

# Extension and application of a tropospheric aqueous phase chemical mechanism (CAPRAM) for aerosol and cloud models

Von der Fakultät für Physik und Geowissenschaften  
der Universität Leipzig  
genehmigte

D I S S E R T A T I O N

zur Erlangung des akademischen Grades

DOCTOR RERUM NATURALIUM

(Dr. rer. nat.)

vorgelegt

von Diplom-Meteorologe Peter Bräuer  
geboren am 16. Juni 1982 in Dresden

Gutachter: Prof. Dr. Hartmut Herrmann  
Prof. Dr. Bernard Aumont

Tag der Verleihung: 12. Oktober 2015

This work was performed between April 2009 and April 2015 at the  
Leibniz Institute for Tropospheric Research (TROPOS), Chemistry Department  
Permoserstr. 15, 04318 Leipzig, Germany

under the supervision of  
Prof. Dr. Hartmut Herrmann.

The work was financially supported by the German Research Foundation  
(Deutsche Forschungsgemeinschaft, DFG) under the project number BO 1714/3-1.



Peter Bräuer

## **Extension and application of a tropospheric aqueous phase chemical mechanism (CAPRAM) for aerosol and cloud models**

University of Leipzig, Dissertation

268 pages, 224 references, 83 figures, 17 tables, 9 appendices

---

### **Abstract:**

The ubiquitous abundance of organic compounds in natural and anthropogenically influenced eco-systems has put these compounds into the focus of atmospheric research. Organic compounds have an impact on air quality, climate, and human health. Moreover, they affect particle growth, secondary organic aerosol (SOA) formation, and the global radiation budget by altering particle properties. To investigate the multiphase chemistry of organic compounds and interactions with the aqueous phase in the troposphere, modelling can provide a useful tool.

The oxidation of larger organic molecules to the final product  $\text{CO}_2$  can involve a huge number of intermediate compounds and tens of thousands of reactions. Therefore, the creation of explicit mechanisms relies on automated mechanism construction. Estimation methods for the prediction of the kinetic data needed to describe the degradation of these intermediates are inevitable due to the infeasibility of an experimental determination of all necessary data. Current aqueous phase descriptions of organic chemistry lag behind the gas phase descriptions in atmospheric chemical mechanisms despite its importance for the multiphase chemistry of organic compounds.

In this dissertation, the gas phase mechanism Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A) has been advanced by a protocol for the description of the oxidation of organic compounds in the aqueous phase. Therefore, a database with kinetic data of 465 aqueous phase hydroxyl radical and 129 aqueous phase nitrate radical reactions with organic compounds has been compiled and evaluated. The database was used to evaluate currently available estimation methods for the prediction of aqueous phase kinetic data of reactions of organic compounds. Among the investigated methods were correlations of gas and aqueous kinetic data, kinetic data of homologous series of various compound classes, reactivity comparisons of inorganic radical oxidants, Evans-Polanyi-type correlations, and structure-activity relationships (SARs). Evans-Polanyi-type correlations have been improved for the purpose of automated mechanism self-generation of mechanisms with large organic molecules. A protocol has been designed based on SARs for hydroxyl radical reactions and the improved Evans-Polanyi-type correlations for nitrate radical reactions with organic compounds. The protocol was assessed in a series of critical sensitivity studies, where uncertainties of critical parameters were investigated.

The advanced multiphase generator GECKO-A was used to generate mechanisms, which were applied in box model studies and validated against two sets of aerosol chamber experiments. Experiments differed by the initial compounds used (hexane and trimethylbenzene) and the experimental conditions (UV-C lights off/on and additional in-situ hydroxyl radical source no/yes). Reasonable to good agreement of the modelled and experimental results was achieved in these studies.

Finally, GECKO-A was used to create two new CAPRAM version, where, for the first time, branching ratios for different reaction pathways were introduced and the chemistry of compounds with up to four carbon atoms has been extended. The most detailed mechanism comprises 4174 compounds and 7145 processes. Detailed investigations were performed under real tropospheric conditions in urban and remote continental environments. Model results showed significant improvements, especially in regard to the formation of organic aerosol mass. Detailed investigations of concentration-time profiles and chemical fluxes refined the current knowledge of the multiphase processing of organic compounds in the troposphere, but also pointed at current limitations of the generator protocol, the mechanisms created, and current understanding of aqueous phase processes of organic compounds.



Peter Bräuer

## **Erweiterung und Anwendung eines troposphärischen Flüssigphasenchemiemechanismus (CAPRAM) für Aerosol- und Wolkenmodelle**

Universität Leipzig, Dissertation

268 Seiten, 224 Literaturzitate, 83 Abbildungen, 17 Tabellen, 9 Anhänge

---

### **Referat:**

Das zahlreiche Vorkommen organischer Verbindungen in natürlichen und anthropogen beeinflussten Ökosystemen hat diese Verbindungen in den Fokus der Atmosphärenforschung gerückt. Organische Verbindungen beeinträchtigen die Luftqualität, die menschliche Gesundheit und das Klima. Weiterhin werden Partikelwachstum und -eigenschaften, sekundäre organische Partikelbildung und dadurch der globale Strahlungshaushalt durch sie beeinflusst. Um die troposphärische Multiphasenchemie organischer Verbindungen und Wechselwirkungen mit der Flüssigphase zu untersuchen, sind Modellstudien hilfreich.

Die Oxidation großer organischer Moleküle führt zu einer Vielzahl an Zwischenprodukten. Der Abbau erfolgt in unzähligen Reaktionen bis hin zum Endprodukt  $\text{CO}_2$ . Bei der Entwicklung expliziter Mechanismen muss deshalb für diese Verbindungen auf computergestützte, automatisierte Methoden zurückgegriffen werden. Abschätzungsmethoden für die Vorhersage kinetischer Daten zur Beschreibung des Abbaus der Zwischenprodukte sind unabdingbar, da eine experimentelle Bestimmung aller benötigten Daten nicht realisierbar ist. Die derzeitige Beschreibung der Flüssigphasenchemie unterliegt deutlich den Beschreibungen der Gasphase in atmosphärischen Chemiemechanismen trotz deren Relevanz für die Multiphasenchemie.

In dieser Arbeit wurde der Gasphasenmechanismusgenerator GECKO-A (*“Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere”*) um ein Protokoll zur Oxidation organischer Verbindungen in der Flüssigphase erweitert. Dazu wurde eine Datenbank mit kinetischen Daten von 465 Hydroxylradikal- und 129 Nitratrakalreaktionen mit organischen Verbindungen angelegt und evaluiert. Mit Hilfe der Datenbank wurden derzeitige Abschätzungsmethoden für die Vorhersage kinetischer Daten von Flüssigphasenreaktionen organischer Verbindungen evaluiert. Die untersuchten Methoden beinhalteten Korrelationen kinetischer Daten aus Gas- und Flüssigphase, homologer Reihen verschiedener Stoffklassen, Reaktivitätsvergleiche, Evans-Polanyi-Korrelationen und Struktur-Reaktivitätsbeziehungen. Für die Mechanismusgenerierung großer organischer Moleküle wurden die Evans-Polanyi-Korrelationen in dieser Arbeit weiterentwickelt. Es wurde ein Protokoll für die Mechanismusgenerierung entwickelt, das auf Struktur-Reaktivitätsbeziehungen bei Reaktionen von organischen Verbindungen mit OH-Radikalen und auf den erweiterten Evans-Polanyi-Korrelationen bei  $\text{NO}_3$ -Radikalreaktionen beruht. Das Protokoll wurde umfangreich in einer Reihe von Sensitivitätsstudien getestet, um Unsicherheiten kritischer Parameter abzuschätzen.

Der erweiterte Multiphasengenerator GECKO-A wurde dazu verwendet, neue Mechanismen zu generieren, die in Boxmodellstudien gegen Aerosolkammerexperimente evaluiert wurden. Die Experimentreihen unterschieden sich sowohl in der betrachteten Ausgangssubstanz (Hexan und Trimethylbenzen) und dem Experimentaufbau (ohne oder mit UV-C-Photolyse und ohne oder mit zusätzlicher partikulärer Hydroxylradikalquelle). Bei den Experimenten konnte eine zufriedenstellende bis gute Übereinstimmung der experimentellen und Modellergebnisse erreicht werden.

Weiterhin wurde GECKO-A verwendet, um zwei neue CAPRAM-Versionen mit bis zu 4174 Verbindungen und 7145 Prozessen zu generieren. Erstmals wurden Verzweungsverhältnisse in CAPRAM eingeführt. Außerdem wurde die Chemie organischer Verbindungen mit bis zu vier Kohlenstoffatomen erweitert. Umfangreiche Untersuchungen unter realistischen troposphärischen Bedingungen in urbanen und ländlichen Gebieten haben deutliche Verbesserungen der erweiterten Mechanismen besonders in Bezug auf Massenzuwachs des organischen Aerosolanteils gezeigt. Das Verständnis der organischen Multiphasenchemie konnte durch detaillierte Untersuchungen zu den Konzentrations-Zeit-Profilen und chemischen Flüssen vertieft werden, aber auch gegenwärtige Limitierungen des Generators, der erzeugten Mechanismen und unseres Verständnisses für Flüssigphasenprozesse organischer Verbindungen aufgezeigt werden.



# Contents

<b>1</b>	<b>Introduction and motivation</b>	<b>1</b>
<b>2</b>	<b>Theoretical background</b>	<b>7</b>
2.1	General overview of the tropospheric multiphase chemistry of organic compounds . . . . .	7
2.1.1	Gas phase chemistry . . . . .	7
2.1.2	Phase transfer . . . . .	9
2.1.3	Aqueous phase chemistry . . . . .	10
2.2	Tropospheric multiphase chemistry mechanisms . . . . .	13
2.2.1	Gas phase mechanisms . . . . .	14
2.2.2	Aqueous phase mechanisms . . . . .	16
2.2.3	The multiphase mechanism MCMv3.1-CAPRAM 3.0n . . . . .	19
	2.2.3.1 MCMv3.1 . . . . .	19
	2.2.3.2 CAPRAM 3.0n . . . . .	21
2.3	Multiphase chemistry box models . . . . .	25
2.3.1	Overview . . . . .	25
2.3.2	The model SPACCIM . . . . .	25
	2.3.2.1 Overview . . . . .	25
	2.3.2.2 The microphysical scheme . . . . .	26
	2.3.2.3 The chemical and phase transfer scheme . . . . .	27
	2.3.2.4 The coupling scheme . . . . .	28
2.4	Prediction of aqueous phase kinetic data . . . . .	29
2.4.1	Simple correlations . . . . .	29
2.4.2	Evans-Polanyi-correlations . . . . .	30
2.4.3	Structure-activity relationships . . . . .	33
2.5	The generator GECKO-A . . . . .	35
<b>3</b>	<b>Evaluation of kinetic data and prediction methods</b>	<b>39</b>
3.1	Compilation and evaluation of aqueous phase kinetic data . . . . .	40
3.2	Extrapolation of gas phase rate constants to the aqueous phase . . . . .	40
3.3	Homologous series of compound classes . . . . .	43
3.4	Radical reactivity comparisons . . . . .	48
3.5	Evans-Polanyi-type correlations . . . . .	50
	3.5.1 OH rate constant prediction . . . . .	50
	3.5.2 NO <sub>3</sub> rate constant prediction . . . . .	55
	3.5.3 Development of an advanced Evans-Polanyi-type correlation . . . . .	57

3.6	Structure-activity relationships . . . . .	67
3.7	Conclusions from the evaluation process . . . . .	70
<b>4</b>	<b>Development of the new aqueous phase protocol and its implementation into GECKO-A</b>	<b>73</b>
4.1	Initialisation and workflow of GECKO-A . . . . .	75
4.2	Estimation of phase transfer data . . . . .	75
4.3	OH reactions of stable compounds . . . . .	77
4.4	NO <sub>3</sub> reactions of stable compounds . . . . .	78
4.5	Hydration of carbonyl compounds . . . . .	81
4.6	Hydrolysis of carbonyl nitrates . . . . .	82
4.7	Dissociation of carboxylic acids . . . . .	83
4.8	Degradation of radical compounds . . . . .	84
4.8.1	RO <sub>2</sub> recombinations and cross-reactions . . . . .	85
4.8.2	HO <sub>2</sub> elimination of $\alpha$ -hydroxy peroxy radicals . . . . .	86
4.8.3	Degradation of acylperoxy radicals . . . . .	87
4.8.4	Degradation of $\beta$ -carboxyl peroxy radicals . . . . .	87
4.8.5	Degradation of alkoxy radicals . . . . .	87
4.8.6	Degradation of acyloxy radicals . . . . .	88
<b>5</b>	<b>Investigation and refinement of crucial parameters in GECKO-A and CAPRAM mechanism development</b>	<b>89</b>
5.1	Formation and degradation of polycarbonyl compounds in the protocol . . . . .	90
5.2	Influence of the mass accommodation coefficient on the organic multiphase chemistry and composition . . . . .	95
5.3	Influence of the cut-off parameter for minor reaction pathways . . . . .	98
5.4	Influence of the chosen SAR in the protocol . . . . .	101
5.5	Processing of organic mass fraction in the protocol . . . . .	104
5.5.1	Parameterisations for radical attack of the overall organic mass fraction	104
5.5.2	Detailed studies of organic nitrate sinks and sources . . . . .	108
5.5.3	Phase transfer of oxygenated organic compounds in the protocol . . . . .	111
5.5.4	Decay of alkoxy radicals in the protocol . . . . .	113
5.5.5	Revision of the GROMHE thermodynamic database . . . . .	114
5.6	Influence of the nitrate radical chemistry . . . . .	117
5.7	The final protocol for aqueous phase mechanism self-generation . . . . .	122
5.8	CAPRAM mechanism development . . . . .	124
5.8.1	CAPRAM 3.0 . . . . .	125
5.8.2	CAPRAM 3.5 . . . . .	126
5.8.3	CAPRAM 4.0 . . . . .	127
<b>6</b>	<b>Model results and discussion</b>	<b>129</b>
6.1	Comparisons of model results with aerosol chamber experiments . . . . .	129
6.1.1	Design of the aerosol chamber experiments . . . . .	130
6.1.1.1	Hexane oxidation experiment . . . . .	130
6.1.1.2	Trimethylbenzene oxidation experiment . . . . .	131

6.1.2	Mechanism generation and model setup . . . . .	132
6.1.2.1	Hexane oxidation experiment . . . . .	132
6.1.2.2	Trimethylbenzene oxidation experiment . . . . .	133
6.1.3	Evaluation of the model versus aerosol chamber results . . . . .	134
6.1.3.1	Hexane oxidation experiment . . . . .	134
6.1.3.2	Trimethylbenzene oxidation experiment . . . . .	137
6.2	Simulations with a ‘real atmosphere’ scenario . . . . .	149
6.2.1	Model setup . . . . .	149
6.2.2	Meteorological and microphysical parameters . . . . .	151
6.2.3	Influence of the extended organic scheme on the particle acidity and SOA formation . . . . .	151
6.2.3.1	Particle acidity . . . . .	152
6.2.3.2	Particle mass . . . . .	155
6.2.4	Influence of the extended organic scheme on inorganic radical oxidants . . . . .	165
6.2.4.1	OH chemistry . . . . .	165
6.2.4.2	NO <sub>3</sub> chemistry . . . . .	169
6.2.4.3	Comparison of OH and NO <sub>3</sub> chemistry . . . . .	173
6.2.4.4	HO <sub>2</sub> /O <sub>2</sub> <sup>-</sup> chemistry . . . . .	177
6.2.5	Influence of the extended organic scheme on inorganic non-radical oxidants . . . . .	182
6.2.5.1	H <sub>2</sub> O <sub>2</sub> chemistry . . . . .	182
6.2.5.2	O <sub>3</sub> chemistry . . . . .	184
6.2.6	Influence of the extended organic scheme on inorganic particulate matter . . . . .	185
6.2.6.1	Sulfate chemistry . . . . .	185
6.2.6.2	Nitrate chemistry . . . . .	186
6.2.6.3	TMI chemistry . . . . .	187
6.2.7	Detailed investigations of selected organic subsystems . . . . .	190
6.2.7.1	Monofunctional organic compounds . . . . .	190
6.2.7.2	Carbonyl compounds . . . . .	192
6.2.7.3	Dicarboxylic acids and functionalised monocarboxylic acids . . . . .	196
<b>7</b>	<b>Conclusions</b>	<b>207</b>
	<b>References</b>	<b>215</b>
	<b>Glossary</b>	<b>237</b>
	<b>Acronyms</b>	<b>241</b>
	<b>List of symbols</b>	<b>245</b>
	<b>List of Figures</b>	<b>247</b>
	<b>List of Tables</b>	<b>255</b>

<b>Acknowledgements</b>	<b>259</b>
<b>Curriculum Vitae</b>	<b>261</b>
<b>List of relevant publications</b>	<b>263</b>
Peer-reviewed publications . . . . .	263
Oral conference contributions . . . . .	263
Poster conference contributions . . . . .	265
<b>Appendix</b>	<b>267</b>
<b>A Overview of selected compound classes of tropospheric relevance</b>	<b>269</b>
<b>B Detailed description of the function of SARs</b>	<b>271</b>
<b>C The kinetic database</b>	<b>275</b>
C.1 Reactions of hydroxyl radicals with organic compounds . . . . .	275
C.2 Reactions of nitrate radicals with organic compounds . . . . .	295
<b>D Detailed information about the evaluation of prediction methods</b>	<b>303</b>
D.1 Rate data used for the derivation and evaluation of gas-aqueous phase correlations . . . . .	303
D.2 Explanation of the use of box plots . . . . .	305
D.3 Additional correlations of homologous series of various compound classes .	306
D.4 Additional information of Evans-Polanyi-type correlations . . . . .	308
D.5 Additional information of structure-activity relationships . . . . .	312
<b>E Additional information for the development of the protocol of GECKO-A</b>	<b>313</b>
E.1 Investigations on the decay of acylperoxy radicals . . . . .	313
E.2 Additional information about the sensitivity of mass accommodation coefficients	314
E.3 Additional information about the sensitivity studies concerning the decay of polycarbonyls . . . . .	315
E.4 Additional information about the sensitivity studies concerning the omission of minor reaction pathways . . . . .	316
E.5 Additional information about the sensitivity studies concerning the processing of the organic mass fraction . . . . .	317
E.6 Additional information about the influence of the nitrate radical chemistry	318
<b>F Additional information about the mechanism generation and model initialisation</b>	<b>325</b>
F.1 List of primary compounds used for the generation of CAPRAM 3.5 . . . .	325
F.2 List of primary compounds used for the generation of CAPRAM 4.0 . . . .	325
F.3 Model initialization of the ‘real atmosphere’ scenarios . . . . .	327



---

<b>G</b>	<b>The CAPRAM oxidation scheme</b>	<b>331</b>
G.1	Photolysis processes . . . . .	332
G.2	Inorganic chemistry . . . . .	333
G.2.1	Phase transfer processes . . . . .	333
G.2.2	Chemical conversions . . . . .	335
G.3	Organic chemistry . . . . .	346
G.3.1	Phase transfer processes . . . . .	346
G.3.2	Chemical conversions . . . . .	365
<b>H</b>	<b>Detailed information about the model validation with chamber experiments</b>	<b>889</b>
H.1	Additional information about the initialisation of the hexane oxidation experiment . . . . .	889
H.2	Additional model results from the hexane oxidation experiment . . . . .	889
H.3	Additional information about the sensitivity runs used in the trimethylbenzene oxidation experiment . . . . .	890
H.4	Additional results from the TMB oxidation experiment . . . . .	897
<b>I</b>	<b>Additional results from the ‘real atmosphere’ scenario</b>	<b>901</b>
I.1	Particle acidity and SOA formation . . . . .	901
I.2	Radical oxidants . . . . .	903
I.3	Organic compounds . . . . .	906
	<b>References of the Appendix</b>	<b>907</b>



# 1 Introduction and motivation

The troposphere is the lowermost part of the earth's atmosphere. This mantle of air is often described as the gaseous shell surrounding the earth. The description is somewhat misleading as the atmosphere is, in fact, a complex multiphase and multicomponent environment. It is a mixture of a multitude of different gases and dispersed solid and aqueous particles such as mineral dust, deliquescent particles, cloud and fog droplets, or ice crystals (*Seinfeld and Pandis, 2006, Solomon et al., 2007*). The dispersion of the solid or liquid particles and the ambient air shell is often referred to as aerosols. Besides external mixtures of solid and aqueous particles, there are internal mixtures as well, where solid parts are dissolved in aqueous parts, different solids are mixed in a particle, such as soot that condenses on dust mineral surfaces, or different liquids are mixed, for example, organic coatings on cloud droplet surfaces. Sources for aerosol particles can be of natural (e.g., sea-salt emissions, soil erosions, particle growth from biogenic activity, pollen, or volcanic eruptions) or anthropogenic origin (e.g., fossil fuel combustion, traffic emissions). In addition to primarily emitted particles, secondary aerosol particles are formed in the atmosphere due to gas-to-particle conversions (*Seinfeld and Pandis, 2006, Hoffmann and Warnke, 2007*). Both, the aerosol origin and the past transformations throughout the atmospheric transportation process determine the physicochemical properties of aerosol particles.

Although most particles are invisible for the naked eye with diameters ranging from a few nanometers up to  $\sim 100\text{ }\mu\text{m}$ , they play an important role in the troposphere (*Seinfeld and Pandis, 2006*). An effect, which can be directly observed, is the reduced visibility in the atmosphere in case of high particle concentrations. It is caused by light scattering on particle surfaces (*Jacob, 1999*). The scattering of solar radiation has a huge impact on our climate as the earth's albedo is increased. The cooling effect of aerosols sums up to about  $-0.9\text{ W m}^{-2}$  (*Jacob, 1999*). Moreover, particles are crucial for cloud formation processes. Without aerosol particles, unrealistically high supersaturations of several 100 per cent would be necessary to form cloud droplets. Therefore, particles acting as cloud condensation nuclei (CCN) are important for tropospheric cloud occurrence.

Aerosol particles contain a wide range of substances including sulfate, nitrate, ammonium, seasalt, crustal material, metal oxides and transition metal ions (TMIs) as well as organic substances such as elemental or organic carbon (*Seinfeld and Pandis, 2006*). The composition is determined by the origin and formation process of the aerosol particle and the transformation during the residence in the troposphere. In the troposphere, particles interact with the ambient air by uptake and release of trace gases. Thus, the aerosol composition is influenced by the environmental regime and, in return, aerosols impact the

gas phase composition of the atmosphere. Besides phase transfer, heterogeneous reactions can occur at the particle surface. Aerosols play an important role for issues concerning air quality and public health as aerosol particles can contain a number of potentially harmful substances or influence the gas phase concentration levels of potentially harmful trace compounds. Moreover, aerosols with a diameter smaller than  $1\text{ }\mu\text{m}$  (fine mode) can intrude deeply in the lungs and are a potential health threat themselves. As a consequence, there have been recent attempts by policymakers to decrease concentration levels of fine particulate matter, e.g., by restrictions of traffic emissions in big European cities (*Durham Environment Watch*, 2014, *Kumar et al.*, 2014, *Panteliadis et al.*, 2014).

A large fraction (between 20 and 90% of the submicron particulate matter) of the aerosols predominantly consists of organic material (*Jimenez et al.*, 2009). Such organic aerosols (OA) can either be primarily emitted (primary organic aerosol, POA), e.g., from fuel combustion or biomass burning, or formed by the oxidation of volatile organic compounds (VOCs) leading to secondary organic aerosol (SOA).

Organic compounds are ubiquitous constituents of the tropospheric multiphase system. They are not only abundant in aerosols, but also as trace gases in the troposphere. They are emitted in large quantities into the atmosphere either from anthropogenic (e.g., traffic or industrial emissions) or natural sources (e.g., plant emissions, emissions from the oceans). The overall emission strength of non-methane volatile organic compounds (NMVOCs) is about  $1300 - 1350\text{ Tg carbon per year}$  ( $1\text{ Tg carbon per year} = 10^{12}\text{ g C a}^{-1}$ ) (*Goldstein and Galbally*, 2007, *Hallquist et al.*, 2009). The largest fraction ( $\sim 1150\text{ Tg C a}^{-1}$ ) can be attributed to natural sources while anthropogenic sources total to just about  $150\text{ Tg C a}^{-1}$ . The largest single source for a compound is that of isoprene with an emission strength of c.  $500\text{ Tg C a}^{-1}$  (*Goldstein and Galbally*, 2007). Isoprene is mainly emitted by deciduous trees and to a smaller extent by phytoplankton. The reason for these emissions is believed to be the protection of plants against heat and oxidative stress (*Sharkey et al.*, 2008).

While the overall source strength of the emissions is relatively well established (*Hallquist et al.*, 2009), numbers in the estimates of the loss fluxes for VOCs and SOA vary greatly and demand further research. *Goldstein and Galbally* (2007) give three removal processes for volatile organic compounds: (i) dry and wet deposition, (ii) tropospheric gas phase oxidation leading to CO/CO<sub>2</sub> production, and (iii) the formation of compounds with a low vapour pressure and thus a generally high water-solubility during the tropospheric oxidation process. In the latter process, VOCs will contribute to SOA formation (*Goldstein and Galbally*, 2007).

Extensive research has been performed concerning the oxidation of volatile organic compounds. While considerable progress has been achieved regarding the gas phase oxidation of VOCs (e.g., *Stockwell et al.*, 2011, *Vereecken and Francisco*, 2012), secondary organic aerosol formation processes are still poorly understood and insufficiently quantified (e.g., *Hallquist et al.*, 2009, *Herckes et al.*, 2013, *Smith et al.*, 2014, *Paglionone et al.*, 2014). Several attempts have been made to close the carbon mass balance. Two different principle methods exist for the closure of the carbon cycle in the atmosphere. In the traditional approach, the *bottom-up approach*, large biogenic, especially isoprene and terpene fluxes, and/or

---

anthropogenic fluxes from other VOCs contributing to SOA formation are combined in global models with laboratory data from oxidation experiments. The model results lead to a better understanding of the turnovers occurring in the atmosphere (*Hallquist et al.*, 2009). The alternative *top-down approach* uses known SOA precursor emissions and constrains their eventual fate to estimate the total SOA production (*Goldstein and Galbally*, 2007, *Hallquist et al.*, 2009). While there are already significant uncertainties within a method, different results from both approaches manifest the necessity for more research. The traditional approaches give SOA production yields of  $12 - 70 \text{ Tg C a}^{-1}$  (*Kanakidou et al.*, 2005). *Goldstein and Galbally* (2007) hypothesize that this number might be substantially underestimated. They used four different *top-down methods* to derive SOA production rates. Their conclusions from the global mass balance of VOC removal result in a SOA production of  $510 - 910 \text{ Tg C a}^{-1}$ . Considerations of the SOA deposition and oxidation yield in  $225 - 575 \text{ Tg C a}^{-1}$ . Comparisons with inorganic aerosols, i.e. sulfate aerosols, give SOA production rates of  $140 - 540 \text{ Tg C a}^{-1}$ . Finally, a SOA production rate of  $223 - 615 \text{ Tg C a}^{-1}$  is estimated when trying ‘*to maintain the assumed global mean vertical SOA distribution*’ (*Goldstein and Galbally*, 2007).

So far, recent research pointed out that SOA can either be formed by thermal (dark) or photochemical reactions. In photochemical reactions, the hydroxyl radical plays the most important role (*Smith et al.*, 2014). The oxidation of gas phase organic precursor compounds leads to less volatile products, which condense on particle surfaces and/or alter the bulk of the particle (*Kanakidou et al.*, 2005, *Hallquist et al.*, 2009). In the particles, conversions may lead to a further reduction of the volatility of the products, so that these compounds stay in the particle phase, even if the remaining water of the deliquescent particles or cloud and fog droplets evaporates (*Kanakidou et al.*, 2005, *Hallquist et al.*, 2009, *Smith et al.*, 2014).

As long as particles contain enough water that they can be considered as deliquescent, they are regarded as part of the aqueous phase along with other hydrometeors such as cloud or fog droplets. In a non-aqueous phase, aerosols have a solid or glassy structure (*Koop et al.*, 2011). Aqueous and non-aqueous aerosols can co-exist in internal and external mixtures (*Jacobson*, 2001). In internal mixtures, solid parts are dispersed in deliquescent particles or in water, such as dissolved parts of a CCN in a cloud droplet. Another possibility are coatings on particle surfaces, e.g., organic material or soot on mineral dust. These mixing states will have an influence either on climate related issues such as the radiation balance as well as on the tropospheric multiphase chemistry (*Jacobson*, 2001, *Kolesar et al.*, 2014).

Further research is needed to clarify the role of the aqueous phase in SOA formation processes. Yet, past research indicates that gas and aqueous phase concentrations are influenced by each other (e.g., *Kanakidou et al.*, 2005, *Tilgner et al.*, 2013) and that particle microphysics and the climate impact of aerosols is changed by interactions with the gas phase (*Kanakidou et al.*, 2005, *Solomon et al.*, 2007, *Hallquist et al.*, 2009). Moreover, particles may relocate certain compounds by long range transport. Further interactions

with the gas phase may alter the chemical composition far away from the aerosol source region (*Kanakidou et al.*, 2005).

However, field, chamber and other laboratory experiments alone are incapable of revealing all secrets of the multiphase chemistry of volatile organic compounds and their contributions to secondary organic aerosol production. *Goldstein and Galbally* (2007) estimated that to date  $10^4 - 10^5$  organic compounds have been measured in the atmosphere. Yet, this is likely to be only a small fraction of the compounds existing in the troposphere. To be able to manage such a large number of different compounds and assess the different formation and degradation pathways, explicit chemistry modelling can provide a useful tool. Numerical box models are able to evaluate or predict concentration profiles of measured organic compounds. Theoretical considerations can be implemented in box models and their plausibility assessed. Detailed mechanisms will give advanced knowledge of the formation and degradation of organic trace gases and secondary organic aerosols. Deviations in the predicted concentration-time profiles of the model runs compared to experimental data from field and laboratory work will demonstrate the constraints of the current knowledge. However, the huge number of possible species and reactions together with the incapability of an experimental determination demands the estimation of kinetic data. Moreover, automation methods have to be applied for the generation of such large oxidation schemes, which will easily reach thousands of compounds and reactions.

Many mechanisms have already been developed to describe the chemistry of organic compounds in the troposphere. In the gas phase, these mechanisms reach from rather compact oxidation schemes to complex near-explicit or explicit mechanisms. In compact mechanisms, compounds of a similar structure are often combined in lumped or surrogate model species (e.g., the Regional Atmospheric Chemistry Mechanism 2 (RACM2) by *Goliff et al.*, 2013). For the creation of the near-explicit and explicit mechanisms, automation routines for the self-generation of the oxidation schemes have already been applied such as the Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A; see *Aumont et al.*, 2005). The description of aqueous phase chemistry lags behind the detailed gas phase oxidation schemes. The currently most detailed aqueous phase mechanism is the Chemical Aqueous Phase RAdical Mechanism 3.0n (CAPRAM 3.0n; see *Bräuer et al.*, 2013, *Tilgner and Herrmann*, 2010). It explicitly describes the aqueous phase chemistry of almost 400 species in 777 reactions. The description includes a detailed oxidation scheme for organic compounds with up to four carbon atoms as well as a more condensed oxidation scheme for a few sample compounds with up to six carbon atoms. However, compared to the  $\sim 2.5$  million species and even 10 times more reactions of the gas phase mechanisms created by GECKO-A, the description of the aqueous phase in CAPRAM 3.0n shows large deficits.

The aim of the present dissertation is to contribute to close this gap between gas and aqueous phase oxidation schemes of organic compounds. Therefore, an aqueous phase protocol has been developed for automated self-generation of large explicit oxidation schemes. The protocol uses up-to-date prediction methods for chemical and kinetic data that have recently become available. An intensive literature study was performed and

---

available kinetic data was evaluated and compiled in a large database. The database was used to investigate the precision of current prediction methods for aqueous phase kinetic data and their practicability for the application in automated computer-assisted mechanism construction. Results from the evaluation process are presented in chapter 3. Before, a more detailed introduction into the topic and an overview of the most important theoretical background information is given in chapter 2.

The protocol for the automated construction of explicit oxidation schemes has been integrated in the mechanism generator GECKO-A. The extension of the generator was a major part of this work and was performed in close cooperation with the group of Bernard Aumont at the Laboratoire Inter-universitaire des Systèmes Atmosphériques (LISA) in Paris, France. The protocol for automated mechanism self-generation and its implementation in the generator is described in chapter 4. Comprehensive sensitivity studies of crucial parameters have been performed, which led to the refinement of the protocol. These test studies and the final protocol is introduced in chapter 5. The new multiphase mechanism generator GECKO-A has been used to advance the organic chemistry in the current CAPRAM version. For the first time, different reaction pathways are introduced in the aqueous phase for a single reaction. Moreover, the chemistry of organic compounds with up to four carbon atoms has been extended. The new self-generated CAPRAM versions are also introduced in chapter 5.

Three different mechanisms with different levels of complexity of the organic oxidation scheme have been generated and applied in sophisticated box model studies. The model framework combines the comprehensive chemical scheme with detailed microphysics using a meteorological scenario with non-permanent clouds. The scenario was designed for realistic remote and urban conditions. Moreover, for a detailed validation of the protocol, experiments in a smog chamber have been performed and compared to the model output of simulations with generated mechanisms that were especially designed for the chamber experiments. Results from the chamber studies and the application in simulations under realistic tropospheric conditions are presented in chapter 6.





## 2 Theoretical background

The current chapter will give an overview of the most important background information required to interpret the results in chapter 6. After a general introduction into the topic in section 2.1, more detailed information about chemical multiphase mechanisms and their processing in box models is given (sections 2.2 and 2.3). Different possibilities to theoretically predict the products and rate constants of a reaction are explained in section 2.4. A computer tool, which applies these prediction methods and was advanced throughout this dissertation is described in section 2.5.

### 2.1 General overview of the tropospheric multiphase chemistry of organic compounds

#### 2.1.1 Gas phase chemistry

The abundance and emission strength of volatile organic compounds (VOCs) has put them into the focus of environmental research. The most abundant organic compound in the atmosphere is methane ( $\text{CH}_4$ ). Natural emissions (predominantly from wetlands, but also from termites or the ocean) and anthropogenic emissions (e.g., from rice agriculture, cattle farming, biomass burning or energy production) total to  $\sim 600 \text{ Tg C a}^{-1}$  and lead to tropospheric concentrations of  $\sim 1.8 \text{ ppm}^1$  (*Seinfeld and Pandis*, 2006). Methane is an important greenhouse gas (GHG) causing global warming and, hence, influencing the earth's climate (*Seinfeld and Pandis*, 2006, *Solomon et al.*, 2007). Besides methane, several non-methane volatile organic compounds (NMVOCs) influence the climate or affect issues such as air quality. Their natural sources, for example from emissions by trees, total to  $\sim 1150 \text{ Tg C a}^{-1}$ . Anthropogenic emissions, e.g., from fuel combustion are one order of magnitude smaller. Yet, emissions of  $150 \text{ Tg C a}^{-1}$  are still a significant environmental issue (*Goldstein and Galbally*, 2007, *Hallquist et al.*, 2009).

Due to the high abundance of VOCs, it is convenient to group compounds with a similar structure into certain classes. As a general rule, organic compounds of a certain compound class have similar properties and obey the same rules for their atmospheric degradation. An overview of the various compound classes of tropospheric relevance can be found in Table A.1 in Appendix A, page 269. The complete dissertation with all appendices is available in electronic form as pdf on a CD attached to this print version, where

---

<sup>1</sup>1.8 parts per million or  $\mu\text{mol/mol}$ , see Glossary for details

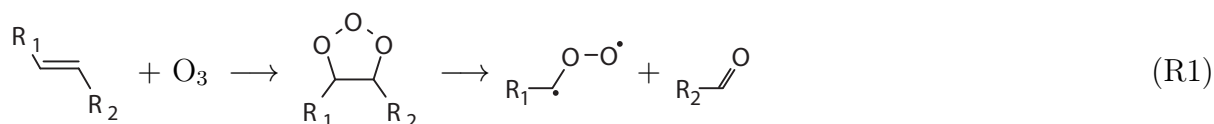
appendices are omitted. Although there is a very large number of different compounds in the troposphere, only a small number of degradation processes exist that are repeatedly observed in the oxidation chain of organic compounds finally leading to the end product CO<sub>2</sub> (Aumont *et al.*, 2005).

The oxidation is started in the gas phase upon the emission from natural or anthropogenic sources. There are three important oxidation processes, which are explained in the following (Aumont *et al.*, 2005, Hallquist *et al.*, 2009):

- Photolysis
- Non-radical oxidation
- Radical oxidation

**Photolysis** is initiated by the excitation of a compound by solar radiation into an excited state and its subsequent fragmentation into smaller pieces. Compounds being able to undergo photolytic degradation must absorb actinic light and have non-negligible decomposition quantum yields. Photolysis is an important degradation process although, in the atmosphere, it is variable depending on the geographic latitude as well as altitude, the annual season, and the time of the day (Seinfeld and Pandis, 2006).

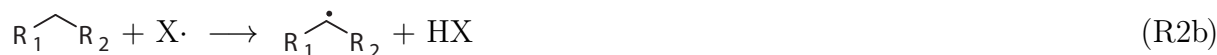
**Non-radical oxidation** is dominated by ozonolysis in the gas phase. It is mainly important for unsaturated compounds such as alkenes. Ozone (O<sub>3</sub>) adds to the double bond of an organic compound forming a so-called ozonide (Seinfeld and Pandis, 2006):



In the following, R in chemical structures denotes any organic rest. Possible differences in the organic rests are indicated by different indices (1, 2, ..., n). The ozonide decays into two fragments by bond breaking between the two carbon atoms originally attached to the double bond and two of the oxygen atoms in the ring of the ozonide. In the reaction, a carbonyl compound and a Criegee biradical is formed (see Reaction R1). The further degradation of the Criegee biradical is discussed elsewhere (Seinfeld and Pandis, 2006, Atkinson *et al.*, 2000, 2006) and beyond the scope of this work. The fate of carbonyl compounds is discussed below.

**Radical oxidation.** Ozone is not only an important oxidant of unsaturated organic compounds, in addition, its photolysis leads to hydroxyl (OH) radicals via excited oxygen atoms O(<sup>1</sup>D) and water molecules. Hydroxyl radicals are the most important radical oxidant in the troposphere (for detailed information, see Seinfeld and Pandis, 2006). Together with other radicals such as nitrogen oxide (NO), the nitrate radical (NO<sub>3</sub>) or halogen atoms (Cl, Br), OH radicals oxidise organic compounds. They react by addition

to double bonds or H-atom abstraction. In both cases, an alkyl radical is formed (*Seinfeld and Pandis, 2006*):



where X is the radical oxidant (OH, NO<sub>3</sub>, Cl...). Due to the excess of oxygen in the air, O<sub>2</sub> will rapidly add to the free radical forming a peroxy radical (R3), which will recombine or react in cross-reactions with other peroxy radicals (R4a, R4b) or peroxy radicals are oxidised by NO (R4c) (*Reimann and Lewis, 2007, Seinfeld and Pandis, 2006*):



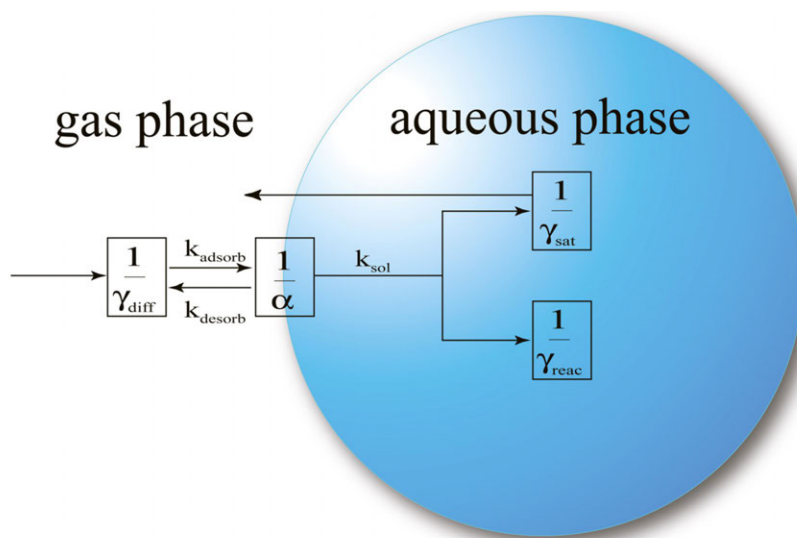
where R<sup>·</sup> is any alkyl radical, RO<sub>2</sub><sup>·</sup> a peroxy radical, R-OH and R=O an alcohol and carbonyl compound, respectively. The alcohol and carbonyl compounds formed in Reaction R4a decay, again, by H-atom abstraction or radical addition to the double bond for unsaturated compounds similar to Reaction R2, while the oxy radicals (RO<sup>·</sup>) formed in the Reactions R4b and R4c degrade either by C-C bond breaking or by reaction with O<sub>2</sub> (*Seinfeld and Pandis, 2006*):



Larger organic compounds are oxidised in a sequence of several reaction steps, where different generations of intermediate organic compounds are formed. During the tropospheric degradation, organic compounds are either fragmented into smaller pieces (by photolysis or C-C bond breaking of intermediate alkoxy radicals) or oxygen adds to the molecule's skeleton. This increase of the O:C ratio increases the polarity and thus the water-solubility of the molecules. Throughout the oxidation process, compounds can evolve that bear several functional groups of the same or of different kind (*Aumont et al., 2005*).

### 2.1.2 Phase transfer

The increase in solubility throughout the atmospheric oxidation process enables the phase transfer into the aqueous phase of a given compound. According to *Schwartz (1986)*, uptake is a dynamic equilibrium, which has several stages. First, the species has to diffuse through the gas phase to the droplet's surface. Upon collision with the droplet surface, a number of molecules will still be reflected back to the gas phase. The fraction entering the bulk of the droplet is described by the mass accommodation coefficient  $\alpha$ . The uptake process is an equilibrium determined by the equilibrium constant – the Henry's Law constant (HLC



**Figure 2.1** Overview of the resistance model by *Schwartz* (1986) (graphic taken from *Tilgner*, 2009).

or  $K_H$ ). In the bulk phase of the droplet, the diffusion and further reactions and equilibria influence the uptake (*Schwartz*, 1986; see also Figure 2.1 for an illustration). Fast aqueous phase degradations will enhance the uptake from the gas phase. This process is known as reactive uptake. Furthermore, some species are known to aggregate on the droplet's surface. They can, at least partially, form surface films. The modified droplet surface has an influence on the phase transfer of further compounds and thus on the tropospheric multiphase composition and chemistry. Moreover, the microphysics such as light absorption and scattering is influenced as well (*Lawrence et al.*, 2005, *Kolesar et al.*, 2014). Besides the uptake, where the compound has to pass the droplet's surface and enter into the bulk phase, heterogeneous reactions are also possible. In these reactions, gaseous oxidants react with compounds attached to the droplet's surface. In these reactions aqueous and/or gaseous products are formed (*Ammann et al.*, 2013).

### 2.1.3 Aqueous phase chemistry

In the aqueous phase, degradation processes follow the same rules as in the gas phase. However, some differentiations have to be drawn due to the different reaction media.

#### Photochemistry

In water, photolysis is generally slower although cloud droplets act as a lens and bundle the light, which increases photolysis rates by a factor of about 1.6 at first (*Madronich*, 1987). However, the surrounding 'solvent cage' prevents the fragments from separating after the photolysis, which reduces the quantum yields (*Herrmann*, 2007). Therefore, quantum yields are provided as effective quantum yields in the aqueous phase, which consider the primary recombination. While quantum yields are typically 1 in the gas phase, they can be decreased by an order of magnitude or even more in the aqueous phase.

## Equilibria

Moreover, water as a solvent causes several equilibria in cloud droplets and deliquescent particles. Carbonyls will react with the surrounding water to form gem-diols (*Monod et al.*, 2005, *Doussin and Monod*, 2013):



Furthermore, carboxylic acids will dissociate in the following equilibrium (*Perrin et al.*, 1981):



Both equilibria (R6 and R7) and thus the speciation of hydrated and dehydrated compounds or dissociated and undissociated species, respectively, can be described with an equilibrium's constant  $K$ . For a more detailed description of the kinetics, the rate constants of the forward ( $k_f$ ) and backward ( $k_b$ ) reaction are needed (see Equation 2.1).

$$K = \frac{k_f}{k_b} \quad (2.1)$$

## Acidity and pH

For dissociations, the equilibrium constants are typically small with an equilibrium constant  $K_a = 10^{-7} \text{ mol l}^{-1}$  for neutral solutions. Therefore it is more convenient to express these equilibria with the negative logarithm of the equilibrium constant, the  $pK_a$  (see *Hazarika et al.*, 2009):

$$pK_a = -\log K_a \quad (2.2)$$

The concentration and type of acids in solution define the acidity of the solution, or in the atmosphere, the acidity of cloud droplets and deliquescent particles. The acidity is defined by the concentration of protons ( $[\text{H}^+]$ ) in a solution, which is again often expressed on a logarithmic scale by the pH value given in Equation 2.3.

$$[\text{H}^+]/\text{mol l}^{-1} = 10^{-\text{pH}} \quad (2.3)$$

## Differences between gas and aqueous phase chemistry

Comparing the aqueous phase chemistry to gas phase chemistry, several differences in the reaction pathways can be noticed although the general reaction mechanisms are the same or at least similar. For example, the  $\text{RO}_2$  radical recombination yields another channel in the aqueous phase leading to 2 carbonyl compounds and hydrogen peroxide.

Another example is that aldehydes form acylperoxy radicals ( $\text{RC}(=\text{O})\text{OO}\cdot$ ) during the tropospheric degradation due to the low bond dissociation enthalpy (*BDE*) between the carbon atom and the hydrogen atom in the aldehyde group. In the gas phase, they react with NO to form acyloxy radicals ( $\text{RC}(=\text{O})\text{O}\cdot$ ), which decay by C–C bond breaking to  $\text{CO}_2$  and alkyl radicals. In the aqueous phase, two facts favour the formation of carboxylic acids rather than acyloxy radicals. Firstly, NO has a low water-solubility ( $K_H = 1.9 \cdot 10^{-3} \text{ M atm}^{-1}$ , see *Sander, 2014*), which makes aqueous phase reactions of this radical unlikely. Moreover, the excess of the surrounding water leads to hydrated acylperoxy radicals ( $\text{RC}(\text{OH})_2\text{OO}\cdot$ ), which will eliminate  $\text{HO}_2$  to form carboxylic acids.

The Henry’s Law equilibrium will regulate the partitioning between the gas and the aqueous phase of the different products formed in a reaction and thus balance the tropospheric multiphase composition. Hence, both compartments interact with each other and neither one can be neglected for a correct description of the chemical composition and conversions in the troposphere.

### Dependencies and variations of aqueous phase reactions

Even within the aqueous phase, differences in the reaction pathways exist due to special conditions. Hydrations depend on the liquid water content (LWC), and dissociations are strongly pH-dependent, which results in different speciations of the various protonation states of a species at different pH levels. Different reaction rate constants of the dissociation states can lead to pH-dependencies of chemical reactions. With decreasing LWC the ionic strength, a measure for the concentration of ions in the solution (see also the explanation in the glossary), increases.

Carboxylic acids dissociate and the increase in the proton concentration causes the pH to decrease. Hence, as deliquescent particles have a lower pH than cloud droplets, where the hydronium ions are diluted (*Tilgner et al., 2013*), significant differences between particle and cloud droplet chemistry can occur. On the other hand, particles and cloud droplets are linked together as well. Particles can act as cloud condensation nuclei (CCN). When a cloud is formed, the CCN partly or fully dissolves in the water of the cloud droplet (*Seinfeld and Pandis, 2006*) altering its chemical composition. In return, the chemical conversions within cloud droplets influence the composition of particles, when clouds evaporate leaving only deliquescent particles behind (*Seinfeld and Pandis, 2006*).

### Non-radical oxidation

Non-radical oxidation can play an important role in the aqueous phase. In addition to the oxidation of unsaturated compounds by ozone similar to the gas phase oxidation, degradation of organic compounds by hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) can be important as well. Investigations are still ongoing and mechanistic details remain unclear at present, however, aldehydes seem to react efficiently with hydrogen peroxide as already investigated in the

1950's by *Satterfield and Case* (1954). Although rate constants in the order of  $10^{-1} \text{ M}^{-1} \text{ s}^{-1}$  of these reactions (see, e.g., *Satterfield and Case*, 1954, *Stefan and Bolton*, 1999) are several orders of magnitude lower than those of the corresponding hydroxyl radical reactions with rate constants in the order  $10^7 - 10^8 \text{ M}^{-1} \text{ s}^{-1}$  (see, e.g. *Stefan and Bolton*, 1999 or the kinetic database of this dissertation introduced in section 3.1), significant turnovers of the  $\text{H}_2\text{O}_2$  channel might be observed in the troposphere. This is due to the significantly higher concentrations of hydrogen peroxide compared to the hydroxyl radical. Aqueous  $\text{H}_2\text{O}_2$  concentrations of about  $10^{-5} - 10^{-4} \text{ M}$  (*Tilgner and Herrmann*, 2010) compared to hydroxyl radical concentrations in the order of  $10^{-13} - 10^{-12} \text{ M}$  (*Tilgner et al.*, 2013) compensate the decreased rate constants. A widely discussed mechanism for  $\text{H}_2\text{O}_2$  reactions with aldehydes and ketones is (*Zhao et al.*, 2012, 2013):



### Accretion reactions

Besides oxidation, organic compounds can participate in non-oxidative reactions. In accretion reactions, two compounds recombine to form a dimer or, in subsequent reactions, oligomers. Thus, high molecular weight compounds can be formed that substantially contribute to aerosol mass and SOA formation (*Ervens and Volkamer*, 2010, *Hallquist et al.*, 2009). The process is catalysed by amino acids, ammonium, carbonate or hydroxide ions (*Ervens and Volkamer*, 2010, *Nozière and Chabert*, 2010). Although the oligomerisation process is still poorly understood, several precursor compounds have been suggested including alcohols, carboxylic acids, carbonyl compounds and stabilised Criegee biradicals (see, e.g., *Hallquist et al.*, 2009 and references therein).

## 2.2 Tropospheric multiphase chemistry mechanisms

The previous sections have shown the importance of the troposphere as a reactive medium. The ultimate goal is to identify and understand the processes, which simultaneously occur in this multicomponent and multiphase environment. Chemical mechanisms aim at the description of the reaction sequences occurring in the tropospheric multiphase system and the identification of reaction pathways. Their description can focus on only one compartment, either the gas or the aqueous phase, or on the multiphase description including partitioning and heterogeneous reactions at the phase interface in more sophisticated mechanisms. Moreover, the description can be of qualitative nature only, or atmospheric mechanisms may try to deliver a quantitative description and assign kinetic and thermodynamic data to the reactions and processes considered in the mechanism (see also *Tilgner*, 2009, *Stockwell et al.*, 2011).

The current section gives an overview of the atmospheric chemical mechanisms available in literature. First, gas phase mechanisms are described in subsection 2.2.1 followed by a description of currently available aqueous phase mechanisms (subsection 2.2.2), which can be combined to multiphase mechanisms. In subsection 2.2.3, the multiphase mechanism used for this study, MCMv3.1-CAPRAM 3.0n, is introduced in detail.

### 2.2.1 Gas phase mechanisms

The tropospheric degradation of most organic compounds is initialised in the gas phase. Important degradation processes are photolysis, radical attack of which the hydroxyl (OH) radical attack plays the dominant role, unimolecular decay and non-radical oxidation, which is mostly important for the ozonolysis of unsaturated compounds. First attempts to describe these processes in chemical mechanisms reach back to the late 70's and early 80's of the 20<sup>th</sup> century (e.g., *Dodge*, 1977, *Whitten et al.*, 1980, *Atkinson et al.*, 1982). These early schemes were very simplified descriptions using condensed reaction mechanisms with only a few tens of species and typically less than 100 reactions. Three different condensation techniques have been developed (*Stockwell et al.*, 1990):

- i) surrogate species
- ii) lumped structure
- iii) lumped molecule

**Surrogate species** are used in the first approach as a representative for a whole compound class. *Dodge* (1977) presented a mechanism using propylene and n-butane as surrogate species to derive ozone-precursor relationships and find a control strategy for urban ozone reduction, which was a primary research topic at that time and is still an issue nowadays, especially in conurbations of developing countries.

**The lumped structure technique** was used in the carbon bond mechanism (CBM) introduced by *Whitten et al.* (1980). In the carbon bond mechanism, the same kinetics are assigned to carbon atoms with similar bondings regardless of the molecule they belong to. *Whitten et al.* (1980) define four carbon classes: paraffins (*PAR*), fast or relatively reactive double bonds (*OLE*), slowly reacting double bonds (*ARO*), and carbonyl groups (*CAR*). A molecule can contain carbon atoms of several types, for example, propylene has an *OLE* and a *PAR* group, benzaldehyde three *ARO* and a *CAR* group. The big advantage of this lumping technique is that carbon mass is preserved. Moreover, as individual carbon atoms are treated, no information about the molecular weight is needed. Furthermore, averaging of the rate constant is narrowed considering the individual groups rather than the whole molecule and no complex parameterisations for the generation of the rate constants are needed (*Whitten et al.*, 1980, *Stockwell*, 1986). The CBM has been used successfully in several studies over the past decades and has been updated several times. The most recent

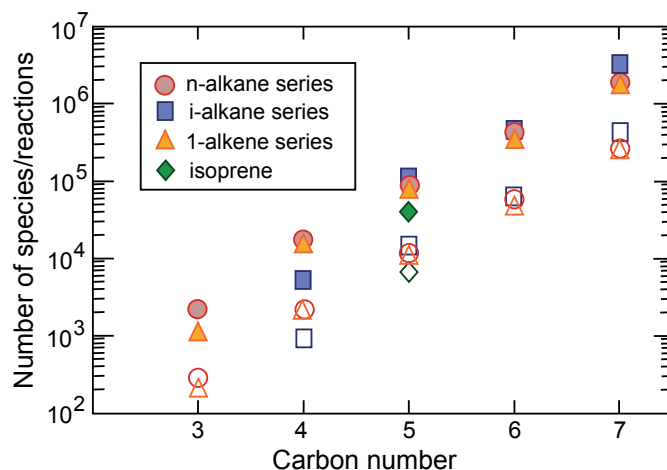


version, the CB05 and the CB05-TU with an updated toluene scheme, have been published by *Yarwood et al.* (2005) and *Whitten et al.* (2010), respectively.

**The lumped molecule technique** is the most widely used method for mechanism condensation. The kinetic schemes comprise compound classes rather than individual species. Compounds with a similar structure are lumped together and an overall average rate constant is synthesised. Several different mechanisms of different complexity have been developed in the past decades. One of the first mechanisms was the Regional Acid Deposition Model (RADM) by *Stockwell* (1986), which was updated several times since then (to RADM2, *Stockwell et al.*, 1990; RACM, *Stockwell et al.*, 1997; and RACM2, *Goliff et al.* (2013)). The latest version treats 17 stable and 4 intermediate inorganic species as well as 55 stable organic model species and 43 organic intermediates. Their degradation is described in overall 363 reactions. The kinetic data of the overall rate constant of a model species is synthesised by scaling the individual rate constants of the compounds of a model species according to the emission strength (see *Middleton et al.*, 1990). Several further mechanisms of this kind exist such as the Caltech Atmospheric Chemistry Mechanism (CACM) by *Griffin et al.* (2002) with 191 compounds and 361 reactions. The Statewide Air Pollution Research Center (SAPRC) chemical mechanism introduced by *Carter* (1990) is the most comprehensive mechanism using the *lumped molecule* technique. The latest published version in a peer-reviewed journal is the SAPRC-07 mechanism by *Carter* (2010a,b) with 222 organic and inorganic species and 640 reactions, which have been further condensed to 49 species and 44 reactions. A more recent update has been made available online, the SAPRC-11 (*Carter*, 2013, <http://www.cert.ucr.edu/~carter/SAPRC>).

**Near-explicit and explicit mechanisms** are the result of recent developments in numerical methods and computational processing leading to advanced models, which are able to treat larger chemical mechanisms. More powerful computers are able to treat larger mechanisms that comprise a high level of detail. A widely used mechanism is the Master Chemical Mechanism (MCM). It aims at a near-explicit description of the degradation of volatile organic compounds in the gas phase. Presented in 1997 by *Jenkin et al.*, it has been updated several times. The latest published version is the MCMv3.1 by *Saunders et al.* (2003) and *Jenkin et al.* (2003). More recently, an update to MCMv3.2 has become available online (<http://mcm.leeds.ac.uk/MCM/>). The latest version MCMv3.2 treats roughly 6700 species in 17 000 reactions. As it is impossible to assign experimentally determined kinetic data to such a large number of reactions, the majority of the data were estimated with structure-activity relationships (SARs).

However, there have also been attempts to condense the mechanism for higher scale modelling. The reduction was performed and evaluated in regard to the ozone formation potential of the VOC oxidation. Besides methane, 115 NMVOCs are considered in the Common Representative Intermediates (CRI) mechanism version 2 (see *Jenkin et al.*, 2008, *Watson et al.*, 2008). The condensed mechanism comprises 434 species and 1183 reactions. Subsequent lumping by redistribution of the mass emissions of the emitted VOCs led to 5



**Figure 2.2** Number of species (open symbols) and reactions (filled symbols) created by GECKO-A for different oxidation series using a 5% threshold for branching (reprinted from *Aumont et al.*, 2005).

reduced schemes with only 196 species and 555 reactions in the most condensed version CRIv2-R5 (see <http://mcm.leeds.ac.uk/CRI/project.htm>).

Automated self-generation methods were used for the development of the National Center for Atmospheric Research (NCAR) Master Mechanism (*Madronich*, 2006). The mechanism contains about 2000 species and 5000 reactions and was used to model the air pollution and ozone formation potential of Mexico City as an example of an important tropical megacity.

The largest mechanism described in literature using a similar self-generation method is the Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A; *Aumont et al.*, 2005). The generator was used to produce explicit mechanisms of organic compounds with up to 24 carbon atoms (*Aumont et al.*, 2012). However, a fully explicit mechanism for such large compounds would result in an enormous number of reaction as the number of reaction increase logarithmically with the number of carbon atoms present in the parent organic compound (see *Aumont et al.*, 2005 and Figure 2.2). The current limit for fully explicit mechanisms is about 2.5 million species and a 10-fold reactions (*Aumont et al.*, 2005), which means that compounds with up to 8 carbon atoms can be described explicitly (*Valorso et al.*, 2011). For the description of the degradation of larger compounds, mechanism reduction has to be performed or only a certain number of generations has to be considered in the mechanism and the oxidation scheme is not completely described to the end product  $\text{CO}_2$  (*Valorso et al.*, 2011, *Aumont et al.*, 2012).

### 2.2.2 Aqueous phase mechanisms

The acidification of rain fostered not only the development of gas phase mechanisms, but also of aqueous phase mechanisms. Early mechanisms date from the beginning of the 1980's (e.g., *Graedel and Weschler*, 1981, *Graedel and Goldberg*, 1983, *Chameides and Davis*,

1982, *Jacob and Hoffmann*, 1983). The early studies of, e.g., *Chameides and Davis* (1982), *Graedel and Goldberg* (1983), and *Schwartz* (1984) were complemented by studies from the *Hoffmann* group (*Jacob and Hoffmann*, 1983, *Hoffmann*, 1986) as well as *Jacob* (1986) and *Pandis and Seinfeld* (1989) throughout that decade. All of these studies demonstrated the importance of the aqueous phase and its influence on either the gas or the particle phase composition and chemistry (*Tilgner*, 2009). The complexity of atmospheric mechanisms and models at that time already allowed for detailed investigations of the tropospheric multiphase chemistry with a focus on acid formation through different reaction pathways as well as on the budget, cycling and interactions of tropospheric radicals and transition metal ions (TMIs) and their contributions to the tropospheric oxidation potential. The investigations included one of the most crucial parameters in the aqueous phase: the pH value as a measure of the acidity (*Tilgner*, 2009). *Jacob* (1986) studied in detail the pH effect on the radical budget, the speciation of different dissociation states of various inorganic and organic compounds and the sulphur(IV) oxidation pathways by different oxidants.

The above-mentioned mechanisms were applied in model studies with a very simplified microphysical and meteorological description although *Chameides and Davis* (1982) and *Jacob* (1986) already postulated a potential importance of certain microphysical parameters such as the cloud droplet surface or the liquid water content (LWC). Investigations of the latter parameter on the S(IV) to S(VI) conversion by *Pandis and Seinfeld* (1989) demonstrated the importance of the LWC in the tropospheric multiphase chemistry and led to an increasing consideration of more detailed microphysical schemes coupled to complex chemical mechanisms in atmospheric models.

In the 1990's, several studies focused on the role of clouds in regard to ozone concentration levels. In a box model study, *Lelieveld and Crutzen* (1991) found up to 50% reduced ozone production rates, when clouds were present. However, in follow-up studies by *Dentener and Crutzen* (1994) and *Matthijsen et al.* (1995), the effect was much smaller. In polluted urban regimes, *Walcek et al.* (1997) modelled up to 90% decreased ozone formation rates due to interactions with the high NO<sub>x</sub> (NO + NO<sub>2</sub>) and NMVOC concentration levels. However, if at all, only very few organic species with only one or two carbon atoms were treated in the aqueous phase mechanisms at that time.

At the beginning of the millennium, a series of more detailed multiphase mechanisms was presented. *Leriche et al.* (2000, 2001, 2003) studied the effects of clouds on acid formation, the partitioning of relevant compounds between the gas phase, aerosols, and cloud droplets, and interactions of the multiphase chemistry with the microphysics. They used a fully explicit aqueous phase mechanism for their studies with 42 compounds and 156 reactions based on the works of *Jacob* (1986) and the CAPRAM 2.3 mechanism by *Herrmann et al.* (2000), which was coupled to a gas phase mechanism with 48 species and 101 reactions (*Leriche et al.*, 2001).

*Deguillaume et al.* (2004) advanced the mechanism by *Leriche et al.* by including a detailed and explicit description of the chemistry of TMIs and aqueous phase photolysis. Overall, 91 aqueous phase TMI reactions and 5 equilibria of TMIs as well as 12 aqueous

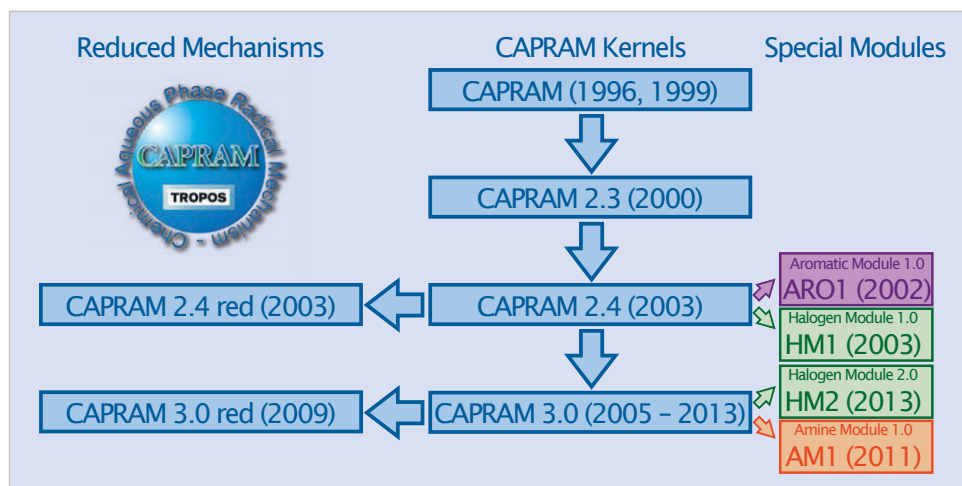
photolysis processes were added. Investigations focused on the role of transition metal ions in cloud chemistry, the  $\text{HO}_x/\text{H}_2\text{O}_2$  cycling, and influences on sulfur chemistry and the chemistry of organic compounds. The model was applied to the same scenarios as used in the CAPRAM 2.4 model studies and results of the two mechanisms were compared and discussed (Deguillaume *et al.*, 2004).

In the late 1990's, the development of the Chemical Aqueous Phase RAdical Mechanism (CAPRAM) series started. As the mechanism was used for this study, it will be explained in great detail in subsection 2.2.3.2. In the present section only a broad historical overview of the different development stages is provided, which is also illustrated in Figure 2.3.

A first version of CAPRAM was introduced by Herrmann *et al.* (1996, 1999). The mechanism focused on an explicit description of the aqueous phase chemistry of inorganic radicals with sulphur, nitrogen, TMIs, and organic compounds. The original mechanism was coupled to the gas phase mechanism RADM2 and, in the aqueous phase, consisted of 201 reactions with 28 acid-base equilibria and 23 uptake processes. The organic scheme treated compounds with up to two carbon atoms. In 2000, a new version with minor updates (CAPRAM 2.3) was presented by Herrmann *et al.*. These first model studies used a simple box model with permanent cloud conditions and a mono-disperse droplet spectrum.

Later mechanism development focused mainly on the extension of the organic scheme. In CAPRAM 2.4 introduced by Ervens *et al.* (2003),  $\text{C}_1$  and  $\text{C}_2$  chemistry was updated to a more explicit mechanism. Further updates concerned the TMI chemistry (Ervens *et al.*, 2003). Moreover, the gas phase mechanism was updated to RACM (Stockwell *et al.*, 1990) and a model scenario was introduced using non-permanent clouds assuming instantaneous cloud formation and evaporation in the study of Ervens *et al.* (2003).

In the latest update CAPRAM 3.0, organic chemistry has been extended to  $\text{C}_3$  and  $\text{C}_4$  compounds as well as a few surrogate compounds up to  $\text{C}_6$ . Aqueous phase chemistry of almost 400 species is described in 777 reactions in this version (Herrmann *et al.*, 2005, Tilgner and Herrmann, 2010). The model scenarios have been further refined using a parcel



**Figure 2.3** Overview of the version history of CAPRAM and CAPRAM special modules.

model where the adiabatic ascend and descend of the air parcel to form and evaporate a cloud can be adjusted to realistic time scales. Three different scenarios have been developed for urban, remote continental and remote marine conditions (*Tilgner, 2009, Tilgner and Herrmann, 2010*). Moreover, a refined microphysical scheme with a fine resolved particle and droplet spectrum has been used in the CAPRAM 3.0 studies (see, e.g., *Herrmann et al., 2005, Tilgner and Herrmann, 2010, Tilgner et al., 2013*).

In addition to the CAPRAM kernels, several special modules, describing the aqueous phase chemistry of specific subsystems have been developed. In 2002, an attempt was made to describe the aqueous phase chemistry of aromatic compounds. *Lahoutifard et al. (2002)* presented an aromatics module for CAPRAM 2.4 and results from investigations of the multiphase chemistry of NO<sub>2</sub> with aromatic compounds. A year later, a special module describing the aqueous phase chemistry of halogen compounds in CAPRAM 2.4 in more detail was presented by *Herrmann et al. (2003)*. It was later updated by *Bräuer et al. (2013)* to a comprehensive module with almost 600 processes. Updates of the halogen chemistry in the CAPRAM kernel led to the most recent version 3.0n. Box modelling studies focused on marine chemistry (*Bräuer et al., 2013*). Another special module aimed at the description of the aqueous phase degradation of organic amines including nitrosamines and amides. It was developed in 2011 as part of an industrial project to investigate environmental impacts of carbon capture attempts with organic amines to reduce CO<sub>2</sub> emissions (*Herrmann et al., 2011*).

The development of CAPRAM led to comprehensive mechanisms, which require very high computational costs. Therefore, reduced mechanisms have been developed from CAPRAM 2.4 on. In CAPRAM 2.4red, reduction led to a decrease of about 50% of the reactions and 20% of the species (*Ervens et al., 2003*). The reduced version of CAPRAM 3.0 treats 130 species in 198 reactions (*Deguillaume et al., 2009*). The reduced versions aim at 2D and 3D model applications. To date, only one study by *Ginnebaugh and Jacobson (2012)* uses the full explicit CAPRAM 3.0i mechanism coupled to the gas phase mechanism MCMv3.1 on a global scale.

A reproduction or prediction of measured concentration levels in local or global 3D-models is the focus of more recent modelling studies. Therefore, the chemical description in these complex model studies is limited due to the high computational costs of global or regional models. The organic schemes in these mechanisms focus mainly on secondary organic aerosol formation from precursor gas and aqueous phase organic compounds. The mechanisms usually treat the chemistry of only a few selected surrogate compounds. In the focus of these studies are isoprene and isoprene oxidation products as potential contributors to SOA production. Several mechanisms were proposed, e.g. by *Lim et al. (2005)* for isoprene and the oxidation products glycolaldehyde, glyoxal, and methylglyoxal; by *Carlton et al. (2006)* for the methylglyoxal oxidation or by *Ervens and Volkamer (2010)* for glyoxal.

Subsequent works of *Ervens et al.* led to more complex multiphase mechanisms, which treat the acid and diacid formation in the aqueous phase in addition to the multiphase degradation of isoprene and its oxidation products (*Ervens et al., 2004*) and the formation

of other high molecular weight compounds (*Ervens et al.*, 2008). The formation of the latter compounds is due to accretion reactions. These non-oxidative processes can significantly contribute to SOA mass and, hence, have been discussed intensively in the recent literature, e.g., by *Altieri et al.* (2008), *Ervens et al.* (2008), *Ervens and Volkamer* (2010), *Carlton et al.* (2010), *Lim et al.* (2010), *Tan et al.* (2012), *Renard et al.* (2013), and *He et al.* (2013).

However, as already mentioned, the chemistry in these mechanisms only is focused on a few surrogate compounds. Any further chemical description in these mechanisms is very limited and feedbacks to others subsystems are not considered. Moreover, *Tilgner and Herrmann* (2010) found that accretion reactions are likely to be insignificant under tropospheric conditions. Contributions were only seen under dark conditions in urban areas in this study.

A more comprehensive mechanism for the investigation of oligomer and organosulfate formation, GAMMA, was developed by *McNeill et al.* (2012). They performed detailed box modelling studies based on the CAPRAM model scenarios under urban and remote continental conditions.

### 2.2.3 The multiphase mechanism MCMv3.1-CAPRAM 3.0n

The present subsection describes the multiphase mechanism MCMv3.1-CAPRAM 3.0n. It was the starting point of the current mechanism development and was advanced during this dissertation by means of automated mechanism self-generation. The mechanism generator GECKO-A, which was extended for the generation of aqueous phase mechanisms in addition to the gas phase generation by *Aumont et al.* (2005), is described in section 2.5.

#### 2.2.3.1 MCMv3.1

As already mentioned earlier, the Master Chemical Mechanism (MCM) is a near-explicit gas phase mechanism, which treats reactions of several inorganic species including  $\text{NO}_x$ ,  $\text{HO}_x$ , ozone ( $\text{O}_3$ ), halogens (Cl and Br) and sulphur species as well as 135 emitted VOCs and more than 4500 intermediate organic species (*Saunders et al.*, 2003, *Jenkin et al.*, 2003, and the MCM website <http://mcm.leeds.ac.uk/MCM>). The treatment of the emitted VOCs includes 22 alkanes, 16 alkenes, 2 dienes, 2 monoterpenes, 1 alkyne, 18 alcohols and glycols, 6 aldehydes, 10 ketones, 3 carboxylic acids, 10 ethers and glycol ethers, 8 esters, 18 aromatic compounds, 15 chlorinated and 2 brominated VOCs, and 2 further aliphatic organic compounds. The overall mechanism treats 4734 organic and 23 inorganic reactive species in 13 567 reactions.

The construction of the mechanism relies heavily on estimated chemical and kinetic data. As such large near-explicit mechanisms can hardly be created manually, automated mechanism construction has been applied (see MCM website for further details). The original protocol was introduced by *Jenkin et al.* (1997). Updates of the latest peer-reviewed

version, MCMv3.1, can be found in *Saunders et al.* (2003), *Jenkin et al.* (2003), and on the MCM website. Reaction products and kinetic data are determined with structure-activity relationships (SARs). In brief, the protocol consists of the following 10 subsections (see also MCM website):

1.  $\cdot\text{OH}$  radical initiation reactions
2.  $\text{O}_3$  initiation reactions
3.  $\text{NO}_3$  radical initiation reactions
4. Initiation by photolysis
5. Reactions of organic radicals
6. Reactions of peroxy radical intermediates
7. Reactions of Criegee biradical intermediates
8. Reactions of alkoxy radical intermediates
9. Removal of chlorine/bromine atoms
10. Reactions of degradation products

Stable compounds are initially attacked by OH radicals and, where appropriate, also by  $\text{NO}_3$  radicals and ozone (1 – 3). For several compound classes, photolysis is important. These compounds are identified in step 4 and photolysis rates are assigned according to the results of the respective SAR. The fate of the multitude of highly reactive intermediate organic compounds is determined in steps 5 – 10.

A fully explicit representation of the organic chemistry in atmospheric mechanisms would lead to an unmanageable large number of species and reactions. Therefore, some rules for mechanism condensation have to be defined in the protocol prior to the generation:

- i) Removal of minor reaction channels
- ii) Parameterisation of cross-reactions of peroxy radicals
- iii) Simplifications of the chemistry of several reaction products, especially from minor reaction pathways

In the following, the parameterisation for the cross-reactions of peroxy radicals is explained. This simplification will lead to an enormous reduction of the final mechanism. In the Master Chemical Mechanism, the concentrations of all peroxy radicals are summed up to an overall concentration. In a fully explicit mechanism, a given peroxy radical had to react with all other peroxy radicals according to Reaction R4. In a simplified description, R4 can be written as:



where  $\text{RO}_2^\bullet$  represents a peroxy radical and  $\text{R}'\text{O}_2^\bullet$  any different or the same peroxy radical. Summing up the concentrations of all peroxy radicals allows the application of pseudo

first-order kinetics, where

$$k_{1st,pseudo} = k_{2nd} \cdot [\Sigma RO_2^\bullet] \quad (2.4)$$

R9 can now be rewritten as:



This way, only one reaction is needed for the representation of all cross reactions of a given peroxy radical. Thus, many thousand reactions can be easily saved in the mechanism.

For the implementation in the model framework of the current study, further mechanism reduction has been performed. In the MCM, reactions with several pathways are written as distinct reactions. To reduce the computational expenses, stoichiometric factors for the different branches have been introduced and the distinct reactions were combined in an overall reaction in previous CAPRAM mechanism developments at the TROPOS. This final reduction step reduced the number of reactions to 11 381.

### 2.2.3.2 CAPRAM 3.0n

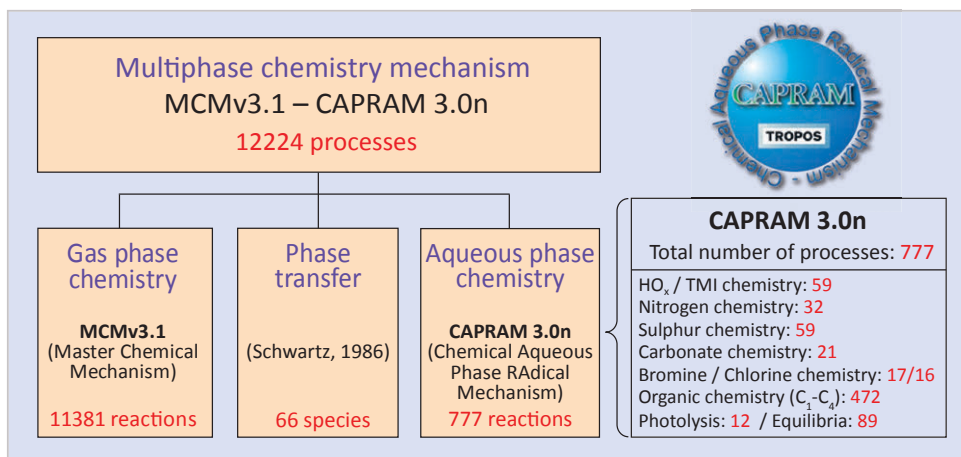
CAPRAM is a detailed aqueous phase chemical mechanism treating the degradation of organic compounds with up to 6 carbon atoms by the most important inorganic radicals along with a detailed HO<sub>x</sub>, NO<sub>x</sub>, sulphur, carbonate, halogen, and TMI chemistry (e.g., *Herrmann et al.*, 2005). A broad overview over the different versions and special modules was given in subsection 2.2.2. This section will provide detailed information about the latest CAPRAM version 3.0n (*Tilgner and Herrmann*, 2010, *Bräuer et al.*, 2013). As this work focuses on the extension of the organic chemistry in CAPRAM 3.0n, a description of the special modules is beyond the scope of this dissertation and the reader is referred to the literature given in subsection 2.2.2.

The latest CAPRAM version treats the aqueous phase chemistry of almost 400 compounds in 671 non-reversible reactions of which 159 are described as temperature dependent. Furthermore, 91 equilibria and 15 photolysis reactions are treated. Due to recent attempts to couple CAPRAM 3.0n to the near-explicit gas phase mechanism MCMv3.1, the number of phase transfers has increased from 52 in the latest published version by *Tilgner and Herrmann* (2010) and *Bräuer et al.* (2013) to 66. All processes implemented in the most recent CAPRAM version are schematically depicted in Figure 2.4.

### Inorganic chemistry

The description of the inorganic chemistry in CAPRAM 3.0n includes (i) an explicit oxidation scheme for the sulphur(IV) to sulphur(VI) conversion by inorganic radical oxidants, ozone, peroxides, and iron(III), (ii) radical reactions of OH, HO<sub>2</sub>/O<sub>2</sub><sup>-</sup>, NO<sub>3</sub>, SO<sub>x</sub><sup>-</sup>, Cl<sub>2</sub><sup>-</sup>, Br<sub>2</sub><sup>-</sup>, and CO<sub>3</sub><sup>-</sup>, and (iii) chemical conversions of the transition metal ions iron (Fe), manganese (Mn), and copper (Cu).





**Figure 2.4** Schematic representation of the multiphase chemical mechanism MCMv3.1-CAPRAM 3.0n.

The aqueous HO<sub>x</sub> (OH + HO<sub>2</sub>/O<sub>2</sub><sup>-</sup>) chemistry is linked to almost all subsystems in the multiphase chemistry mechanism MCMv3.1-CAPRAM 3.0n. Direct uptake of these radicals causes interactions with the gas phase, photochemistry produces HO<sub>x</sub> radicals, and chemical conversions and interactions with other reaction cycles are both a sink and a source for OH and HO<sub>2</sub>/O<sub>2</sub><sup>-</sup> radicals. Close interactions with the TMI chemistry have been implemented in the mechanism as described by *Graedel et al.* (1986) and *Weschler et al.* (1986). The redox reactions of Fe(II)/Fe(III) and Cu(I)/Cu(II) cause quick conversions between the species OH, HO<sub>2</sub>/O<sub>2</sub><sup>-</sup>, and H<sub>2</sub>O<sub>2</sub>. Moreover, reactions with TMIs are one of the most important in-situ sources for aqueous hydroxyl radicals in the so-called Fenton reaction as described by *Zepp et al.* (1992). Further important aqueous OH sources besides the direct uptake from the gas phase are the photolysis of H<sub>2</sub>O<sub>2</sub>, iron-hydroxy complexes and NO<sub>3</sub><sup>-</sup>, whose photolysis leads to OH radicals in subsequent reactions (see also *Benkelberg et al.*, 1991, *Sedlak and Hoigné*, 1993, *Benkelberg and Warneck*, 1995). HO<sub>2</sub>/O<sub>2</sub><sup>-</sup> are produced in the aqueous phase by reactions of oxidised TMIs with H<sub>2</sub>O<sub>2</sub> and the photolysis of Fe(III) complexes with organic ligands (*Zuo and Hoigné*, 1992, *Faust and Zepp*, 1993). For a complete overview of the 59 processes of HO<sub>x</sub> and TMI chemistry implemented in CAPRAM 3.0n, the reader is referred to Table G.4/G.5 in Appendix G.2 and the CAPRAM website (<http://projects.tropos.de/capram>), where, among additional information, the whole mechanism is available for download.

More than 30 reactions in CAPRAM 3.0n concern nitrogen species. NO<sub>x</sub> (NO + NO<sub>2</sub>) and NO<sub>y</sub> (NO + NO<sub>2</sub> + NO<sub>3</sub> + HONO + HNO<sub>3</sub> + HNO<sub>4</sub>) are especially important in urban areas. NO<sub>3</sub> and NO<sub>x</sub> are important tropospheric oxidants. However, the importance of the nitrate (NO<sub>3</sub>) radical is mainly restricted to night-time as, during the day, it is rapidly photolysed. Yet, not only the radical budget and thus the self-cleaning capacity of the troposphere is influenced by nitrogen compounds, but also the non-radical oxidant budgets. Among the most important interactions are reactions of nitrogen containing radicals that lead to ozone formation and destruction, which is especially important for environmental and health concerns. Another important nitrogen compound is nitrous acid (HONO). Its photolysis is a direct source of OH and NO radicals. *Ren et al.* (2005), *George et al.* (2005),

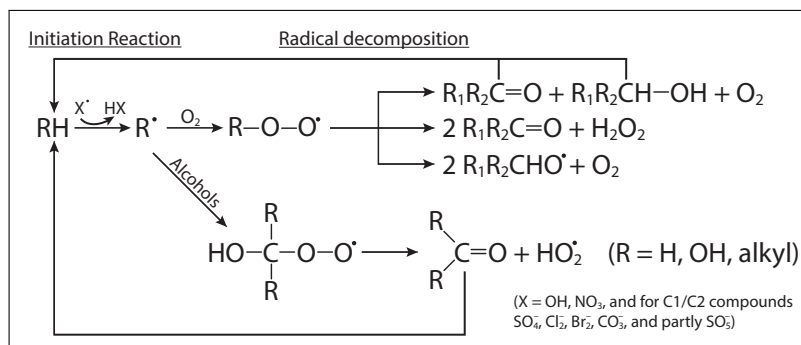
and *Stemmler et al.* (2006) have shown the potential of the HONO photolysis as OH source, which can even exceed the OH production by ozone photolysis.

A large number of reactions in CAPRAM 3.0n concern sulphur chemistry. 59 reactions describe the sulphur(IV) to sulphur(VI) conversion. *Warneck* (1999) and *Berglen et al.* (2004) have shown that about 80% of the S(IV) oxidation occurs in the aqueous phase. The predominant sulphur oxidants are ozone and hydroperoxides including hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), organic peroxides such as methyl hydroperoxide ( $\text{CH}_3\text{OOH}$ ), and organic peracids such as peroxyacetic acid (PAA,  $\text{CH}_3\text{C}(=\text{O})\text{OOH}$ ). All reactions show a strong pH dependency. The oxidation of sulphur(IV) by ozone increases with decreasing acidity and dominates in alkaline solutions. The pH dependency can be explained by different reactivities of the different dissociated forms of sulphurous acid. The sulphite dianion ( $\text{SO}_3^{2-}$ ), which is the dominant form of sulphurous acid in alkaline solutions, reacts  $10^4$  times faster than hydrogen sulphite ( $\text{HSO}_3^-$ ) favouring more acidic solutions. At lower pH values, oxidation of S(IV) by  $\text{H}_2\text{O}_2$  and other hydroperoxides dominates. The strong pH dependency of these reactions is realised in CAPRAM 3.0n using third-order reactions according to the experimental studies of *Lind et al.* (1987). *Amels et al.* (1996) have shown that the rate constants of the S(IV) oxidation by  $\text{HNO}_4$  are comparable to that by  $\text{H}_2\text{O}_2$ , this oxidation pathway can play an important role in urban polluted areas. Therefore, it was implemented in the CAPRAM mechanism. Moreover, several multi-step oxidation pathway initialised by aqueous radicals, namely OH,  $\text{NO}_3$ ,  $\text{SO}_4^-$ ,  $\text{SO}_5^-$ ,  $\text{Cl}_2^-$ ,  $\text{Br}_2^-$ , and  $\text{CO}_3^-$ , leading to S(VI) are implemented in CAPRAM 3.0n.

CAPRAM 3.0n comprises a basic description of the aqueous phase halogen chemistry in 33 reactions. The chemistry includes interactions of chloride, bromide, chlorine and bromine atoms and the radical anions  $\text{Cl}_2^-$  and  $\text{Br}_2^-$  with other inorganic species such as the radicals OH,  $\text{NO}_3$ ,  $\text{SO}_4^-$ , or  $\text{HO}_2$  as well as the transition metal ions manganese and iron. Moreover, the oxidation of several organic compounds by  $\text{Cl}_2^-$  and  $\text{Br}_2^-$  is described explicitly in CAPRAM 3.0n.

## Organic chemistry

In contrast to most other aqueous phase mechanisms, CAPRAM 3.0n includes a detailed description of the degradation of organic compounds. Up to two carbon atoms, the description comprises a high level of detail and stable organic compounds such as alcohols, aldehydes, carboxylic acids and bases, and the difunctional compounds glyoxal, glyoxylic acid, and oxalic acid are oxidised by a great variety of different radical oxidants, namely OH,  $\text{NO}_3$ ,  $\text{SO}_4^-$ ,  $\text{Cl}_2^-$ ,  $\text{Br}_2^-$ ,  $\text{CO}_3^-$ , and partly  $\text{SO}_5^-$ . For  $\text{C}_3$  and  $\text{C}_4$  compounds, only the oxidation by OH and  $\text{NO}_3$  radicals is implemented due to missing kinetic data. Moreover, the oxidation of a few sample compounds with up to six carbon atoms including a heterocyclic compound with evaluated kinetic data from the European Multiphase chemistry of Oxygenated Species in the Troposphere (MOST) project (*George et al.*, 2005) are implemented in CAPRAM 3.0n. In principle, the oxidation of the organic compounds in CAPRAM 3.0n follows the same rules as demonstrated in Figure 2.5.



**Figure 2.5** Principles of the oxidation scheme of organic compounds in CAPRAM 3.0n (reprinted and modified after *Tilgner*, 2009).

The oxidation is initialised by H-atom abstraction of stable organic compounds by the radicals OH and NO<sub>3</sub> as well as SO<sub>4</sub><sup>-</sup>, Cl<sub>2</sub><sup>-</sup>, Br<sub>2</sub><sup>-</sup>, CO<sub>3</sub><sup>-</sup> for C<sub>1</sub> and C<sub>2</sub> compounds. Additional oxidation by the peroxomonosulphate radical SO<sub>5</sub><sup>-</sup> is considered for glyoxal and oxalic acid according to the work of *Herrmann et al.* (2000). So far, no branching ratios are considered in CAPRAM 3.0n and only the weakest bound H-atom is abstracted. The oxalate dianion forms an exception as no abstractable H-atoms are available. This compound is oxidised by electron transfer reaction (ETR) rather than H-atom abstraction. For such a large mechanism as CAPRAM 3.0n, kinetic data is not entirely available and has to be estimated for several species. The estimation is based either on the reactivities of species with similar structures or on Evans-Polanyi-type correlations as described in detail in subsection 2.4.2 or in literature (see, e.g., *Herrmann and Zellner*, 1998, *Monod et al.*, 2005, *Herrmann et al.*, 2010).

The alkyl radicals formed in the H-atom abstraction reactions react immediately with dissolved oxygen to form peroxy radicals. The fate of the peroxy radicals follows the suggestions of *von Sonntag* (1987) and *von Sonntag et al.* (1997) (see also Figure 2.5). If a hydroxyl group is in α-position to the peroxy functional group, the peroxy radical decomposes to a carbonyl compound and an HO<sub>2</sub> radical. Otherwise, peroxy radicals will recombine forming either two carbonyl compounds and hydrogen peroxide, a carbonyl and an alcohol plus O<sub>2</sub> (non-radical pathways), or two alkoxy radicals and oxygen (radical pathway). More details can be found in the dissertation by *Tilgner* (2009) and the respective publications of the different CAPRAM versions (*Herrmann et al.*, 2005, *Tilgner and Herrmann*, 2010).

## 2.3 Multiphase chemistry box models

### 2.3.1 Overview

The processing of complex multiphase chemistry mechanisms such as MCMv3.1-CAPRAM 3.0n can be achieved with box models. Box models form the basis of detailed fundamental studies. They can be used to investigate chemical processes at a molecular level under

predefined conditions. Therefore, no interactions with other microphysical parameters disturb numerical experiments unless the investigation of their influence is desired.

Two basic types of box models exist – *Eulerian* and *Lagrangian* models. In a *Eulerian* model, a cell in a fixed geographic region is defined. The walls of the cell are permeable, so that there is typically an inflow at one side of the box and an outflow at the opposite side. Mixing with the free troposphere or stratosphere can occur at the upper wall of the box and emissions and depositions cause exchanges of molecules at the lower boundary of the box. Microphysical parameters such as temperature, pressure, radiation, and liquid water content can be adjusted to simulate different conditions.

*Lagrangian* models use a box with a defined volume, where no exchange with the ambient air is allowed except for emissions and depositions at the lower boundary and in some models intrusions from the free troposphere at the upper boundary. Therefore, the box acts as a large simulated closed reaction system, where the microphysical parameters can be adjusted. Hence, it is possible to simulate the movement of the box along a predefined trajectory by changing the ambient microphysical parameters. More information about Eulerian and Lagrangian type models can be found in the publication of *Jacob* (1999). The book gives furthermore an introduction to the formulation of the prognostic equations.

### 2.3.2 The model SPACCIM

#### 2.3.2.1 Overview

The SPectral Aerosol Cloud Chemistry Interaction Model (SPACCIM) is a Lagrangian 0-dimensional box model, which comprises both, a detailed microphysical and chemical scheme. Both separate processes are described for a highly size-resolved particle and droplet spectrum (*Wolke et al.*, 2005, *Tilgner*, 2009). The coupling is performed for a fixed coupling time step allowing interactions of the microphysical parameters with the chemical composition and conversions.

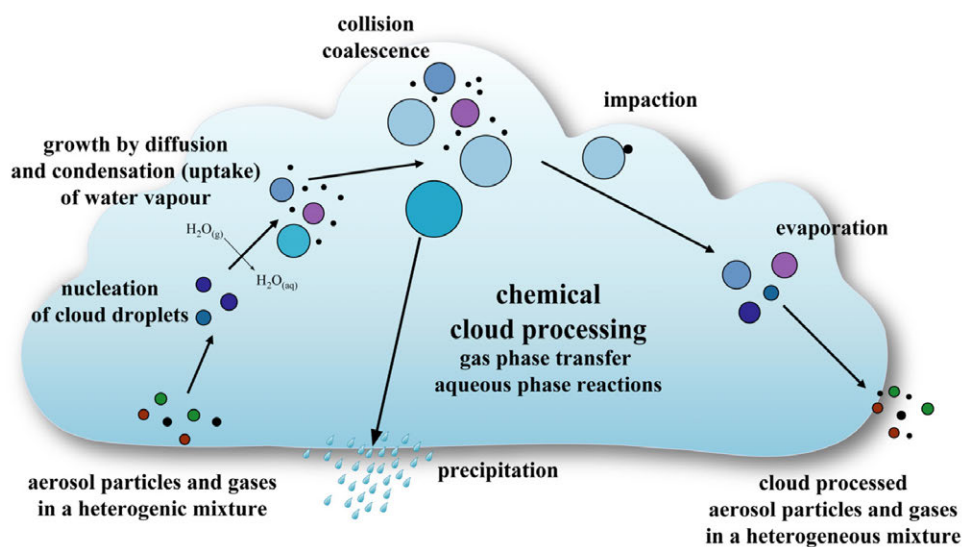
In the parcel model SPACCIM, a box is moved along a predefined trajectory. The microphysical scheme includes the description of all relevant processes during the dry and wet adiabatic ascent or descent of the air parcel. Therefore, it is possible to study chemical and microphysical processes under cloud formation and evaporation conditions with SPACCIM. The ascending and descending times can be adjusted to simulate realistic conditions. A detailed description of the model can be found in the publications of *Wolke et al.* (2005) and *Tilgner* (2009). The described features of the model made it an excellent choice for the current study.

#### 2.3.2.2 The microphysical scheme

The microphysical model implemented in SPACCIM is based on the works of *Simmel et al.* (2002, 2005) and *Simmel and Wurzler* (2006). Here, only a short overview of the

microphysical model is given. Figure 2.6 shows the most important microphysical and chemical processes implemented in SPACCIM concerning the multiphase chemistry in a cloud. A detailed description of the microphysical scheme can be found in the above-mentioned publications as well as in the dissertation of *Tilgner* (2009).

Cloud formation and evaporation is realised in SPACCIM by adiabatic cooling and heating through lifting or descending an air parcel. CCN are activated to cloud droplets by condensation of water vapour on the aerosol surface due to the supersaturations of typically less than 1%. The condensation and droplet growth is described with the *Köhler* theory (see, e.g., *Pruppacher and Klett*, 1997, *Jacobson*, 2005). Particles and cloud droplets are represented as fine-resolved spectrum in SPACCIM. For the current study, the *moving bin* approach has been used. The initial aerosol particle population is classified in regard to the non-water particle mass independently from the relative humidity. The initial spectrum is divided into 66 discrete size bins or classes. The individual size bins will grow or shrink according to the liquid water content available in their droplet class. There is no mass exchange between the individual size bins. The mean radii of each size class will increase or decrease individually. In each size bin, the prognostic variables are the water mass, the total and soluble particulate mass and the particle number concentration. Moreover, SPACCIM is able to simulate further microphysical processes such as impaction of aerosol particles, collision coalescence of cloud droplets, entrainment and detrainment, or wet deposition as described by *Simmel et al.* (2005). However, the complexity of the current multiphase chemical scheme demands such high computational costs that these processes are not considered in the current model study. Moreover, only a mono-disperse aerosol class with a mean radius of  $0.2\text{ }\mu\text{m}$  and a particle density of  $1770\text{ kg m}^{-3}$  (for ammonium sulfate) has been used for the current study. The particle number concentration has been set to  $100\text{ cm}^{-3}$  for remote continental conditions and to  $300\text{ cm}^{-3}$  under urban conditions. Feedbacks of the chemistry on the microphysics and vice versa have been shut off to study the chemical effects only and to further reduce the computational costs.



**Figure 2.6** Overview of the most important microphysical processes along with the multiphase chemical processes implemented in SPACCIM (taken from *Tilgner*, 2009).

### 2.3.2.3 The chemical and phase transfer scheme

In SPACCIM, the multiphase chemistry mechanism MCMv3.1-CAPRAM 3.0n as described in subsection 2.2.3 and Figure 2.4, page 22, is processed. The concentrations of the individual compounds are determined separately for every particle/droplet class in the moving bin approach. The number of species can vary between the aqueous and the gas phase. In each time step, the chemical source and loss fluxes are determined and the corresponding new concentrations according to these fluxes are calculated for every compound. Photolysis rates are calculated and the concentrations of the corresponding species are adjusted. No correction factors for shading or enhanced radiation effects of clouds are applied during cloud periods. As there are regions at the edge and the top of a cloud with intensified solar radiation and regions with a decreased supply of solar radiation inside and below a cloud and the exact position of the air parcel during cloud periods is not specified in the model scenarios, no correction factors have been applied for the photolysis rates during that time in SPACCIM.

Phase transfer between the gas and the aqueous phase is realised in SPACCIM following the resistance model by *Schwartz* (1986) (see *Wolke et al.*, 2005). In this approach, a gas phase compound has to overcome several resistances to enter the aqueous phase as expressed in Figure 2.1, page 10. At first, the compound has to diffuse to the particle or droplet surface expressed by the resistance  $\frac{1}{\gamma_{diff}}$ . This resistance depends on the gas phase diffusion coefficient ( $D_g$ ). When the droplet's surface is reached, only a certain number of molecules actually enter the bulk of the droplet passing the phase interface, the rest is reflected back to the gas phase. This process is expressed as a function of the mass accommodation coefficient ( $\alpha$ ). In the bulk of the droplet, aqueous phase diffusion, solution effects ( $\gamma_{sol}$  in Figure 2.1 and Equation 2.5) and chemistry ( $\gamma_{reac}$  in Figure 2.1 and Equation 2.5) determine the uptake of further molecules of that compound. The overall resistance  $\frac{1}{\gamma}$  can be expressed as:

$$\frac{1}{\gamma} = \frac{1}{\gamma_{diff}} + \frac{1}{\alpha} + \frac{1}{\gamma_{sol} + \gamma_{reac}} \quad (2.5)$$

The transition at the phase interface is considered as a dynamic equilibrium, with the Henry's Law constant (HLC), also denoted as  $K_H$ , as equilibrium's constant:

$$K_H = \frac{k_{g \rightarrow aq}}{k_{aq \rightarrow g}} \quad (2.6)$$

The mass fluxes of the phase transfer process ( $k_{g \rightarrow aq}/k_{aq \rightarrow g}$ ) can be described with the mass transfer function ( $k_T$ ). For a species entering the aqueous phase from the gas phase, the mass transfer function is given by Equation 2.7. For the release of an aqueous species to the gas phase,  $k_T$  has to be divided by the Henry's Law constant  $K_H$  in Equation 2.7 (see also *Wolke et al.*, 2005):

$$k_T = \left( \frac{r^2}{3D_g} + \frac{4r}{3\bar{v}\alpha} \right)^{-1} \quad (2.7)$$

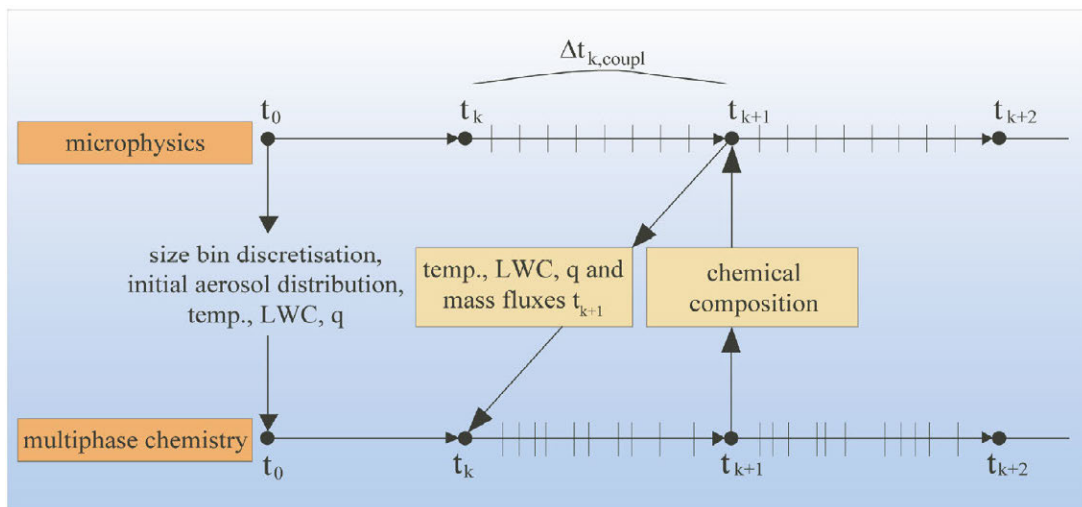
$k_T$  ..... Mass transfer function in  $\text{s}^{-1}$   
 $r$  ..... Particle or droplet radius in m  
 $D_g$  ..... Gas phase diffusion coefficient in  $\text{m}^2 \text{s}^{-1}$   
 $\bar{v}$  ..... Mean molecular speed (in  $\text{m s}^{-1}$ ) expressed as  $\bar{v} = \sqrt{\frac{8RT}{\pi M}}$ ;  
 $M$  = molar mass,  $R$  = universal gas constant,  $T$  = temperature  
 $\alpha$  ..... Mass accommodation coefficient (unitless)

The first term in Equation 2.7 represents the diffusion resistance ( $\frac{1}{\gamma_{diff}}$ ), the second term the mass accommodation ( $\frac{1}{\alpha}$ ). The other resistances for the solubility and aqueous phase reactions are determined by the chemistry model.

### 2.3.2.4 The coupling scheme

Microphysical and chemical processes occur simultaneously in the atmosphere and interact with each other. Microphysical parameters such as the liquid water content or the particle/droplet surface determine the uptake process and therefore the chemical composition and multiphase chemistry. In return, multiphase chemical production and decomposition influence microphysical parameters such as the surface tension, which in turn affects uptake and CCN activation to cloud droplets due to a decrease in vapour pressure compared to pure water.

To integrate both separate processes, the microphysics and the chemistry, into the SPACCIM model framework, but allow for interactions, a detailed coupling scheme has been developed (see *Wolke et al.*, 2005). The scheme enables the processing of gases, deliquescent particles and cloud droplets under non-cloud and in-cloud conditions as well as under cloud formation and evaporation conditions for a highly size-resolved particle and droplet spectrum. The approach uses the *operator splitting technique* and is illustrated in Figure 2.7. A strict separation of all microphysical and chemical variables is necessary, when using this technique. The parameters of both, the microphysics and the chemistry



**Figure 2.7** Coupling scheme of the microphysics and chemistry module in SPACCIM (graphic taken from *Tilgner*, 2009 after *Wolke et al.*, 2005).

module, are determined separately using their individual and, depending on the model conditions, variable time steps in the integration schemes of both models. Information is exchanged for a fixed coupling time step, which was set to 5 s in the current model studies. This technique allows the continuous interaction of distinct processes, which demand different numerical costs due to different complexities.

The coupling is realised in SPACCIM by first integrating all microphysical parameters, which are then sent to the chemistry model. Thereafter, the chemical fluxes and concentrations are determined in the chemistry model using the information from the microphysics module for this coupling time step. Afterwards, the chemical information is returned to the microphysics module, which uses the data for the calculation of the next time step.

## 2.4 Prediction of aqueous phase kinetic data

The complex multiphase chemical mechanisms introduced in section 2.2 along with the incapability to determine all necessary kinetic data to describe the chemical processes quantitatively make estimations necessary. The following section introduces the most important approaches to fill the gaps of missing experimental aqueous phase kinetic data in current oxidation mechanisms.

### 2.4.1 Simple correlations

A very basic approach for the determination of missing kinetic data are conclusions drawn by analogy to other compounds or subsystems. Assumptions that certain compound classes or subsystems have the same or similar reactivities lead to regressions, which allow the estimation of missing rate data. Three examples are given below.

#### Gas-aqueous phase correlations

Gas phase kinetics have been determined experimentally for several decades by now and large compilations and evaluations exist in literature, e.g., from the panels of the National Aeronautics and Space Administration's (NASA) Jet Propulsion Laboratory (JPL) (*Sander et al.*, 2011) and the International Union of Pure and Applied Chemistry (IUPAC) (*Atkinson et al.*, 2006). The gas phase kinetic database exceeds that of the aqueous phase by far, which becomes obvious by comparing gas phase databases in reviews by, e.g., *Atkinson et al.* (2000), *Atkinson and Arey* (2003), *Atkinson et al.* (2006), and *Sander et al.* (2011) with databases in aqueous phase kinetic reviews, e.g., by *Herrmann* (2003), *Herrmann et al.* (2010), and the National Institute of Standards and Technology (NIST) database (*Ross et al.*, 1998). Therefore, attempts have been made to correlate the gas and the aqueous phase reactivities for a 'first guess' approximation of missing aqueous phase rate constants. As the results in section 3.2 show, the regression of gas and aqueous phase



data lead to correlations of moderate quality with correlation coefficients  $R^2$  typically between 0.4 and 0.6. However, an intersecting dataset large enough to derive a correlation is only found for reactions of organic compounds with the hydroxyl radicals. Moreover, the prediction methods depend on available experimental data in the gas phase. If these are obsolete, the method fails to extend the predictions of the known data to unknown rate constants.

### Homologous series of compound classes

Another correlation uses the fact that different compounds with a similar structure behave in a comparable manner. Species belonging to a certain compound class will often lead to products, which belong again to another specific compound class, which makes a prediction of reaction products possible. In the approach using a homologous series of compounds belonging to a given compound class, the attempt is made to predict the reaction rate constants as well. For organic compounds, the most noticeable difference of species of the same compound class is the number of carbon atoms that the individual compound bears. Measurements exist mainly for low molecular weight compounds. The prediction method tries to correlate the reaction rates of these compounds to the number of carbon atoms borne by these species. The resulting linear regression allows the extension of the kinetic data to compounds with a higher molecular weight. As shown in section 3.3, the method works astonishingly well with correlation coefficients  $R^2$  of up to 0.99, however, only for a very restricted number of compound classes with a strictly defined structure.

### Radical reactivity comparisons

The last simple correlation described in this context does not focus on the compound to be oxidised but on the oxidant. In general, most measurements exist for reactions with the hydroxyl radical. Kinetic data of reactions with other oxidants such as  $\text{NO}_3$ ,  $\text{SO}_x^-$  or  $\text{Cl}_2^-/\text{Br}_2^-$  are sparse. Therefore, attempts have been made, where the data of the various oxidants is pooled and correlations to the OH reactivity are determined. Thus, the limited databases of still rather unexplored radical oxidants can be extended by scaling it to the already quite comprehensive dataset of OH radical reactivities. It is noted, however, that the prediction method relies on measured aqueous phase OH radical kinetic data.

#### 2.4.2 Evans-Polanyi-correlations

The current and the next subsection will introduce more sophisticated estimation methods to derive the second order rate constants of organic compounds with inorganic radicals. The correlations are advanced to the use of information of increments of the molecule only, instead of information about the molecule as a whole, which gives refined and more precise correlations.

## Derivation of activation energies and rate constants

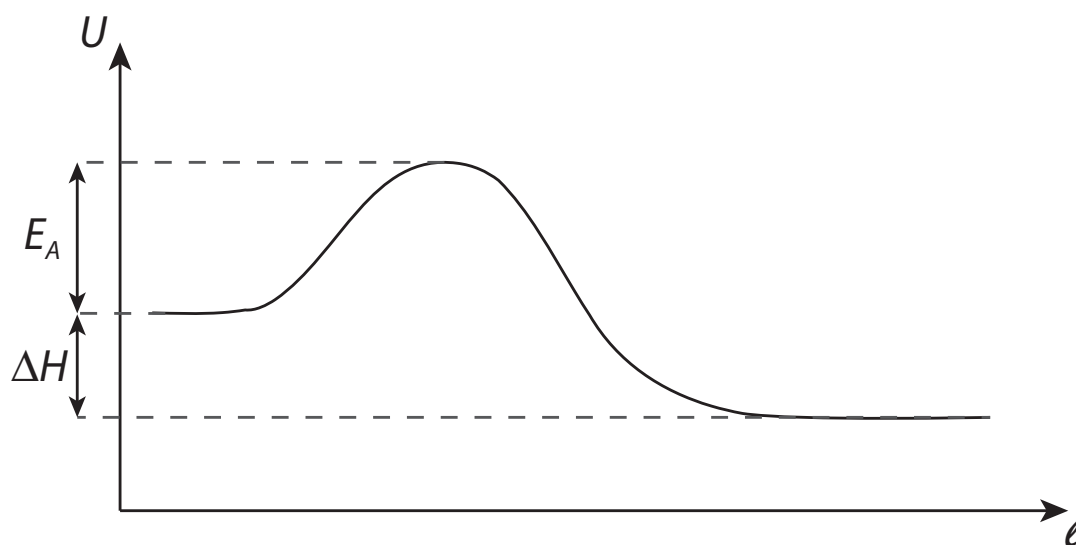
To derive more sophisticated estimation methods for the prediction of kinetic data, it is necessary to understand the nature of a chemical reaction. Already in the 1930's, *Evans and Polanyi* (1938) described the '*inertia and driving force of chemical reactions*.' They described the nature of a chemical reaction as the rearrangement of atoms in molecules, where new molecules are formed at the expenditure of old ones. In a chemical reaction, bonds between atoms or molecular groups are broken and new bonds are formed. The strength of these bonds can be measured with the bond dissociation enthalpy (*BDE*; see Glossary and below for more explanation). The inertia in a chemical reaction is the necessity of bond breaking and the repulsion of different atoms and molecules, while the driving force is the rearrangement and new formation of bonds in order to minimise the energy of the chemical system (*Evans and Polanyi*, 1938).

A reaction can be described as a function of potential energy  $U$  along a reaction path  $\ell$  (see Figure 2.8 and *Evans*, 1938). To pass from the initial state to the final state having the least possible potential energy, the system has to overcome the activation energy  $E_A$ . The reaction path  $\ell$  always chooses the way with the least expenditure of energy. During a reaction, the reaction enthalpy  $\Delta H$  is produced as the potential energy is transformed into heat (*Evans*, 1938).

*Evans and Polanyi* (1938) have shown that there is a linear relationship between the bond dissociation enthalpy (*BDE*) and the activation energy ( $E_A$ ):

$$E_A = a' + b' \cdot BDE(\text{C-H}) \quad (2.8)$$

where  $a'$  and  $b'$  are coefficients of the linear regression and C-H symbolizes the bond between the C and the H atom. Thus, the strength of a chemical bond can be viewed as a



**Figure 2.8** Progress of the potential energy  $U$  during a chemical reaction along a reaction coordinate  $\ell$  after *Evans* (1938).

measure of the heat produced in a reaction. Moreover, the activation energy is a measure for the temperature dependency of a reaction expressed in the Arrhenius equation:

$$k = A \cdot \exp \left\{ -\frac{E_A}{RT} \right\} \quad (2.9)$$

with  $k$  being the reaction rate constant,  $A$  the pre-exponential factor,  $R$  the universal gas constant, and  $T$  the temperature. While the Evans-Polanyi correlation has initially been developed for the gas phase, it has been shown in various studies, e.g. by *Hoffmann et al.* (2009), that it can also be applied to the aqueous phase. Combining equations 2.8 and 2.9 results in a method to estimate the reaction rate constants  $k$  for H-abstraction reactions (*Herrmann et al.*, 2010, *Hoffmann et al.*, 2009, *Monod et al.*, 2005):

$$\log \left( \frac{k}{n_H} \right) = \log k_H = \left( \log A' - \frac{a''}{RT} \right) - \frac{b''}{RT} BDE(\text{C-H}) = a - b \cdot BDE(\text{C-H}) \quad (2.10)$$

where  $A' = \frac{A}{n_H}$ ,  $a'' = \frac{a'}{\ln 10}$ ,  $b'' = \frac{b'}{\ln 10}$ , and  $n_H$  stands for the number of weakest bound H-atoms in a molecule. It should be noted that only the main channel of a chemical reaction is considered with Evans-Polanyi-type correlations as only the weakest bound H-atoms are considered in the correlation of the  $BDE$  to the reaction rate constants. Yet, the main attack of radicals in an H-abstraction reaction is expected at the weakest bound H-atom. Therefore, the overall second order rate constant is scaled by the number of H-atoms with the weakest bond dissociation energy ( $n_H$ ). For large molecules, however, there might be a significant fraction of H-atoms abstracted besides the weakest bound ones (*Hoffmann et al.*, 2009). Therefore, the method is likely to underestimate rate constants for these species as only the main branch is considered and is, hence, limited to rather small molecules. Furthermore, the method works properly only for compounds with the same pre-exponential factor as can be concluded from Equation 2.10. Equation 2.10 shows that the pre-exponential factor  $A$  is part of the regression coefficient  $a$ . Therefore, all reaction rates used for the regression must have a similar  $A$ -value. Moreover, the method relies on available bond dissociation energies. A large compilation of measured  $BDEs$  can be found in the work of *Luo* (2003). Yet again, as it is impossible to measure all necessary data needed to generate oxidation schemes of an appreciable complexity, estimation methods for missing  $BDEs$  become necessary. The most widely used estimation method by *Benson* (1976) is introduced in the following.

## BDE correlations

The bond dissociation energy or enthalpy ( $BDE$ ) is a measure for the strength of a chemical bond between two atoms. It is defined as the change of the standard enthalpy  $\Delta H$  after a homolytic bond cleavage at 0°C. Thus, the  $BDE$  can be calculated from the standard enthalpy of the whole molecule  $\Delta H(AB)$  and the two resulting radical fragments after the bond cleavage  $\Delta H(A\cdot)$  and  $\Delta H(B\cdot)$ :

$$BDE = \Delta H(A\cdot) + \Delta H(B\cdot) - \Delta H(AB) \quad (2.11)$$

For the estimation of the standard enthalpies, *Benson* (1976) developed a method that calculates missing data with a precision of  $\pm 8 \text{ kJ mol}^{-1}$ . The method works for molecules bearing C, H, O, N, S, F, Cl, Br, I, and/or even some metallic atoms. To predict the thermochemical data, the molecules are split into their individual atoms and bonds. To each internal atom an individual partial enthalpy is assigned according to the neighbouring atoms and the type of bond to these atoms. The incremental enthalpies are tabulated and can be found, e.g., in the work of *Benson* (1976). For example, ethanol is composed of three increments:  $\text{C}-(\text{H})_3(\text{C})$ ,  $\text{C}-(\text{H})_2(\text{C})(\text{O})$ , and  $\text{O}-(\text{H})(\text{C})$ . The individual groups are summed up to derive the overall enthalpy of the molecule. The method provides also increments for radical compounds, e.g.  $\text{CH}_3\text{CH}(\text{OH})$  would be composed of  $\text{C}-(\text{H})_3(\text{C}\cdot)$ ,  $\cdot\text{C}-(\text{H})_2(\text{C})(\text{O})$ , and  $\text{O}-(\text{C}\cdot)(\text{H})$ . Therefore, it is possible to calculate the individual *BDEs* of any molecule according to Equation 2.11 by calculating the overall enthalpy of that molecule and the enthalpies of the resulting fragments or single atoms after bond cleavage. The resulting *BDEs* can then be used for further estimates of reaction rate constants with Evans-Polanyi-type correlations, as described above.

### 2.4.3 Structure-activity relationships

Recently, more sophisticated prediction methods for reaction rate constants in the aqueous phase have become available. Among those are structure-activity relationships (SARs; see *Monod and Doussin*, 2008, *Minakata et al.*, 2009, or *Herrmann et al.*, 2010 for an overview). SARs are especially suitable for computerised mechanism construction. Among the many advantages is the simple use of SARs as the only input needed is the chemical structure of the compound of interest.

SARs are developed for reactions of organic compounds with the hydroxyl radical. In a structure-activity relationship, the kinetic rate data of chemical reactions is brought into relation to the structure of the organic compound. An SAR, like the *BDE* prediction of *Benson* (1976), is an incremental method, where the molecule is split into distinct parts. The method provides a partial rate constant for every reactive group, i.e. a molecular group with an abstractable H-atom or a double bond. These partial rate constants are then modulated by a correction factor taking into account effects of the neighbouring groups and, in more sophisticated SARs, effects of the second neighbour as well. Moreover, a correction factor is applied to atoms being part of a ring structure. The partial rate constants and all correction factors are determined by means of multi-linear regression and simultaneous error minimisation during the development process of the structure-activity relationship. After the determination, they are universally applicable to all kinds of molecules, which incorporate the molecular groups provided by the SAR. The overall rate constant is derived by summing up all modulated partial rate constants. The distinction of discrete molecular groups with their own individual rate constants allows the determination of different reaction pathways, which are just the relation of the individual partial rate constants to the overall rate constant. The determination of branching ratios is one of the biggest advantages of SARs, which distinguishes this method from all other prediction methods.

Two recently introduced structure-activity relationships are those by *Monod and Doussin* (2008) and *Minakata et al.* (2009). Both SARs incorporate the principles described above, but vary in the extent of the database of kinetic data used to derive the structure-activity relationship, the number of descriptors needed, and thus the complexity of the SAR. *Monod et al.* (2005) came up with a first approach of a structure-activity relationship for the aqueous phase, where they tried to adopt the gas phase SARs by *Atkinson* (1987) and *Kwok and Atkinson* (1995) to the aqueous phase. Their simple approach included four descriptors for the partial rate constants at a primary, secondary or tertiary carbon atom and at a hydroxyl group and ten descriptors to account for the neighbouring effects of molecular groups consisting of pure hydrocarbons, alcohols, carbonyl compounds, carboxylic acids or ethers. The accuracy was still moderate, and the authors state that 84% of the 128 predicted rate constants tested were within a factor of 5 of the experimentally determined rate constants. In 2008, *Monod and Doussin* refined the SAR for alkanes, alcohols, and carboxylic acids and bases. The major advancement was the introduction of a descriptor taking into account the effects of the second neighbour in addition to the effects of the direct neighbour on the partial rate constants. Moreover, four descriptors have been introduced for carbon atoms, which are part of an aliphatic ring structure with four to seven carbon atoms to account for ring strain effects on the reaction rate constant. In the new SAR, the partial rate constants of the primary, secondary, and tertiary carbon atoms and the hydroxyl function have been recalculated taking into account the product studies of *Asmus et al.* (1973). During the development of the current SAR, the parameters were forced to reflect the fact that the main H-atom abstraction will occur at the carbon atom rather than the hydroxyl group in conclusion with the product studies of *Asmus et al.* (1973) and the bond strength of the corresponding bonds (*Monod and Doussin*, pers. comm.). The improvements led to a significantly increased accuracy and *Monod and Doussin* (2008) state that now 60% of the calculated data lie within 80% of the experimental range and 80% of the predicted data lie within 60% of the experimental values. However, due to the high number of descriptors (22 descriptors derived from a dataset of 72 aliphatic compounds), over-fitting is likely. More recent work of *Doussin and Monod* (2013) has focused on the advancement of the 2008-SAR to carbonyl compounds. Therefore, a new partial rate constant for aldehyde groups and four group contribution factors for the  $\alpha$ - and  $\beta$ -effects of carbonyls and gem-diols have been added to the SAR from 2008. The previous parameters are left unchanged. The authors comment on the accuracy of the new SAR that 58% of the compounds tested were predicted within  $\pm 20\%$  of the experimental values and 76% within  $\pm 40\%$ .

Another SAR was presented by *Minakata et al.* (2009). The prediction method is similar to the one by *Monod et al.* (2005) and includes only the  $\alpha$ -effects for the variation of the partial rate constants. However, the major advantage is the huge database and the very thorough determination of the parameters of the SAR. For the derivation of the structure-activity relationship, a dataset of 310 experimental values was used, which was then tested against a set of 124 organic compounds. The method includes 66 partial rate constants and 80 group contribution factors for the variation of the partial rate constants. The SAR of *Minakata et al.* (2009) allows a broad applicability as it covers the reactions of

the most important organic compounds of atmospheric relevance including aliphatic and aromatic compounds, cyclic aliphatic molecules, unsaturated compounds, and a wide range of functional groups. The authors give an accuracy of a factor of 2 for 83% of the calibrated data and 62% of the predicted rate constants. As SARs are essential for the current study, a more detailed explanation along with an example is given in Appendix B.

## 2.5 The generator GECKO-A

Both the *BDE* prediction by *Benson* (1976) and SARs have originally been developed for the prediction of gas phase kinetic and thermodynamic data. They have been applied in the mechanism generation process of large semi-explicit and explicit mechanisms like the MCM (see section 2.2). An even more complex mechanism generator is the Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A, *Aumont et al.*, 2005), which is based on the mechanism construction routines of the MCM. However, more reaction pathways with minor branches are allowed in GECKO-A, leading to more complex mechanisms with generated oxidation schemes including about 2.5 million species (*Aumont et al.*, 2005). As the aim of the current study is to advance the aqueous phase mechanism CAPRAM 3.0n by means of automated mechanism construction, a generator like GECKO-A seems a very practical and suitable tool. Therefore, the routines of the generator were chosen as a starting point and were then advanced to the description and generation of aqueous phase oxidation schemes. For this reason, the basic principles and the workflow of the original gas phase generator is explained in this section. A more detailed explanation can be found in the publication by *Aumont et al.* (2005).

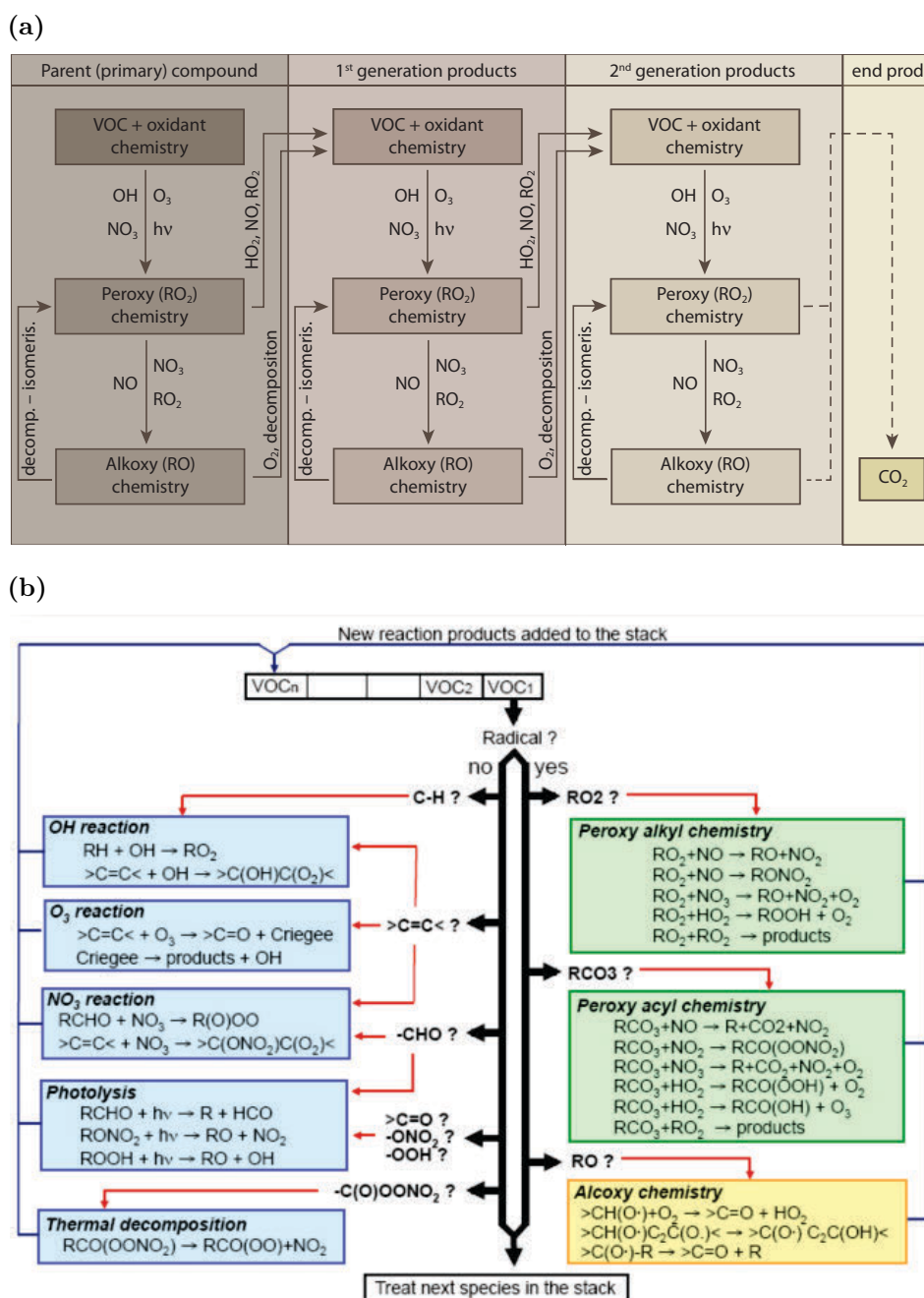
GECKO-A uses the principle that even though there are innumerable different compounds in the atmosphere, there is only a finite number of chemical reaction types that can be repeatedly applied during the oxidation process until the parent compound and all intermediates are oxidised to the end product  $\text{CO}_2$ . In general, these oxidation steps include the following (see also Figure 2.9):

- Oxidation of stable organic compounds by OH,  $\text{NO}_3$ ,  $\text{O}_3$ , bond breaking or photolysis and initiation of the radical degradation chain
- Peroxy radical degradation by reaction with NO,  $\text{NO}_2$ ,  $\text{NO}_3$ ,  $\text{HO}_2$  or by recombination or cross-reaction
- Alkoxy radical decomposition by bond breaking, isomerisation, or reaction with  $\text{O}_2$

The generator GECKO-A is a computer tool, which automatically self-generates oxidation schemes of the parent (emitted) compounds and all evolving intermediates after rules defined in a protocol. A simplified schematic of the protocol is depicted in Figure 2.9a while the workflow of the generator and the numerical processing of the protocol is shown in Figure 2.9b.

At first, the generator analyses the chemical structure of the parent compound and assigns a list of possible reactions to the compound. In a next step, the kinetic data is assigned

to these reactions. Therefore, the generator checks a kinetic database for available rate constants and assigns them to reactions, where possible. Otherwise, as it is the case for most intermediate compounds, GECKO-A estimates the missing rate data (including educts, products, stoichiometric coefficients, rate constants and temperature dependencies) using mainly structure-activity relationships. Finally, the generator checks whether the reaction products have been treated previously in the protocol and adds new reaction products to a 'stack'. After all reactions are assigned to a compound including radical oxidation, photolysis, decomposition and isomerisation as well as uptake processes into



**Figure 2.9** Simplified representation of the gas phase protocol for the VOC oxidation in GECKO-A (a) and its processing in the generator (b) according to *Aumont et al.* (2005).

either the aqueous or the particle phase, the generator moves on to the next compound in the stack.

The procedure is repeated for the following compounds until all parent compounds and their oxidation products are treated and a complete mechanism is generated for all species up to the end product  $\text{CO}_2$ . A complete description of the processes implemented in the current generator gas phase protocol along with an evaluation of the generated oxidation schemes can be found in the work of *Aumont et al.* (2005).



### 3 Evaluation of kinetic data and prediction methods

For the construction of a protocol for mechanism self-generation, a large database with kinetic data is essential. The data are either used directly to assign rate constants to reactions created by the mechanism generator or indirectly to evaluate and further develop prediction methods for missing aqueous phase rate constants based on known experimental values. The aim of the kinetic database is to deliver a comprehensive set of reviewed rate constants in the aqueous phase for reactions of hydroxyl and nitrate radicals with a wide range of organic compounds. While this includes aromatic compounds, for the rate prediction methods only aliphatic compounds are considered at the current state.

Therefore, an intense review and evaluation of available kinetic data from literature has been undertaken. Overall, a database with 465 aqueous phase reactions of the hydroxyl radical with organic compounds and 129 reactions of the nitrate radical with organic compounds has been created and is introduced in section 3.1. Table with a listed recommended values can be found in Appendix C.

Furthermore, the literature review was focused on already available prediction methods for radical reactions with organic compounds. Prediction methods investigated include:

- Gas-aqueous phase correlations
- Homologous series of various compound classes
- Reactivity comparisons between radicals
- Evans-Polanyi-type correlations (including the *BDE* prediction method after *Benson*, 1976)
- Structure-activity relationships (SARs)

The current chapter presents results from an intensive literature review. The evaluated OH and NO<sub>3</sub> radical reactions are introduced in section 3.1. The kinetic database has been used to evaluate the prediction methods listed above. Results from the assessment are presented in sections 3.2 – 3.6. The evaluation process includes an assessment of the accuracy of the respective prediction method as well as an evaluation of the applicability of the method for the incorporation in computer-assisted tools for automated mechanism self-generation. Moreover, the kinetic database was used to advance the Evans-Polanyi-type correlations with a focus on increased accuracy for higher weight organic compounds. The methodology and results with a new correlation are presented in subsection 3.5.3. Final

conclusions and the decision on the choice of the respective prediction methods for the use in the expert system GECKO-A are provided in section 3.7.

## 3.1 Compilation and evaluation of aqueous phase kinetic data

Several comprehensive compilations and recommendations exist for aqueous phase kinetic data (e.g., *Buxton et al.*, 1988, *Ross et al.*, 1998, *Herrmann*, 2003, *Herrmann et al.*, 2010). Experimental data relevant for tropospheric chemistry of organic compounds were collected from these compilations and assembled in a large kinetic database. Moreover, kinetic data from further laboratory experiments were collected from literature and from unpublished TROPOS measurements. Rate constants were carefully revised. In general, already recommended values from compilations were taken over from literature if no updated value from more recent reliable literature could be found. Further experimental data were selected by actuality, but also quality of the data. If no clear preference could be obtained, averaging was used for the recommendation of the kinetic data.

A database was created with a total of 465 reactions of OH radicals with organic compounds and 129 reactions of NO<sub>3</sub> radicals with organic compounds. The data are provided in the Appendix C, page 275 in Table C.1 and C.2, respectively. For clarity, only the recommended values are given in these tables, thus it is no compilation of all available rate data of the reactions considered.

So far, only the reactions of aliphatic compounds (including 282 OH and 76 NO<sub>3</sub> reactions) have been used to design a protocol for automated mechanism construction. Besides the use of the database to assign kinetic data to the constructed mechanisms, it has also been used for testing and advancing the prediction methods. Those prediction methods are introduced in the next sections.

## 3.2 Extrapolation of gas phase rate constants to the aqueous phase

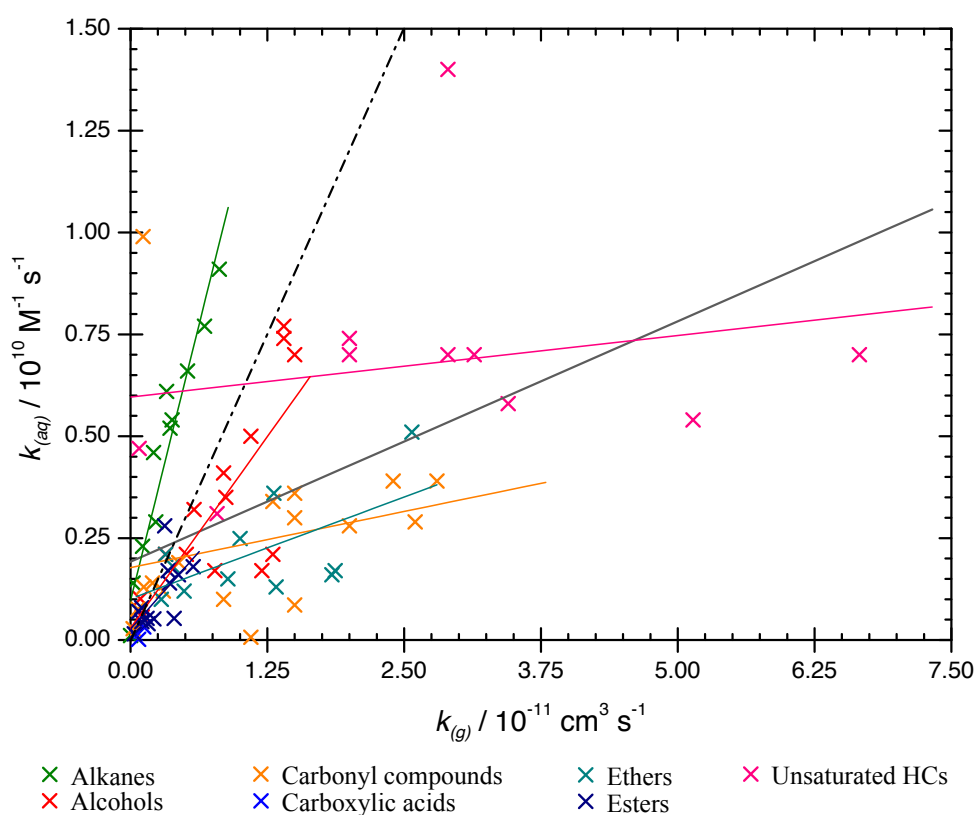
The current section evaluates gas–aqueous phase correlations as described in subsection 2.4.1. For the evaluation, the kinetic database presented in section 3.1 is used to derive a correlation between the gas phase and the aqueous phase rate constants. Gas phase rate constants for hydroxyl radical reactions with organic compounds have been taken from the recommendations of *Atkinson and Arey* (2003), *Atkinson et al.* (2006), *Sander et al.* (2011) and the GECKO-A database. After the derivation of the regression line, the kinetic data are used again to assess the precision of the prediction method.

The major advantage of this method is that it is very easy to use and can be readily implemented in computer assisted rate prediction tools. However, as already stated in

subsection 2.4.1, the method relies on gas phase kinetic data. The data used to derive a correlation can be found in Table D.1, page 303, in Appendix D.1. Only hydroxyl radical reactions with organic compounds have been correlated. Kinetic data for the nitrate radical in the aqueous phase is sparse and the intersecting subset of gas and aqueous phase rate constants is too small for a reliable correlation.

For the derivation of the regression lines and later the assessment of the quality of the different prediction methods with box plots and linear regressions of the scatter plots of predicted versus calculated data, the commercial software Origin 7.0 (<http://www.originlab.com>) has been used. The software was also used for the derivation of the errors and statistical data such as the standard deviation ( $\sigma$ ) or the correlation coefficient ( $R^2$ ). For more details, the reader is referred to the homepage of the OriginLab company or the Origin 7.0 manual.

The resulting regression lines from the correlation of OH reactions with organic compounds in the gas and the aqueous phase as well as important statistical data are given in Table 3.1. The data have been analysed separately for the different compound classes. Moreover, an overall correlation of all data has been performed. For more clarity, the data are plotted in Figure 3.1 and the respective regression lines are shown.



**Figure 3.1** Regression lines derived from the correlation of gas and aqueous phase kinetic data of hydroxyl radical reactions with organic compounds for the various compound classes. Regression lines for the various compound classes are shown in the same colour as the respective data points. The grey line represents the correlation of the overall data, the black dashed dotted line is the line of same reactivity.

**Table 3.1** Parameters for the regression equations  $k_{(aq)}/\text{M}^{-1}\text{s}^{-1} = A \cdot (k_{(g)}/\text{cm}^3\text{s}^{-1}) + B$  and statistical data derived from the correlation of gas and aqueous phase kinetic data of hydroxyl radical reactions with organic compounds for the various compound classes.

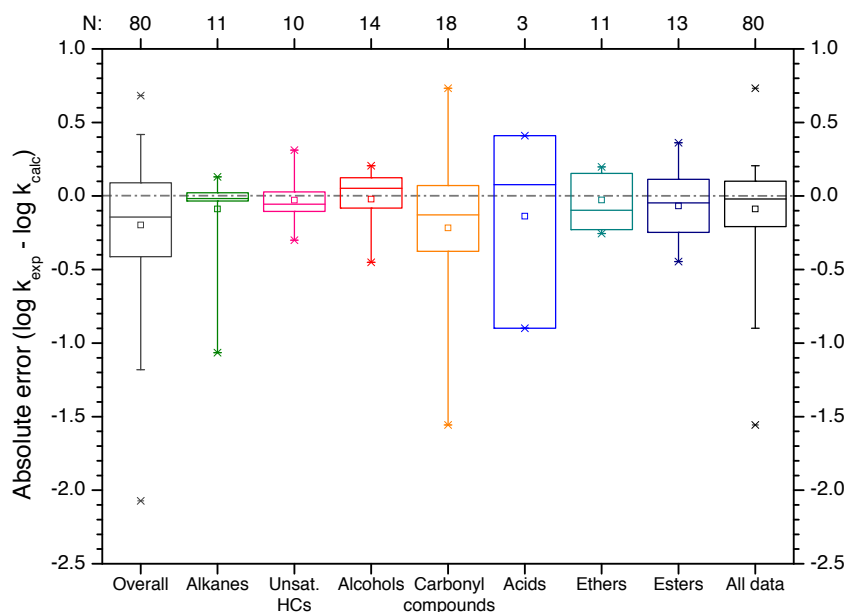
Compound class	$10^{-20}A / \text{M}^{-1}\text{cm}^{-3}$	$10^{-9}B / \text{M}^{-1}\text{s}^{-1}$	$R^2$	$10^{-9}\sigma / \text{M}^{-1}\text{s}^{-1}$	$N$
Alkanes	$10.2 \pm 1.0$	$1.27 \pm 0.41$	0.921	0.8	11
Unsaturated organics	$0.30 \pm 0.51$	$5.96 \pm 1.76$	0.042	3.0	10
Alcohols	$3.76 \pm 0.94$	$0.29 \pm 0.92$	0.570	1.6	14
Carbonyls	$0.55 \pm 0.59$	$1.77 \pm 0.82$	0.052	2.3	18
Carboxylic acids	$2.90 \pm 2.82$	$-0.08 \pm 0.24$	0.514	0.2	3
Ethers	$1.00 \pm 0.43$	$1.01 \pm 0.57$	0.375	1.0	11
Esters	$3.03 \pm 1.07$	$0.27 \pm 0.32$	0.422	0.6	13
Overall	$1.17 \pm 0.23$	$1.94 \pm 0.35$	0.248	2.4	80

For such a simple approach, the method works sufficiently and correlation coefficients of up to 0.92 are reached for alkanes. No correlation could be obtained for carboxylic acids due to missing data. With only 3 values for formic, acetic, and propanoic acid, the resulting regression line is not reliable despite a correlation coefficient of 0.51 (compare Table 3.1). Moreover, the gas and aqueous phase data of carbonyl compounds and unsaturated hydrocarbons show no correlation having correlation coefficients of 0.05 and 0.04, respectively, although there has been a sufficient data set for the derivation of the regression lines.

A likely explanation for the failure of this estimation method to predict the rate constants of representatives of the two compound classes are differences between the gas and the aqueous phase reaction mechanisms. In the aqueous phase, carbonyls hydrate (see subsection 2.1.3). For the correlation, only the unhydrated forms have been considered. The hydration and parallel oxidation of the gem-diol forms is very likely to disturb the correlation. Unsaturated compounds react predominantly by radical addition rather than H-atom abstraction. The different reaction mechanism might cause the problems to predict rate constants properly with this prediction method compared to the other compound classes.

Apart from the above-mentioned exceptions, correlation coefficients are generally in the range of 0.4 – 0.6. It should be noted that correlations should be derived for the different compound classes separately as there is almost no correlation, when using the regression for the whole dataset, resulting in a correlation coefficient of  $R^2 = 0.25$ . However, overall, one can expect to meet at least the correct order of magnitude with gas–aqueous phase correlations and the method will deliver an appropriate ‘first guess’.

For further assessment of the method, the data of Table D.1 were used again to predict aqueous rate constants with the aid of the gas phase values and the correlation lines presented in Table 3.1. Deviations of the logarithmised predicted values to the experimental values ( $\log k_{exp} - \log k_{calc}$ ) were evaluated statistically with box plots. A short explanation of this kind of statistical analysis and the graphical output is provided in Appendix D.2, page 305. Results for gas–aqueous phase correlations are provided in Figure 3.2. Besides the analysis of every compound class separately, the absolute errors of the individual correlations have been accumulated and analysed for the whole dataset (last box of Figure 3.2: ‘All data’). Moreover, the absolute errors of the overall regression line (black



**Figure 3.2** Box plots (as described in Appendix D.2) of the absolute errors of the correlation of gas and aqueous phase rate constants of hydroxyl radical reactions with organic compounds. The box ‘Overall’ represents the statistical data for the overall correlation of the whole data while the box ‘All data’ is an overall evaluation of the accumulated data of the individual correlations of the various compound classes.

line in Figure 3.2 and last line in Table 3.1) have been evaluated in the first box labelled ‘Overall’.

The box plot confirms the initial impression of a robust prediction method, which is suitable to be used as a first guess. The reaction rate constants are predicted in the right order of magnitude as all boxes and most whiskers of the absolute errors stay between -1 and 1 (see Figure 3.2). Furthermore, it can be seen that a majority of the data in the box plot lies below the zero-line, which indicates a tendency of the correlation to overestimate. Moreover, for the use in automated mechanism generators, the correlations are too weak to produce reliable results. The necessity of available gas phase rate constants constrains the implementation in mechanism generators. The insufficient dataset of gas phase rate constants of carboxylic acids allows no prediction of kinetic data of these compounds. Finally, only hydroxyl radical reactions can be estimated with this method as the intersecting dataset of gas and aqueous phase kinetic data of further radical oxidants is too small to produce reliable correlations.

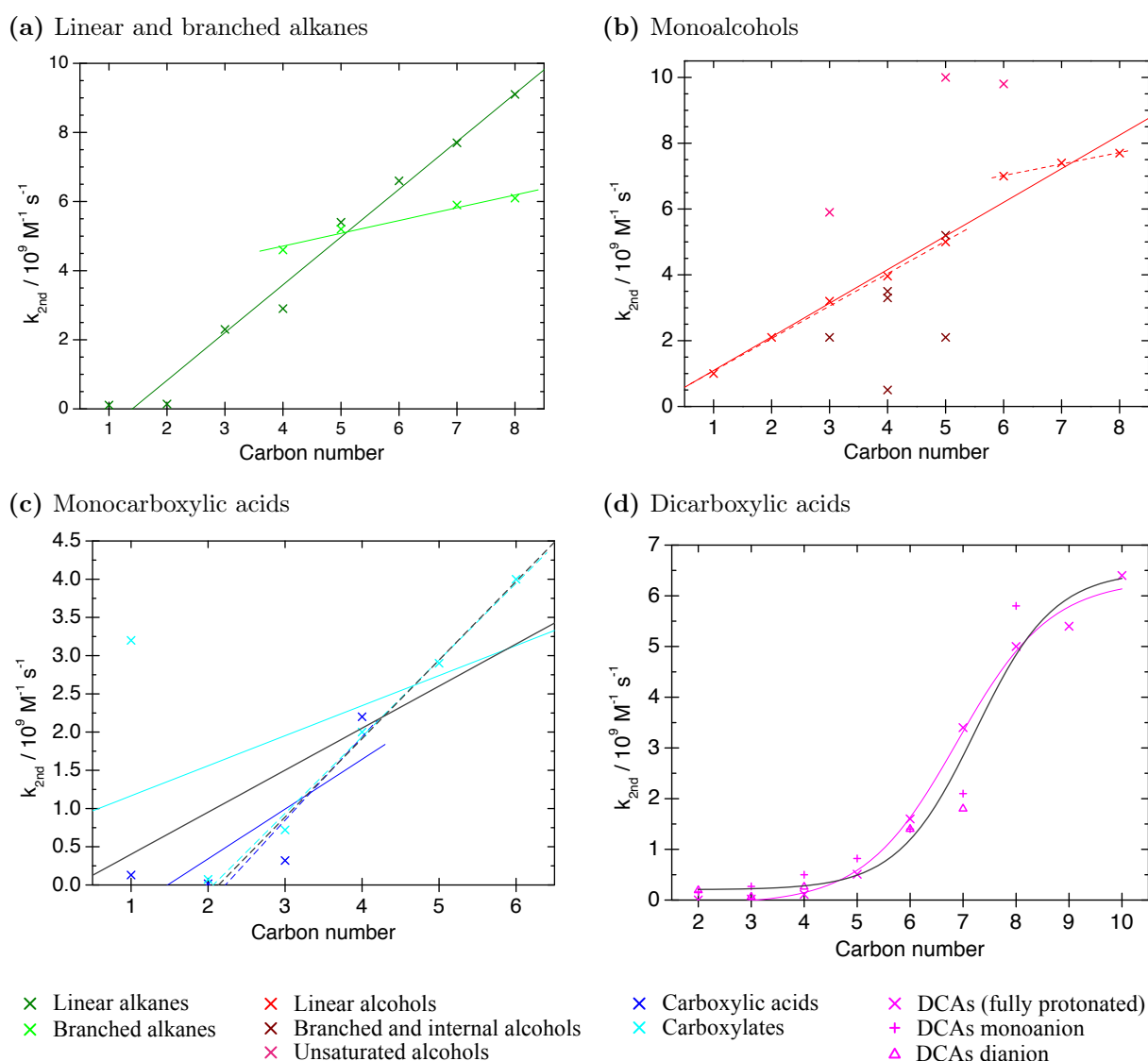
### 3.3 Homologous series of compound classes

#### OH rate prediction

Another, very simple approach is the extrapolation of kinetic data for a homologous series of a certain compound class. Although this method can be readily implemented in computer assisted prediction tools, its applicability is limited. The method works well only

for simple molecules of the same structure such as monoalcohols with a terminal hydroxyl group. If enough data are available, a regression line can be derived from the lower weight compounds of the homologous series, where experimental data typically exists, and then be used to extend the rate constant data to higher carbon numbers. However, for higher weight molecules, the reactivities may get close to the diffusion limit of a reaction and the behaviour in the transition region is unclear. Nevertheless, for a complete overview, the extrapolation of homologous series is discussed in this section.

In a first attempt, the method was tested for alkanes. Even for this most simple compound class, the restrictions of the method can be seen. Figure 3.3a shows the regression of the



**Figure 3.3** Correlation of hydroxyl radical reaction rate constants of the respective compound classes against the carbon number. Correlation lines are shown in the same colour as the data points. The dashed lines in subfigure b are separate correlations for C<sub>1</sub> to C<sub>5</sub> and C<sub>6</sub> to C<sub>8</sub> compounds. Dash lines in subfigure c refer to correlations without formic acid/formate. In subfigure d, the pink line represents the best fit of the Markov distribution of the fully protonated acids and the grey line is the fit of all protonation states. The respective equations for the regression lines can be found in Table 3.2 and Equation 3.1 and 3.2.

**Table 3.2** Parameters for the regression equations  $k_{2nd}/M^{-1}s^{-1} = A \cdot CN + B$  ( $CN$  = carbon number) and statistical data derived from the correlation of hydroxyl radical reaction rate constants of organic compounds plotted against the carbon number of the various organic compounds.

Compound class	$10^{-9}A / M^{-1}s^{-1}$	$10^{-8}B / M^{-1}s^{-1}$	$R^2$	$10^{-8}\sigma / M^{-1}s^{-1}$	$N$
Linear alkanes	$1.38 \pm 0.08$	$-(19.4 \pm 4.1)$	0.980	5.2	8
Branched alkanes	$0.37 \pm 0.40$	$32 \pm 3$	0.971	1.4	4
Terminal monoalcohols	$1.02 \pm 0.06$	$0.7 \pm 3.3$	0.977	4.2	8
– C1 – C5	$0.99 \pm 0.03$	$0.9 \pm 1.2$	0.996	1.1	5
– C6 – C8	$0.35 \pm 0.03$	$49 \pm 2$	0.993	0.4	3
Terminal diols	$0.77 \pm 0.07$	$3.0 \pm 3.0$	0.975	2.2	5
Monocarboxylic acids	$0.5 \pm 0.2$	$1.0 \pm 9.0$	0.378	12.0	10
	$(1.03 \pm 0.08)^*$	$-(22 \pm 3)^*$	$(0.966)^*$	$(2.9)^*$	$(8)^*$
– protonated	$0.7 \pm 0.3$	$9.6 \pm 9.0$	0.667	7.3	4
	$(1.1 \pm 0.5)^*$	$-(24 \pm 14)^*$	$(0.852)^*$	$(6.4)^*$	$(3)^*$
– deprotonated	$0.4 \pm 0.4$	$8 \pm 13$	0.236	15.0	6
	$(1.00 \pm 0.05)^*$	$-(21 \pm 2)^*$	$(0.993)^*$	$(1.6)^*$	$(5)^*$

\*C1 data omitted due to bad correlation.

homologous series of alkanes. The dataset demonstrates the necessity for a distinction of the chemical structure and two regression lines can be found – one for linear and one for branched alkanes. The regression lines, however, show a high accuracy (compare Table 3.2) with correlation coefficients  $R^2$  of 0.98 and 0.97, respectively.

Figure 3.3b shows the data for monoalcohols, which underlines the importance of the structure of the molecules. The rate constants of unsaturated alcohols have a very poor correlation with the carbon number and internal monoalcohols seem to be totally uncorrelated. Only the regression of linear terminal monoalcohols shows satisfactory results, which is, therefore, the only regression line for monoalcoholic compounds shown in Figure 3.3b. From this regression, another crucial parameter becomes obvious, which is valid for all estimation methods; that is the dependency on the experimental dataset. From Figure 3.3b can be seen that  $C_6$  to  $C_8$  compounds show a different behaviour than the lower weight compounds up to  $C_5$ . The data of the  $C_6$  to  $C_8$  compounds is taken from *Scholes and Willson* (1967), while the rate data of the other compounds is from different sources. Therefore, it cannot be clarified, whether this effect is due to the experimental determination of the data or really an effect of the carbon number of larger compounds. While the correlation of the overall data is still very good with an  $R^2$  of 0.98, a consideration of a different correlation for  $C_6$  and higher compounds would have a significant effect, as the slope of the regression line is considerably lower. Large deviations arise especially for higher molecular weight compounds. For example, a predicted rate constant of a  $C_{12}$  alcohol with separate correlations would be only 74% of the rate constant predicted with the overall correlation.

Another group of alcohols, for which the extrapolation of a homologous series works well, are terminal diols with an alcohol function at every end of the molecule. The correlation is shown in the Appendix in Figure D.2, page 306, and the equation and the statistical data are given in Table 3.2.

Linear carboxylic monoacids are another compound class for which the method was tested and works well with some constraints. The results are given in Figure 3.3c and Table 3.2. From the data in Figure 3.3c can be seen that no big differences in the rate constants exist for protonated and deprotonated acids. Also, for both forms the C<sub>1</sub> acid forms an exception with higher rate constants than the ones expected from a linear regression. This effect is much stronger for the deprotonated form. When omitting formic acid, however, the good performance of the prediction method can be confirmed with a correlation coefficient  $R^2$  of 0.97 for the regression line using both, the dissociated and undissociated forms. When investigating both forms separately, the deprotonated form correlates better with an  $R^2$  of 0.99 compared to  $R^2 = 0.85$  of the protonated form. However, all three regression lines are very similar so that the overall regression should be used, which is more reliable due to a larger data set.

Another interesting example is the correlation of linear dicarboxylic acids (DCAs). The dataset for all three forms, the protonated forms, the monoanions, and the dianions, is shown in Figure 3.3d. From this figure can be seen that no linear regression is valid for DCAs. There is only a moderate, non-linear increase in the rate constants for DCAs with less than 7 carbon atoms. Rate constants stay below  $2 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . Then, the rate constants jump to values above  $5 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for dicarboxylic acids with more than 7 carbon atoms and do, again, only moderately increase for larger diacids. For such a distribution, a sigmoidal function can be used and the Markov distribution has been applied resulting in the following regression line:

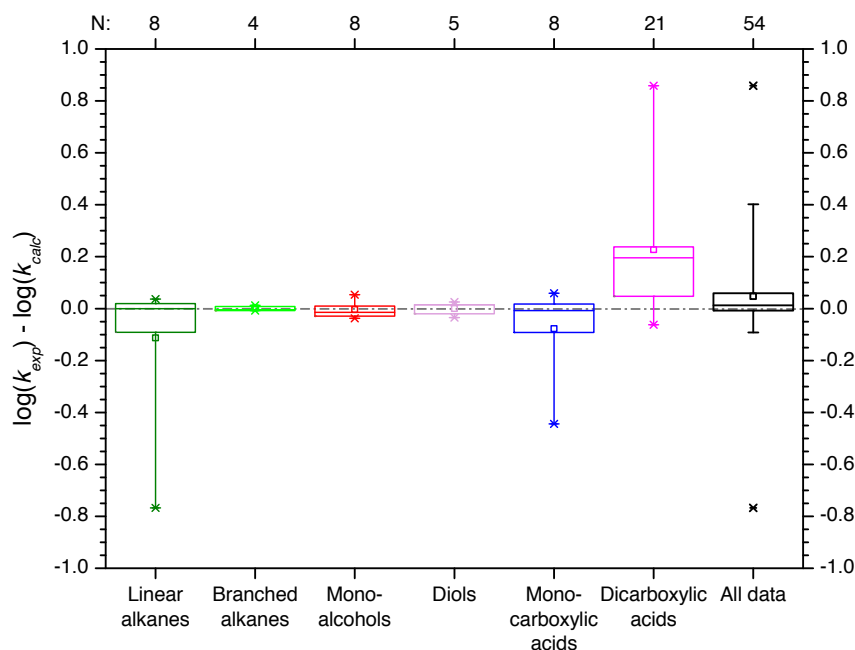
$$k_{2nd} = \frac{-(9 \pm 15) \cdot 10^7 - (6.3 \pm 0.3) \cdot 10^9}{1 + \exp \left\{ CN - \frac{6.9 \pm 0.1}{0.9 \pm 0.1} \right\}} + (6.3 \pm 0.3) \cdot 10^9 \quad (3.1)$$

Overall, 21 values were used to derive the correlation of which 9 belonged to the fully protonated dicarboxylic acids, 5 to the monoionic and 7 to the dianionic forms. Again, there is a good correlation with an  $R^2$  of 0.96 for the overall data. Taking only the fully protonated forms leads to correlation with an  $R^2$  of 0.995 and a regression equation of:

$$k_{2nd} = \frac{-(2 \pm 2) \cdot 10^8 - (6.5 \pm 0.5) \cdot 10^9}{1 + \exp \left\{ CN - \frac{7.2 \pm 0.2}{0.7 \pm 0.1} \right\}} + (6.5 \pm 0.5) \cdot 10^9 \quad (3.2)$$

It can only be speculated on the reason why a linear correlation does not apply to dicarboxylic acids. A likely explanation is the special structure of this compound class. Carbon atoms in a carboxyl group are highly oxidised. They are attached to an oxygen atom by a double bond and a hydroxyl group by a single bond. The carboxyl group is, therefore, very polar and has a large diffusion volume. Therefore, steric effects could suppress hydrogen abstraction at further carbon atoms in the carbon skeleton of lower weight compounds leaving only the hydrogen atoms in the carboxyl group for radical attack. However, these hydrogen atoms are attached to oxygen atoms and the bond dissociation enthalpy (BDE), which is a measure for the bond strength, is much larger resulting in a lower reactivity. Therefore, the reactivity could be reduced for smaller molecules due to these effects. As the chain length increases, steric effects are reduced, which results





**Figure 3.4** Box plots (as described in Appendix D.2) of the absolute errors of the correlation of hydroxyl radical reactions with organic compounds against the carbon number.

in a sudden unproportional increase of the rate constants to values, which are expected without these effects.

For a complete evaluation, all of the above correlations were used again to predict rate data for compounds, where experimental data is available. The absolute errors of the logarithmised experimental versus predicted data are then compared in box plots as explained in the previous section. Results are shown in Figure 3.4. The method seems to work extremely well with small boxes usually hitting the zero-line. It should be noted that the datasets for the box plots are usually small, such as in the case of branched alkanes and diols, where the datasets contain only 4 and 5 compounds, respectively. Furthermore, only the regression lines, which use the overall data of these compound classes, have been used for the comparison in the box plots.

### NO<sub>3</sub> rate prediction

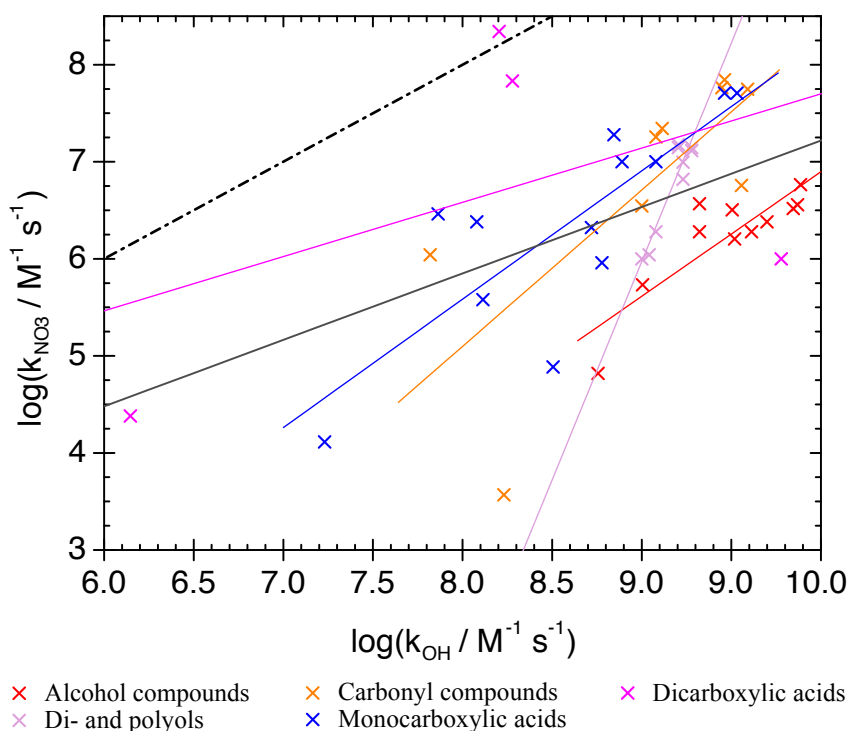
As seen for the correlation of gas and aqueous phase rate constants, homologous series are impractical to predict NO<sub>3</sub> rate constants due to the limited experimental dataset. The dataset allowed the determination of regression lines only for several alcohols and for aldehydes. However, for the regressions no more than 8 data points could be used (see Table D.2, page 307). An exception is the correlation of all alcohols including linear, branched and substituted saturated monoalcohols and gem-diols with 13 data points. However, the correlation is weak with a correlation coefficient  $R^2$  of 0.5. All correlation data can be found in Table D.2 besides a more detailed discussion in Appendix D.3. Moreover, Figure D.3, page 307, shows the dataset and regression lines of the correlation of NO<sub>3</sub> rate constants with various alcohols and aldehydes plotted against the carbon

number. Further compound classes show a weak correlation and are therefore not shown. The derived correlations have also been evaluated by means of box plots. The discussion can be found in Appendix D.3, page 306, as well.

### 3.4 Radical reactivity comparisons

The kinetic database has been used to compare the reactivities of hydroxyl and nitrate radicals. Results from the evaluation are shown in Figure 3.5. The data is plotted on a double logarithmic scale and the correlation equations (see Table 3.3) are valid for the logarithmised rate constants as well. In general, the reactivity of  $\text{NO}_3$  is smaller than that of OH. On average, the decrease in the reactivity is about 2 orders of magnitude as can be seen from the data points as well as the correlation line of all data (grey line) in Figure 3.5. The only exception is oxalic acid, where the ETR of oxalate with the nitrate radical is so fast that the reactivity of the monoanion is close to the reactivity of the corresponding OH reaction. The oxalate dianion is reacting even faster with  $\text{NO}_3$  than with OH.

The regression lines were used to predict the reaction rate constants of the nitrate radical with the respective organic compounds for which the aqueous OH rate constants are known. Results are, again, satisfactory for such a simple approach and regression equations with correlation coefficients  $R^2$  of up to 0.93 could be achieved. However, as for the other correlations, there should be a distinction between the different compound classes as a



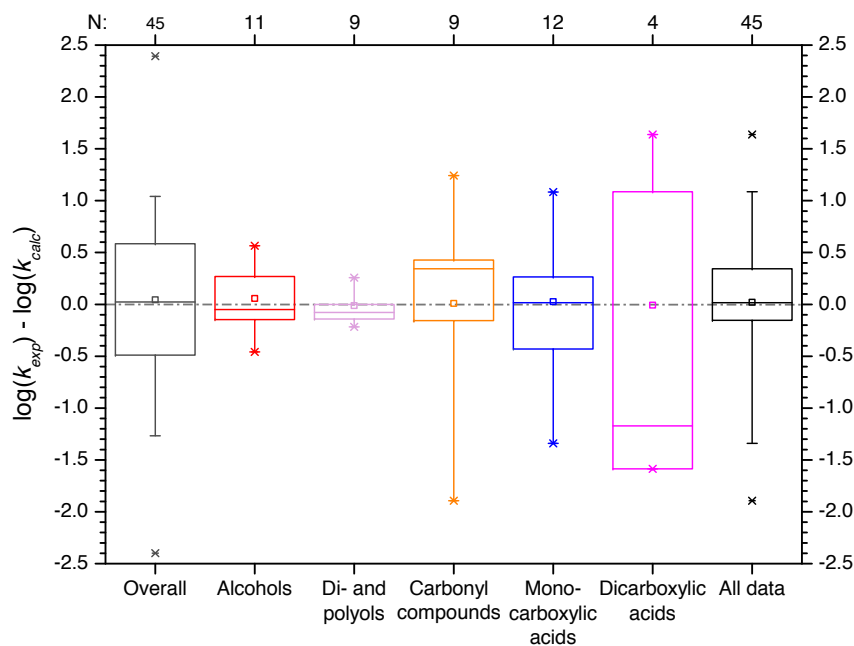
**Figure 3.5** Correlation of the OH versus  $\text{NO}_3$  radical rate constants in the aqueous phase for the respective compound classes and the overall data. Regression lines for the various compound classes are shown in the same colour as the respective data points. The grey line represents the correlation of the overall data, the black dashed dotted line is the line of same reactivity.

**Table 3.3** Parameters for the regression equations  $\log(k_{NO_3}/M^{-1}s^{-1}) = A \cdot \log(k_{OH}/M^{-1}s^{-1}) + B$  and statistical data derived from the correlation of hydroxyl radical and nitrate radical kinetic data of the reactions with organic compounds for the various compound classes.

Compound class	<i>A</i>	<i>B</i>	<i>R</i> <sup>2</sup>	$\sigma$	<i>N</i>
Alcohols	1.28±0.25	-(5.9±2.4)	0.741	0.29	11
Di- and polyols	4.50±0.60	-(34.5±5.5)	0.889	0.18	9
Carbonyls	1.61±0.55	-(7.8±5.0)	0.934	0.97	9
Monocarboxylic acids	1.32±0.30	-(5.0±2.6)	0.654	0.68	12
Dicarboxylic acids	0.56±0.76	2.1±6.3	0.212	1.97	4
Overall	0.68±0.18	0.4±1.6	0.253	0.88	45

correlation of the overall data is poor with a correlation coefficient  $R^2$  of 0.25. The analysis with box plots (see Figure 3.6) details the precision of the correlations. The method works extremely well for alcohol compounds with only small deviations of the predicted data from the experimental values. There is a slight increase in the errors of the predicted data for carbonyl compounds and monocarboxylic acids. The method fails for dicarboxylic acids. Only 4 data points could be used for the derivation of the regression line and only a weak correlation was seen. Hence, the errors of the predicted data span three orders of magnitude. The reason for the failure of the method to predict nitrate radical rate constants with dicarboxylic acids based on hydroxyl radical rate constants might be different reaction mechanisms. The nitrate radical is known to react by ETR, while OH radicals typically react by H-atom reactions.

Although it is strongly recommended to use different regression lines for every compound class, even the overall regression of all data shows reasonable results predicting most



**Figure 3.6** Box plots (as described in Appendix D.2) of the absolute errors of the correlation of hydroxyl and nitrate radical aqueous phase rate constants of reactions with organic compounds. The box ‘Overall’ represents the statistical data for the overall correlation of the whole data while the box ‘All data’ is an overall evaluation of the accumulated data of the individual correlations of the various compound classes.

data within the correct order of magnitude. It should be noted again that the method is restricted to the dataset of the hydroxyl radical reactions in the aqueous phase and therefore impractical for automated rate constant prediction. However, if hydroxyl radical rate constants are missing, these reactions might be estimated with another estimation method. The estimated OH reaction rate constant could then be used in the correlation to predict the NO<sub>3</sub> rate constants. Yet, the errors of the results of this prediction would be increased by the errors of the OH prediction method.

## 3.5 Evans-Polanyi-type correlations

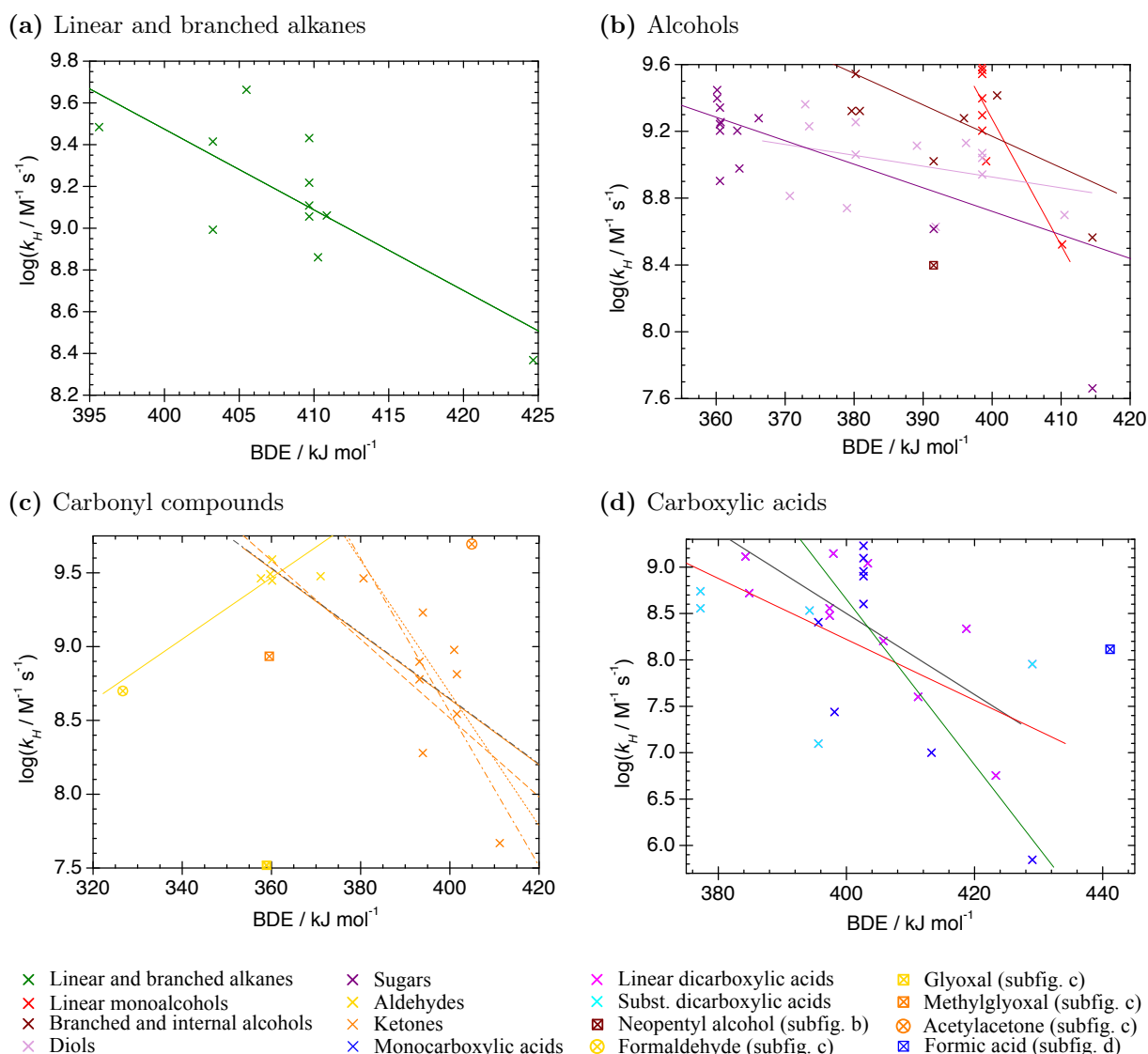
A more advanced correlation is investigated in the current section. Evans-Polanyi-type correlations use the bond dissociation enthalpy (*BDE*) of the weakest bound hydrogen atom and correlate it to the experimentally determined logarithmised reaction rate constant, which is divided by the number of weakest bound H-atoms ( $\log k_H$ ; see also subsection 2.4.2). The *BDEs* needed for the correlations have been calculated with the method described by *Benson* (1976). To have a consistent dataset, these calculations were performed even if experimental data for *BDEs* were available, e.g. from the compilation by *Luo* (2003).

The method has been evaluated for hydroxyl radical reactions with aliphatic organic compounds. Results are given in the next subsection. In subsection 3.5.2, the method was evaluated for nitrate radical reactions with aliphatic organic compounds.

### 3.5.1 OH rate constant prediction

Overall, 97 OH radical reactions with aliphatic organic compounds have been used for the evaluation process. The data of the kinetic database (see section 3.1 and Appendix C) has been used again for this purpose. Compound classes investigated include alkanes, alcohol and carbonyl compounds as well as carboxylic acids and diacids. The calculated *BDEs* range from about 360 to 440 kJ mol<sup>-1</sup>, the experimental rate constants are between 10<sup>6</sup> and 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup> (see Figure 3.7). Besides the data used for the regressions, Figure 3.7 shows the calculated regression lines. The values of the calculated slopes and y-intercepts of the linear regressions as well as the statistical data are given in Table 3.4, page 52.

From Figure 3.7 it becomes obvious that a critical assessment of the experimental data is essential for the proper derivation of a regression line when using Evans-Polanyi-type correlations. The method seems to work reasonably well for pure hydrocarbons giving a moderate correlation coefficient  $R^2$  of 0.6 (see Figure 3.7a and Table 3.4). The data of alcohol compounds (see Figure 3.7b) have to be chosen with more care. Using the data of all monoalcohols would result in only a weak correlation with a correlation coefficient of  $R^2 = 0.32$  and one should treat the predicted rate data with caution. Therefore, it is suggested to use the correlation only for linear terminal monoalcohols and omit internal or branched monoalcohols, which increases the  $R^2$  to 0.73. Moreover, separate correlations for diols and sugars result in weaker correlations than an overall regression (compare Table 3.4).



**Figure 3.7** Evans-Polanyi-type correlations of hydroxyl radical reactions with the respective compound classes. Linear fits are shown as solid lines in the same colour as the data points. Moreover, in subfigure c, the dotted line represents the linear fit of ketones excluding methylglyoxal, the dashed line represents the correlation of ketones without acetylacetone. For the dashed-dotted line, both compounds have been omitted. The grey dashed-dotted line in subfigure c is the overall correlation of all carbonyl compounds except glyoxal and formaldehyde. The respective equations for the regression lines can be found in Table 3.4.

The critical data assessment is even more crucial for carbonyl compounds. Figure 3.7c shows the data used for the regression. Four data points attract the attention as they do not align very well with the other data. These four data points belong to formaldehyde (yellow circled cross), glyoxal (yellow boxed cross), methylglyoxal (orange boxed cross) and acetylacetone (orange circled cross). Formaldehyde has a decreased  $BDE$  and reaction rate constant compared to the other aldehydes. The  $BDE$  of glyoxal falls in the range of the other aldehydes, however, the rate constant is significantly decreased. For ketones, methylglyoxal seems to have a decreased reactivity towards hydroxyl radicals compared to the other ketones and the reactivity of acetylacetone seems to be increased. Therefore, several regression lines are shown in Figure 3.7c to assess the reliability of the experimental

**Table 3.4** Parameters for the regression equations  $\log(k_H/\text{M}^{-1}\text{s}^{-1}) = A \cdot (BDE/\text{kJ mol}^{-1}) + B$  and statistical data derived from the Evans-Polanyi-type correlations of aqueous phase hydroxyl radical reactions with organic compounds for the various compound classes.

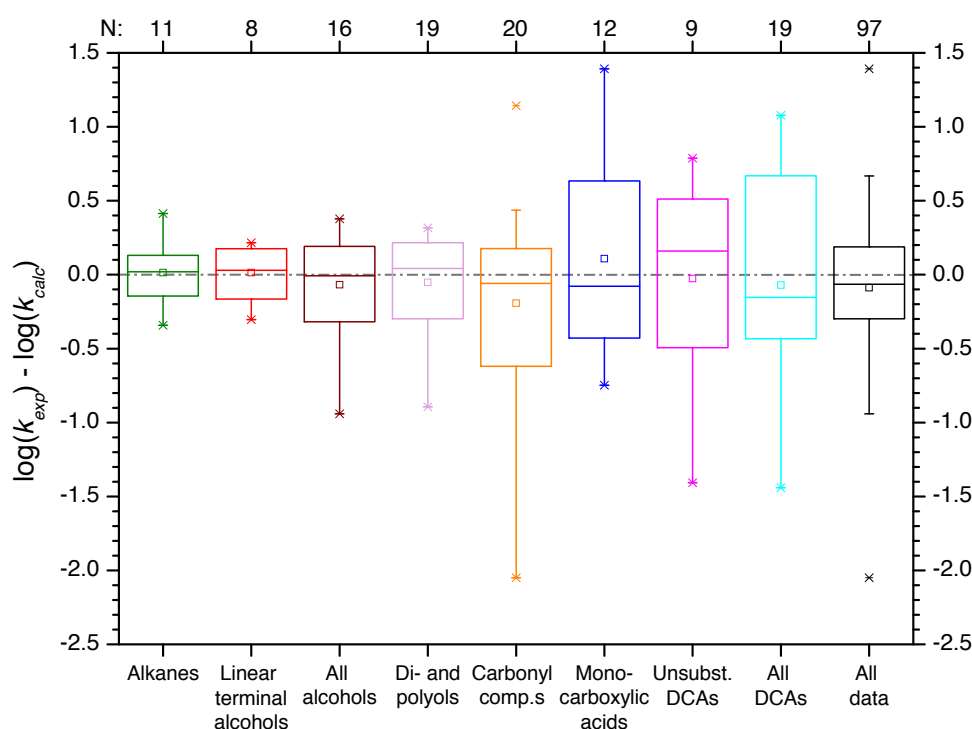
Compound class	$10^2 A$	$10^{-1} B$	$R^2$	$\sigma$	$N$
Alkanes	$-(3.86 \pm 1.1)$	$2.49 \pm 0.4$	0.595	0.24	11
Linear terminal monoalcohols	$-(7.56 \pm 1.9)$	$3.95 \pm 0.7$	0.732	0.20	8
All monoalcohols	$-(1.88 \pm 0.8)$	$1.67 \pm 0.3$	0.315	0.28	15
Diols	$-(0.65 \pm 0.5)$	$1.15 \pm 0.2$	0.126	0.22	13
Diols and sugars	$-(1.41 \pm 0.3)$	$1.44 \pm 0.1$	0.439	0.28	25
Monoaldehydes	$2.08 \pm 0.4$	$0.20 \pm 0.1$	0.852	0.13	7
Ketones and diketones	$-(2.21 \pm 1.2)$	$1.75 \pm 0.5$	0.254	0.60	12
– without methylglyoxal	$-(4.49 \pm 1.7)$	$2.67 \pm 0.7$	0.444	0.54	11
– without acetylacetone	$-(2.67 \pm 1.0)$	$1.92 \pm 0.4$	0.453	0.48	11
– without both	$-(5.21 \pm 1.1)$	$2.94 \pm 0.4$	0.745	0.35	10
Carbonyl compounds (without glyoxal and formaldehyde)	$-(2.21 \pm 0.6)$	$1.75 \pm 0.2$	0.497	0.48	18
Monocarboxylic acids (without formic acid)	$-(4.37 \pm 1.3)$	$2.60 \pm 0.5$	0.573	0.52	10
All dicarboxylic acids	$-(3.29 \pm 1.6)$	$2.14 \pm 0.6$	0.257	0.88	14
Unsubstituted dicarboxylic acids	$-(8.93 \pm 2.8)$	$4.44 \pm 1.1$	0.601	0.78	9

values of these crucial compounds as well as the resulting regression lines. Glyoxal as only representative of dialdehydes has not been considered in the correlations due to the significantly decreased reactivity. The correlation of ketones was tested either for the full dataset, with the methylglyoxal value omitted, with acetylacetone omitted and with both outliers omitted. The resulting regression lines are plotted in Figure 3.7c. The values of the regression parameters and further statistical data is given in Table 3.4. The best correlation is found for the regression omitting both, methylglyoxal and acetylacetone. Monoaldehydes show a very good correlation to the bond dissociation energy with an  $R^2$  of 0.85. However, aldehydes are the only compound class that contradict the theory of a decreased reactivity with increasing  $BDE$ . Yet, omitting the outlying value of formaldehyde results in an overall dataset for all carbonyl compounds with aldehydes at the upper left end in Figure 3.7c meaning slightly lower  $BDE$ s and increased reactivities. Ketones are found at the lower left end of the dataset meaning higher  $BDE$ s of the abstractable H-atoms and decreased reactivities compared to aldehydes. An overall regression of all carbonyl compounds except formaldehyde and glyoxal results in exactly the same regression line as that for all ketones. This fact demonstrates that aldehydes behave the same as ketones and the value of formaldehyde should not be considered for the derivation of the regression line. It is rather suggested that the overall correlation of all carbonyls is used, when using Evans-Polanyi-type correlations.

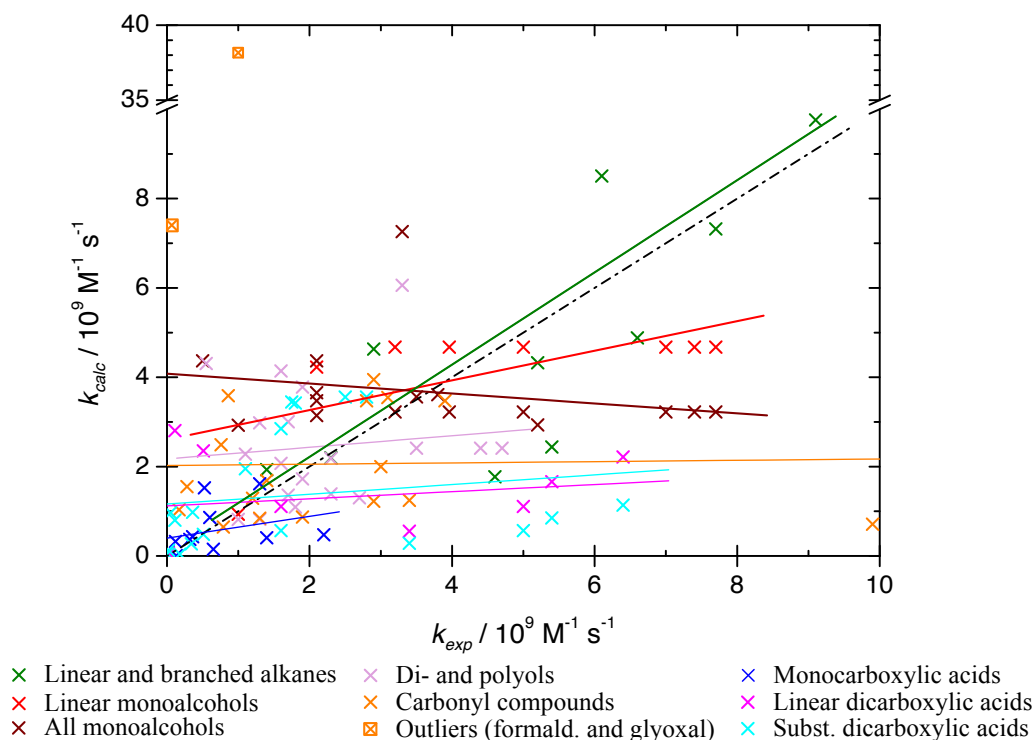
Carboxylic acids and diacids belong to the last compound class investigated with Evans-Polanyi-type correlations (see Figure 3.7d). Moderate quality of the regressions is obtained for monocarboxylic acids with a correlation coefficient of 0.57. DCAs show a weak correlation (see Table 3.4) and the predicted data should be treated with care. However, using only linear unsubstituted dicarboxylic acids for the correlation increases the correlation coefficient from 0.26 to 0.60 compared to all DCAs.

Again, the data of the kinetic database has been reused together with the regression lines of Table 3.4 to predict the rate constants of the compounds with known kinetic data and assess the accuracy of the prediction method with box plots (see Figure 3.8). Very good results are obtained for alkanes with small absolute errors. Errors increase slightly, when an alcohol group is added. For carbonyl compounds and carboxylic acids errors are rather large, but stay within an order of magnitude compared to the experimental data for most of the predicted rate constants. Despite the recommendations made in this subsection, the overall correlations of all monoalcohols and all dicarboxylic acids have been used besides the regressions of only linear terminal monoalcohols and unsubstituted DCAs. The use of these regression lines regardless of their weak correlation in the development process was to further evaluate the quality of Evans-Polanyi-type correlations and is no suggestion for the application of any of the correlations. Furthermore, for the evaluation of all data in the last box in Figure 3.8, the correlation of the more accurate regression lines have been used when possible and the overall correlations have been used only for internal and branched alcohols or substituted DCAs. Figure 3.8 shows the absolute errors increase only slightly with the more inaccurate overall regressions despite only a weak correlation during the development process. Moreover, the correct order of magnitude is predicted for almost all compounds evaluated in Figure 3.8.

For a more detailed investigation, further analysis was performed, where the predicted data were plotted against the experimental data and linear regressions have been performed for every compound class (see Figure 3.9). In such a scatter plot, all data should be on the 1:1 line for a perfect correlation, thus the regression should have a slope of 1 and a y-intercept of 0. The correlation coefficient  $R^2$  of the regression line should be 1. Any deviations in the



**Figure 3.8** Box plots (as described in Appendix D.2) of the absolute errors of the Evans-Polanyi-type correlation of hydroxyl radical reactions with the respective compound classes.



**Figure 3.9** Plot of predicted versus experimental data for hydroxyl radical reactions predicted with Evans-Polanyi-type correlations. The data is separated by compound class and linear regression lines are shown in the same colour as the data points. For the calculation of the predicted values, the regression lines of Table 3.4 together with the data from the kinetic database have been used. The cyan line represents the overall regression line of linear and substituted DCAs. The black dashed-dotted line is the line of same reactivity.

slope and the y-intercept of the regression line indicate a bias of the prediction method. A decrease in the correlation coefficient is an indication of the scatter in the predicted values and indicates individual errors. For a complete overview, all parameters of the regression lines and the statistical information is given in Table D.3, page 309, in the Appendix.

From Table D.3 and Figure 3.9 can be seen that the only regression line to show a slope of  $\sim 1$  is that of alkanes. All other compound classes have slopes significantly smaller than 1 ( $\leq 0.33$ ). For the more inaccurate overall correlation of all monoalcohols, the slope is even negative ( $-0.11$ ). The good performance of alkanes, confirms the results from the analysis of the box plots and the sufficient correlation with an  $R^2$  of almost 0.6 during the development process. For the other compound classes it can be seen from Figure 3.9 that for fast reacting compounds reaction rate constants are underestimated and for slowly reacting compounds reaction rate constants are overestimated. The intercept with the 1:1 line depends on the compound class.

The reason for this failure is due to the correlation of the rate constant to the *BDE* of the weakest bound H-atom. Within a certain compound class, the weakest *BDE* in a molecule is generally similar. However, the reactivity increases with increasing chain length of a molecule for a specific compound class as there are more reactive sites within a molecule. The increased reactivity is caused by side attacks in longer chained molecules. With a increasing chain length, the probability rises for H-atom abstractions at other sites even



if there is a lower *BDE* elsewhere in the molecule. The correlation against the weakest *BDE* only is not capable to reflect this fact. Moreover, when calculating *BDEs* with the method developed by *Benson* (1976), bond dissociation energies are exactly the same for longer chained compounds as the prediction method considers only the direct neighbouring atoms and bonds for the calculation. On the other hand, due to the parameterisation, low molecular weight compounds are overestimated as the high molecular weight compounds tilt the slope of the regression line and, hence, cause this overestimation at the lower end of the regression line.

Besides this general bias, there is a large scatter in the predicted data, which can be seen from the correlation coefficients in Table D.3, page 309. Thus, the method does not only fail to reflect the general trend of the reaction rates, moreover, the single predicted values inherit large errors. Figure 3.9 demonstrates more clearly than the box plots in Figure 3.8, why the predicted data with the overall correlation of all monoalcohols should be treated with caution. Although the correct order of magnitude is predicted for the current data set, there is an increased bias from the overall correlation as can be seen from the regression line in Figure 3.9 (compare also Table D.3). There is already a severe underprediction of fast reacting (i.e. large) compounds, when only the data of linear terminal monoalcohols is used, which can be seen by the slope of the regression line of only 0.33 in Figure 3.9 and Table D.3. For the overall correlation, the error increases dramatically and the slope becomes even negative (−0.11). However, for substituted DCAs, this effect is not seen. Although the overall correlation of all dicarboxylic acids was very weak and an appreciable correlation was only found for unsubstituted DCAs, the parameters of the regression lines of the predicted versus experimental data do not show a decreased bias for the correlation of the unsubstituted DCAs only. Both, the regression equations and the correlation coefficients do not differ a lot (compare Table D.3, page 309).

Furthermore, from Figure 3.9 can be seen that there is a severe overestimation of the rate constants of formaldehyde and glyoxal. The reason is the omission of these compounds in the derivation process of the regression line for rate constant predictions. Due to the reasons discussed above, formaldehyde and glyoxal have not been considered in the Evans-Polanyi correlation. As these compounds show significantly decreased reaction rate constants compared to other aldehydes, their rate constants are consequently heavily over-predicted with the current correlation.

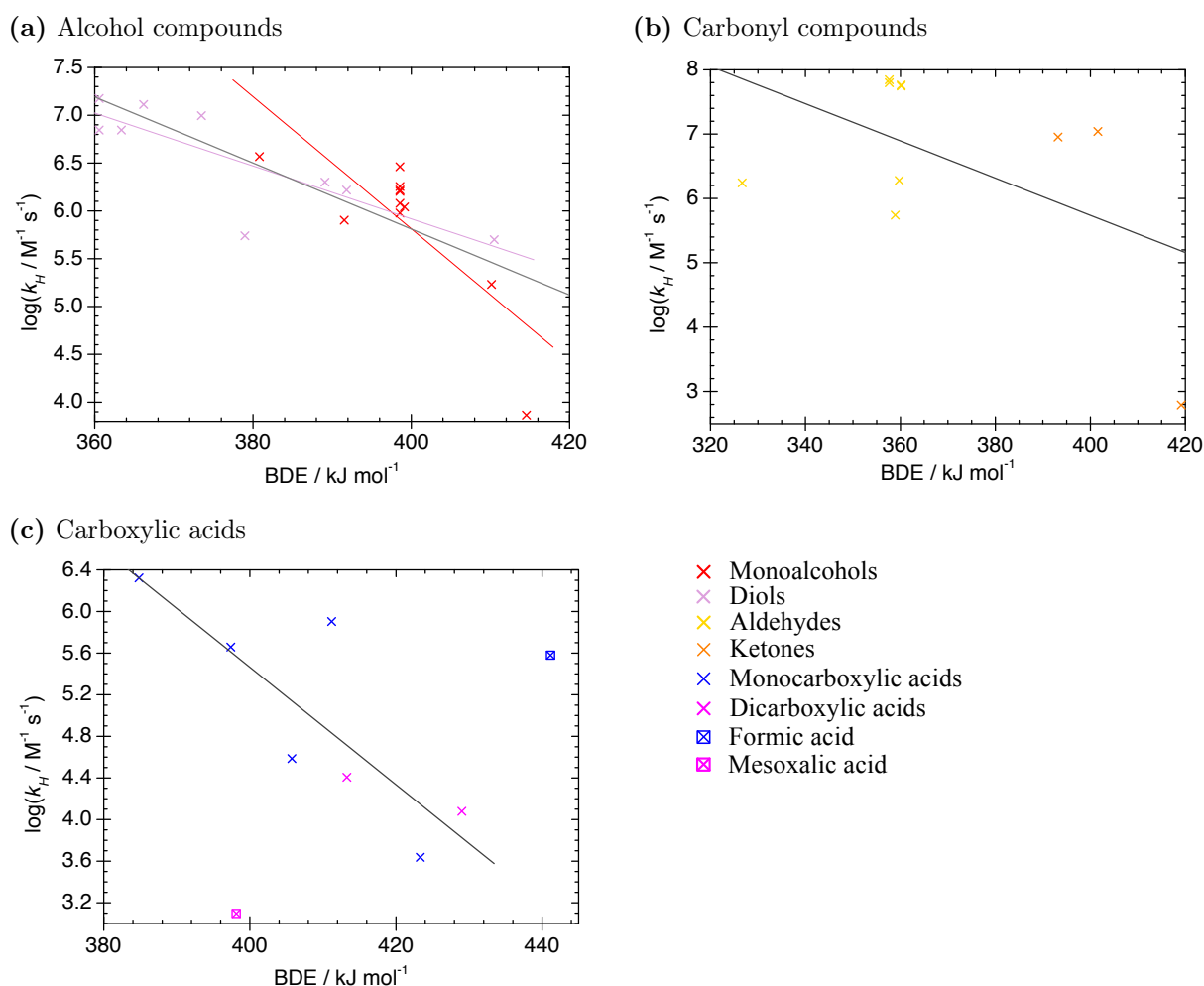
It can be concluded that Evans-Polanyi-type correlations are a good estimation method as they are widely applicable. However, the method fails for charged or unsaturated compounds. The precision is appreciable, but should be improved for the intended aim of automated mechanism self-construction, especially, for higher molecular weight compounds.

### 3.5.2 NO<sub>3</sub> rate constant prediction

The evaluation of Evans-Polanyi-type correlations has been extended to nitrate radical reactions with organic compounds. As no experimental data for nitrate radical reactions with alkanes exist, this compound class has been omitted in the evaluation process.

The results show again a moderate correlation of the logarithmised experimental rate constant divided by the number of weakest bound H-atoms ( $\log k_H$ ) against the  $BDE$  with correlation coefficients  $R^2$  between 0.6 and 0.7. Only for carbonyl compounds the method fails and the correlation coefficient  $R^2$  of 0.26 indicates no correlation (see Table 3.5 and Figure 3.10).

No significant improvement is obtained by separate regression lines for monoalcohols and diols, so that the overall regression can be used (compare Figure 3.10a and Table 3.5). For aldehydes and ketones, an overall correlation is given as in the case of the Evans-Polanyi-type correlations for the hydroxyl radical reactions. This is also due to the very limited dataset of ketone reactions bearing only three experimentally determined rate constants. However, no correlation was found (see Figure 3.10b) and the values scatter over several orders of magnitude. At around  $360 \text{ kJ mol}^{-1}$ , the range of rate constants spans over 2 orders of magnitude (between 5.5 and 8). Acetone with a  $BDE$  of  $419 \text{ kJ mol}^{-1}$  has a 2.4 times smaller  $\log k_H$  with a value of 2.79 than expected from the regression line. For carboxylic acids some critical data assessment has to be performed in advance of the derivation of the regression line. Analogous to the homologous series of carboxylic



**Figure 3.10** Evans-Polanyi-type correlations of nitrate radical reactions with the respective compound classes. The respective equations for the regression lines can be found in Table 3.5.

**Table 3.5** Parameters for the regression equations  $\log(k_H) = A \cdot (BDE/\text{kJ mol}^{-1}) + B$  and statistical data derived from the Evans-Polanyi-type correlations of aqueous phase nitrate radical reactions with organic compounds for the various compound classes.

Compound class	$10^2 A$	$10^{-1} B$	$R^2$	$\sigma$	$N$
Monoalcohols	$-(6.91 \pm 1.8)$	$3.35 \pm 0.7$	0.628	0.49	11
Diols	$-(2.76 \pm 0.7)$	$1.70 \pm 0.3$	0.680	0.35	9
All alcohols	$-(3.45 \pm 0.6)$	$1.96 \pm 0.3$	0.616	0.47	20
All carbonyls	$-(2.89 \pm 1.7)$	$1.73 \pm 0.6$	0.256	1.41	10
Carboxylic acids*	$-(5.65 \pm 1.7)$	$2.80 \pm 0.7$	0.698	0.61	7

\*without mesoxalic and formic acid

acids (see section 3.3), formic acid shows an unexpectedly high reactivity than it would be expected from the Evans-Polanyi-type correlations. Moreover, the highly oxidised DCA mesoxalic acid ( $\text{C}(=\text{O})(\text{C}(=\text{O})\text{OH})_2$ ) has a significantly reduced reaction rate constant compared to the other acids. Therefore, these two values were excluded, when deriving the regression line. The resulting correlation, however, shows a reasonable  $R^2$  of 0.7.

The conclusions drawn from the investigations of the Evans-Polanyi-type correlations of hydroxyl radical reactions with organic compounds are also valid for nitrate radical reactions. Yet, due to a much smaller dataset with overall 41 reactions considered, the errors increase significantly for nitrate radical reactions. The dataset for alcohol compounds is of comparable size and, therefore, the errors are small as can be seen from the box plot in Figure D.5 on page 310 in Appendix D.4. With dataset sizes of only about 10, the precision decreases for the other compound classes. Moreover, only an overall correlation of aldehydes and ketones could be used to predict rate constants of carbonyl compounds with the nitrate radical and, for carboxylic acids, an overall correlation of the rate constants of the nitrate radical with the protonated and deprotonated forms had to be used. Poor results are not surprising for carbonyl compounds since they have initially shown a weak correlation with an  $R^2$  of 0.26 and the use of the correlation is not recommended. However, also carboxylic acids show large errors in the predicted results (compare Figure D.5, page 309 in the Appendix) despite a correlation coefficient  $R^2$  of 0.70 for the derived regression line. This is caused by the inclusion of outliers during the evaluation process, yet an exclusion during the derivation process of the regression line. There is an underestimation of fast reaction rate constants and an overestimation of slow reaction rate constants in all compound classes as seen for the hydroxyl radical (see Figure D.6, page 310). However, an experimental dataset with measurements of continuous homologous series to high carbon numbers exists only for alcohol compounds. For carbonyl compounds and carboxylic acids, measurements for homologous series exist only up to  $\text{C}_3$  compounds. Therefore, effects of an underestimation of large molecules could not be evaluated due to the limited experimental database. The evaluated data and the derived regression lines can be found in Figure D.6, page 309. For a better legibility, a double logarithmic scale has been used in the plot. The parameters of the regression equations of Figure D.6 and the statistical data are given in Table D.4, page 309, in Appendix D.4.

### 3.5.3 Development of an advanced Evans-Polanyi-type correlation

Overall, Evans-Polanyi-type correlations give suitable results for a first guess, but advantages towards the other much simpler estimation methods are minor. Especially the bias that derives from the consideration of only the weakest bound H-atoms is unsatisfying as the prediction methods investigated in this context are meant for automated mechanism self-construction, which aims at the description of the oxidation of large organic compounds. Moreover, for nitrate radical reactions, reliable correlations could be derived only for alcohol compounds and carboxylic acids. Furthermore, the method cannot be applied to unsaturated compounds as it is intended for H-abstraction reaction and not for addition reactions to double bonds. Evans-Polanyi-type correlations also fail for reactions of dissociated acids, since the *BDE* prediction method by *Benson* (1976) was developed for the gas phase and no increments exist for carboxylate groups. Thus, it is not possible to estimate the *BDEs* of dissociated carboxylic acids, which are, however, needed as input for the Evans-Polanyi correlation. Moreover, electron transfer reactions become likely for dissociated carboxylic acids, especially, in reactions with the nitrate radicals. As Evans-Polanyi-type correlations are only meant for H-abstraction reactions, deprotonated acids have to be omitted.

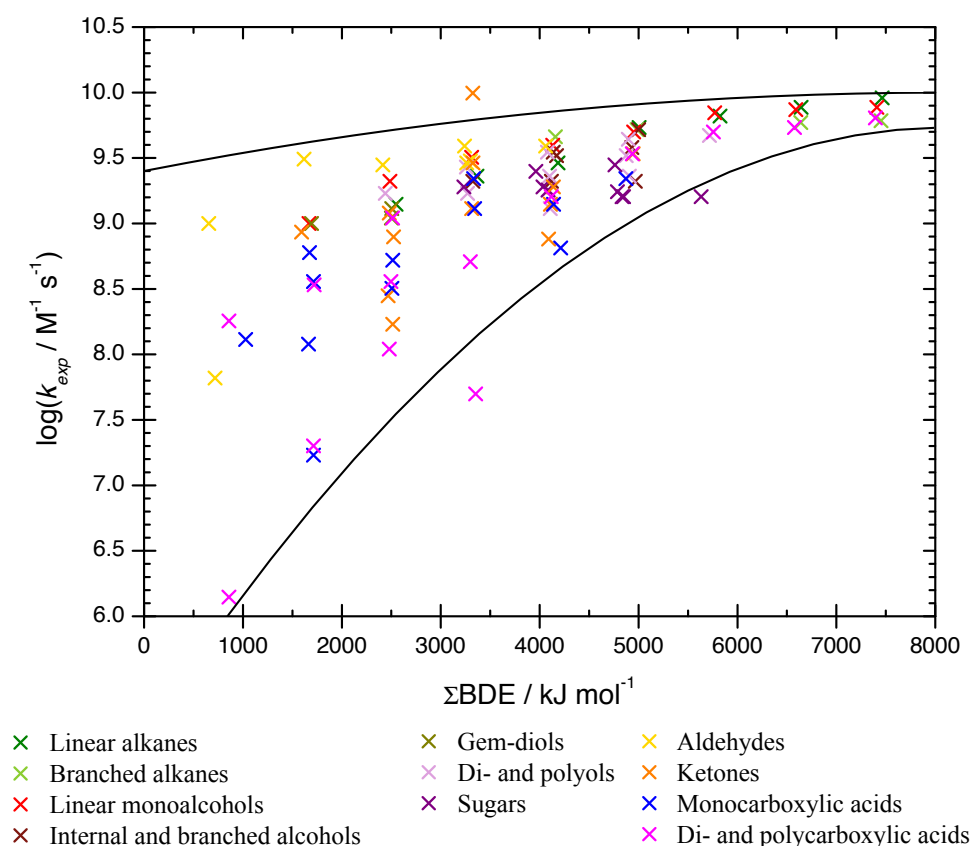
Despite the limited use for the prediction of saturated, neutral, aliphatic organic compounds only, an improvement of the prediction method was tempted. The aim was to diminish the biases caused by the correlation with the weakest *BDE* of the organic molecule. The original intention of the correlation with only the weakest *BDE* was to be able to predict the reaction products as well. As Evans-Polanyi-type correlations are meant for H-abstractions only, an immediate determination of the reaction product is possible, when the position of the weakest *BDE* is known. Previous studies focused mainly on smaller compounds bearing up to four carbon atoms, which are not so much affected by the bias. Moreover, only the main reaction channel was considered in previous studies. Hence, it was sufficient to correlate the rate constants to the weakest *BDE* only, as the main abstraction site in a molecule is found at the weakest *BDE*. For larger compounds, the organic rest has to be considered besides the main attack site. Therefore, not only the weakest *BDE*, but all *BDEs* of bonds including H-atoms in a molecule should be considered. The idea is to correlate the sum of all *BDEs* to the logarithmised experimental overall rate constant rather than only the weakest *BDE* to  $\log k_H$  in Equation 2.10, page 32:

$$\log k_{exp} = a - b \cdot \Sigma BDE(X-H) \quad (3.3)$$

where  $\Sigma BDE(X-H)$  is the sum over all *BDEs* of bonds including an H-atom and X, which is either a carbon or an oxygen atom. By summing up all individual *BDEs* to an overall *BDE*, the organic rest is considered. However, information about the reaction products is lost. Estimates can be made from the strength of the individual *BDEs*, but an exact calculation of branching ratios is not possible.

### Hydroxyl radical rate constant prediction

Figure 3.11 shows experimental rate constants for hydroxyl radical reactions with organic compounds plotted against the sum of all  $BDEs$  of bonds including a hydrogen atom ( $\Sigma BDE$ ) for the individual compound classes. When the rate data are correlated against  $\Sigma BDE$ , the linear regression has to be extended to a quadratic regression. It can be seen from Figure 3.11 that nearly all data lie within a sector that is marked by an upper and a lower boundary. Both boundaries follow quadratic equations as well as the data of each compound class within this sector. At first glance, the sector seems to converge to a limit value of  $1 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  at a  $\Sigma BDE$  of about  $8000 \text{ kJ mol}^{-1}$ . This value corresponds to the approximate diffusion limit of the reaction of hydroxyl radicals with organic compounds in the aqueous phase (see, e.g., *Haag and Yao*, 1992, *Schöne et al.*, 2014) and might explain the different behaviours of the old and the new correlations. The previous Evans-Polanyi-type correlations considered  $\log k_H$ , where only partial rate constants of H-abstraction reactions from the carbon atom with the weakest bound H-atoms were considered. Therefore, in the old method, the diffusion limit was never reached with the correlations to  $\log k_H$ . Considering the overall experimental value of the rate constant and all bonds with abstractable H-atoms changes this fact and a linear regression is not valid any more. The derived equations in the improved Evans-Polanyi-type correlations should



**Figure 3.11** Improved Evans-Polanyi-type correlation of the experimental rate constants plotted against the sum of all  $BDEs$  of bonds including a hydrogen atom. The black lines mark the upper and lower boundaries of most of the data following a quadratic equation. Colours represent different compound classes as given in the figure legend.

be used only up to the maximum value of the quadratic equation. This point should mark the diffusion limit of the respective compound class and the maximum value should be used from this point on.

Another difference to the old correlation are much higher *BDE* values, which are directly proportional to the experimental second order rate constants in contrast to the inversely proportional *BDEs* and  $\log k_H$  previously. The previous inverse proportionality represented the fact that the reactivity decreases with increasing bond strength. Considering all bonds relevant for H-atom abstractions, *BDEs* increase with larger molecules. As these molecules have more sites to attack, their reactivity increases and a direct proportionality is observed.

Quadratic regressions have been performed to derive regression equations for rate constant predictions. The results are plotted in Figure 3.12 for the various compound classes and detailed information is given in Table 3.6. The extended Evans-Polanyi-type correlations show significant improvements in most cases, which can be seen from Figure 3.12 and the correlation coefficients in Table 3.6. However, for optimal results a thorough analysis of the dataset is essential and few adjustments are necessary in the database to derive the correlations.

The method is immediately applicable to alkanes with correlation coefficients  $R^2$  close to 1, when distinguishing between linear and branched alkanes. The use of an overall correlation for alkanes gives still excellent results with an  $R^2$  of 0.92. For alcohols, the method works very well only for linear monoalcohols with a correlation coefficient of 0.99. Internal functionalisations, branches or more than one alcohol group in the molecules decrease the reaction rate constants compared to the rate constants of linear monoalcohols with the same *BDE* (compare Figure 3.12b). For these compounds, a clear trend in the correlation of the rate constant and the *BDE* is not visible and the correlation coefficient

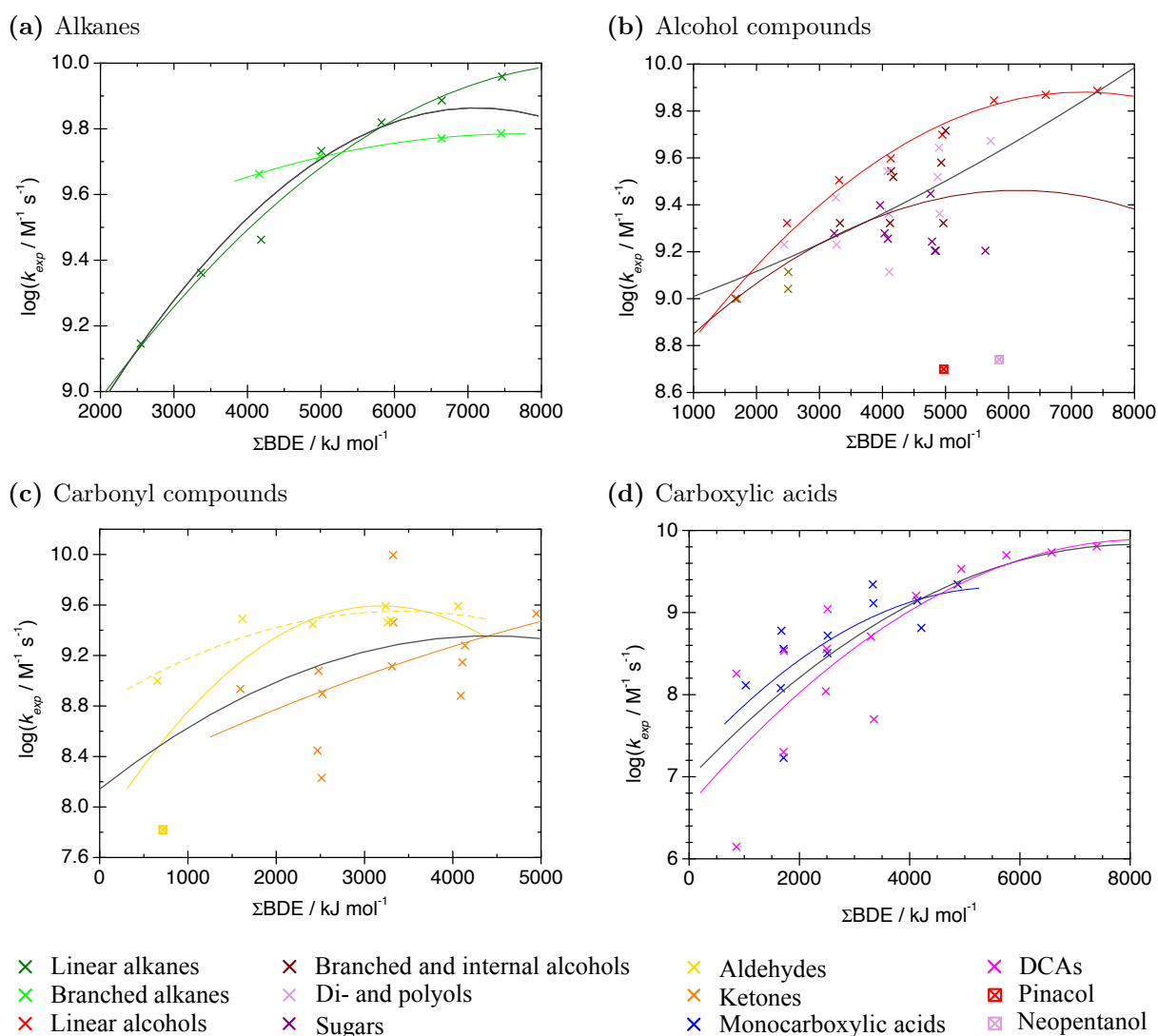
**Table 3.6** Parameters for the regression equations  $\log(k_{exp}/M^{-1}s^{-1}) = A \cdot (\Sigma BDE/kJ mol^{-1})^2 + B \cdot (\Sigma BDE/kJ mol^{-1}) + C$  and statistical data derived from the advanced Evans-Polanyi-type correlations of aqueous phase hydroxyl radical reactions with organic compounds for the various compound classes.

Compound class	$10^8 A^{(a)}$	$10^4 B^{(b)}$	$C^{(c)}$	$R^2$	$\sigma^{(c)}$	$N$
Linear alkanes	-(2.21±0.7)	3.90±0.7	8.29±0.17	0.986	0.04	7
Branched alkanes	-(0.94±0.2)	1.46±0.2	9.22±0.07	0.998	0.04	4
All alkanes	-(3.46±1.0)	4.92±1.1	8.11±0.26	0.923	0.08	11
Linear terminal monoalcohols	-(2.77±0.5)	3.97±0.4	8.46±0.09	0.987	0.04	8
All other alcohols*	-(2.31±2.5)	2.84±2.0	8.59±0.36	0.346	0.15	30
All alcohols*	0.55±1.2	0.90±1.0	8.91±0.22	0.523	0.17	38
Monoaldehydes	-(6.44±3.8)	4.39±1.8	8.80±1.09	0.810	0.11	7
All aldehydes	-(17.5±14.5)	11.2±6.6	7.81±0.61	0.630	0.43	8
Ketones	-(1.67±14.3)	3.49±9.5	8.14±1.50	0.238	0.46	12
All carbonyls	-(6.19±5.2)	5.48±3.1	8.14±0.43	0.288	0.41	25
Monocarboxylic acids	-(6.62±11.1)	7.49±6.6	7.19±0.86	0.548	0.46	12
Di- and polycarboxylic acids	-(4.70±4.7)	7.81±3.9	6.65±0.66	0.665	0.66	14
All carboxylic acids	-(4.33±3.3)	7.04±2.6	6.97±0.44	0.602	0.57	26

(a) in  $\frac{mol^2}{kJ^2 s^2}$ ; (b) in  $\frac{1}{kJ s}$ ; (c) in  $M^{-1} s^{-1}$

\*except the outliers neopentanol and pinacol

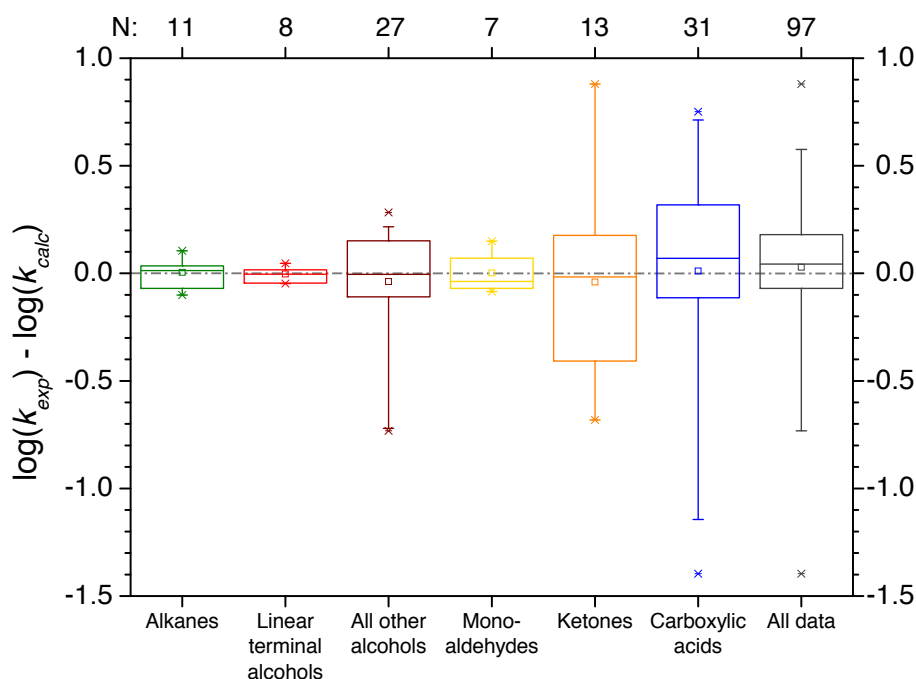
decreases to 0.35. The overall correlation coefficient of all alcoholic compounds is still moderate with a value of 0.52 although the advantage of the improved Evans-Polanyi-type correlation compared to the original correlation is minor for all alcohol compounds except linear monoalcohols. Moreover, using the overall correlation of all alcohols including linear terminal monoalcohols gives a parabola as regression equation, which is opened upward. Thus, the regression equation has a minimum rather than a maximum, which contradicts the theory of a correspondence with the diffusion limit. Furthermore, it should be noted that the highly branched di- and polyols pinacol and neopentanol have not been considered for the derivation of the regression line as the decrease of the rate constants of these compounds is particularly enhanced. For carbonyl compounds, the method works well only



**Figure 3.12** Improved Evans-Polanyi-type correlations of hydroxyl radical reactions with organic compounds for the respective compound classes. Lines of regressions for the individual compound classes are shown in the same colour as the corresponding data points or in grey for the correlation of the overall data. The grey line in plot b represents the quadratic regression of all alcohols except linear monoalcohols and the dashed orange line in plot c is the regression line of all monoaldehydes and glyoxal. The respective equations for the regression lines can be found in Table 3.6.

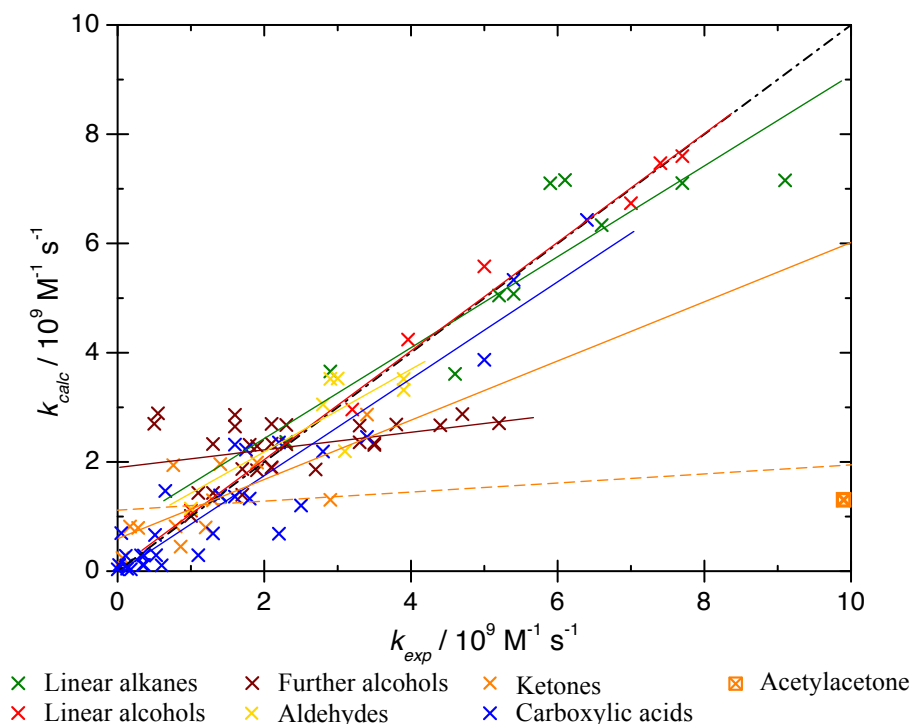
for aldehydes, who show an appreciable correlation coefficient of 0.63. On the contrary, the rate constant prediction for ketones fails and a correlation is barely visible ( $R^2 = 0.24$ ). For carboxylic acids, moderate correlation coefficients are found again in the range of 0.55 – 0.67.

The regression lines were used to predict rate constants for the compounds listed in the kinetic database. The data has been analysed with box plots (see Figure 3.13). Moreover, the predicted data has been plotted against the experimental data in Figure 3.14 and linear regressions have been performed as explained in subsection 3.5.1. From the box plots in Figure 3.13, a slightly increased accuracy is visible compared to the original Evans-Polanyi-type correlations (compare with Figure 3.8). It is furthermore most noticeable that less parameterisations are needed, as the correlations with the improved Evans-Polanyi-type correlations work for more general compound classes. For example, there is no distinction between mono- and dicarboxylic acids in the improved predictions. The major improvements become visible from the more detailed investigations by plotting the predicted data against the experimental data in a scatter plot (compare Figures 3.9 and 3.14 as well as Tables D.3 and D.5 in Appendix D.4). The general bias of decreased rate constant predictions of large or fast reacting compounds is significantly diminished. For alcoholic compounds except terminal linear monoalcohols, only slight improvements could be achieved and the slope of the regression line is still a lot smaller than one with a value of 0.16. Errors in the single predicted values are large, represented by an  $R^2$  of the regression line of 0.15. For ketones, acetylacetone shows a significantly reduced value in the predicted rate constants compared to the experimental value. Omitting this outlier, the slope of the regression line improves to 0.54 and  $R^2$  to 0.53. All other compound classes give regressions with slopes between 0.76 and 0.99 and correlation coefficients between 0.66



**Figure 3.13** Box plots of the absolute errors of the improved Evans-Polanyi-type correlation of hydroxyl radical reactions with organic compounds of the respective compound class.



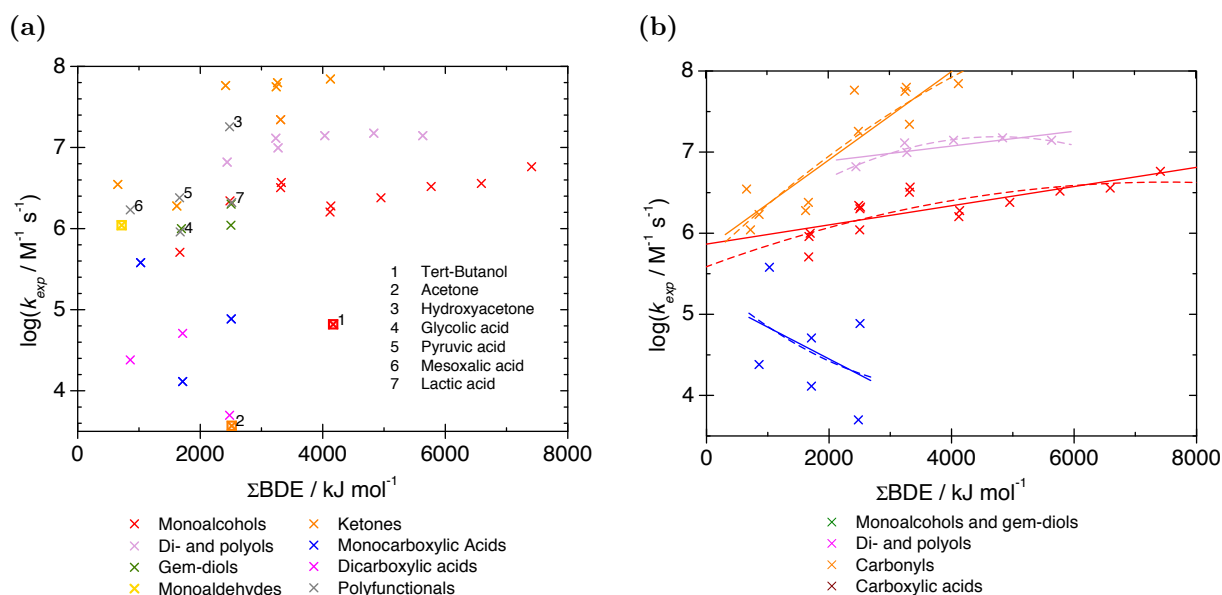


**Figure 3.14** Plot of predicted versus experimental data for hydroxyl radical reactions separated by compound class together with the linear regression lines for the improved Evans-Polanyi-type correlations. For the calculation of the predicted values, the regression lines of Table 3.6 together with the data from the kinetic database have been used. The regression lines have the same colour code as the data points. For ketones, the dashed line includes the outlier acetylacetone while the solid line does not. The black dashed-dotted line is the line of same reactivity.

and 0.99 compared to slopes less than 0.33 in the original Evans-Polanyi correlation for all compound classes except alkanes and correlation coefficients less than 0.42. Overall, the improvements increase the reliability of the prediction method and make it a considerable tool for automated rate constant prediction although some compound classes still show noticeable errors.

### Nitrate radical rate constant prediction

Improved Evans-Polanyi-type correlations were also derived for nitrate radical reactions with organic compounds using the kinetic database from section 3.1. Results from the correlation are shown in Figure 3.15. Figure 3.15a shows the raw data of the database. In contrast to the advanced Evans-Polanyi-type correlations of the hydroxyl radical reactions, a quadratic dependency is not visible for nitrate radical reactions. The only exceptions are di- and polyols. An explanation for this behaviour might be the significantly reduced rate constants by about 2 orders of magnitude, but similar diffusion limits of nitrate radical reactions compared to hydroxyl radical reactions (see *Schöne et al.*, 2014, *Hoffmann*, 2007).  $\text{NO}_3$  reaction rate constants stay below  $10^8 \text{ M}^{-1} \text{ s}^{-1}$  and, hence, significantly below the diffusion limit. Thus, the diffusion limit might not affect the correlations in this range and linear regressions are still valid. The curvature of the quadratic behaviour of diols is small



**Figure 3.15** Improved Evans-Polanyi-type correlations of nitrate radical reactions for the respective compound classes. Figure (a) shows the raw data and Figure (b) the derived correlations and the data used to derive these correlations. Lines of regressions for the individual compound classes are shown in the same color as the corresponding data points. Solid lines represent linear regressions and dashed lines quadratic regressions. The respective equations for the regression lines can be found in Table 3.7 and Table D.6, page 311.

and only 6 data points belong to the correlation, so that this effect could be a coincidence. Moreover, the correlation coefficient of the linear regression is still appreciable with a value of 0.61 (compare Table 3.7). In general, the correlation coefficients for the linear regressions are about equal to the quadratic regressions (compare Table 3.7 and Table D.6, page 311). As previous Evans-Polanyi-type correlations showed a linear dependency of the *BDE* versus the logarithmised rate constants and the precision of the linear and quadratic equations is about equal for nitrate radical reactions, linear regressions were preferred over quadratic.

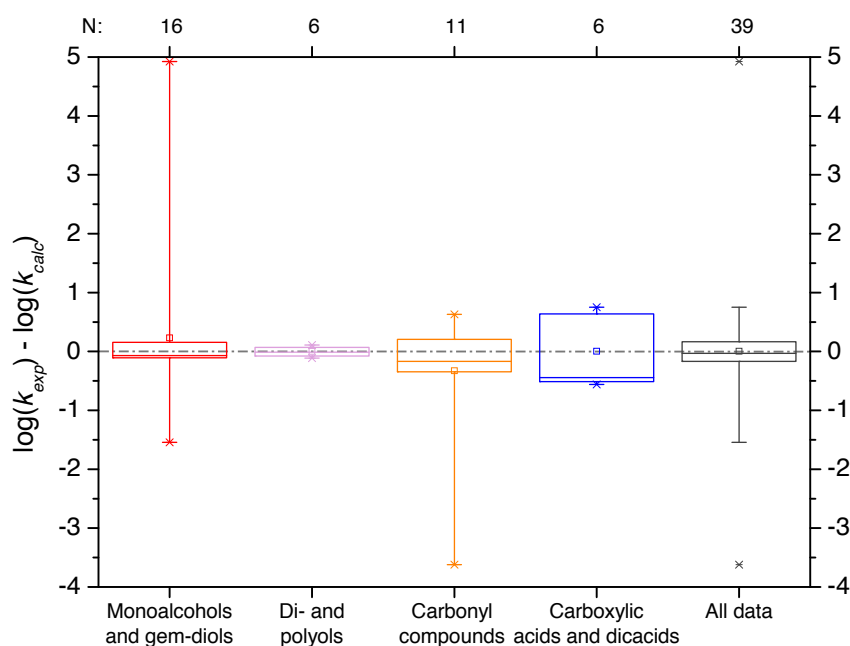
To derive the correlations two outliers had to be excluded (acetone and tert-butanol, both with significantly reduced reaction rate constants). Moreover, it can be seen from Figure 3.15a that substituted carboxylic acids correlate with the compound class of the substitution rather than the dataset of carboxylic acids. Hydroxyacetone is the only polyfunctional compound with a hydroxyl and a carbonyl group. According to Figure 3.15a, these polyfunctionals correlate better with carbonyl compounds. All polyfunctional compounds and outliers have been labelled in Figure 3.15a for more convenience. The final regressions with the consideration explained above are plotted in Figure 3.15b. The parameters of the regression lines and further statistical information is given in Table 3.7 for the linear equations and in Table D.6, page 311, for the quadratic equations. As for hydroxyl radicals, only a few correlations are needed to describe the whole set of reaction rate constants needed for this study. This is a big advantage over the original Evans-Polanyi-type correlations as in the advanced Evans-Polanyi correlations larger subsets can be used to produce more reliable correlations.

**Table 3.7** Parameters for the regression equations  $\log(k_{exp}/M^{-1} s^{-1}) = A \cdot (\Sigma BDE/kJ mol^{-1}) + B$  and statistical data derived from the improved Evans-Polanyi-type correlations of aqueous phase nitrate radical reactions with organic compounds for the various compound classes.

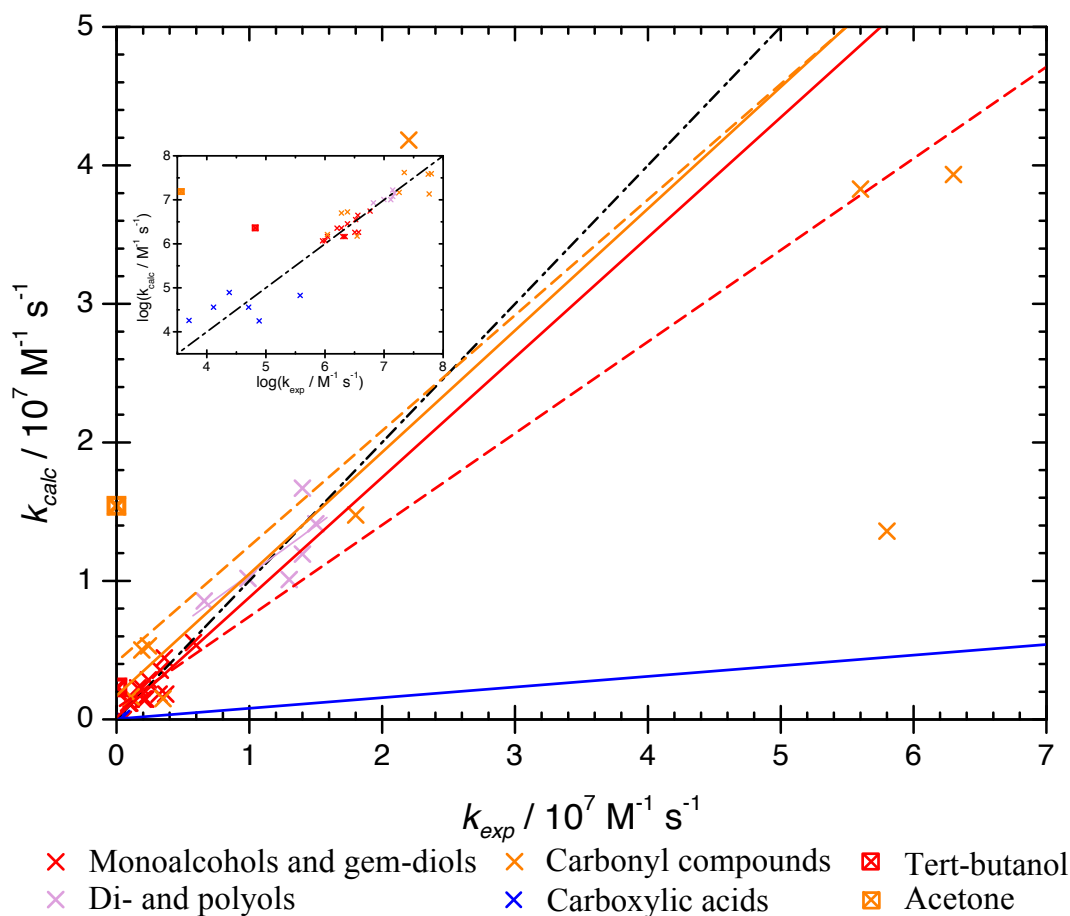
Compound class	$10^4 A / \frac{1}{kJ s}$	$B / M^{-1} s^{-1}$	$R^2$	$\sigma / M^{-1} s^{-1}$	$N$
Monoalcohols <sup>(a)</sup> and gem-diols	$1.18 \pm 0.27$	$5.87 \pm 0.11$	0.601	0.18	15
Di- and polyols	$0.91 \pm 0.36$	$6.71 \pm 0.15$	0.611	0.10	6
Carbonyl compounds <sup>(b)</sup>	$5.44 \pm 0.91$	$5.82 \pm 0.23$	0.799	0.34	11
Carboxylic acids <sup>(c)</sup>	$-(3.92 \pm 4.28)$	$5.23 \pm 0.78$	0.173	0.67	6

<sup>(a)</sup>except tert-butanol; <sup>(b)</sup>except acetone; <sup>(c)</sup>substituted carboxylic acids count to the respective compound class of the functional group

In the following, the linear regressions have been used to predict the kinetic data of nitrate radical reactions with organic compounds from the kinetic database. The predicted data was compared to the experimental data either with box plots (see Figure 3.16) or a scatter plot, where regressions were performed for the predicted versus experimental data (see Figure 3.17). As the outliers tert-butanol and acetone have been excluded during the development process of the Evans-Polanyi-type correlation, but are included in the evaluation process, large errors can be seen in the whiskers of the box plots for monoalcohols and carbonyl compounds in Figure 3.16. Moreover, large errors exist for carboxylic acids as the correlation was weak. Yet, the errors stay within an order of magnitude. Underestimation cannot totally be neglected for  $NO_3$  reactions as can be seen from Figure 3.16 and Figure 3.17. The whisker of the overall box in Figure 3.16 shows values down to -1.5. These values are from reactions of nitrate radicals with monoalcohols and gem-diols as can be seen from the first box. The large positive whisker in the first box derives from the outlier tert-butanol. From Figure 3.17 can be seen that this underestimation is not necessarily a bias from underpredicted rate constants of large compounds. Generally,



**Figure 3.16** Box plots of the absolute errors of the improved Evans-Polanyi-type correlation of nitrate radical reactions with organic compounds of the respective compound class.



**Figure 3.17** Plot of predicted versus experimental data for nitrate radical reactions with organic compounds of the different compound classes together with the linear regression lines. For the calculation of the predicted values the regression lines of Table 3.7 together with the data from the kinetic database have been used. The regression lines have the same colour code as the data points. Dashed lines include the values of the outliers of the respective compound class. The black dashed-dotted line is the line of same reactivity.

the data points follow the 1:1 line. However, between  $2 \cdot 10^6$  and  $4 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$  of the experimental values a substantial number of values is underpredicted.

In general, the improved Evans-Polanyi-type correlations reduce the bias of underpredicted fast reaction rate constants, which is noticeable from the regression lines in Figures D.6, page 310, and 3.17 as well as Tables D.4 and D.7, pages 309 and 311, respectively. Except for carboxylic acids, the slopes of the regression lines increase (to values between 0.7 and 0.9). For carboxylic acids, the slope of the regression line is close to 0, and no clear trend of the predicted data is visible to follow the 1:1 line. As the carboxylic acid react very slowly with rate constants in the order of  $10^3 - 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , the data has been replotted on a double logarithmic scale for more clarity in Figure 3.17. Besides the general reduction of the bias, the precision of the single predictions increases as well, which can be inferred from an increase in the correlation coefficients of the regression lines in the scatter plot of the experimental versus predicted data (compare Table D.4 and Table D.7.).

Overall, with the improvements introduced in this subsection, Evans-Polanyi-type correlations are a prediction method, which can be considered for automated mechsims

construction. Although errors are still noticeable, the right order of magnitude of the rate constant is predicted. Moreover, the method is widely applicable and reliable for all saturated, neutral organic compounds. The only necessary input are *BDEs*, which can be estimated with the prediction method of *Benson* (1976) with a satisfactory accuracy of  $\pm 8 \text{ kJ mol}^{-1}$  (*Benson*, 1976).

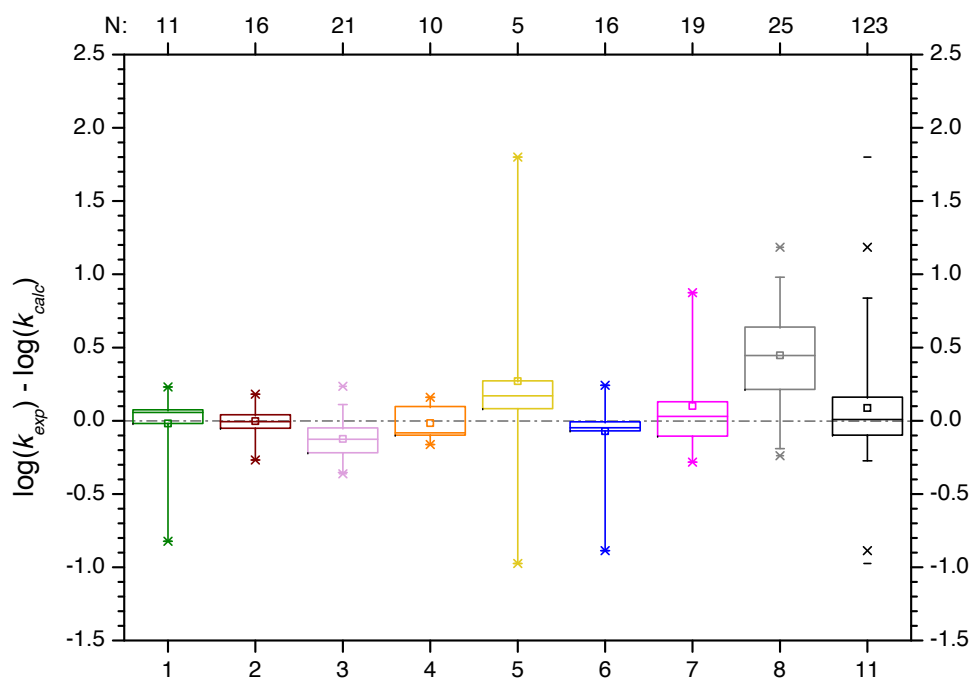
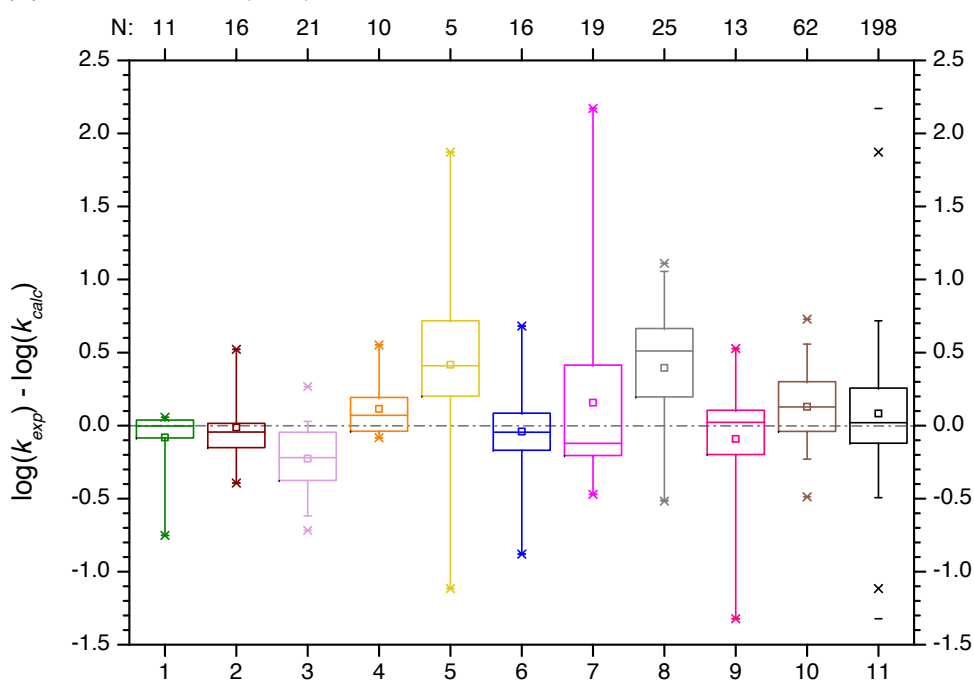
## 3.6 Structure-activity relationships

This section evaluates and compares the two SARs of *Monod and Doussin* (2008)/*Doussin and Monod* (2013) and *Minakata et al.* (2009) introduced in subsection 2.4.3. For the evaluation process, rate constants have been predicted for reactions of hydroxyl radicals with organic compounds, where reactions were available in the kinetic database. Parameters for the rate constant predictions have been taken from the publications mentioned above.

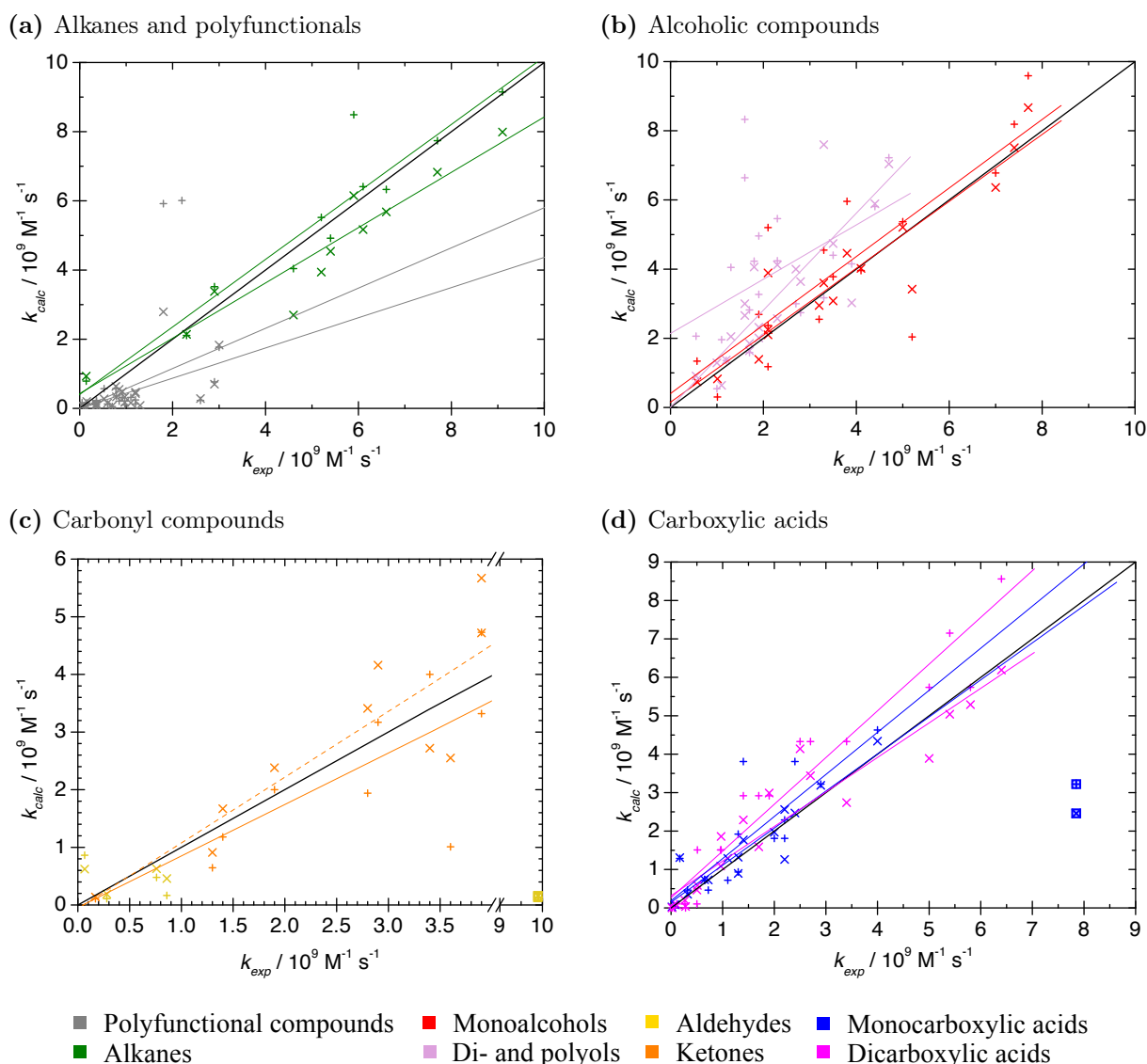
The accuracy of both SARs can be assessed from the box plots given in Figure 3.18. In general, both SARs predict the rate constants very precisely. Errors are small. This is especially the case for pure hydrocarbons or organic compounds with just one functional group, e.g., monoalcohols or monocarboxylic acids. Two functional groups of the same kind increase the errors somewhat and a mixture of different functional groups (polyfunctionals, No. 8 in Figure 3.18) even more. For polyfunctional compounds the box (25% median) does not even hit the zero-line anymore in the SAR by both authors. Both SARs seem to have difficulties with the prediction of carbonyl compounds. For monocarbonyl compounds the precision is still very good although errors are already larger than for the other single substituted organic compounds (monoalcohols and monocarboxylic acids). Rate constants of dicarbonyl compounds are underestimated by both SARs as the boxes are above the zero-line in Figure 3.18 either for the SAR by *Doussin and Monod* (2013) or the one by *Minakata et al.* (2009).

The comparison of both SARs shows similar results – a high precision in the predicted rate constants and no clear bias although the current evaluation showed a small overestimation of rate constants of di- and polyols and an underestimation of dicarbonyl and polyfunctional compounds. Yet, overall, errors are nearly equally distributed around the zero-line. These conclusions are manifested by the plots given in Figure 3.19, page 69, where the predicted data is plotted against the experimental data. The slopes of the regression lines of these plots are generally close to 1 and the correlation coefficients as a measure of the quality of the single predictions are high.

In the structure-activity relationship by *Monod and Doussin* (2008)/*Doussin and Monod* (2013) absolute errors are a little smaller than in the one by *Minakata et al.* (2009) (compare Figure 3.18). While deviations in the slopes and y-intercepts are similar for both SARs, the correlation coefficients as a measure for the accuracy of the single predictions are higher for the structure-activity relationship by *Monod and Doussin* (2008). However, one should keep in mind that due to the large number of descriptors, overfitting is more likely for the SAR by these authors. Moreover, *Minakata et al.* (2009) cover more compound classes such as

(a) *Monod and Doussin (2008)/Doussin and Monod (2013)*(b) *Minakata et al. (2009)*

**Figure 3.18** Box plots of the absolute errors of the logarithmised experimental minus predicted rate constants for the prediction with the SAR by *Monod and Doussin* (a) and *Minakata et al.* (b). Numbers of the boxes in the abscissa refer to the compound class: 1 – alkanes, 2 – monoalcohols, 3 – di- and polyols, 4 – carbonyl compounds, 5 – dicarbonyl compounds, 6 – monocarboxylic acids, 7 – dicarboxylic acids, 8 – polyfunctional compounds, 9 – unsaturated compounds, 10 – aromatics, 11 – all data.



**Figure 3.19** Scatter plot of the rate constants predicted with the SARs by *Monod and Doussin* (2008)/*Doussin and Monod* (2013) and by *Minakata et al.* (2009) over experimental rate constants for aqueous phase reactions of hydroxyl radicals with organic compounds of the various compound classes. Regression lines are shown in the same colour as the respective data points. Oblique crosses and solid regression lines belong to the SAR by *Monod and Doussin* (2008)/*Doussin and Monod* (2013), upright crosses and dashed regression lines belong to the SAR by *Minakata et al.* (2009). For carbonyl compounds an overall regression of all carbonyl and dicarbonyl compounds is shown. The boxed values in subfigure c and d are outliers, which have been excluded in the linear regression. Parameters for the regression lines and statistical information can be found in Table D.8 and Table D.9, page 312, for the SARs by *Monod and Doussin* and *Minakata et al.*, respectively.

ethers, esters, unsaturated compounds and aromatic compounds. Overall, both SARs are a very suitable prediction tool for automated mechanism self-generation. A clear preference cannot be given. For the current study, the SAR by *Monod and Doussin* (2008)/*Doussin and Monod* (2013) was used due to the higher accuracy in the predictions and more reasonable branching ratios. The latter statement can be assessed with measurements by *Asmus et al.* (1973), who found 7% H-atom abstraction at the hydroxyl group for

methanol and even lower values for further alcohols. For methanol, 1/3 of the H-atom abstraction occurs at the hydroxyl group in the SAR by *Minakata et al.* (2009) and only 11% of the H-atom abstraction occurs at the hydroxyl group in the SAR by *Monod and Doussin* (2008). Yet, for higher carbon numbers, both SARs give reasonable results.

### 3.7 Conclusions from the evaluation process

The discussions of this chapter have shown that to date already accurate methods for the prediction of kinetic data for reactions of organic compounds with inorganic radicals of environmental interest exist. This allows the creation of a protocol for computerised mechanism self-construction. This section gives only an overview of the choice of prediction methods used for the protocol of automated mechanism self-generation within GECKO-A. The prediction methods are listed in Table 3.8. A detailed discussion of the reasons for the choice and a description of the implementation into the expert system GECKO-A is given in chapter 4.

**Table 3.8** Choice of the prediction methods in the final revised GECKO-A protocol to generate rate constants for the indicated reactions.

Prediction method	Application in the protocol
GROMHE ( <i>Raventos-Duran et al.</i> , 2010)	Henry's Law constants (needed for phase transfer) and hydration constants
SAR by <i>Minakata et al.</i> (2009)	Hydroxyl radical reactions with/influenced by unsaturated groups within organic compounds and carboxyl groups <sup>(a)</sup>
SAR by <i>Doussin and Monod</i> (2013)	Hydroxyl radical reactions with/influenced by carbonyl and gem-diol groups <sup>(a)</sup>
SAR by <i>Monod and Doussin</i> (2008)	Hydroxyl radical reactions with/influenced by all remaining functional groups within stable organic compounds <sup>(a, b)</sup>
Fuller-Schettler-Giddings (FSG) method ( <i>Fuller</i> , 1986)	Gas phase diffusion coefficients (needed for phase transfer)
Correlation of Taft parameters ( <i>Perrin et al.</i> , 1981)	Dissociations
Advance Evans-Polanyi-type correlations with branching ratios as from the corresponding OH radical reactions	Nitrate radical reactions of stable saturated and neutral organic compounds
Estimates with fixed rate constants and branching ratios as for the corresponding OH radical reactions	Nitrate radical reactions with unsaturated organic compounds
Estimates with fixed rate constants and fixed branching ratios	Nitrate radical reactions with deprotonated carboxylic acids and diacids, monomolecular decay of polycarbonyl compounds as well as radical decomposition

<sup>(a)</sup>SARs are applied group-wise in a molecule as described in detail in section 4.3. Parts of the molecule might be described with the SAR by *Minakata et al.* (2009) and parts with the SAR by *Monod and Doussin* (2008)/*Doussin and Monod* (2013). <sup>(b)</sup> $\alpha/\beta$ -parameters of NO<sub>3</sub>-functions in organic nitrates have been estimated with the corresponding parameters of the OH-function.



It was shown that structure-activity relationships are of special value for automated mechanism self-construction. Among the prediction methods tested, they showed the highest accuracy. Moreover, in addition to the other prediction methods, they allow conclusions about the products formed in a reaction and the branching ratios between the different reaction channels. Therefore, SARs have been used for the prediction of hydroxyl radical rate constants for all stable organic compounds.

SARs demand a large dataset for the derivation of this prediction method. Therefore, to date SARs exist only for hydroxyl radical reactions with organic compounds. For nitrate radical reactions, the presently most precise prediction method are Evans-Polanyi-type correlations. The improvements of using the sum of all bond dissociation enthalpies of bonds including a hydrogen atom instead of using the *BDEs* of the weakest hydrogen bonds only as described in subsection 3.5.3 resulted in a reliable prediction method. Difficulties of the previous Evans-Polanyi-type correlations to predict the correct rate constants for larger molecules have been overcome with this advancement. However, for the reactions of nitrate radicals with unsaturated compounds and deprotonated carboxylic acids and diacids, the method is not applicable and estimates with fixed rate constants and branching ratios had to be used as shown in Table 3.8 and explained in detail in section 4.4.

Estimation methods for the aqueous phase equilibrium processes hydration and dissociation as well as for the phase transfer process between the gas and the aqueous phase have been developed at the LISA. They have been adapted to the protocol (see Table 3.8) and were, therefore, not evaluated in this study.

As radical compounds are very unstable, they decompose rapidly, which makes an experimental determination of the rate constants difficult. Therefore, only a few measurements exist, which do not allow the derivation of a prediction method for radical decomposition. Therefore, only estimates with fixed rate constants and branching ratios could be used based on the few experimental data available in literature (e.g., *von Sonntag and Schuchmann*, 1991, *von Sonntag et al.*, 1997).



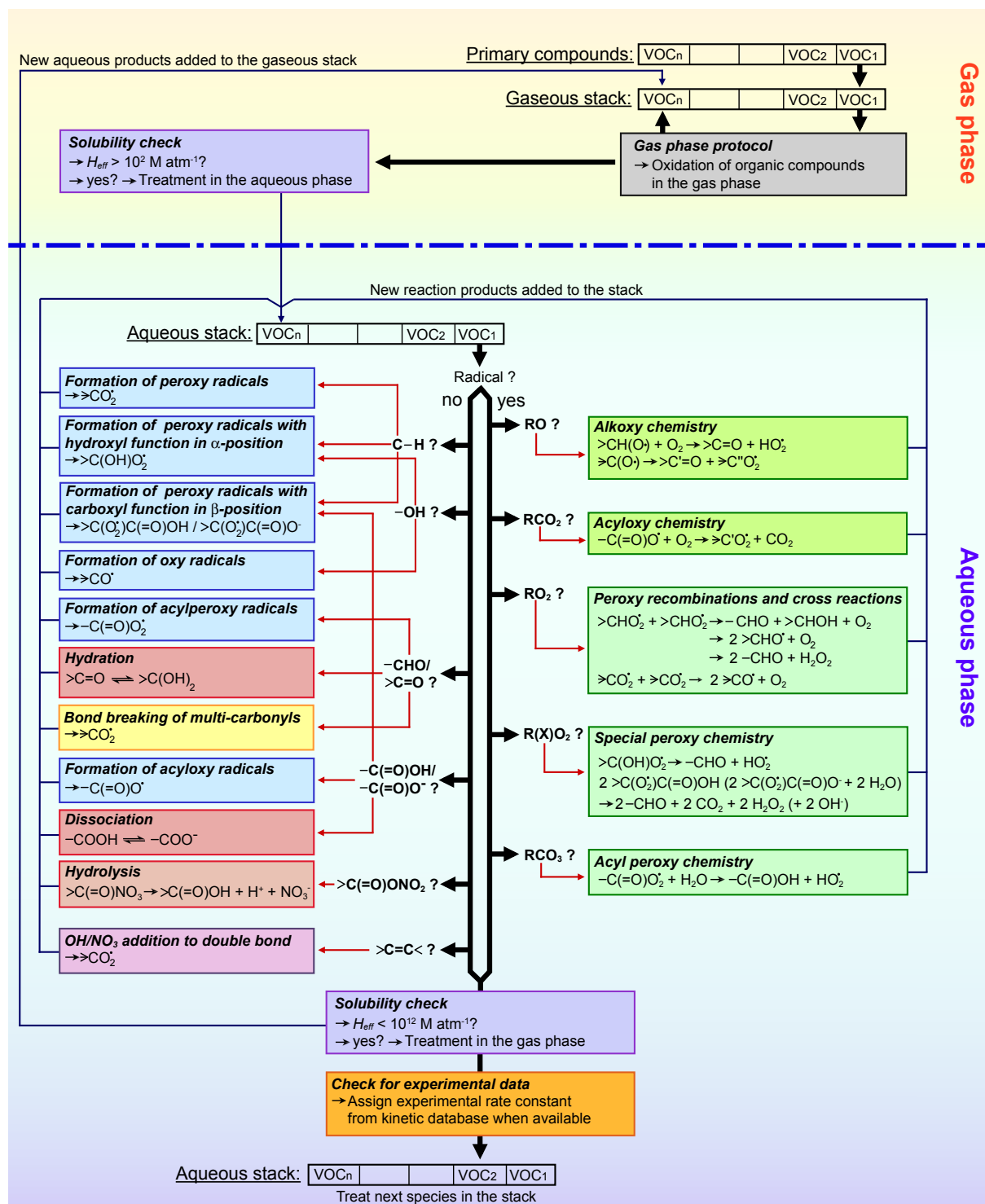
## 4 Development of the new aqueous phase protocol and its implementation into GECKO-A

The current chapter describes the development of the protocol for automated mechanism self-construction and its implementation in the expert system GECKO-A. The protocol is based on the evaluated results of the kinetic data and the prediction methods discussed in chapter 3. A detailed description of all implemented processes arranged by reaction type can be found in this chapter. When no advanced estimation methods have been available, ‘first guess’ approximations had to be used. These approximations have been taken over from previous CAPRAM studies (see, e.g. *Tilgner and Herrmann, 2010, Tilgner et al., 2013*). In the course of this dissertation, these simple estimations with mostly fixed rate constants and branching ratios have been tested intensively in sensitivity studies described in chapter 5. While this chapter describes the protocol and all initial guesses for its parameters, the final revised protocol from the sensitivity studies with all the final estimation methods and parameters is presented in section 5.7.

Moreover, this chapter details the implementation of the aqueous phase protocol into the generator and explains the principles of the work flow of the new multiphase mechanism Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere. However, for this dissertation, only the generated aqueous phase mechanisms have been used. For the gas phase, the more condensed, yet, still near-explicit mechanism MCMv3.1 (*Saunders et al., 2003, Jenkin et al., 2003*) has been used.

This chapter focuses solely on the newly developed aqueous phase protocol for the Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere (see also *Aumont et al., 2005*). The gas phase protocol has been briefly introduced in section 2.5. A detailed description is given by *Aumont et al. (2005)*. The adoption of the new aqueous phase routines and the workflow of the overall multiphase generator GECKO-A are explained in this chapter. The original gas phase generator has been left unchanged. New routines were programmed to describe the phase transfer between the gas and the aqueous phase based on the *Schwartz* approach as well as the subsequent aqueous phase chemistry. The implementation of these routines was mainly performed by the French cooperation partner at the Laboratoire Inter-universitaire des Systèmes Atmosphériques (LISA) and was part of another dissertation (*Mouchel-Vallon, 2013*). However, several adjustments had to be performed to adopt the generator to the needs of the box model SPACCIM, which were applied in this study.

A schematic depiction of the workflow of the generator is given in Figure 4.1. As only the aqueous phase protocol was used for this dissertation, the gas phase routines are shown



**Figure 4.1** Workflow of the generator GECKO-A with a detailed depiction of the final implemented aqueous phase protocol. Blue boxes represent H-abstraction reactions, the pink box represents radical addition to double bonds of unsaturated organic compounds, red boxes represent equilibria, the yellow box represents C–C bond breaking of polycarbonyl compounds, the light brown box represents the hydrolysis of carbonyl nitrates, and green boxes represent radical chemistry (different shades differentiate between alkoxy and peroxy radical chemistry).

in a simplified manner in Figure 4.1. The gas phase routines are depicted in detail in Figure 2.9 in section 2.5. Moreover, the schematic in Figure 4.1 shows the final revised version of the protocol as presented in section 5.7.

## 4.1 Initialisation and workflow of GECKO-A

The generator is initialised in the gas phase. All emitted or primary compounds are listed in a ‘*primary stack*’. The first species of this primary stack is taken and moved to the ‘*gaseous stack*’, where the gas phase routines are applied to describe the gas phase oxidation.

For stable compounds the generator has been extended with routines to describe the phase transfer to the aqueous phase. These routines were supplied by the LISA and have been modified throughout this dissertation for needs of the box model SPACCIM as described in the next subsection. A standard threshold has been implemented for the effective HLCs to reduce the number of reactions in the generated mechanisms. Species with an effective HLC lower than  $10^2 \text{ M atm}^{-1}$  are expected to stay exclusively in the gas phase and their uptake is not treated. Species entering the aqueous phase are put to an ‘*aqueous stack*’. Oxidation routines are applied to the gas phase and the aqueous phase in an alternating manner. Rules for the gas phase oxidation are presented in *Aumont et al.* (2005), aqueous oxidation rules are given in the following (section 4.3 – 4.8 and chapter 5). Evolving intermediates are added to the end of the stack of the respective compartments unless they have already been treated in the protocol. Compounds produced in the aqueous phase are checked for their solubility as well. Release to the gas phase is treated unless the standard threshold of  $10^{12} \text{ M atm}^{-1}$  is exceeded.

The generator processes the oxidation of all intermediates in the gaseous and aqueous stack until the end product  $\text{CO}_2$ . Then, the generator checks the primary stack for further compounds and adds them to the gaseous stack unless they have already been treated as intermediates in the oxidation chain of previous primary compounds. If this is not the case, new compounds are oxidised up to  $\text{CO}_2$  as well until all species in the primary stack are treated. For more clarity, the workflow is depicted in Figure 4.1.

## 4.2 Estimation of phase transfer data

The generator provides model input to describe the uptake process according to the resistance model by *Schwartz* (1986) (see subsection 2.3.2.3 for a detailed explanation). This dynamic equilibrium can be described with the mass transfer function ( $k_T$ ; see Equation 2.7, page 28) and the HLC as the equilibrium’s constant (see Equation 2.6, page 27). For the estimation of the Henry’s Law constant, routines have been supplied by the LISA using the structure-activity relationship GROMHE (GROUp contribution Method for Henry’s law Estimate; *Raventos-Duran et al.*, 2010). Moreover, a database with experimental values as given in *Raventos-Duran et al.* (2010) is used preferably in

the protocol. To reduce the number of uptake processes and reactions in the generated mechanisms, upper and lower thresholds have been assigned in the protocol between which uptake is allowed as already mentioned in section 4.1. These thresholds can be varied in the generator. The standard values, which were used throughout the current studies, are  $10^2$  and  $10^{12} \text{ M atm}^{-1}$  for the lower and upper boundary, respectively. Moreover, for pure aqueous phase species, release to the gas phase is prohibited. Therefore, uptake is suppressed for hydrated carbonyl compounds (gem-diols) and dissociated carboxylic acids.

From the mass transfer function (Equation 2.7, page 28) can be seen that uptake is dependent on the gas phase diffusion coefficient ( $D_g$ ) and the mass accommodation coefficient ( $\alpha$ ) besides the Henry's Law constants ( $K_H$ ). In contrast to previous studies at the LISA (see *Mouchel-Vallon et al.*, 2013), in this dissertation missing gas phase diffusion coefficients were calculated with the Fuller-Schettler-Giddings (FSG) method as described by *Fuller* (1986). Former studies at the LISA estimated  $D_g$  by scaling the gas phase diffusion coefficient of an unknown compound to the gas phase diffusion coefficient of a reference compound (water in previous LISA studies) and the square root of the quotient of the molar masses of both compounds:

$$D_g = D_{g,ref} \sqrt{\frac{M_{ref}}{M}} \quad (4.1)$$

The FSG method calculates  $D_g$  according to the atomic volumes present in the considered molecule ( $v_i$ ) and the molecules of the ambient gas/mixture of gases (e.g., air with a mean molar volume of  $20.1 \text{ cm}^{-3}$ ;  $v_{air}$ ) as well as the molar mass of the considered molecule ( $M$ ) and the ambient gas (e.g.,  $M_{air} = 29 \text{ g mol}^{-1}$ ). Furthermore, calculations are pressure ( $p$ ) and temperature ( $T$ ) dependent (*Fuller*, 1986):

$$D_g = \frac{0.0101 T^{1.75} \sqrt{\frac{1}{M} + \frac{1}{M_{air}}}}{p \left[ (\sum v_i)^{1/3} + v_{air}^{1/3} \right]^2} \quad (4.2)$$

Parameters for the diffusion volumes of all necessary atoms (C, H, O, and N) are provided in the work of *Fuller* (1986). Calculations are performed for 1000 hPa and 288 K.

Measurements of mass accommodation coefficients are rare and only a few values exist in the literature (see *Ammann et al.*, 2013). Moreover, due to the missing experimental data, no reliable prediction method is available. Therefore,  $\alpha$ -values had to be estimated with a constant value. The experimental values of  $\alpha$  at 288 K in the CAPRAM database range from  $4 \cdot 10^{-3}$  to 0.5 with a mean value of 0.093 (see Table E.1, page 314, in the Appendix). Therefore,  $\alpha$  was estimated with a constant value of 0.1 in this study. However, for organic compounds this value should be seen as an upper limit as most experimental values of the organic compounds are much lower. They range from  $6.76 \cdot 10^{-3}$  to 0.032 with a mean value of 0.02. Therefore, further tests have been performed in section 5.2 to evaluate the sensitivity of this parameter and the plausibility of the current estimate.

## 4.3 OH reactions of stable compounds

The new aqueous phase protocol distinguishes between stable and radical compounds. Based on the results of the evaluation process in chapter 3, SARs seem the most practical tool for the prediction of missing kinetic data for reactions of stable organic compounds with the hydroxyl radical. They predict OH rate constants with a high accuracy, are easy to implement in the FORTRAN routines of GECKO-A, and are applicable for all compound classes of organic compounds. The introduction of a second descriptor accounting for the  $\beta$ -effects of the neighbouring functional groups increases the accuracy in the SAR by *Monod and Doussin* (2008)/*Doussin and Monod* (2013) compared to the one of *Minakata et al.* (2009). Therefore, the SAR of *Monod and Doussin* is preferably chosen in the protocol for the prediction of hydroxyl radical rate constants. However, only the rate constants of alkanes, alcohol and carbonyl compounds, and carboxylic acids and bases are covered by this SAR. Unsaturated stable compounds are covered by the SAR of *Minakata et al.* (2009) in the generator. Only for organic nitrates, no estimation method exists. Currently, these compounds are treated with the SAR by *Monod and Doussin* (2008) estimating the same group contribution factors for the  $\alpha$ - and  $\beta$ -effects of the  $\text{NO}_3$ -function than that of the OH-function. An overview of the application of the different SARs in the GECKO-A protocol can be found in Table 3.8, page 70, introduced in section 3.7.

To estimate missing rate constants, the generator splits the molecules into increments with each increment bearing exactly one carbon atom. To every carbon atom bearing group several functions can be attached. The current version of the generator treats the following groups in the aqueous phase:

- $\text{CH}_X$  (pure hydrocarbons)
- $\text{CH}_X\text{OH}$  (alcohols)
- $\text{CH}_X(\text{OH})_2$  (gem diols)
- $\text{CH}=\text{O}/\text{C}=\text{O}$  (carbonyl compounds)
- $\text{C}(=\text{O})\text{OH}/\text{C}(=\text{O})\text{O}^-$  (carboxylic acids and bases)
- $\text{C}_d=$  (unsaturated organic compounds)
- $\text{CH}_X\text{ONO}_2/\text{C}(=\text{O})\text{ONO}_2$  (organic nitrates and carbonyl nitrates)

For every group, a partial rate constant for the reaction with hydroxyl radicals is generated with the respective SAR as defined above and in Table 3.8, page 70. A special case can occur for unsaturated compounds. As unsaturated compounds are the only compounds currently treated in the generator for which the SAR of *Monod and Doussin* (2008) does not apply, for these functional groups the SAR of *Minakata et al.* (2009) is used. However, as the generator applies the SARs groupwise, it can happen that in an unsaturated compound functional groups exist, which can be calculated with the structure-activity relationship by *Monod and Doussin* (2008). This is the case for any saturated  $\text{CH}_X$  or OH group that does not have an unsaturated group in  $\alpha$ - or  $\beta$ -position. For these groups, the SAR by *Monod and Doussin* (2008)/*Doussin and Monod* (2013) is applied rather than the one by

*Minakata et al.* (2009). Only for the unsaturated groups or groups having an unsaturated function in  $\alpha$ - or  $\beta$ -position, the SAR of *Minakata et al.* (2009) is used. Moreover, the partial rate constant for carboxyl groups ( $k_{\text{COOH}} = 7 \cdot 10^5 \text{ M}^{-1} \text{ s}^{-1}$ ) is always used for carboxylic acids. Thus, in carboxylic acids the SAR of *Minakata et al.* (2009) is applied for carboxyl groups and the SAR of *Monod and Doussin* (2008)/*Doussin and Monod* (2013) is applied for the remaining functional groups. Hence, it can happen that the two SARs are applied within one molecule.

After the determination of all partial rate constants, the overall  $k_{2\text{nd}}$  is synthesised. A major advantage of structure-activity relationships over all other estimation methods is the possibility to determine the branching ratios as explained in Appendix B. Branching ratios are calculated by the generator based on the partial rate constants and the overall rate constant according to Equation B.9, page 273. Minor branches are removed according to the following scheme. The generator can be run at 10 levels of detail. The following thresholds are possible for the removal of minor branches: 25% – 20% – 15% – 10% – 5% – 3% – 2% – 1% – 0.5% – 0.1%. However, for very large molecules, it would be possible that even the omission of minor branches would result in a great loss of mass as many minor branches might sum up to a significant percentage of all turnovers. Therefore, a value can be defined (arbitrary between 0 and 1), how much mass in a reaction should be preserved (called the mass preservation factor in the following). After the removal of all minor branches, GECKO-A checks whether the remaining branches stay above the defined mass preservation threshold. If not, the generator reduces the cut-off parameter for this single reaction to the next smaller value and repeats the routine until the mass preservation condition is fulfilled or the lowest cut-off value of 0.1% is reached. After the removal of minor branches, the overall second order rate constant is recalculated by summing up just the individual rate constants of the remaining reaction pathways. The branching ratios are recalculated for the final determination of the reaction. If no specifications are made, a standard threshold of 3% for the cut-off parameter and a mass preservation factor of 0.8 is used. The coarse cut-off levels are mainly used for sensitivity studies, which focus only on the main reaction channel.

After the cut-off process, the kinetic database is checked for experimental values. If available, they are assigned to the reaction together with the calculated branching ratios. The final reaction with all remaining products is written into the mechanism and another routine checks whether the products have already been treated in the mechanism before. If so, no further consideration is necessary, otherwise, they are put to the end of the aqueous stack and the oxidation routines are applied to these products at a later point as well (see also Figure 4.1, page 74).

## 4.4 NO<sub>3</sub> reactions of stable compounds

In a next step, the generator estimates NO<sub>3</sub> reaction rate constants. As SARs exist only for hydroxyl radical reactions, the next best estimation method was chosen. Based on



the results of chapter 3, these are the improved Evans-Polanyi-type correlations. The method is widely applicable. Only for unsaturated compounds and deprotonated carboxylic acids, fixed reaction rate constant estimates have to be used based on the experimental dataset described in section 3.1 (see also Table 3.8, page 70). However, the extended Evans-Polanyi-type correlations correlate the overall experimental reaction rate constants to the overall *BDE*, which allows no estimation of the branching ratios of the different reaction channels. Therefore, branching ratios are taken over from the corresponding hydroxyl radical reaction.

For the general prediction, the improved linear Evans-Polanyi-type correlations from Table 3.7 were used. Polyfunctional compounds are ranked according to considerations in subsection 3.5.3. It was shown that substituted carboxylic acids correlate better, when they are assigned to the compound class of the substitution. Polyfunctional compounds including hydroxyl and carbonyl groups are assigned to the compound class including monoalcohols and gem-diols. Therefore, the various compound classes are ranked the following:

1. Carbonyl compounds
2. Alcohol compounds (including gem-diols, di- and polyols)
3. Carboxylic mono- and diacids

Any polyfunctional compound is treated with the correlation of the compound class with the substitution listed the highest in the above enumeration.

As described in section 3.5, Evans-Polanyi-type correlations are incapable to predict the rate constants of unsaturated compounds and deprotonated carboxylic acids. Therefore, ‘first guess’ approximations with fixed rate constants and branching ratios based on the experimental values of the kinetic database (see section 3.1) have initially been implemented in the protocol as already indicated in Table 3.8, page 70.

Reaction rate constants vary for the different compound classes, which is considered in the generator. The initial estimates used for nitrate radical reactions with unsaturated organic compounds are listed in Table 4.1. Estimates of polyfunctional compounds are assigned to a reaction according to the rank of a compound class. A compound is assigned to the compound class with lowest possible rank in Table 4.1. Thus, for, e.g. hydroxy-butenal, the rate constant for alcohols would be used as the rank is lower than that for carbonyl compounds. Table 4.2 shows the estimated nitrate radical rate constants for the different carboxylate mono- and dianions.

**Table 4.1** Estimated rate constants for reactions of nitrate radicals with unsaturated organic compounds.

Compound	$k_{2nd}/\text{M}^{-1}\text{s}^{-1}$	Rank
Unsaturated alcohols	$1.5 \cdot 10^9$	1
Unsaturated carbonyls	$2.5 \cdot 10^9$	2
Unsaturated carboxylic acids	$3.0 \cdot 10^7$	3
Further unsaturated compounds	$1.0 \cdot 10^9$	4

**Table 4.2** Estimated rate constants for reactions of nitrate radicals with deprotonated carboxylic acids.

Compound	$k_{2nd}/\text{M}^{-1}\text{s}^{-1}$
Monocarboxylate	$2.00 \cdot 10^7$
DCA monoanion	$2.50 \cdot 10^7$
DCA dianion	$7.75 \cdot 10^7$

Due to the scarcity of the kinetic data on which these initial estimations are based, intensive testing has been performed and is presented in section 5.5. The sensitivity studies let to a refinement of parameters. The final set of kinetic parameters used to estimate nitrate radical reactions with organic compounds for which the advanced Evans-Polanyi-type correlations are not applicable are given in section 5.7.

As no product information is available, the estimates of the OH radical reactions are also used for reactions of unsaturated organic compounds with  $\text{NO}_3$  radicals. For reactions with deprotonated carboxylic acid, electron transfer of the carboxylate group with the nitrate radical is assumed to be the only reaction channel. Thus, the only reaction product is an acyloxy radical. This is the only reaction type besides the radical addition to unsaturated organic compounds, where different products are formed in a reaction of an organic compound with either OH or  $\text{NO}_3$  radicals.

Estimates of the rate constants are assigned to the reaction by the generator unless experimental data is available. Acyloxy radicals resulting from the electron transfer reactions of nitrate radicals with deprotonated carboxylic acids are checked for their previous treatment in the protocol. Untreated products are added to the end of the aqueous stack for their later treatment as also shown in Figure 4.1, page 74.

To reduce computing time, mechanism reduction is given special attention. In remote environments with low  $\text{NO}_x$  concentrations,  $\text{NO}_3$  reactions might be negligible. Moreover, even in urban influenced regimes  $\text{NO}_3$  addition to double bonds might be of minor importance compared to the addition of the OH radicals due to the lower reactivities of the nitrate radical in addition to lower concentration levels. Omitting the  $\text{NO}_3$  addition to double bonds, however, will result in significantly reduced mechanisms. As  $\text{NO}_3$  is built into the molecular structure of the educt in addition reactions, organic nitrates are formed, which have to be oxidised by the generator up to  $\text{CO}_2$ . For H-abstraction by  $\text{NO}_3$ , potential for mechanism reduction is less since the resulting products are the same as for the corresponding OH reaction. Therefore, GECKO-A is equipped with 3 options resulting in a different complexity of the generated mechanism and thus accuracy of the model results:

- *The  $\alpha$  subversion:* The full mechanism without any restrictions of the  $\text{NO}_3$  chemistry is generated.
- *The  $\beta$  subversion:* Nitrate radical chemistry of unsaturated organic compounds is suppressed in the generator.
- *The  $\gamma$  subversion:* All reactions of nitrate radicals with organic compounds are prohibited in the generator.

While in the  $\alpha$  subversion all  $\text{NO}_3$  reactions are allowed, nitrate radical chemistry is prohibited for unsaturated compounds in the  $\beta$  subversion. H-abstraction reactions are still allowed in this subversion to consider nitrate radical chemistry at least to some extent. However, for unsaturated compounds,  $\text{NO}_3$  addition is omitted. To prevent a shift in the reaction pathways, H-abstraction reactions by  $\text{NO}_3$  are also omitted for these compounds in the  $\beta$  subversion. Thus, nitrate chemistry is allowed only for unsaturated compounds. In the  $\gamma$  subversion, nitrate radical chemistry is completely omitted.

The applicability of the different mechanisms strongly depends on the  $\text{NO}_x$  regime. For all CAPRAM versions later than 3.0, all  $\text{NO}_3$  reduction schemes are generated. Same reactions in the different subversions are labelled with the same reaction numbers for more clarity. However, this will cause missing reaction numbers in the reduced  $\beta$  and  $\gamma$  subversion or even disordered reaction labelling due to different treatment of the intermediates in the oxidation chains of the different subversions.

## 4.5 Hydration of carbonyl compounds

Besides the radical oxidation of organic compounds by OH and  $\text{NO}_3$ , several compound classes take part in further aqueous phase processes. Among these processes is the hydration of carbonyl compounds according to Reaction R6, page 11. Thus, if the generator identifies a carbonyl group in a molecule, further routines are called in advance of the OH and  $\text{NO}_3$  oxidation routines to estimate the hydration equilibrium constants  $K_{hyd}$ . For gem-diol groups dehydrations are calculated. For the estimation of  $K_{hyd}$ , the GROUp contribution Method for Henry's law Estimate (GROMHE; see *Raventos-Duran et al.*, 2010) is used in the generator. Furthermore, the first order or pseudo first order rate constants of the hydration equilibrium are estimated. A fixed value of  $5.69 \cdot 10^{-3} \text{ s}^{-1}$  based on previous CAPRAM estimations (*Herrmann et al.*, 2005, *Tilgner and Herrmann*, 2010) has been used for the backward reactions. The rate constants of the forward reactions are calculated according to Equation 2.1, page 11, using the predicted  $K_{hyd}$  and the estimated backward rate constants.

The SAR was already part of the generator provided by the LISA and has, therefore, not been evaluated again in this context. *Raventos-Duran et al.* (2010) give a precision of the predicted hydration constants  $K_{hyd}$  of a factor of 3 equivalent to an root mean square error (RMSE) of 0.47 log units.

To reduce the number of species, minor branches are omitted in the generated mechanisms. The standard threshold is 5% of the overall hydration constant, but may be varied in the generator if desired. It should be noted that the cut-off of minor branches based on percentages of the overall equilibrium constant contains difficulties. Even if the equilibrium constant suggests that certain pathways are of minor importance, significant turnovers might be obtained due to different reactivities of the carbonyl and the gem-diol form. Thus, if products in a minor pathway are formed that react significantly faster than all other products, the balance of the equilibrium is shifted towards this product as the product will

stay at low concentrations levels due to the high reactivity. To balance the equilibrium, more of these minor products are formed. Hence, minor pathways based only on the calculations using the equilibrium constant might be able to reach significant turnovers. That such a case is not totally negligible shows the data of the kinetic database. For example, the hydrated form of glyoxal reacts about 17 times faster with OH than the unhydrated form, however, for formaldehyde and acetaldehyde the reactivities towards OH of both forms are about equal (compare kinetic database, Table C.1, page 275, in Appendix C.1). Thus, as there is no general rule for the reactivities of the hydrated and unhydrated forms, it would be better to consider the subsequent reactions of all products, i.e. all hydration forms, in the calculations of the cut-off parameters as well. The initial branching ratio  $r_i^0$  of the  $i$ -th hydrated form should be scaled by the reactivity of the  $i$ -th hydrated form towards OH and NO<sub>3</sub> ( $k_i^{OH}$  and  $k_i^{NO_3}$ ) compared to the sum of all reactivities ( $\Sigma k_i^{OH} / \Sigma k_i^{NO_3}$ ) to account for the consideration of the different turnovers of the different hydrated forms:

$$r_i = r_i^0 \cdot \alpha \frac{k_i^{OH}}{\Sigma_i k_i^{OH}} \cdot \beta \frac{k_i^{NO_3}}{\Sigma_i k_i^{NO_3}} \quad (4.3)$$

$\alpha$  and  $\beta$  determine the ratio of the OH and NO<sub>3</sub> reaction fluxes, which can be adjusted for every mechanism according to the meteorological scenario for which the mechanism is designed.

The present form of the generator, however, just includes the cut-off of minor branches according to the percentage of the overall hydration constant. After the removal of the minor branches, branching ratios are rescaled. The remaining hydrations are written into the mechanism in addition to the reactions with OH and NO<sub>3</sub>. Equilibrium constants are assigned from a kinetic database given in *Raventos-Duran et al. (2010)* or estimates are used otherwise. If a nitrate function is attached to a keto group, GECKO-A generates a hydrolysis reaction rather than a hydration equilibrium as described in the next subsection.

## 4.6 Hydrolysis of carbonyl nitrates

In the protocol, nitrate radicals add to the double bonds of unsaturated compounds. In the course of the further oxidation of the evolving intermediates, compounds can be generated, which are totally lacking of hydrogen atoms, such as C(=O)(O<sup>-</sup>)C(=O)ONO<sub>2</sub>. To consider the further degradation of these carbonyl nitrates, their hydrolysis was implemented in the protocol. The mechanism and rate constants were estimated according to the peroxyacyl nitrate (PAN) hydrolysis. According to *Li and Francisco (2005)*, PANs will hydrolyse forming a carboxylic and peroxonitric acid. Accordingly the hydrolysis of carbonyl nitrates has been estimated with:



The second order rate constant has been estimated with  $7.5 \cdot 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$  based on data presented in *Kames and Schurath (1995)* for PANs. To derive  $k_{1st}$  of the pseudo first order

reaction in R11,  $k_{2nd}$  has to be multiplied by the concentration of water, i.e. 55.5 M. The activation energy  $E_A/R$  has been estimated with 6600 K according to the data in *Kames and Schurath* (1995).

Thus, for any compound bearing an C(=O)ONO<sub>2</sub> function, the decay according to Reaction R11 is implemented with the above mentioned estimations for the rate constants. The produced carboxylic acid is checked by the generator and added to the end of the aqueous stack if it has not been treated before (see also Figure 4.1, page 74).

## 4.7 Dissociation of carboxylic acids

Besides hydrolysis, dissociation of carboxylic acids is another additional process in the aqueous phase protocol of GECKO-A. The equilibrium constants are derived from the  $pK_a$  values according to Equation 2.2. Missing  $pK_a$  values are estimated using Taft parameters according to the method described by *Perrin et al.* (1981). For a complete description of the equilibrium, rate constants for the backward reactions are estimated with a fixed value of  $5 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  and rate constants of the forward reactions are calculated based on Equation 2.1, page 11.

Thus, if the generator finds a carboxyl or carboxylate functional group in the current compound, it calls the respective routines to estimate the dissociation equilibrium. If more than one acid group is present, the dissociation is estimated for every functional group by determination of the different  $pK_a$  values. Unsymmetrical di- or polycarboxylic acids will lead to different dissociation products. For the determination of branching ratios, any considered dissociated form is divided by the sum of all dissociation states:

$$r_{A_i^-} = \frac{[A_i^-]}{[HA] + [A_1^-] + [A_2^-] + \dots + [A_i^-] + \dots + [A_n^-]} = \frac{\frac{[A_i^-]}{[HA]}}{1 + \sum_i \frac{[A_i^-]}{[HA]}} \quad (4.4)$$

The *Henderson-Hasselbalch equation* (Equation 4.5; see, e.g., *Po and Senozan*, 2001), which relates the concentrations of the protonated and deprotonated forms of an acid to the  $pK_a$  and the pH, can be used to rewrite Equation 4.4 as given in Equation 4.6.

$$pH = pK_a + \log \frac{[A^-]}{[HA]} \quad (4.5)$$

$$r_{A_i^-} = \frac{10^{pH-pK_{a,i}}}{1 + \sum_i 10^{pH-pK_{a,i}}} \quad (4.6)$$

Thus, the determination of branching ratios depends on the pH and  $pK_a$  values. The  $pK_a$  values are calculated by the generator as described above. At the current state of the generator, fixed prescribed pH values are used for the calculation of branching ratios. Again, a threshold for minor branches has been implemented in the aqueous phase protocol

of the generator. The threshold for the cut-off of minor dissociation pathways is variable in GECKO-A. If minor branches are omitted, these reaction pathways are set to zero. The remaining ‘microscopic’  $pK_a$  values are recalculated and scaled to leave the ‘macroscopic’  $pK_a$  value unchanged. In the standard mode, however, no cut-off is used. This is due to the following considerations. First of all, the determination of branching ratios can only be performed for a fixed pH value. In the box model studies, especially, when using a non-permanent cloud scenario, large fluctuations of the pH value are possible resulting in significant changes in the speciation of the different protonation states of di- and polycarboxylic acids. This leads to uncertainties, which could result in the omission of important reaction pathways.

Moreover, the different protonation states of a diacid may react with different reaction rates as can be seen for the reaction of oxalic acid with the hydroxyl radical (see Table C.1 in Appendix C.1), where the reactivity for the protonated form is about 2 orders of magnitude lower than that of the deprotonated forms. For reactions with the nitrate radical this fact is even more important as electron transfer reactions (ETRs) are expected for the deprotonated forms, which are much faster than the H-abstraction reactions (see Table C.2 in Appendix C.2). For the reaction of  $\text{NO}_3$  with oxalic acid, more than 3 orders of magnitude difference are seen in the reactivities of the protonated and the deprotonated forms. Hence, an omission of reaction pathways based only on calculations of the acid-base equilibrium without the consideration of the subsequent degradation of the reaction products by OH and  $\text{NO}_3$  might omit important turnovers as already discussed for the hydration of carbonyl compounds. Therefore, no cut-off is used in the current standard mode of the generator. Future versions of GECKO-A might overcome this problem by scaling the determined branching ratio with weighted reactivities of the hydroxyl and the nitrate radical:

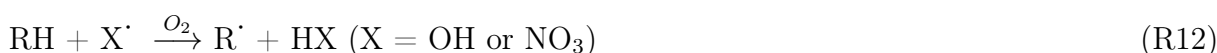
$$r_{A_i^-} = \frac{10^{pH-pK_{a,i}}}{1 + \sum_i 10^{pH-pK_{a,i}}} \cdot \alpha \frac{k_i^{OH}}{\sum_i k_i^{OH}} \cdot \beta \frac{k_i^{NO_3}}{\sum_i k_i^{NO_3}} \quad (4.7)$$

where  $k_i^{OH}$  and  $k_i^{NO_3}$  are the OH and  $\text{NO}_3$  rate constants, respectively.  $\alpha$  and  $\beta$  are, again, a prescribed ratio between the OH and  $\text{NO}_3$  reactivities depending on typical turnovers in the meteorological scenario of the simulations. However, the problem with a largely varying pH value would remain.

After the kinetic data are assigned either from the kinetic database or, if not available, from the generator protocol, the dissociation is written into the mechanism. No further processes for stable compounds are treated in the protocol at this stage. If the species was produced in-situ in the aqueous phase and does not bear any carboxylate or gem-diol functions, the generator will check the water solubility and treat the release of the species into the gas phase if the effective HLC is below a prescribed threshold. The standard value for this threshold is  $10^{12} \text{ M atm}^{-1}$ . Thereafter, the generator can move on to the next stable species in the stack (see Figure 4.1, page 74). When all stable species are treated, GECKO-A will continue with radical compounds as given in the following subsection.

## 4.8 Degradation of radical compounds

The degradation of stable organic compounds, whether by H-atom abstraction or OH/NO<sub>3</sub> addition to double bonds of unsaturated compounds, results in the formation of an alkyl radical. The only exceptions are H-atom abstraction reactions from hydroxyl groups, where oxy radicals are formed, and H-atom abstraction from carboxyl groups as well as electron transfer reactions of carboxylate functions, where acyloxy radicals are formed. Immediate oxygen addition is assumed for carbon centered radicals in the generator and the reactions are combined with the parent reaction. Therefore, no alkyl radicals are formed in the mechanisms created by GECKO-A and the oxidation of stable organic compounds results directly in the formation of peroxy radicals:



Kinetic data for radical compounds is limited. Moreover, no prediction methods exist for these compounds. Only in the study of *Li and Crittenden* (2009), a computerised protocol for the decay of organic compounds including radical compounds has been presented. However, no kinetic data for radical compounds is given. Only the degradation pathways are shown.

In literature, several studies with proposed reaction mechanisms exist (see, e.g., *von Sonntag and Schuchmann*, 1991, *von Sonntag et al.*, 1997 for the peroxy radical decay). The generator protocol is based on such mechanistic studies, but has to use fixed estimates for the reaction rate constants based on values either given in these studies or derived from further experiments. The following oxygen centered radical processes are implemented in the protocol and explained in detail in the following subsections (subsection 4.8.1 – 4.8.6):

- Peroxy radical recombinations and cross-reactions
- HO<sub>2</sub> elimination of peroxy radicals with hydroxyl functions in  $\alpha$ -position
- Hydration and immediate HO<sub>2</sub> elimination of acylperoxy radicals
- Decarboxylation of peroxy radicals with carboxyl/carboxylate function in  $\beta$ -position
- Carbonyl formation of alkoxy radicals by reaction with oxygen
- Monomolecular decay of alkoxy radicals by C–C bond-breaking
- Decarboxylation of acyloxy radicals by C–C bond-breaking

### 4.8.1 RO<sub>2</sub> recombinations and cross-reactions

In general, peroxy radicals decay after the mechanism of *von Sonntag and Schuchmann* (1991) according to Reaction R13. For primary and secondary peroxy radicals, 3 reaction pathways exist:



where  $\text{RO}_2\cdot$  symbolises a peroxy radical,  $\text{R-OH}$  the corresponding alcohol,  $\text{R=O}$  the resulting carbonyl compound, and  $\text{RO}\cdot$  the corresponding alkoxy radical.  $\text{R}'$  may be the same organic rest in a given peroxy radical to recombine with the considered peroxy radical or any different organic rest to react in a cross-reaction with the considered  $\text{RO}_2\cdot$ .

Branching ratios are estimated in the protocol with 50% for channel R13a, 30% for channel R13b, and 20% for channel R13c following the most recent determination by *Schaefer et al.* (2012) for the acetylperoxy radical. Besides the branching ratios, second order rate constants of all peroxy radical recombinations and cross-reactions are, as well, estimated with the value of the acetylperoxy radical recombination given in this publication. A fixed value of  $7.3 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$  has been used for all  $\text{RO}_2 + \text{R}'\text{O}_2$  reactions (see *Schaefer et al.*, 2012). For tertiary peroxy radicals, only the last pathway (R13c) is possible with an assumed rate constant of  $1.0 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$  based on previous CAPRAM estimations (see *Herrmann et al.*, 2005, *Tilgner and Herrmann*, 2010). The second order peroxy radical decay has been implemented in the generator protocol as a pseudo first order monomolecular decay according to the MCM as described in subsection 2.2.3.1 (see Reaction R10 and Equation 2.4, page 21).

According to Figure 4.1, page 74, if the generator detects a peroxy function in a molecule, it checks the functional groups in the  $\alpha$ - and  $\beta$ -position. If a hydroxyl or oxo group is detected in  $\alpha$ -position or a carboxyl or carboxylate group in  $\beta$ -position, special routines are called for these compounds. Additionally, GECKO-A checks whether the peroxy function is attached to a tertiary or any other carbon atom. The above-mentioned reaction pathways, rate constants and branching ratios are assigned accordingly except for peroxy radicals with hydroxyl or oxo function in  $\alpha$ -position. These compounds follow special degradation rules as described in subsection 4.8.2 and in subsection 4.8.3. For peroxy radicals with a carboxyl/carboxylate group in  $\beta$ -position both degradation pathways are implemented, the recombination/cross reactions and the special degradation pathways as described in subsection 4.8.4.

New products formed during the decay of the peroxy radicals are put to the end of the aqueous stack (as can be seen from Figure 4.1) and the generator continues to treat either the special decay of peroxy radicals with a  $\text{C(=O)OH/C(=O)O}^-$ -function in  $\beta$ -position or the next compound in the aqueous stack.

## 4.8.2 $\text{HO}_2$ elimination of $\alpha$ -hydroxy peroxy radicals

If the generator identifies a hydroxyl group is in  $\alpha$ -position to the peroxy function,  $\text{HO}_2$  elimination is expected rather than  $\text{RO}_2$  recombination. Rate constants for  $\text{HO}_2$  elimination have been estimated with  $2.0 \cdot 10^2 \text{ M}^{-1} \text{ s}^{-1}$  for peroxy radicals with only one hydroxyl group in  $\alpha$ -position, and with a rate constant of  $1.0 \cdot 10^3 \text{ M}^{-1} \text{ s}^{-1}$ , when 2 hydroxyl groups



are adjacent to the carbon atom with the peroxy function. The rate constants have been based on experimental data and estimations of previous CAPRAM versions (*Herrmann et al.*, 2005, *Tilgner and Herrmann*, 2010). Thus, for the recombinations (with an estimated  $k_{2nd}$  of  $7.3 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ) to be competitive with this fast monomolecular decay, peroxy radical concentrations in the order of at least  $10^{-6} \text{ mol l}^{-1}$  would be needed, which is unrealistically high under atmospheric conditions. Therefore, for these peroxy radicals, only the monomolecular decay is treated in the protocol.

The peroxy radical decay results either in a carbonyl compound or, if two hydroxyl functions are present, in a carboxylic acid. After the reaction and the respective kinetic data is written into the mechanism, the generator adds new reaction products not yet treated in the mechanism to the end of the aqueous stack as it is depicted in Figure 4.1.

### 4.8.3 Degradation of acylperoxy radicals

If the peroxy function is attached to a carbonyl group, immediate hydrolysis is assumed followed by  $\text{HO}_2$  elimination following the suggestions of *von Sonntag* (1987) and previous CAPRAM estimates (*Herrmann et al.*, 2005, *Tilgner and Herrmann*, 2010):



Due to the excess of water, hydrolysis is expected to proceed fast and the rate determining step is the decay of the resulting peroxy radical by  $\text{HO}_2$  elimination. Therefore, the same estimate for the rate constant of  $1.0 \cdot 10^3 \text{ M}^{-1} \text{ s}^{-1}$  has been used as for the decay of a peroxy radical with two hydroxyl functional groups in  $\alpha$ -position. Again, no  $\text{RO}_2$  recombinations and cross-reactions are considered due to the considerations described in the last subsection. Sensitivity studies confirm the validity of these assumptions and are shown in Appendix E.1, page 313.

Therefore, the only reaction product besides  $\text{HO}_2$  is a carboxylic acid, which is checked by the generator for the previous treatment and added to the end of the aqueous stack, when necessary, as shown in Figure 4.1, page 74.

### 4.8.4 Degradation of $\beta$ -carboxyl peroxy radicals

According to previous CAPRAM versions (*Herrmann et al.*, 2005, *Tilgner and Herrmann*, 2010), an additional decay pathway for peroxy radicals with a carboxyl or carboxylate functional group in  $\beta$ -position has been added to the protocol. Reaction products and rate constants have been taken over from the previous version and are extended to further compounds of this kind. Thus, for any peroxy radical with a  $\text{C(=O)OH/C(=O)O}^-$  group in  $\beta$ -position, the generator will add a reaction according to Reaction R15 in addition to the recombination and cross reaction channels. The estimated rate constants are  $1.9 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$  derived from the decay of the acetate radical ( $\text{CH}_2(\text{OO}\cdot)\text{C(=O)O}^-$ ) given in *Schuchmann et al.* (1985).



After the determination of the products, new compounds are added to the end of the aqueous stack and the generator treats the next aqueous species.

### 4.8.5 Degradation of alkoxy radicals

In the generator, alkoxy radicals are either formed in the radical channel of the recombinations and cross-reactions of peroxy radicals or by H-abstraction of the oxygen bound H-atom in alcohols. Two reaction channels are possible (see R5a, R5b, page 9) as given in section 2.1. The monomolecular degradation (channel R5a) results in smaller fragments of the initial alkoxy radical. The reaction with oxygen (channel R5b) leads to stable products, i.e. a carbonyl compounds.

Thus, if the generator identifies an alkoxy radical, two reactions are written into the mechanism except for tertiary alkoxy radical, where the reaction with oxygen is not valid as an H-atom is needed. As for the other organic radicals, rate constants and branching ratios had to be estimated with fixed values due to missing prediction methods. The values are taken over from CAPRAM 3.0n (*Herrmann et al.*, 2005, *Tilgner and Herrmann*, 2010). The initial estimates in the protocol are  $5 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$  for the reaction with oxygen and  $5 \cdot 10^5 \text{ s}^{-1}$  for the fragmentation by C–C bond breaking. For unsymmetrical molecules, an equally distributed fragmentation is assumed due to missing data. The assumptions of the kinetic data have been tested in sensitivity studies and are presented later in subsection 5.5.4. The sensitivity studies led to a refinement of the protocol. The final revised protocol with the suggested kinetic parameters is given in section 5.7.

After both reaction channels are treated in the protocol of GECKO-A, reaction products are identified and checked for their previous treatment. New compounds are added to the end of the aqueous stack according to Figure 4.1, page 74.

### 4.8.6 Degradation of acyloxy radicals

The oxidation of carboxylic acids at the carboxyl group and the electron transfer reactions of carboxylic bases with the nitrate radical lead to acyloxy radicals ( $\text{RC}(=\text{O})\text{O}\cdot$ ). These organic radicals decay by C–C bond breaking leading to carbon dioxide and an alkyl radical with a shortened carbon skeleton by one carbon atom ( $\text{R}'\cdot$ ). In the generator, immediate oxygen addition is assumed and the resulting reactions are represented by R16:



The initial estimate for a fixed rate constant for this monomolecular decay is  $5 \cdot 10^5 \text{ M}^{-1} \text{ s}^{-1}$ . In the course of the refinement of alkoxy radical reactions, kinetic parameters of acyloxy radicals have been adjusted as well. Recommendations of the final protocol are presented in section 5.7. The generator assigns the rate constant and determines the reaction products.

If the resulting peroxy radical has not been treated previously in the generator, it is added to the end of the aqueous stack as shown in Figure 4.1, page 74.



## 5 Investigation and refinement of crucial parameters in GECKO-A and CAPRAM mechanism development

The protocol was implemented into the FORTRAN routines of the generator. The implementation was mainly performed at the LISA (see *Mouchel-Vallon*, 2013). The delivered routines have been adapted and further developed to the needs of the box model and the pre-processor used at the TROPOS as a part of this dissertation. With the aid of the generator new mechanisms have been designed according to the following concept. Automated mechanism self-generation with GECKO-A was used to extend the current CAPRAM mechanism in two steps. In a first step, for OH and NO<sub>3</sub> radical reactions with stable organic compounds, branching ratios are introduced in the current CAPRAM version. Resulting intermediate organic compounds not yet part of the CAPRAM oxidation scheme are oxidised to species, which have previously already been implemented. In a second step, the aqueous phase chemistry of organic compounds with up to four carbon atoms is compared to the gas phase chemistry of the MCMv3.1. For gas phase species part of the MCMv3.1, yet missing in the CAPRAM oxidation scheme, the generator is applied to describe the uptake from the gas phase with GROMHE (see *Raventos-Duran et al.*, 2010) and the further oxidation in the aqueous phase according to the new protocol described in chapter 4. For each extension step, all levels of complexity of nitrate radical chemistry are generated (see section 4.4). Mechanisms of the first extension step are called CAPRAM 3.5, the second extension step produces CAPRAM 4.0. A detailed description of the extension process is given in section 5.8 at the end of this chapter.

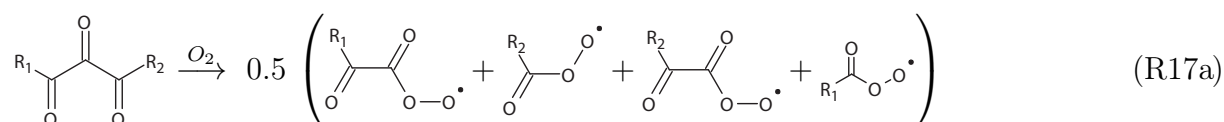
Various simulations were run with the air parcel model SPACCIM (*Wolke et al.*, 2005, see also subsection 2.3.2, page 25). Before the actual model runs, test studies were performed to assess the sensibility of critical parameters and to validate the plausibility of the generated mechanisms. For these test cases, mechanisms based on the same extension concept have been generated. These test mechanisms resemble the mechanisms used later in a revised form for the actual model simulations.

The sensibility runs, the final revised protocol, and the mechanisms generated with this protocol are described in the current chapter. In the following chapter, the further validation of the generated mechanisms with smog chamber experiments and results from the actual model studies under real tropospheric conditions are presented and discussed.

## 5.1 Formation and degradation of polycarbonyl compounds in the protocol

To validate the GECKO-A protocol and its generated mechanisms, smog chamber experiments have been performed at the LEAK chamber (*Iinuma et al.*, 2009, *Kahnt*, 2012) of the Leibniz Institute for Tropospheric Research. The experiments and their results are described in the results part in section 6.1. In a hexane oxidation experiment, the generated mechanisms showed unrealistically high concentrations of polycarbonyl compounds. Compounds with three or four neighbouring carbonyl functions were found in the generated mechanisms. The carbonyl functions were mostly in their hydrated forms. To prevent these unrealistically high concentrations, a monomolecular decay for polycarbonyl compounds has been added to the protocol. The decay is estimated according to assumptions made for the decay of polycarbonyl compounds in the gas phase mechanism MCM.

In the MCM, the oxidation of the n-alkane series leads to several polycarbonyl compounds. However, independently of the chain length of the initial alkane, no more than three carbonyl groups are found within four carbon atom bearing groups. This rule has been taken over to the aqueous phase protocol. In addition to the gas phase, the carbonyl groups may be hydrated (or not). If the condition is fulfilled, a monomolecular decay has been implemented in the protocol based on sensitivity studies given in the following. When three adjacent carbonyl groups are found, bond breaking occurs to either side of the central carbonyl group with equal branching ratios. For three carbonyl groups within four carbon bearing groups, the bond breaking occurs between the two adjacent carbonyl groups. Thus, the polycarbonyls may be split in up to four smaller fragments:



Sensitivity studies were performed to estimate the order of magnitude of the decay rate. Moreover, the importance of hydroxyl radical reactions in addition to the monomolecular decay have been investigated. Estimations of the decay of such highly functionalised compounds should compromise between a guarantee for low concentrations of polycarbonyl compounds on one side and, on the other hand, warrant realistic degradation times of higher weight compounds, i.e., the C–C bond breaking should not lead to a sudden decay of long-chained carbonaceous aerosol constituents.

In the sensitivity runs, the monomolecular decay was estimated with three different decay rates ranging from  $10^{-2}$  to  $10^0 \text{ s}^{-1}$ . Moreover, an additional sensitivity run without a decay by C–C bond breaking was performed (woBB) to serve as a benchmark. For every decay rate, runs have been performed, where additional oxidation of the polycarbonyl compounds by hydroxyl radicals has been either allowed or prohibited. The whole set of

sensitivity runs is given in Table 5.1. The generator with the protocol described in chapter 4 and the rules for the decay given in the description above and in Table 5.1 was used to generate several mechanisms that resemble CAPRAM 3.5 $\gamma$  as described above and in detail in subsection 5.8.2. The mechanisms were tested in a ‘real atmosphere’ scenario with non-permanent clouds under remote continental conditions as given in subsection 6.2.1.

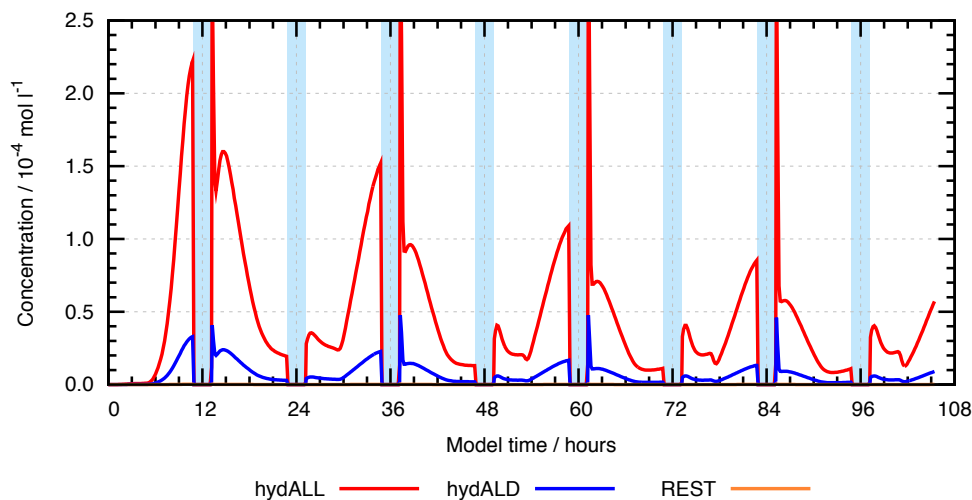
Results are shown for 2-oxo-3-hydroxy succinaldehyde, whose unhydrated form was already implemented in CAPRAM 3.0n. However, with the applied GROMHE hydration routine (*Raventos-Duran et al.*, 2010), this compound is present mostly in its hydrated form (see Figure 5.1a). Therefore, investigations focused on the hydrated form, which is present in  $10^4$  times higher concentrations than the unhydrated forms (compare Figure 5.1). It can be seen that the shape of the concentration-time profile is the same and, due to the hydration constant  $K_{hyd}$ , only the absolute values are decreased (see Figure 5.1). Hence, the discussion is valid for all hydration forms, however, only shown for the most important one. Furthermore, the effect of the monomolecular decay of polycarbonyl compounds by C–C bond breaking can be studied from Figure 5.1. The runs with bond breaking show significantly decreased concentrations of 2-oxo-3-hydroxy succinaldehyde. Only the runs with a decay rate of  $10^{-2} \text{ s}^{-1}$  show slightly higher concentrations, when additional oxidation by OH is allowed (BBE-2+OH) and significantly higher concentration without additional oxidation by hydroxyl radicals (BBE-2woOH) compared to the other sensitivity runs with bond breaking. With decay rates of  $0.1 \text{ s}^{-1}$  or less, concentrations are decreased close to zero independently from additional oxidation by OH.

Another example, oxo-succinaldehyde, confirms the tendency of polycarbonyl compounds to fully hydrate (compare Figure E.2a, page 315, in the Appendix). Moreover, differences between the various sensitivity runs are a little more obvious although the general trend remains (Figure E.2b): (i) With a decay rate of  $10^{-2} \text{ s}^{-1}$  still significant concentration levels of oxo-succinaldehyde are found. (ii) Concentrations of the polycarbonyls are of minor importance for the monomolecular decay in the runs BBE-1+OH/BBE-1woOH. (iii) In the runs with a decay rate of  $1 \text{ s}^{-1}$ , concentrations are indistinguishable from the zero-line. (iv) Only for runs with a slow monomolecular decay rate of  $10^{-2} \text{ s}^{-1}$ , additional oxidation by OH makes a difference. Without additional oxidation by OH, concentrations are even higher during the day compared to the run without bond breaking (woBB) at the end of the model run in the scenario BBE-2woOH.

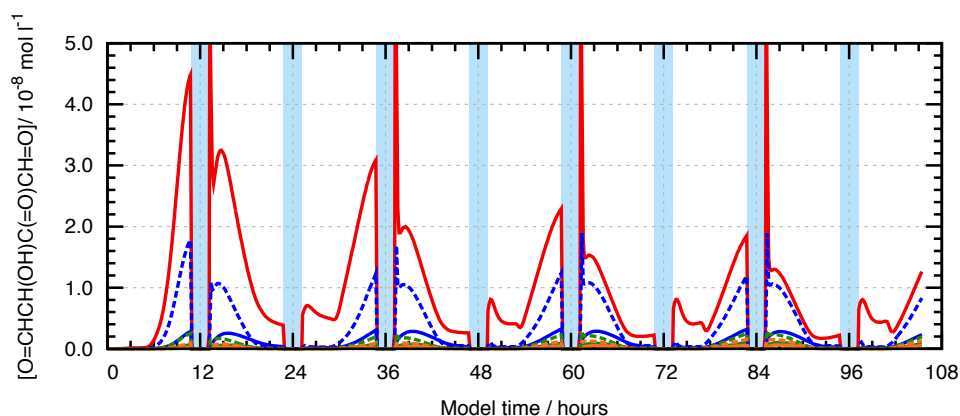
**Table 5.1** Overview of the conditions of the sensitivity runs performed to derive a suitable parameterisation for the monomolecular decay of polycarbonyl compounds.

Sensitivity run	$k_{1st}/\text{M}^{-1} \text{ s}^{-1}$	OH attack
woBB	—	yes
BBE-2+OH	$10^{-2}$	yes
BBE-2woOH	$10^{-2}$	no
BBE-1+OH	$10^{-1}$	yes
BBE-1woOH	$10^{-1}$	no
BBE0+OH	$10^0$	yes
BBE0woOH	$10^0$	no

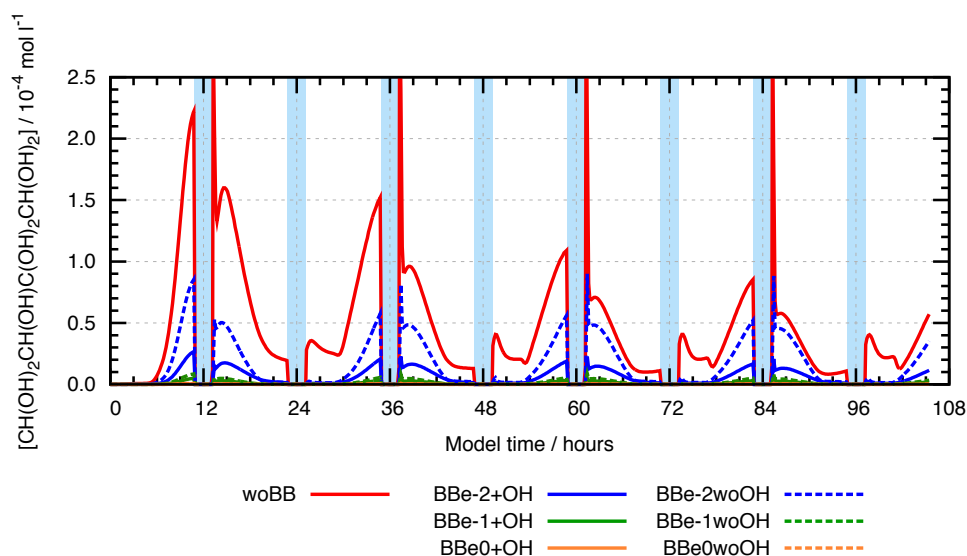
(a) Speciation of 2-hydroxy-3-oxo butanedial in the run woBB



(b) Concentration of the unhydrated form in all sensitivity runs



(c) Concentration of the fully hydrated form in all sensitivity runs



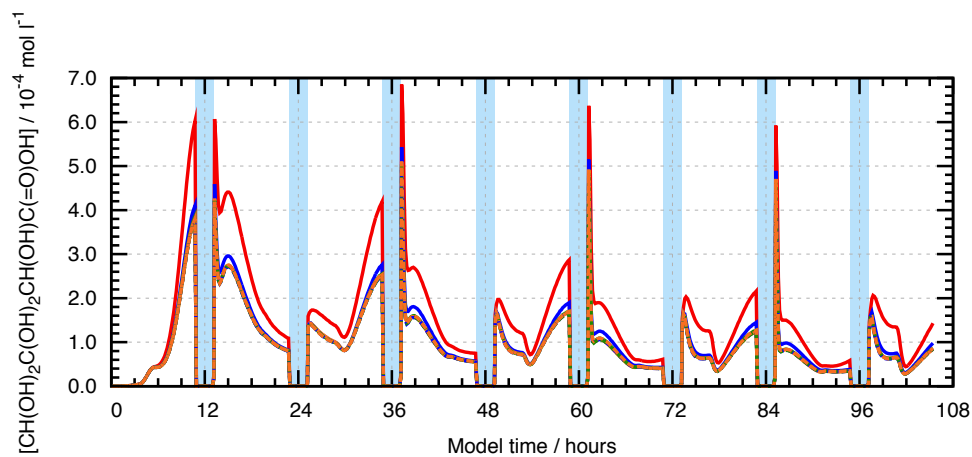
**Figure 5.1** Speciation of the different hydration forms of 2-hydroxy-3-oxo butanedial in the sensitivity run woBB (a) and concentrations of the unhydrated (b) and fully hydrated (c) forms of 2-hydroxy-3-oxo butanedial in the different sensitivity runs. hydAll stands for the hydration of all carbonyl groups, hydALD indicates the hydration of only the terminal aldehyde groups and REST is the sum of all other hydration forms. Blue bars represent cloud periods.



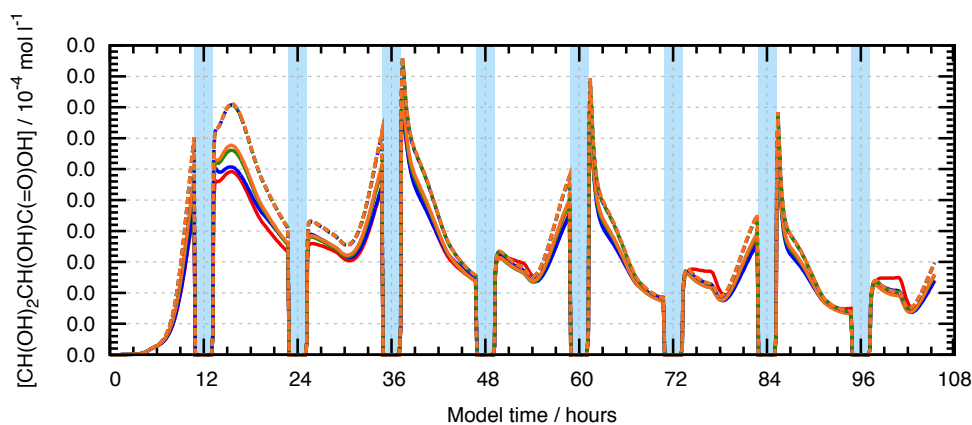
Figure 5.2 shows concentration-time profiles of different products from the degradation of 2-oxo-3-hydroxy succinaldehyde. The concentration over time of 1,1,2,3,3-pentahydroxy butyric acid ( $\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{C}(=\text{O})\text{OH}$ ) is shown in Figure 5.2a for the different sensitivity runs. The molecule is the direct stable product from the main oxidation channel of the OH initiated oxidation of 2-oxo-3-hydroxy succinaldehyde. While there is a clear decrease in the concentrations of 1,1,2,3,3-pentahydroxy butyric acid in the runs with bond breaking (no matter whether OH oxidation is calculated or not), no significant differences in-between these sensitivity runs can be found. Moreover, the concentrations of the direct stable product of the monomolecular decay (dihydroxy-lactic acid,  $\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{C}(=\text{O})\text{OH}$ ) show increased values in the runs with bond breaking (Figure 5.2b). With additional oxidation by OH, concentrations are only slightly increased and a dependence on the rate constant of the decay can be seen. When no additional oxidation by hydroxyl radicals is calculated, concentrations of dihydroxy-lactic acid increase more, however, differences in-between the runs with the various decay rates vanish. The reason for the increased dihydroxy-lactic acid concentration, when no oxidation by OH is calculated, is the shift in the reaction products. In the runs with oxidation by OH, more 1,1,2,3,3-pentahydroxy butyric acid is produced and the bond breaking channel is decreased. Only with the smaller concentrations in the runs, where oxidation by OH is calculated, the differences of the decay rates of the bond breaking can be observed in the concentration-time profiles of the products. For tartronic acid, the direct oxidation product of dihydroxy-lactic acid, the increase in concentrations for the runs, where both bond breaking and oxidation by OH is calculated, compared to the run woBB is even bigger than for  $\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{C}(=\text{O})\text{OH}$  (see Figure 5.2c). On the other hand, differences of the various decay rates are not visible for either the runs with or without additional oxidation by OH. It should also be noted that for dihydroxy-lactic acid, differences are especially large during the first two model days and vanish thereafter (see Figure 5.2b). From Figure 5.2c can be seen that there is a difference in the runs with or without OH oxidation throughout the first two model days, which vanishes thereafter. However, a significant increase in all sensitivity runs compared to the run woBB is observed throughout the whole modelling period.

Thus, as expected, bond breaking shifts the reaction products away from the products of the OH oxidation to smaller products (with less carbon mass). However, the shift is not unrealistically high and will not result in a dramatically enhanced shortening of the chain length of the organic compounds in the mechanism. For the decay rate,  $0.1\text{ s}^{-1}$  was chosen as the best estimate based on the results as shown for the decay of 2-oxo-3-hydroxy (Figure 5.1) and oxo-succinaldehyde (Figure E.2, page 315, in the Appendix) in the different sensitivity runs. Although OH oxidation does not significantly further reduce the concentrations of polycarbonyl compounds with the implemented monomolecular decay rate of  $0.1\text{ s}^{-1}$ , it causes a shift in the reaction products. Therefore, OH oxidation is calculated besides the monomolecular decay in the standard version of the generator. An additional routine was added to the generator, which treats the decay of polycarbonyl compounds using the above-mentioned specifications (see also, Figure 4.1, page 74).

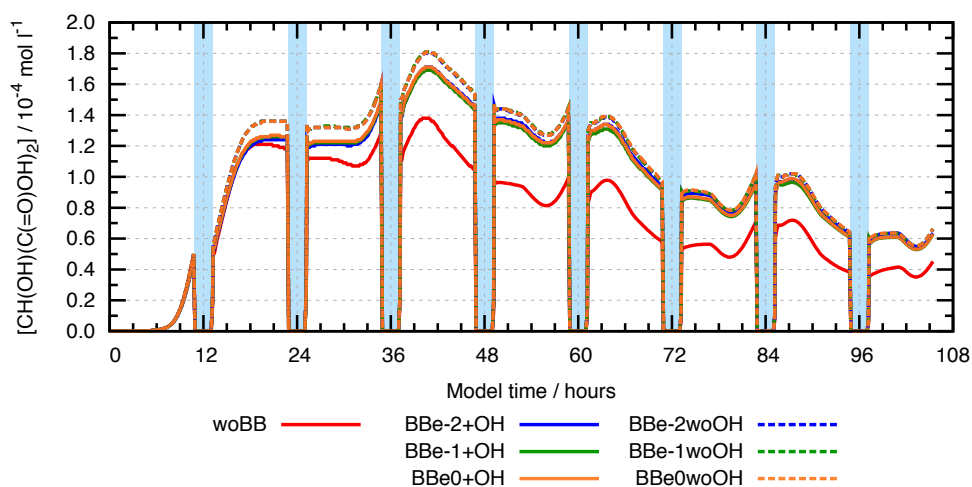
(a) 1,1,2,3,3-pentahydroxy butyric acid



(b) Dihydroxy lactic acid



(c) Tartronic acid



**Figure 5.2** Concentration-time profiles for various products of the 2-hydroxy-3-oxo butanedial oxidation for the different sensitivity runs. Blue bars represent cloud periods.

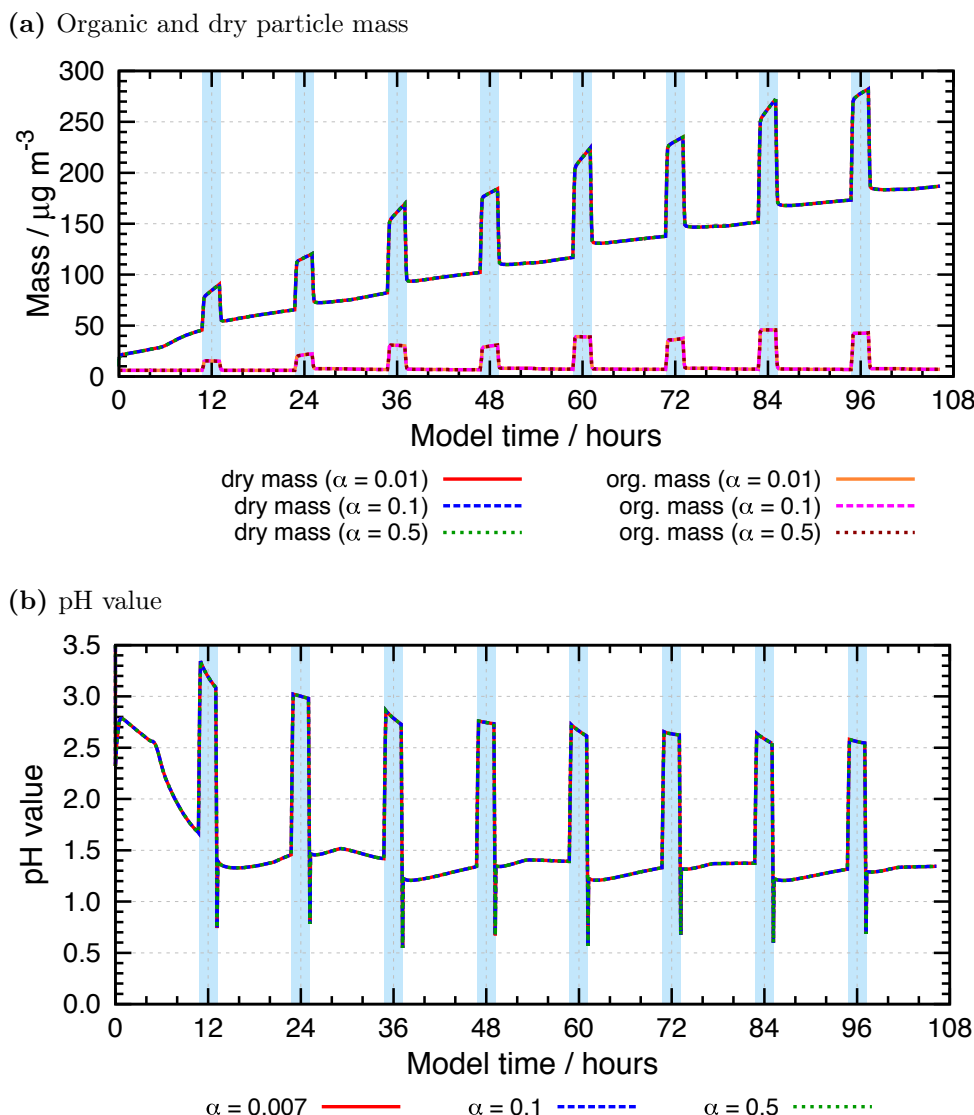
## 5.2 Influence of the mass accommodation coefficient on the organic multiphase chemistry and composition

Experimental data for mass accommodation coefficients ( $\alpha$ ) are very sparse, which can be seen from the CAPRAM database, the review of *Davidovits et al.* (1995) or the latest IUPAC recommendation No. VI by *Ammann et al.* (2013) and references within these publications. Therefore, all mass accommodation coefficients have to be estimated in the mechanisms generated by GECKO-A. To evaluate the sensitivity of this parameter and assess the accuracy of the generated mechanisms, model simulations have been performed, where the estimated  $\alpha$  values for organic compounds were varied from 0.007 to 0.5. Three different sensitivity runs have been performed based on experimental  $\alpha$ -values taken from the CAPRAM database as published by *Herrmann et al.* (2005) or given on the CAPRAM website (<http://projects.tropos.de/capram>).

Table E.1, page 314 in the Appendix, shows the available experimental data of mass accommodation coefficients from the CAPRAM database. Based on these values, three sensitivity runs were performed. In the base case, a mechanism that resembles CAPRAM 3.5 $\alpha$  (see description above and subsection 5.8.2) with mass accommodation coefficients  $\alpha = 0.1$  is used. For the model runs, the standard ‘real atmosphere’ scenario as described in detail in subsection 6.2.1 was used, however, this time under urban conditions with higher concentrations of organic compounds. In this scenario, any differences between the various sensitivity runs can be better seen than under remote conditions with smaller concentrations of organic compounds.

From Table E.1 in the Appendix can be seen that the experimental  $\alpha$ -values range from 0.004 for the nitrate radical to 0.5 for nitrous acid. Mass accommodation coefficients of organic compounds vary around 0.02. Therefore, a sensitivity run was used with  $\alpha = 0.007$ , the approximate minimum value for organic compounds of 0.0067 for methyl hydroperoxide (see Table E.1, page 314). For a complete evaluation, a sensitivity run to estimate the upper limit was created, where all mass accommodation coefficients of organic compounds in the generated mechanism were estimated with the maximum value of 0.5.

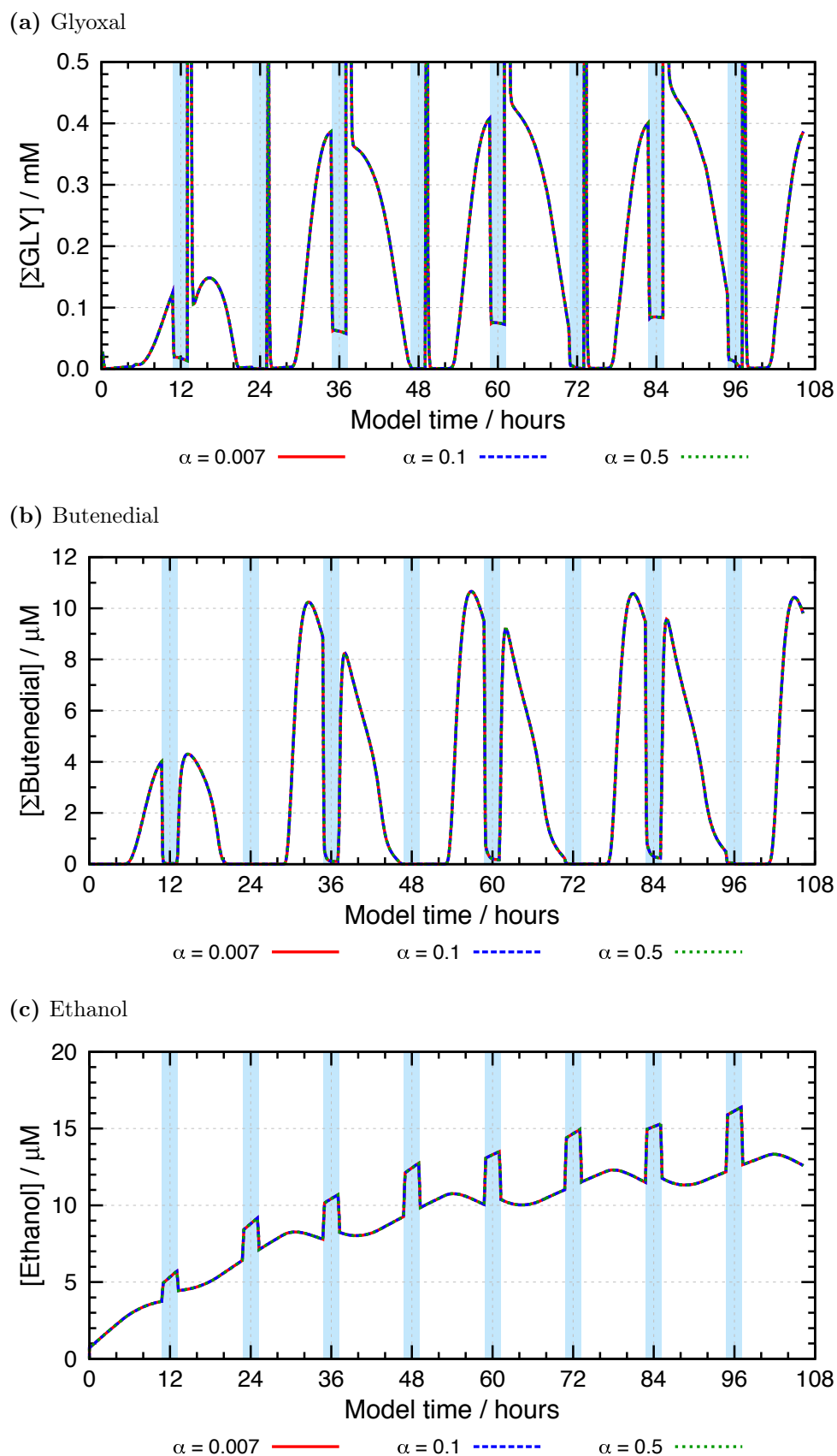
The sensitivity studies show that mass accommodation coefficients are insensitive in the range investigated. No influence of the variation of the  $\alpha$  parameter is seen on the dry or organic particle mass or particle acidity in Figure 5.3. Moreover, the concentration-time profiles of single species have been investigated thoroughly, but an influence was seen for neither compound. Figure 5.4 shows the concentration-time profiles for the examples glyoxal (5.4a), butenedial (5.4b), and propionaldehyde (5.4c). Glyoxal is very soluble in aqueous solutions, where it hydrates. The equilibrium decreases the concentrations of the unhydrated forms in the aqueous phase, which causes further uptake from the gas phase as a consequence of the Henry’s Law equilibrium. A sensitivity of the mass accommodation coefficient is, therefore, likely to be seen (as a deviation in the concentration-time profiles of this compound between the different sensitivity studies). However, no variation in the



**Figure 5.3** Time profile of the organic and dry mass (a) and the pH-value (b) for varying mass accommodation coefficients. Blue bars represent cloud periods.

concentration of glyoxal in the different sensitivity runs is observed as can be seen in Figure 5.4a.

Butenedial is another compound, where effects of a varying  $\alpha$ -value are likely to be seen. Due to the double bond, butenedial has a high reactivity with a rate constant of  $2.31 \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  for hydroxyl radical reactions and an estimated rate constant of  $2.5 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for nitrate radical reactions. The fast rate constants cause a permanent strong degradation of this compound in the aqueous phase and, hence, a decrease in the concentrations. As a consequence, more butenedial can be taken up from the gas phase in this *reactive uptake*. Due to the fast sink reactions in the aqueous phase, mass accommodation coefficients might be the limiting factor in the uptake process. However, model results in Figure 5.4b confirm that  $\alpha$  is not the most crucial parameter and no differences in the concentration-time profiles are seen. For completeness, a compound with



**Figure 5.4** Concentration-time profiles of selected compounds for varying mass accommodation coefficients. The concentrations in subfigure a and b are the sum of all hydration forms. Blue bars represent cloud periods.

a relatively low HLC is shown, i.e. ethanol with an HLC of  $1.9 \cdot 10^2 \text{ M atm}^{-1}$ . Again, no effects of the  $\alpha$  variation is seen in Figure 5.4c.

As no significant influence of the mass accommodation coefficients was seen in the sensitivity studies, the previously used  $\alpha$ -value of 0.1 has been used in the protocol as well.

### 5.3 Influence of the cut-off parameter for minor reaction pathways

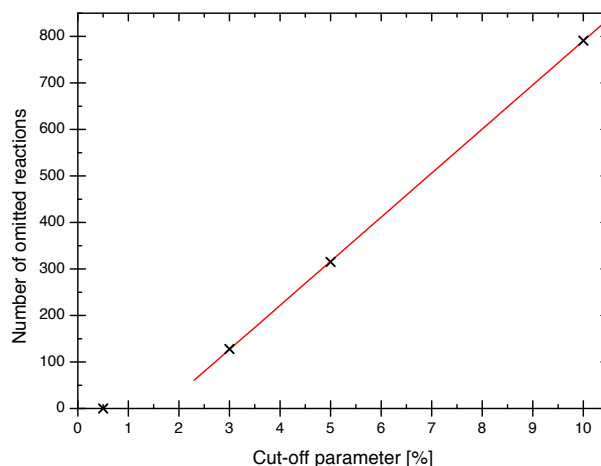
A major advantage of the newly developed protocol for automated aqueous phase mechanism generation is the introduction of a branched radical attack leading to different reaction channels. However, to reduce the size of the generated mechanism, minor reaction pathways are omitted (see section 4.3). To investigate the sensitivity of the threshold for the cut-off of minor reaction channels, four different mechanisms have been created. These mechanisms range from a very detailed mechanism with a 0.5% threshold for minor branches to the overall turnover in this reaction to a more simplified reaction scheme omitting branches with up to 10% of the overall turnovers. Again, the generator was used to introduce branching ratios in CAPRAM 3.0n. The generated mechanisms resemble the new CAPRAM 3.5 $\alpha$  version (as discussed above and in subsection 5.8.2). The total number of aqueous phase reactions depending on the threshold for the cut-off of minor reaction pathways as well as the cut-off parameter used in these sensitivity studies is given in Table 5.2. For the generation of the last mechanism with a cut-off parameter of 10%, the mass preservation factor described in section 4.3 was decreased to 0.6 to allow for even more reduction. Thus, the 10% case is a rather extreme example to evaluate the limits of such a cut-off process.

Figure 5.5 demonstrates the potential for mechanism reduction by plotting the number of reduced reactions over the threshold of the cut-off parameter. For branching ratios greater or equal 3% the increase is linear. For very small branching ratios, the reduction potential is less. Thus, significant potential for mechanism reduction is given only for rather crude cut-off parameters.

Sensitivity runs have been performed using the standard scenario with non-permanent clouds for either urban or remote continental conditions. The scenario is described in detail in subsection 6.2.1. Again, a few sample compounds are used to demonstrate the influence of the investigated parameter. Results are shown in Figure 5.6. Dicarboxylic

**Table 5.2** Overview of the different conditions used for the mechanism generation of the sensitivity runs concerning the cut-off of minor branches and the resulting number of reactions.

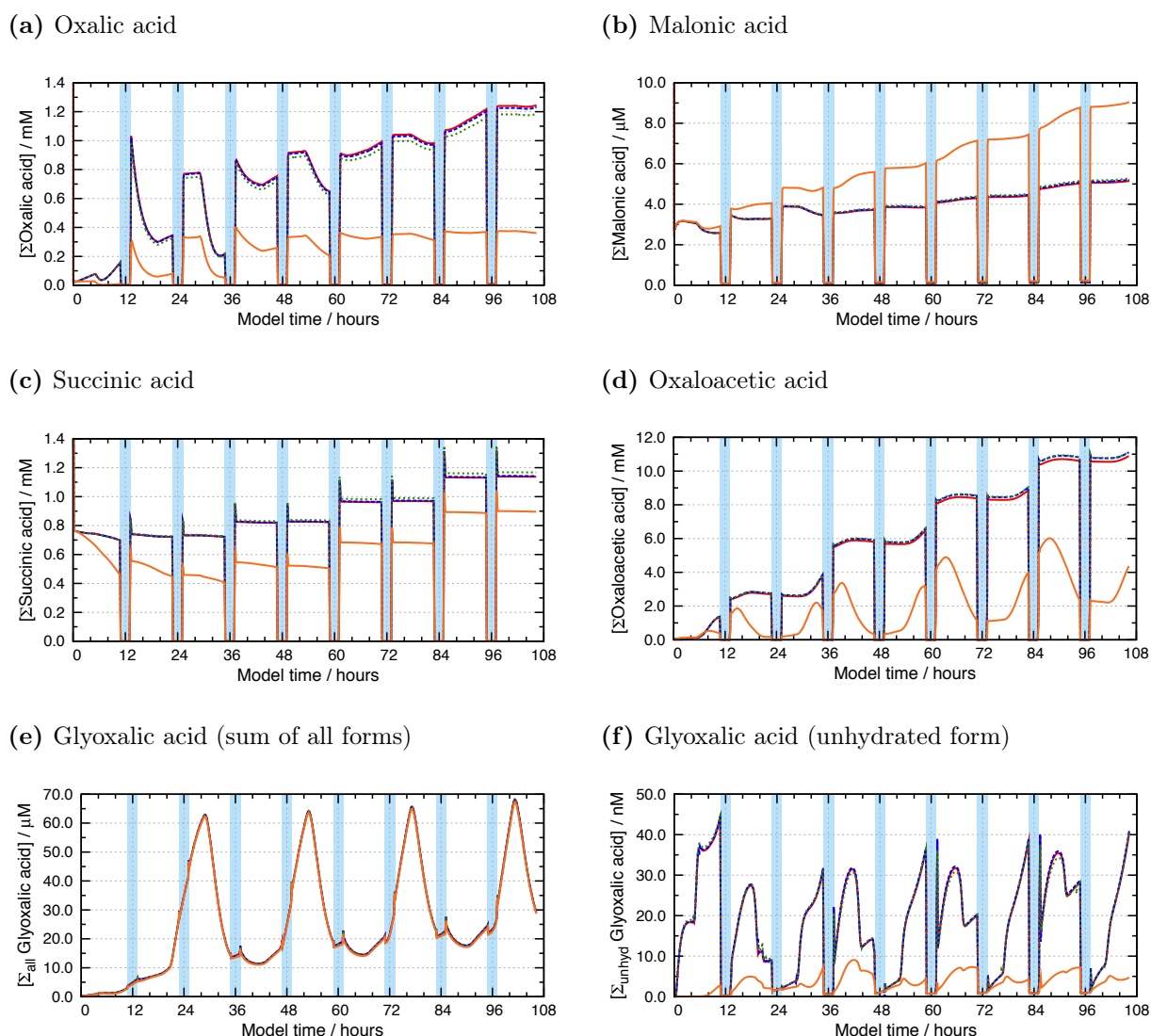
Cut-off	Mass preservation	No. of reactions
0.5	80	4454
3.0	80	4326
5.0	80	4139
10.0	60	3663



**Figure 5.5** Overview of the potential of mechanism reduction by omitting minor reaction pathways.

acids are a very good example to demonstrate the influence of the cut-off parameter, as only a small percentage of H-atoms is abstracted at the carboxyl group. For malonic acid, 30.5% percent of the H-atoms are abstracted at either of the carboxyl groups in the fully protonated form and only 6% of the H-atoms are abstracted at the carboxyl group of the mono-anion. As the mono-anion is the predominant form under tropospheric conditions, concentrations of the 10% run are significantly increased in Figure 5.6b due to the missing oxidation of the latter channel. On the other hand, no big differences are seen in the concentration-time profiles of the other runs, which all include the oxidation pathway at the carboxyl group. For succinic acid (Figure 5.6c), large deviations exist again for the 10% run. However, this time the 10% case shows decreased concentrations compared to the other runs. As only 1.8% of all H-atoms are abstracted at both carboxyl groups in the fully protonated form, this would only affect the 0.5% runs, but effects are too small to be seen. In the predominant mono-anionic form less than 0.5% of the H-atoms are abstracted at the carboxyl group and, thus, the decay is equal for all runs. Deviations derive, therefore, from the formation process. The study of the direct precursors allows no conclusions of this big differences in the concentration profiles as the cut-off is the same for all four sensitivity runs. However, investigating more precursors of the oxidation chain leads to the monohydrated form of butanedial ( $\text{CHOCH}_2\text{CH}_2\text{CH}(\text{OH})_2$ ). 9.8% of the H-atoms are abstracted at the hydroxyl group, which is oxidised to oxo-butyric acid and subsequently to succinic acid. Thus, the omission of this reaction pathway could explain the decreased concentrations of succinic acid in the 10% run, but detailed analyses of the chemical fluxes would be needed to assure this assumption. As for succinic acid, decreased concentrations in the 10% run are also seen for oxalic acid (Figure 5.6a). This time, minor deviations can also be seen for the 5% run with slightly decreased concentrations compared to the 3% run and the 0.5% run. Deviations in the concentration-time profiles of the latter two runs are negligible. Since oxalic acid has only one possible degradation channel by H-abstraction, reasons for the differences in the concentration-time profiles of the various sensitivity runs must be found in different formations pathways.

Another interesting example is the oxidised DCA oxaloacetic acid (see Figure 5.6d). The 10% threshold in the cut-off parameter does not only lead to significantly decreased



**Figure 5.6** Concentration-time profiles for selected organic compounds in the sensitivity runs investigating the influence of the omission of minor reaction pathways under urban conditions. Red solid lines belong to mechanisms using a 0.5% threshold, for blue dashed lines a 3% threshold is used, for green dotted lines a 5% threshold is used and for orange solid lines a 10% is used. Moreover, for the 10% run the mass preservation factor was reduced from 0.8 to 0.6 (see section 4.3 for details). The blue bars mark cloud periods.

concentrations compared to the other runs, moreover, a diurnal variation is seen in the concentration of oxaloacetic acid in the 10% run, which is not present in the concentration-time profiles of the other sensitivity studies. In the runs with a threshold of 5% or less of the cut-off parameter, oxaloacetic acid accumulates over the whole modelling period. Detailed flux analyses would be needed to investigate this behaviour, which are beyond the scope of this simple sensitivity analysis.

Glyoxalic acid shows the necessity of detailed and thorough analysis. No big differences are seen for all four runs, when investigating the overall concentration of all hydration and dissociation states of this compound (see Figure 5.6e). However, when looking only



at the unhydrated forms in Figure 5.6f, deviations of the 10% runs are visible again. Yet, concentrations of the unhydrated forms are in the nM range and, therefore, negligible.

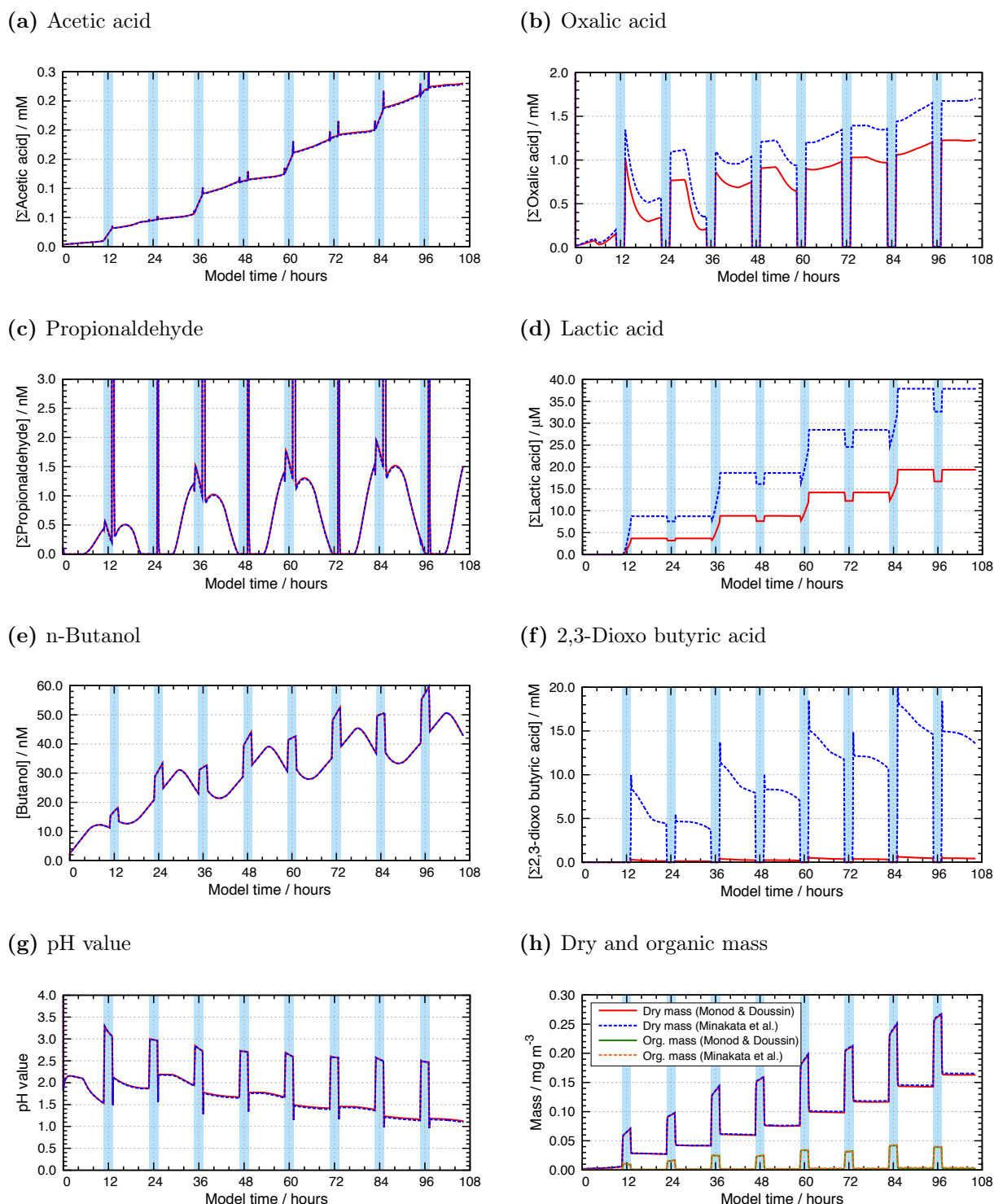
Overall, it can be concluded that most potential for mechanism reduction is found for high thresholds of the cut-off parameter. However, for crude cut-off parameters, significant deviations in the model output were observed. Major deviations in the concentration-time profiles of the 10% run are seen in almost all concentration-time profiles compared to the other sensitivity studies. Differences between the other runs are mostly negligible although minor deviations are seen for the 5% threshold in the concentration-time profiles of oxalic acid compared to the 3% and 0.5% run. As the potential for mechanism reduction with a 5% threshold is small compared to the 3% threshold, a cut-off parameter of 3% was chosen as the standard value in the generator for a better accuracy in the description of the aqueous phase chemistry.

Furthermore, model runs have also been performed under remote continental conditions. The tendency of the urban results with major deviations in the model results mainly for the higher thresholds of the cut-off parameters is confirmed under remote conditions. However, deviations are smaller. Moreover, no differences in the diurnal variations of the oxaloacetic acid concentrations of the 10% run were seen for these conditions. Results for the remote case studies are given in Figure E.3 on page 316 in the Appendix.

## 5.4 Influence of the chosen SAR in the protocol

The generator protocol is, to the main part, based on structure-activity relationships. Although all data prediction methods have been chosen with great care and, in the case of Evans-Polanyi-type correlations, even been improved for the needs of automated mechanisms self-generation, some uncertainties remain. Therefore, the issue of the chosen SAR has been addressed in another sensitivity study.

The generator with the protocol described above and given in Table 3.8 in section 3.7 was used to generate a mechanism that resembles CAPRAM 3.5 $\alpha$  (see subsection 5.8.2 and explanations above). A second mechanism was generated, where the routines in GECKO-A were changed in a way that the SAR of *Minakata et al.* (2009) was always used instead of preferring the SAR by *Monod and Doussin* (2008) and *Doussin and Monod* (2013). Hence, all hydroxyl radical reactions with stable organic compounds are estimated with the SAR of *Minakata et al.* (2009) and the protocol was modified in rows 3 – 5 in Table 3.8 in the respective manner. Moreover, branching ratios of nitrate radical reactions have been adjusted to the results of the SAR by *Minakata et al.* (2009). Sensitivity runs were performed with the standard meteorological scenario under remote conditions (see subsection 6.2.1). Resulting concentration-time profiles of important organic compounds have been compared for the two generated mechanisms and are shown for selected compounds in Figure 5.7.



**Figure 5.7** Concentration-time profiles for selected organic compounds (plots a – f), as well as pH value (plot g) and dry and organic mass (plot h) in the sensitivity runs investigating the influence of the chosen SAR. Red solid lines belong to compounds of the mechanisms created with the standard protocol of GECKO-A, blue dashed belong to compounds of the mechanism using only the SAR of *Minakata et al.* (2009) instead of preferring the SAR by *Monod and Doussin* (2008) and *Doussin and Monod* (2013). The legend for plot h is directly given in that plot. The blue bars mark cloud periods.

In Figure 5.7, some concentration-time profiles match almost perfectly while other differ by orders of magnitude. At a closer investigation, concentrations that match well (Figure 5.7a, 5.7c, and 5.7e) belong to compounds that are not very oxidised and have uptake from the gas phase as main source or are the direct main oxidation product of such compounds. Examples are terminal monoalcohols, monoaldehydes, and monocarboxylic acids. The chain length of the molecules does not influence the results. The concentration-time profiles of acetic acid (Figure 5.7a), propionaldehyde (5.7c), and butanol (5.7e) are exemplarily shown to demonstrate this fact. More oxidised compounds with aqueous phase in-situ sources can show large deviations in the concentration-time profiles of the different sensitivity studies as demonstrated by the plots 5.7b, 5.7d, and 5.7f for oxalic, lactic, and 2,3-dioxo butyric acid, respectively. Furthermore, ‘macroscopic’ parameters such as the particle or cloud droplet pH (Figure 5.7g) or the dry or organic mass (Figure 5.7h) do not show large deviations.

The behaviour of these discrepancies can be explained with the results of the evaluation process of the two SARs given in section 3.6. Both SARs showed a high accuracy in the prediction of the overall second order rate constants of organic compounds with hydroxyl radicals. However, differences were seen in the predicted products as explained for the branching ratios of terminal monoalcohols. The high precision of the rate constant prediction is reflected by the fact that the concentration-time profiles of organic compounds that have mainly gas phase sources are almost equal. However, differences in the predicted products can lead to different oxidation pathways and, thus, different intermediate compounds. Therefore, the concentration-time profiles of more oxidised compounds with predominantly aqueous phase in-situ sources can show large deviations. However, the impact of these differences is not large enough to affect macroscopic parameters such as the pH value or particle mass. Therefore, significant differences exist in the single predicted compounds and the particular oxidation pathways, yet different reaction pathways do not lead to, e.g., large deviations in the solubility of the products and thus a shift in the speciation of gas and aqueous phase organic mass. Furthermore, particle acidity is not influenced by the different SARs, e.g., by producing more carboxylic acids in either of the two prediction methods.

In conclusion, the structure-activity relationships of *Monod and Doussin* (2008)/*Doussin and Monod* (2013) are preferred in the GECKO-A protocol. While the accuracy of both SARs is equally high, differences arise in the predicted reaction pathways. More experimental product studies would be needed to develop more precise SARs. The only known detailed product study is that of *Asmus et al.* (1973), which was used to derive the SAR by *Monod and Doussin* (2008). Parameters have been constrained to reflect the reaction products of linear monoalcohols determined by *Asmus et al.* (1973) (*Monod and Doussin*, pers. comm.). However, more studies for more homologous series of compound classes are needed to develop SARs with reliable product determination in addition to the already very precise second order rate constant prediction. It must be concluded that up to date a high uncertainty is found in the predicted products and the oxidation pathways have to be treated with care.

## 5.5 Processing of organic mass fraction in the protocol

From Figure 5.7h, page 102, an insufficient organic mass production during non-cloud periods becomes clear. Therefore, the processing of the organic particulate mass fraction is addressed in a series of sensitivity studies in the present section. To study the organic scheme in the generator protocol and the extended CAPRAM mechanisms in great detail, a more advanced mechanism has been used, where the organic chemistry in CAPRAM 3.0n has been extended for organic compounds with up to four carbon atoms. The mechanisms used in the sensitivity studies in this section resemble CAPRAM 4.0 $\alpha$  (see discussion at the beginning of this chapter and subsection 5.8.3.) For detailed studies, an urban ‘real atmosphere’ scenario was used as presented in subsection 6.2.1. The aim of the sensitivity studies was to point out weaknesses in the protocol and possibly present solutions for the auto-generation of realistic chemical oxidation schemes. The studies were performed successively and successful methods have been applied in the following studies, too, unless stated otherwise. Therefore, mechanisms of sensitivity runs later in this section will incorporate new reaction schemes discussed previously in this section.

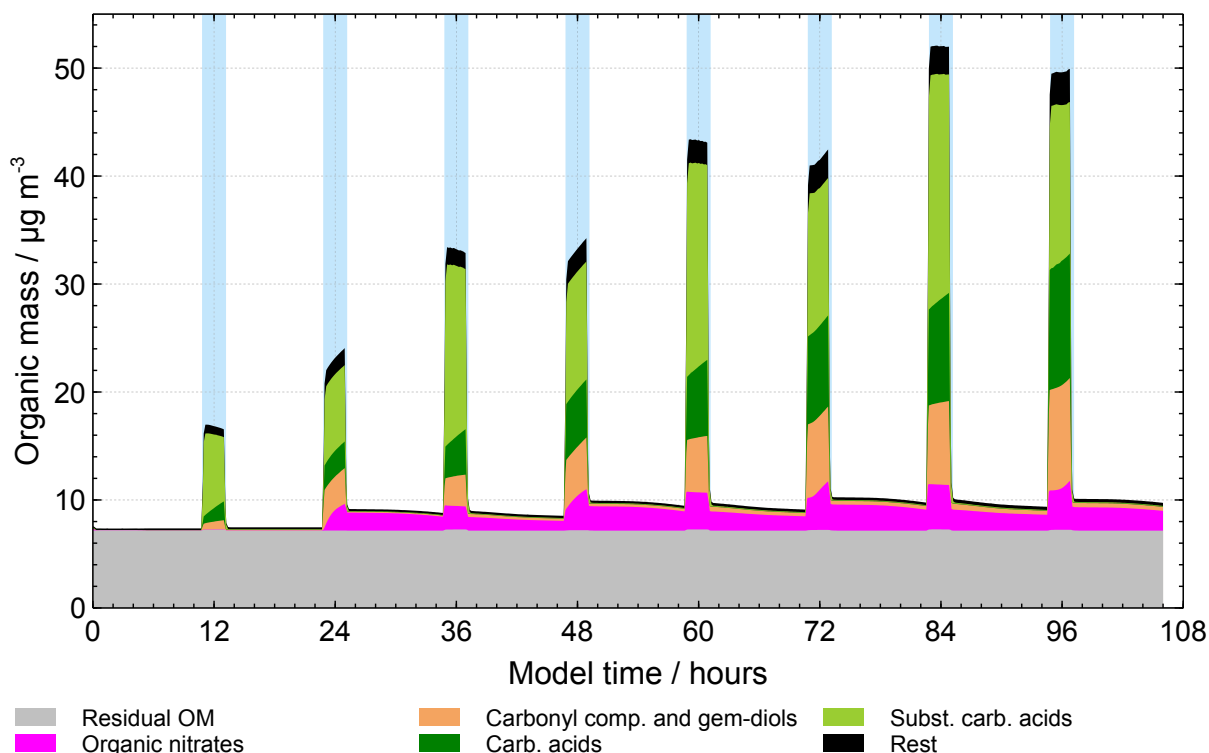
### 5.5.1 Parameterisations for radical attack of the overall organic mass fraction

One reason for the insufficient mass production might be the restricted size of the chemical mechanism CAPRAM to just compounds with up to four carbon atoms. CAPRAM is designed as a fully explicit chemical mechanism, however, as no auto-generation methods have been applied previously, this means that it is restricted to a certain size. Currently, only the C<sub>1</sub> and C<sub>2</sub> chemistry are treated with a high detail, and a sufficient description of the C<sub>3</sub>/C<sub>4</sub> chemistry is available in CAPRAM 3.0n. Missing chemistry from C<sub>3</sub>/C<sub>4</sub> and even larger compounds might lead to an underprediction of the production of organic mass fraction. Moreover, and equally important, missing organic compounds in the mechanism can lead to an overestimation of hydroxyl radical concentrations as OH rapidly reacts with the dissolved organic material and is transformed into water in this reaction. Overestimated hydroxyl radical concentrations can cause a too rapid oxidation of organic compounds in the aqueous phase and, therefore, an insufficient organic mass production. To account for the additional hydroxyl radical scavenging by organic compounds, several reactions with water-soluble organic carbon (WSOC) and humic-like substances (HULIS) have been parameterised and added to a mechanism resembling CAPRAM 4.0 $\alpha$  in a sensitivity study called ‘WSOC<sub>OH</sub>’.

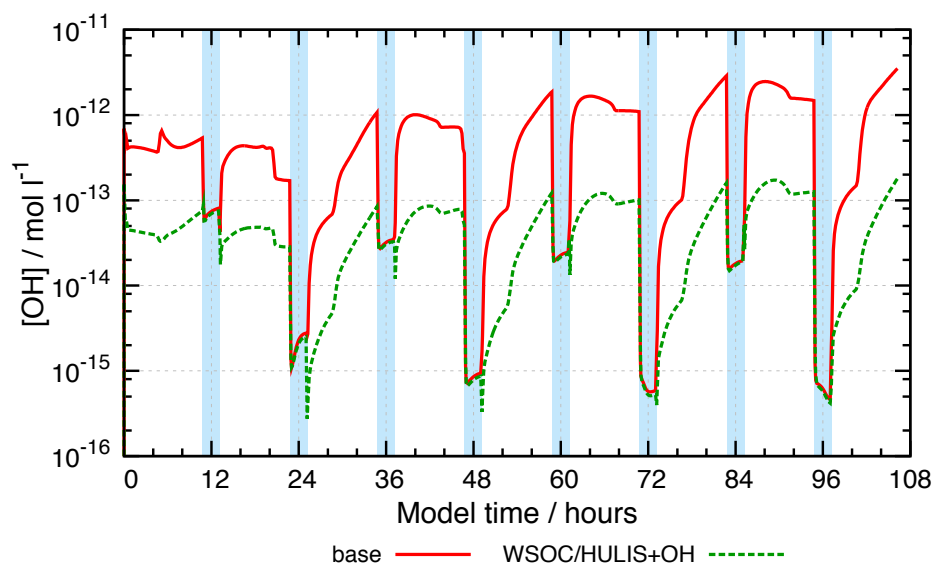
## Hydroxyl radical reactions with dissolved organic material

The additional sink reactions for OH radicals include the model species WSOC and HULIS. The same rate constant has been used for WSOC and HULIS with an estimated value of  $3.8 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$  after *Arakaki et al.* (2013). Furthermore, HULIS can dissociate. The dissociated HULIS form ( $\text{HULIS}^-$ ) reacts with OH radicals with the same estimated rate constant by *Arakaki et al.* (2013) of  $3.8 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ . Moreover,  $\text{HULIS}^-$  subsequently forms complexes with iron(II) and iron(III). Photolysis can release the HULIS bound in the iron(III) complex and convert iron(III) to iron(II). The dissociation of HULIS has been estimated with the  $pK_a$  of fulvic acid after *Salma and Lang* (2008). The complexation of iron with HULIS has been estimated with the respective equilibrium constants of the iron-oxalato complex from the CAPRAM 3.0n database, because humic-like substances are known to be effective complexing agents (see, e.g., *Skogerboe and Wilson*, 1981, *Vione et al.*, 2004, *Arakaki et al.*, 2010). The iron-HULIS complex photolysis has been estimated with a value for the iron-hydroxy complex photolysis according to *Arakaki et al.* (2010). A summary of all reactions can be found in Table G.12 in Appendix G.3. For the current sensitivity run  $\text{WSOC}_{\text{OH}}$ , reactions  $\text{R}_000305 - \text{R}_000307$ , equilibria  $\text{E}_000015 - \text{E}_000017$ , and the photolysis  $\text{P}_00003$  has been used.

The parameterisations in the  $\text{WSOC}_{\text{OH}}$  run have the desired effect and the organic mass fraction increases from initially  $\sim 7.5 \mu\text{g m}^{-3}$  to about  $10 \mu\text{g m}^{-3}$  (compare Figure 5.8) due to a strong decrease in hydroxyl radical concentrations of about 1 order of magnitude during non-cloud periods (see Figure 5.9). During cloud periods, the effect of the additional



**Figure 5.8** Time-resolved evolution of the organic mass fraction distinguished by compound classes in the sensitivity run  $\text{WSOC}_{\text{OH}}$  under urban conditions.



**Figure 5.9** Logarithmised concentration-time profiles of OH radicals in the aqueous phase over the whole modelling period. Results are shown for the sensitivity run  $\text{WSOC}_{\text{OH}}$  and the base case under urban conditions.

parameterisations of reactions of OH radicals with dissolved WSOC and HULIS is marginal. Moreover, the overall effect is small, and the organic mass production is only a few micrograms per cubic meter.

For a more detailed analysis, the organic mass fraction has been distinguished by compound classes of the organic constituents in Figure 5.8. The model is initialised with about  $7.3 \mu\text{g m}^{-3}$  residual organic matter (OM), which consists of elemental carbon (EC), water-insoluble organic carbon (WISOC), WSOC, HULIS/HULIS<sup>-</sup>, and the iron-HULIS complexes. This mass fraction does not change over time and the constituents of this class are only transformed into different forms. Additional mass production derives from the explicit chemical scheme in CAPRAM. During cloud periods, the largest fraction of the organic mass are carboxylic acids and diacids of which a major fraction is substituted (see dark and light green colour, respectively, in Figure 5.8). There is also a substantial fraction of carbonyl compounds (mono-, di- and polycarbonyl compounds, which may be partly or fully hydrated and/or hydroxy-substituted; orange colour in Figure 5.8). A minor fraction are organic nitrates (pink colour in Figure 5.8) or further compounds (black colour).

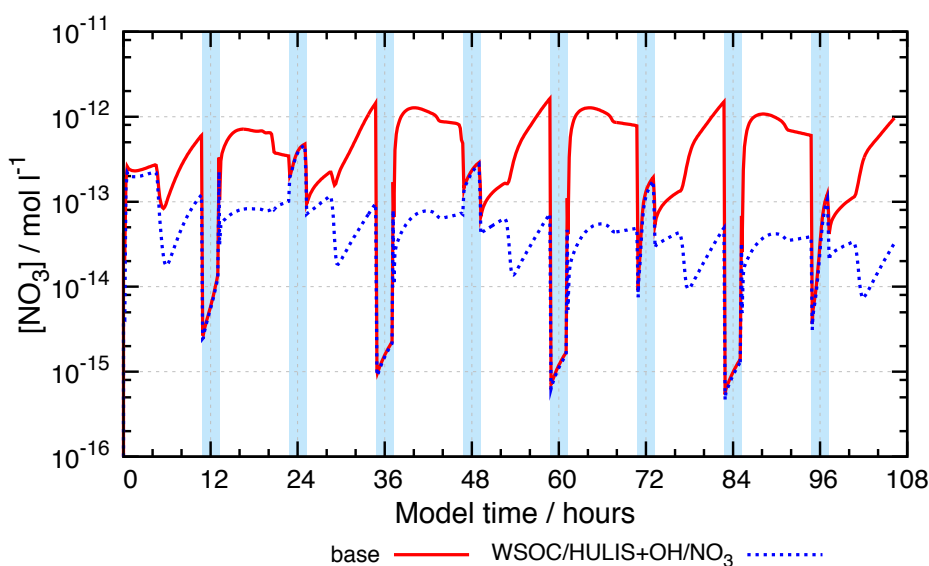
However, during non-cloud periods, particulate organic matter consists mainly of organic nitrates besides the residual OM with which the model was initialised. Only one group has seen very high secondary organic aerosol (SOA) loadings with organic nitrates. *Fry et al.* (2009) conducted chamber experiments at the SAPHIR chamber in Jülich, Germany, simulating remote conditions. Their  $\beta$ -pinene oxidation experiment yielded 40% organic nitrates under dry conditions and 45% organic nitrates in organic particles were found at 60% relative humidity. In field experiments, *Fry et al.* (2013) found about  $0.1 \mu\text{g m}^{-3}$  particulate organic nitrates. Up to 20% of the particulate matter was found to be organic nitrates in the flight samples during the INTEx-NA campaign (*Perring et al.*, 2009). In general, about 10 – 20% of the organic mass can be organic nitrates (see *Day et al.*, 2010

and references therein). This is, however, still considerably lower than the predicted model output in the explicit scheme of the WSOC<sub>OH</sub> sensitivity study. Only when assuming that all the residual OM with which the model was initialised does not have the same composition as the explicit scheme in CAPRAM and would not comprise any organic nitrates, the organic nitrate fraction would meet the upper end of the measurements. However, there is no reason why the residual OM should be assumed organic nitrate free, when this is the main component in the explicit scheme. Therefore, further sensitivity studies have been performed to resolve the overestimation of organic nitrate concentrations.

### Nitrate radical reactions with dissolved organic material

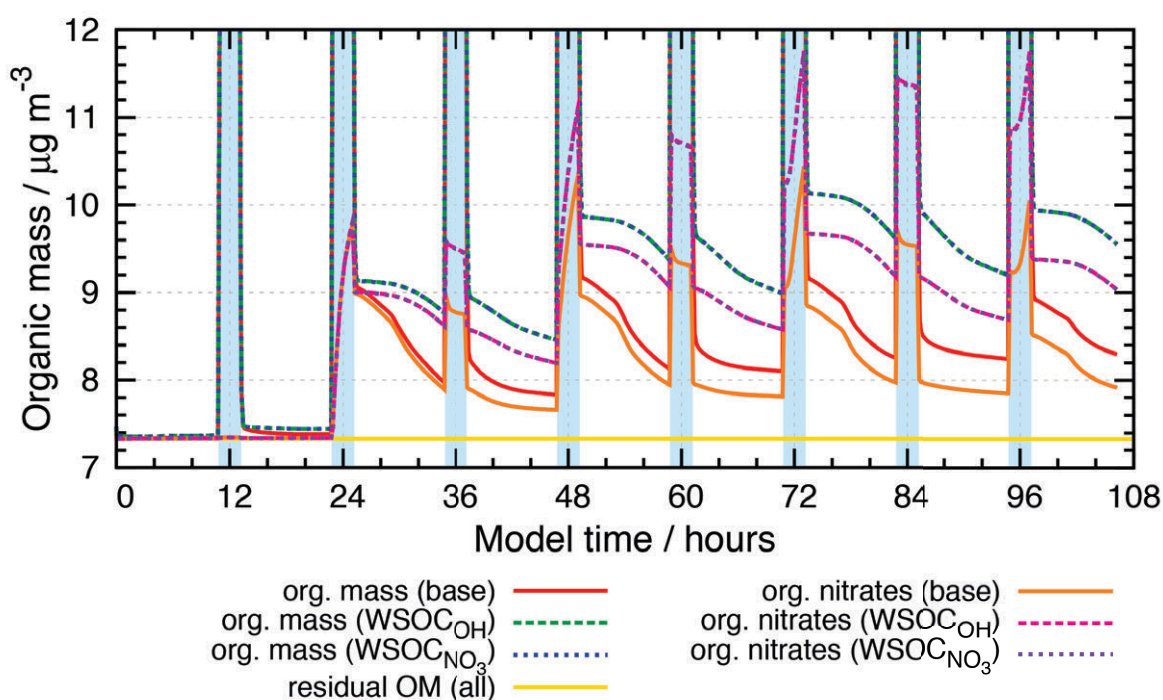
Further sensitivity runs were conducted to resolve the overestimation of the organic nitrate fraction in the particulate organic matter. Only two processes are implemented in the GECKO-A protocol, which can be responsible for the organic nitrate formation. The organic nitrate fraction can either derive from uptake from the gas phase or from in-situ production by NO<sub>3</sub> addition reactions to unsaturated organic compounds.

In a first approach, further parameterisations were introduced for nitrate radicals with WSOC and HULIS/HULIS<sup>-</sup> in order to consider further aqueous phase sinks of the nitrate radical and, hence, achieve realistic concentration levels in either the aqueous or the gas phase. Consequently, the formation of organic nitrates by reaction of NO<sub>3</sub> with unsaturated organic compounds (see reactions R<sub>o</sub>00308 – R<sub>o</sub>00310, Table G.12, page 395) should be suppressed with the more realistic aqueous phase NO<sub>3</sub> concentrations. The reactions of nitrate radicals with WSOC and HULIS were estimated with a rate constant of  $1 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$  according to typical rate constants of NO<sub>3</sub> with aliphatic organic compounds



**Figure 5.10** Logarithmised concentration-time profiles of NO<sub>3</sub> radicals in the aqueous phase over the whole modelling period. Results are shown for the sensitivity runs WSOC<sub>OH</sub>, WSOC<sub>NO<sub>3</sub></sub>, and the base case under urban conditions.





**Figure 5.11** Time-resolved evolution of particulate OM, residual OM and organic nitrate concentrations in the sensitivity runs  $\text{WSOC}_{\text{OH}}$ ,  $\text{WSOC}_{\text{NO}_3}$ , and the base case under urban conditions.

(see, e.g., *Alfassi et al.*, 1993, *Herrmann*, 2003). For the reaction of  $\text{NO}_3$  with  $\text{HULIS}^-$ , electron transfer was assumed with a rate constant of  $5 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$ .

As for the hydroxyl radical, the parameterisations led to a significant reduction in nitrate radical concentrations of one to two orders of magnitude during non-cloud periods (see Figure 5.10). Again, during cloud periods, nitrate radical concentrations stayed unaffected. However, no effect is seen on the organic matter and organic nitrate concentrations. Figure 5.11 shows the concentrations-time profiles of the overall organic mass, the residual OM as described above, and organic nitrates in the different sensitivity runs, respectively. These are identical for the sensitivity studies  $\text{WSOC}_{\text{OH}}$  and  $\text{WSOC}_{\text{NO}_3}$ . Furthermore, in this figure, high concentrations during cloud periods are cut off and the plot is zoomed in to the particulate matter during non-cloud periods for a better resolution in Figure 5.11. For a complete overview of the processing of the organic mass fraction, the complete graphs are shown in Figure E.4, in Appendix E.5, page 317.

### 5.5.2 Detailed studies of organic nitrate sinks and sources

As the overall parameterisations of nitrate radical reactions with dissolved organic matter were ineffective, more detailed investigations of the explicit chemical scheme in the generated CAPRAM mechanisms were performed. If the reason for the overestimation of organic nitrates in CAPRAM is the aqueous phase chemistry and not uptake processes then there must be either an overestimation of the sources or an underestimation of the sinks. Both



possibilities are addressed in further sensitivity studies and results are shown in this subsection.

### Organic nitrate photolysis

In this paragraph, possible missing sinks are discussed as one reason for the overprediction of the organic nitrate aqueous phase concentrations. The oxidation of organic nitrates can lead to organic compounds without any hydrogen atoms. For these carbonyl nitrates, hydrolysis was estimated as degradation process with an assumed rate constant of  $7.5 \cdot 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$  based on the PAN hydrolysis. This process is, however, very slow and can lead to a significant enrichment of organic nitrates if no further sinks are implemented in the mechanism.

At the current state of the protocol, aqueous phase photolysis is neglected. However, photolysis might be an important sink for slowly reacting compounds. Therefore, photolysis was implemented for all organic nitrates according to Reaction R18 in a sensitivity study called ‘Phot’.



The photolysis was estimated twice the value for organic nitrates in the gas phase mechanism MCMv3.1. The value was chosen to account for often similar extinction coefficients in the gas and the aqueous phase and a lens effect resulting from the spheric shape of the cloud droplets (see, e.g., *Madronich*, 1987). A cage effect of the solvent water was not considered to have an upper limit estimate of the aqueous organic nitrate sinks by photolysis. Moreover, the chosen value is close to the value of the photolysis of inorganic nitrate ( $\text{NO}_3^-$ ).

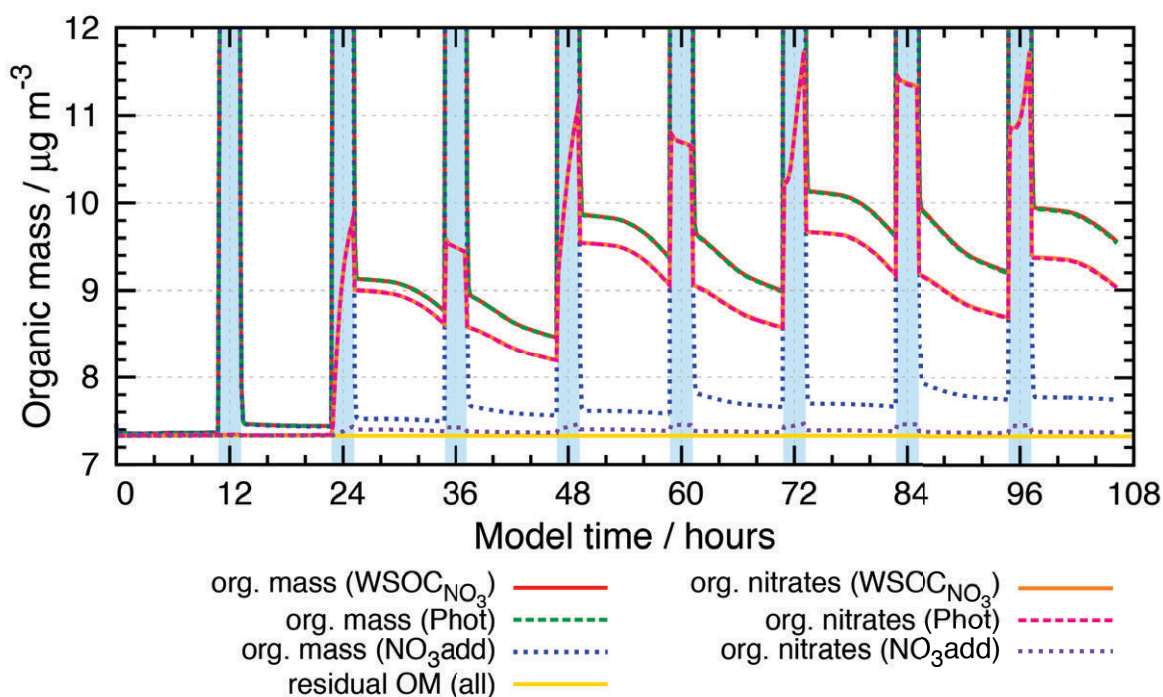
Results of the comparison of the mechanism without organic nitrate photolysis in the scenario  $\text{WSOC}_{\text{NO}_3}$  and with organic nitrate photolysis (scenario Phot) are shown in Figure 5.12. This plot zooms again into the concentrations of the non-cloud periods, while the complete graphs are provided in the Appendix in Figure E.5, page 317. The additional sink of organic nitrate photolysis has no effect on organic nitrate concentrations and, hence, the overall organic matter. In Figure 5.12, the concentration-time profiles of the scenarios  $\text{WSOC}_{\text{NO}_3}$  and Phot are indistinguishable from one another for organic nitrates (orange solid line and pink dashed line, respectively) and the overall organic matter (red solid line and green dashed line). As photolysis is currently not treated in the protocol, this additional sink was omitted in the following studies for consistency and as it had no effect on multiphase processing of organic compounds.

### $\text{NO}_3$ reactions with unsaturated organic compounds

As the sinks seem to be described adequately to our current knowledge, further investigations aimed at the sources of organic nitrates to detect the cause of the overestimation of their concentrations in the model runs. Although, the rate constants of nitrate radical

additions to double bonds of unsaturated aliphatic compounds have been chosen with great care based on the kinetic database described in section 3.1, a revision of the data has been performed. These data resemble our current knowledge and are assumed to be true within the experimental errors. However, data are sparse and simple estimations with fixed rate constants had to be made based on only a very few measurements (compare Table 4.1 and Table C.2 in Appendix C.2). The estimations have been distinguished by compound class, which further decreased the number of data points in the set of data to develop a reliable estimation for the reaction of nitrate radicals with unsaturated aliphatic compounds. Moreover, new data by *Schöne et al.* (2014) has become available since the development of the parameterisations, which contradicts the previous measurements. *Schöne et al.* (2014) present kinetic data for the reaction of nitrate radicals with unsaturated compounds, which vary around  $1 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$ . This is significantly lower than the estimates except for unsaturated carboxylic acids and in the order of other nitrate radical reactions with saturated organic compounds (see, e.g., *Alfassi et al.*, 1993, *Herrmann*, 2003). The new values by *Schöne et al.* (2014) have been added to the database and based on this new knowledge all nitrate radical reactions with unsaturated organic compounds have been estimated with a constant value of  $1 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$ .

A sensitivity study has been performed with the urban ‘real atmosphere’ scenario described in subsection 6.2.1, where the new value for nitrate radical addition to double bonds has been adjusted in the scenario  $\text{WSOC}_{\text{NO}_3}$ . This sensitivity study is addressed as ‘ $\text{NO}_3\text{add}$ ’ in the following. Results are shown in Figure 5.12.



**Figure 5.12** Time-resolved evolution of particulate OM, residual OM and organic nitrate concentrations in the sensitivity runs  $\text{WSOC}_{\text{NO}_3}$ , Phot, and  $\text{NO}_3\text{add}$  under urban conditions.

The reduced rate constant of  $\text{NO}_3$  addition to unsaturated compounds has a big impact on the processing of the organic mass fraction. With the new rate constants, the organic nitrate fraction decreases to marginal concentrations (compare violet dotted line with orange solid line in Figure 5.12). However, organic mass production is reduced by the same extent leaving less than half a microgram per cubic meter in 4.5 days in the sensitivity run  $\text{NO}_3\text{add}$  (blue dotted lines vs. red solid line).

### 5.5.3 Phase transfer of oxygenated organic compounds in the protocol

The sensitivity studies described in this section have pointed out two main problems: (i) an insufficient organic mass production through aqueous phase chemistry and (ii) an overestimation of the organic nitrate fraction in the aqueous phase. The two problems are contradicting and trying to resolve one will enhance the other discrepancy. The current studies have led to mechanisms that either predict an adequate organic mass production, but overestimate the organic nitrate fraction; or, if organic nitrate concentrations are reduced, only an insufficient organic mass production is observed in the particles.

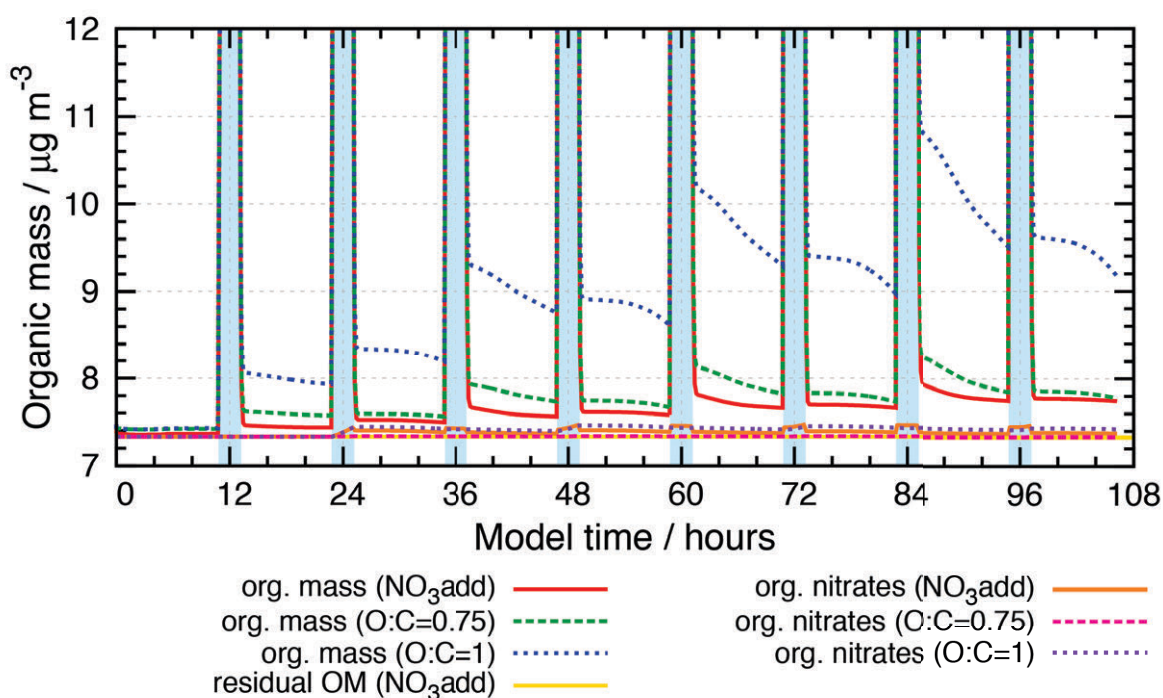
Thus, the current explicit mechanism is not able to reproduce the processing of the organic mass fraction to our current knowledge as it is seen in field measurements (see, e.g., *Seinfeld and Pandis*, 2006 and references therein). *Ervens and Volkamer* (2010) suggested an organic particle growth rate of  $5 \mu\text{g m}^{-3}$  in 12 hours during daytime conditions oxidising glyoxal in their multiphase model study.

However, at the current state there are still processes missing in CAPRAM. Firstly, the mechanism as designed by the protocol is a purely oxidative mechanism and non-oxidative processes such as accretion reactions have been omitted at present. Moreover, organic compounds can form salts with inorganic particle components such as potassium, magnesium or trace metals (see, e.g. *Jin et al.*, 2014, *Drozd et al.*, 2014). Measurements will identify these organic compounds bound in salts as organic mass fraction. Salt formation will reduce the oxidation of organic compounds as organic compounds bound in salts are believed to be unreactive (*Scheinhardt et al.*, 2013, *Drozd et al.*, 2014). Another issue is the current size of the mechanism. Only organic compounds with up to four carbon atoms are treated, which is not sufficient to describe atmospheric chemistry realistically. Moreover, the gas phase chemical mechanism might need adjustments as well. Current studies suggest the formation of extremely low-volatility organic compounds (ELVOCs) by H shifts of organic peroxy-radicals. In the ELVOC formation process, highly soluble organic oligomers are formed, which enter the aqueous phase. With carbon numbers that can easily reach 20, these compounds are not captured with the current aqueous phase oxidation scheme.

Despite known problems of currently missing issues in either the gas or the aqueous phase mechanism, further processes might take place, which are not yet understood. To address these issues, another sensitivity study has been performed. The study focuses on

uptake as a likely parameter to influence the particle mass production. As the current mechanism is not able to reproduce a plausible mass production, the current sensitivity study suppresses the release to the gas phase for highly oxygenated compounds. This measure is meant to simulate processes currently not well understood that keep compounds in the aqueous phase despite different suggestions from the Henry's Law equilibrium. The currently poor description could result from HLCs, which are determined too low, or from missing transformations of species such as salt formation/complexations or further aqueous phase equilibria, which increase the effective HLC. Two studies have been performed, where phase transfer (in either direction gas – aqueous phase) was prohibited for compounds with more than two carbon atoms and an oxygen-to-carbon (O:C) ratio greater or equal to 0.75 and 1, respectively. These studies try to compromise between the uptake of organic compounds from the gas phase as a source for organic mass production in the aqueous phase and the suppression of release of highly oxidised organic compound from the aqueous to the gas phase. Results from these studies are shown in Figure 5.13, where they are compared to the sensitivity run  $\text{NO}_3\text{add}$  as the mechanism of these studies is based on the scenario  $\text{NO}_3\text{add}$ . While high concentrations in cloud periods are cut off to better resolve particulate concentrations of the organic mass, the complete concentration-time profiles are given in the Appendix in Figure E.6, page 318.

The exclusion of phase transfer processes of highly oxidised organic compounds has a great impact on the organic mass production. As can be seen from Figure 5.13, the exclusion of organic compounds with more than two carbon atoms and an O:C ratio of 1 leads to a significant increase in organic mass. Organic matter is produced during cloud periods and degraded during non-cloud periods. However, production over-compensates degradation



**Figure 5.13** Time-resolved evolution of particulate OM, residual OM and organic nitrate concentrations in the sensitivity runs  $\text{NO}_3\text{add}$ ,  $\text{O:C}=0.75$ , and  $\text{O:C}=1$  under urban conditions.

so that at the end of the model run organic mass has increased to about  $9.2 \mu\text{g m}^{-3}$ . Lowering the O:C ratio to 0.75 decreases the organic mass almost to values of the reference scenario  $\text{NO}_3\text{add}$ . OM is slightly increased only after cloud periods and is degraded during non-cloud periods. Before the start of next cloud period, oxidation of the dissolved organic compounds has decreased the particulate organic matter to values close to the reference scenario (compare Figure 5.13). Therefore, the O:C ratio has to be chosen with care. Prohibiting the phase transfer of organic compounds, which are not enough oxygenated, will result in a decreased uptake of organic compounds from the gas phase and, hence, in decreased sources from the gas phase rather than decreased sinks from the release to the gas phase.

From Figure E.6 in the Appendix can be seen that during cloud periods the omission of phase transfer processes leads to a slight decrease in OM in the scenario O:C=1 and a significant decrease in the scenario O:C=0.75. In these periods of increased LWC, even more oxygenated organic compounds are taken up by the aqueous phase leading to a significant decrease in the organic matter, if the O:C ratio is chosen too low. Another important fact is that the suppression of the release of organic compounds does result in an increase in OM, yet organic nitrate concentrations stay at a very low concentration level (see Figure 5.13).

The sensitivity studies in this paragraph have pointed at probable uncertainties in the current knowledge of the processing of organic particulate matter. Based on these sensitivity studies, the mechanism, where uptake is suppressed for organic compounds with more than two carbon atoms and an O:C ratio of 1, is chosen as the new reference compound for further sensitivity studies. As current knowledge is unable to explain OM production, it is advisable to include these rules in the generator protocol at the current state for a more realistic simulation of organic particulate matter. The studies have shown that only the uptake of very soluble species with an O:C ratio greater or equal one should be suppressed. With these adjustments it was possible to increase the organic mass while organic nitrate concentrations remained at realistic concentration levels.

#### 5.5.4 Decay of alkoxy radicals in the protocol

Another study focused at organic radical chemistry, in particular, the degradation of alkoxy radicals. Determinations of the kinetic data for the degradation of organic radicals are sparse. Therefore, all estimations concerning organic radicals in the GECKO-A protocol rely on a few experimental determinations only and are rather simple compared to the estimation methods for the prediction of kinetic data of stable organic compounds with, e.g., structure-activity relationships. Therefore, estimations for radical compounds have been carefully re-investigated.

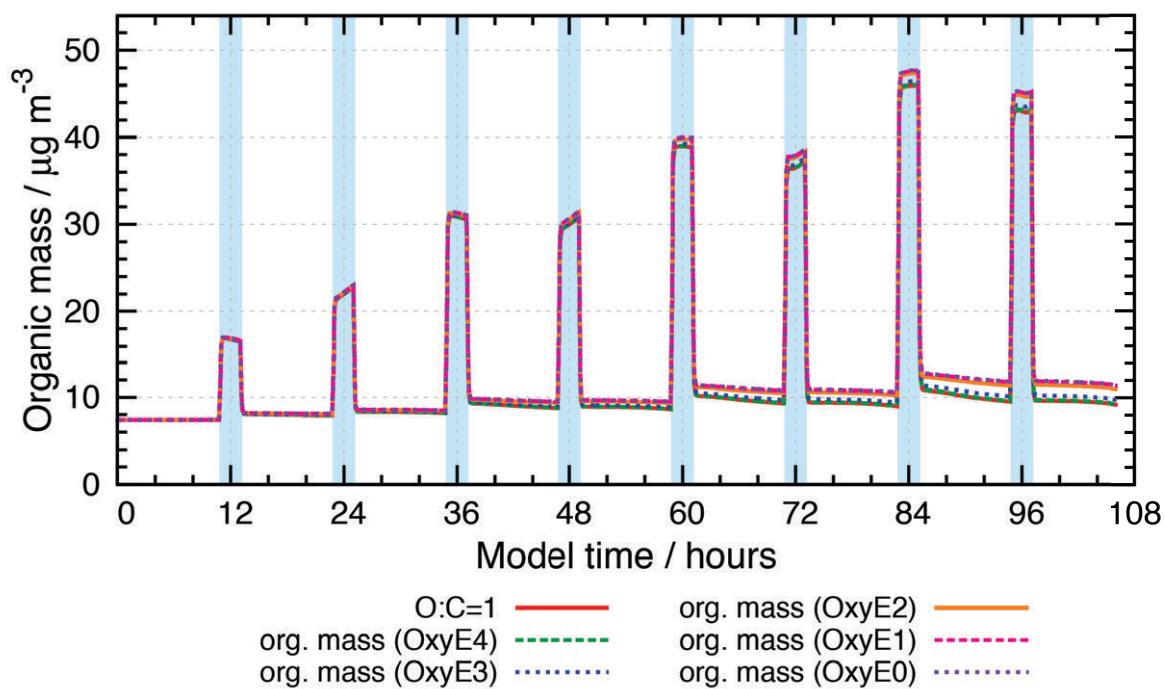
For the degradation of alkoxy radicals, previous CAPRAM estimates have been incorporated in the generator protocol according to reaction R5, page 9. For the reaction of alkoxy radicals with oxygen an estimated value of  $5 \cdot 10^6 \text{ M}^{-1} \text{ s}^{-1}$  has been used in the protocol and the monomolecular decomposition has been estimated with  $5 \cdot 10^5 \text{ s}^{-1}$  according to

Tilgner and Herrmann (2010), respectively. Both values are assumptions, which could not be validated by experimental data due to the scarcity of experimental determinations of kinetic data of organic radical compounds (see also subsection 4.8.5). The rate constant of the monomolecular decay is first order, while the rate constant of the reaction with oxygen is second order. Yet, the values of both rate constants differ by only one order of magnitude. This fact makes the reaction with oxygen uncompetitive, even with the very large concentrations of dissolved oxygen of about  $3.5 - 4 \cdot 10^{-4} \text{ mol l}^{-1}$ . In the oxygen channel, a carbonyl compound is formed and oxygen is built into the structure of the molecule, which makes the organic compound more polar and, therefore, more water-soluble. On the other side, the monomolecular decay breaks the parent alkoxy radical into smaller fragments. No oxygen is added to the molecular structure. In this reaction channel, the oxidation of organic compounds is increased leading rapidly to smaller compounds and ultimately  $\text{CO}_2$ . The smaller fragments are more likely to be released to the gas phase than the more oxygenated larger molecules formed in the reaction with oxygen. Hence, an artificial shift towards the monomolecular decay increases the oxidation of organic compounds and reduces organic mass production. Therefore, the rate constant of the monomolecular degradation channel has been re-investigated by variation over a range of  $5 \cdot 10^5 \text{ s}^{-1}$  (reference case,  $\text{O:C}=1$ ) to  $5 \cdot 10^0 \text{ s}^{-1}$  (sensitivity runs OxyE4 – OxyE0). Moreover, the decay rate of acyloxy radicals by C–C bond breaking to release  $\text{CO}_2$  and a peroxy radical, whose skeleton is shortened by one carbon atom, has been adjusted in this context. The original value of  $5 \cdot 10^5 \text{ s}^{-1}$  has been reduced by the same amount as the monomolecular decay of alkoxy radicals in the respective sensitivity runs.

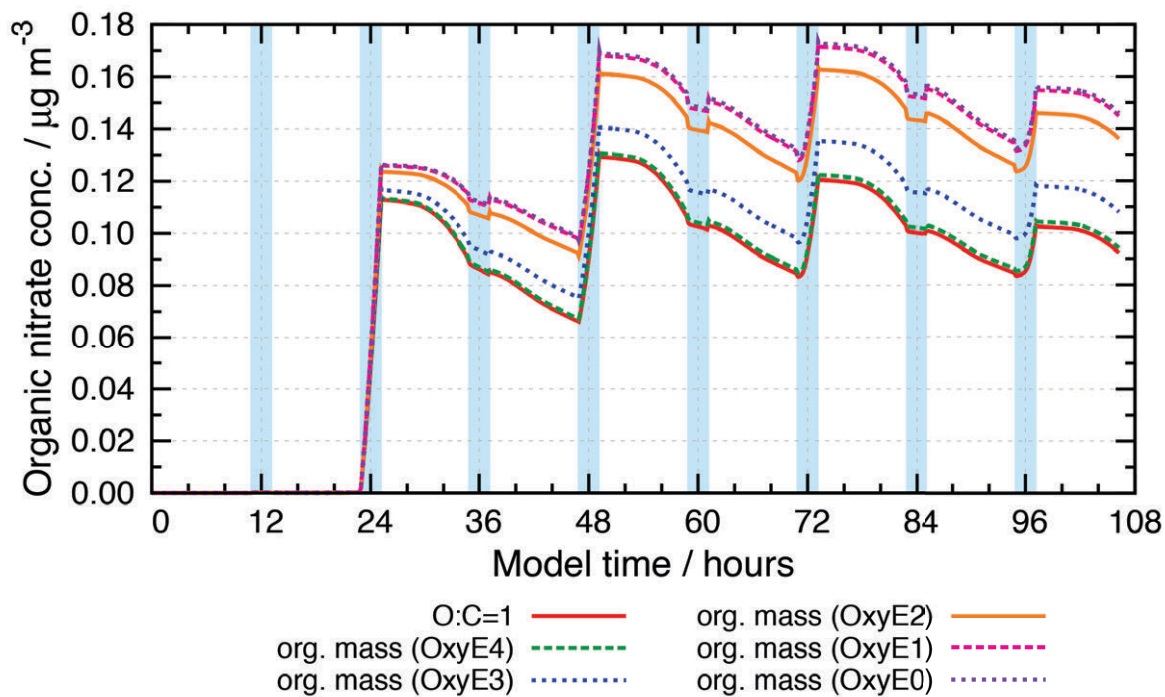
The sensitivity runs confirm the initial assumptions and an increase in organic mass is seen with decreasing rate constants of the monomolecular degradation channel (see Figure 5.14). Organic mass is increased by up to  $2 \mu\text{g m}^{-3}$  at the end of the sensitivity runs with the lowest molecular degradation rate constants. A major increase is seen between the sensitivity studies OxyE3 (blue dotted line) and OxyE2 (orange solid line in Figure 5.14). The sensitivity runs with higher rate constants ( $\text{O:C}=1$  and OxyE4) or lower rate constants (OxyE1 and OxyE0) show only minor changes in the organic mass due to the change of the degradation rate. This is, because of shift of the reaction channels towards the reaction with oxygen. The shift occurs at a rate constant of the monomolecular degradation channel that is about 4 orders of magnitude smaller than the reaction with oxygen. This ratio is determined by the oxygen concentration (in the order  $10^{-4} \text{ M}$ ) as the second order rate constant of the oxygen channel has to be multiplied by these concentrations, but not the first order rate constant of the monomolecular decomposition. Therefore, highest changes are seen for rate constants 4 orders of magnitude smaller than the oxygen channel, i.e. about  $10^2 \text{ s}^{-1}$ .

Organic nitrates show the same behaviour as the overall organic mass and concentrations increase with decreasing rate constants of the monomolecular degradation channel. The major changes occurs in the of decay rates between  $10^{-3}$  and  $10^{-2} \text{ s}^{-1}$  (see Figure 5.15). However, the increases are moderate and concentrations of organic nitrates stay below  $0.18 \mu\text{g m}^{-3}$ , which is realistic for tropospheric conditions (compare, e.g., Day *et al.*, 2010).





**Figure 5.14** Time-resolved evolution of particulate organic matter in the sensitivity runs O:C=1 and OxyE4 – OxyE0 under urban conditions.

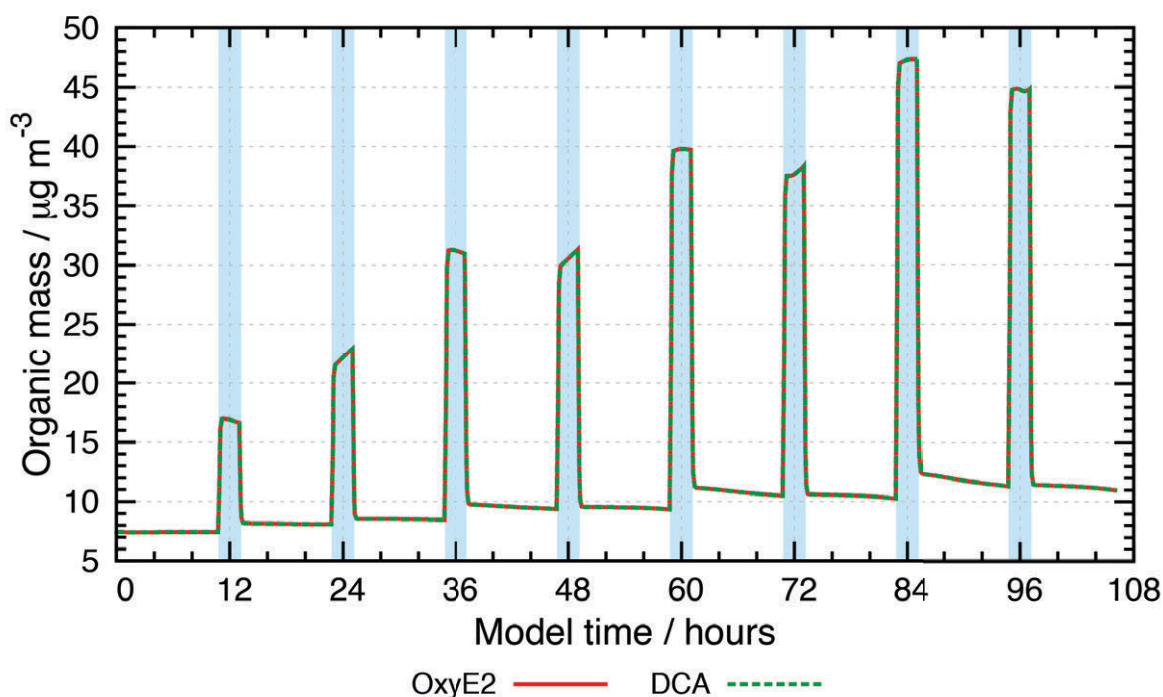


**Figure 5.15** Aqueous phase concentration-time profiles of organic nitrates in the sensitivity runs O:C=1 and OxyE4 – OxyE0 under urban conditions.

### 5.5.5 Revision of the GROMHE thermodynamic database

Uptake is critical for a correct description of tropospheric multiphase chemistry as it was demonstrated in subsection 5.5.3. Therefore, the GROMHE database has been carefully revised. This database is used to assign Henry's Law constants to phase transfer processes in the generated mechanisms, but was also used to derive the structure-activity relationship in the first place. Recently, more data has become available (see, e.g., *Compernelle and Müller*, 2014a,b and references therein). The more recent values for DCAs given in *Compernelle and Müller* (2014a) are all significantly higher than in the GROMHE database (up to three orders of magnitude). Moreover, values in the GROMHE database are taken from the EPI Suite database from the U.S. Environmental Protection Agency. However, these values are partly estimates themselves and not experimentally determined. It was therefore decided to replace the values of dicarboxylic acids in the GROMHE database with the more recent values given in *Compernelle and Müller* (2014a). As DCAs have at least four oxygen atoms and therefore an O:C ratio of one or greater for organic compounds with up to 4 carbon atoms only the Henry's Law constant of the remaining C<sub>2</sub> DCA oxalic acid had to be replaced in the current mechanism with phase transfer suppressed for species with an O:C ratio greater or equal one and a carbon number greater than two.

A sensitivity run under urban conditions has been performed with the scenario OxyE2 as a reference case and a scenario labelled 'DCA', where the value of the HLC of oxalic acid has been changed to  $6.2 \cdot 10^8 \text{ M atm}^{-1}$ . No effect is seen on the total organic mass (see Figure 5.16) even when performing a sensitivity run with a mechanism in which phase



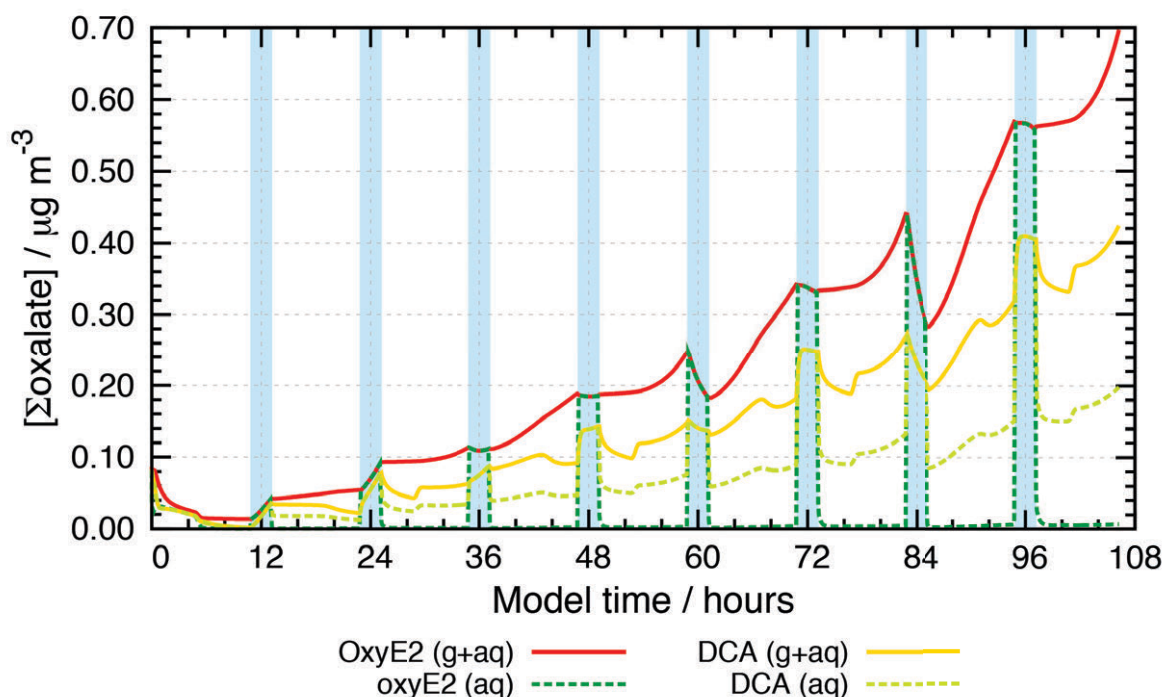
**Figure 5.16** Time-resolved evolution of particulate organic matter in the sensitivity runs OxyE2 and DCA under urban conditions.



transfer for species with an O:C ratio  $\geq 1$  is allowed and all values of dicarboxylic acids are replaced (not depicted).

The adjustments are, however, important for the individual compounds as can be seen in Figure 5.17 for oxalic acid. In the reference scenario, oxalic acid is found exclusively in the aqueous phase only during cloud periods. During non-cloud periods almost all oxalic acid is released to the gas phase. In the scenario DCA, this release is decreased and oxalic acid is found in either compartment in about equal concentrations. Moreover, the overall gas and aqueous concentrations of oxalic acid are decreased in the scenario DCA compared to the scenario OxyE2. The reason for this can be found in the gas phase mechanism MCMv3.1. Currently no dicarboxylic acids are treated in the MCM. Therefore, oxalic acid is not further oxidised after the release to the gas phase. It can only re-enter the aqueous phase with an increasing LWC during later cloud periods. With a decreased release to gas phase in the scenario DCA, the remaining aqueous phase fraction of oxalic acid is oxidised throughout non-cloud periods and, hence, overall concentrations are decreased. Therefore, it is important to keep the GROMHE database updated for a precise description of the multiphase chemistry of single organic compounds.

The current sensitivity runs have shown the importance of constant updates in the kinetic data in chemical mechanisms and continuous mechanism development to a state-of-the-art description of current knowledge. Furthermore, for mechanism self-generation it is equally important to keep the estimation methods updated. There is a need especially for older estimation methods, which rely on outdated experimental data, for a revision and further advancement.



**Figure 5.17** Aqueous phase concentration-time profiles of oxalic acid in the sensitivity runs O:C=1 and OxyE4 – OxyE0 under urban conditions.

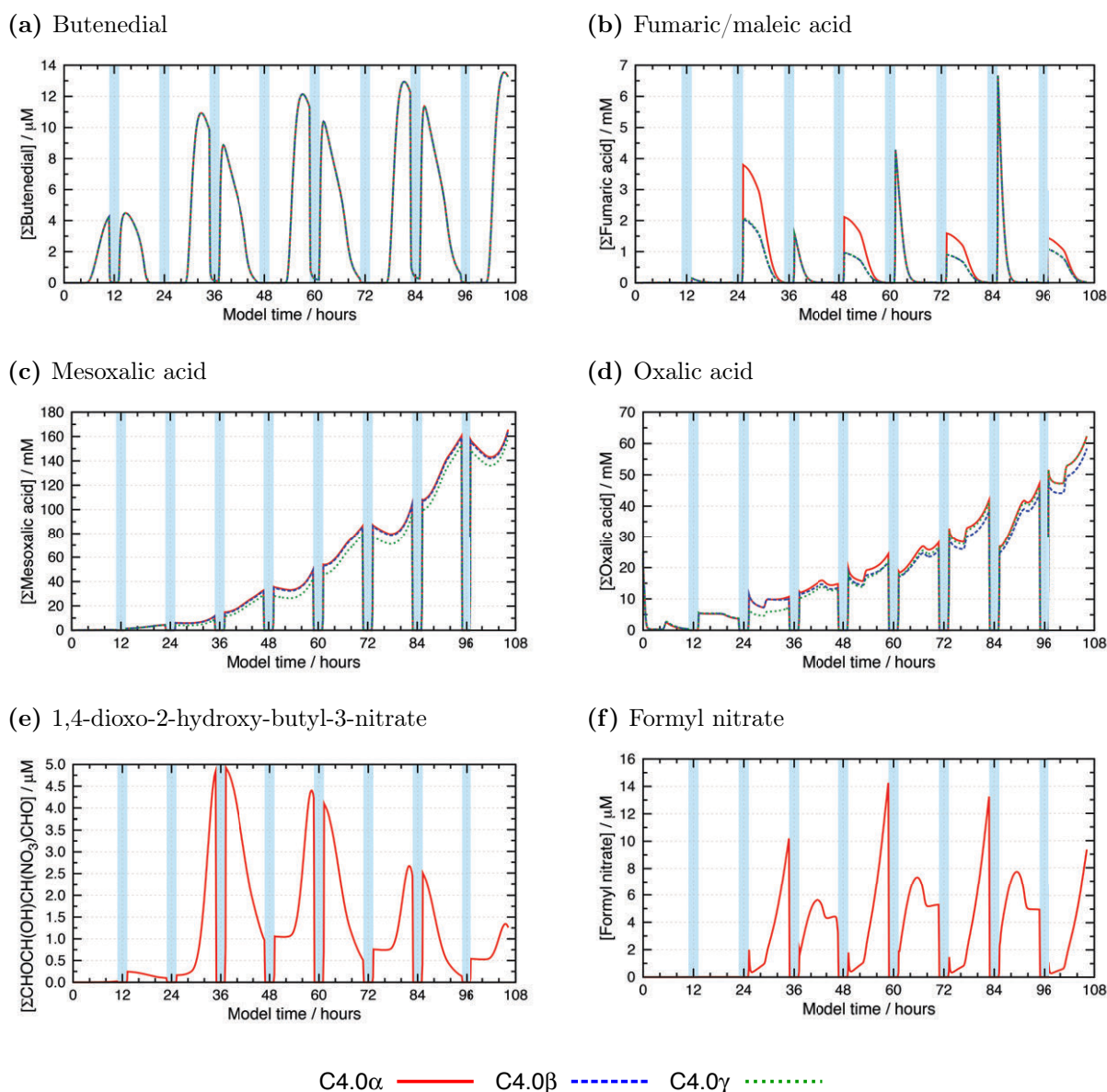
## 5.6 Influence of the nitrate radical chemistry

Section 4.4 described the possible generation of three different mechanisms with detailed levels of the nitrate radical chemistry by GECKO-A. In the  $\alpha$  subversion, the full mechanism is generated. In the  $\beta$  subversion, nitrate radical addition to double bonds is suppressed, and in the  $\gamma$  subversion, H-abstraction reactions by  $\text{NO}_3$  is omitted as well. The current section investigates the influence of the level of detail of nitrate radical chemistry on the model output for various scenarios. The chemistry up to  $\text{C}_4$  has been extended in CAPRAM 3.0n according to the description given at the beginning of this chapter and in subsection 5.8.3. Three mechanisms, CAPRAM 4.0 $\alpha$ ,  $\beta$ , and  $\gamma$ , have been generated. All three mechanisms were used in an urban and a remote continental ‘real atmosphere’ scenario with non-permanent clouds as described in subsection 6.2.1. Additionally, a winter run has been performed for both environments to investigate the importance of the nitrate radical chemistry under conditions of reduced availability of solar radiance. Results of these sensitivity studies led to a recommendation for the use of the different subversions.

The previous sensitivity studies in subsection 5.5.1 have shown that nitrate radical chemistry can have a significant influence in urban environments. It is therefore important to do model simulations with the full  $\alpha$ -version of the mechanism under these conditions as nitrate radical addition to double bonds can lead to a significant build up of organic nitrates (compare subsection 5.5.1). Current investigations show that the complexity of the description of nitrate radical chemistry is also important for a correct description of the concentration-time profiles of single organic constituents.

Figure 5.18 shows the influence of the level of complexity of nitrate radical chemistry in the different CAPRAM subversions on selected organic compounds. Butenedial has been chosen as representative for unsaturated compounds in Figure 5.18a as it has already been incorporated in CAPRAM 3.0n. No big influence of the nitrate radical chemistry is seen for this compound. Due to the significantly lower nitrate radical concentration under daytime conditions and due to a decreased reaction rate constant of the nitrate radical by over three orders of magnitude in the revised mechanism compared to the hydroxyl radical, turnovers in the different subversions are not influenced. In the new protocol, a minor fraction (6.2%; see Reaction  $\text{R}_{02806}/\text{R}_{02807}$  in Table G.13, page 588) of the OH and  $\text{NO}_3$  radicals reacts by H-atom abstraction at the aldehyde group besides the addition to the double bond. This reaction pathway will lead to fumaric or maleic acid in subsequent reactions. It should be noted that no distinction between cis and trans compounds occurs at the current state of the generator. However, from the kinetic database (see Appendix C) can be seen that both forms react with the same rate constant of  $6.0 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . For a better legibility, in the following the compound  $\text{C}(=\text{O})(\text{OH})\text{CH}=\text{CHC}(=\text{O})\text{OH}$  is referred to as fumaric acid although both forms fumaric (trans) and maleic (cis) acid are possible.

From Figure 5.18b can be seen that differences between the various subversions increase for fumaric acid. Although only a minor pathway in the butenedial oxidation, significant concentrations of fumaric acid up to almost 7 mM are found. While concentrations are insignificantly low on the first day, a large in-cloud production is seen from the second



**Figure 5.18** Concentration-time profiles of selected organic compounds in the sensitivity runs investigating the nitrate radical chemistry under urban conditions.

cloud period on (see Figure 5.18b). Due to the decreasing LWC and, hence, increasing number of fumaric acid molecules per available liquid water, concentrations peak right after the cloud period. During non-cloud periods, fumaric acid is oxidised in the liquid phase. Oxidation is much slower during night and rapidly decreases fumaric acid to insignificant concentrations levels during the day. During the night, fumaric acid in the  $\alpha$ -version of the mechanism can double concentrations of the other two runs. This is due to the importance of nitrate radical chemistry during night. Fumaric acid is produced from the H-abstraction channel of butenedial. The additional increase in the  $\alpha$  run results from H-abstraction by  $\text{NO}_3$ . Although H-abstraction by  $\text{NO}_3$  is allowed in the  $\beta$  subversion as well, it is not treated for unsaturated compounds in CAPRAM 4.0 $\beta$  due to the considerations explained in section 4.4. Therefore, in CAPRAM 4.0 $\beta$  and  $\gamma$ , no fumaric acid is produced from the

H-abstraction channel of the butenedial oxidation by  $\text{NO}_3$  and, hence, the concentrations are lower.

Another class of compounds, for which the differences between the different levels of details in the nitrate radical chemistry become obvious, are very oxidised dicarboxylic acids. Figure 5.18c and 5.18d show the examples of mesoxalic acid and oxalic acid. In both acids, the only abstractable H-atoms are found at the carboxyl group. For the dissociated forms, ETRs become likely. This type of reaction is favoured by the nitrate radical and rate constants become comparable to hydroxyl radical reaction rate constants or even succeed them (see kinetic database in Appendix C). Thus, differences occur between the  $\beta$  and the  $\gamma$  subversions. Differences to the  $\alpha$  subversions are the result of the oxidation of unsaturated compounds of which both acids can be an oxidation product. Nitrate radicals can influence this oxidation as they add to the double bond. In consequent reactions, the carbonyl nitrate  $\text{C}(=\text{O})(\text{OH})\text{C}(=\text{O})\text{C}(=\text{O})\text{ONO}_2$  is formed, which hydrolyses to mesoxalic acid. Thus,  $\text{NO}_3$  addition to double bonds can have an impact on these diacid concentrations besides the electron transfer reactions.

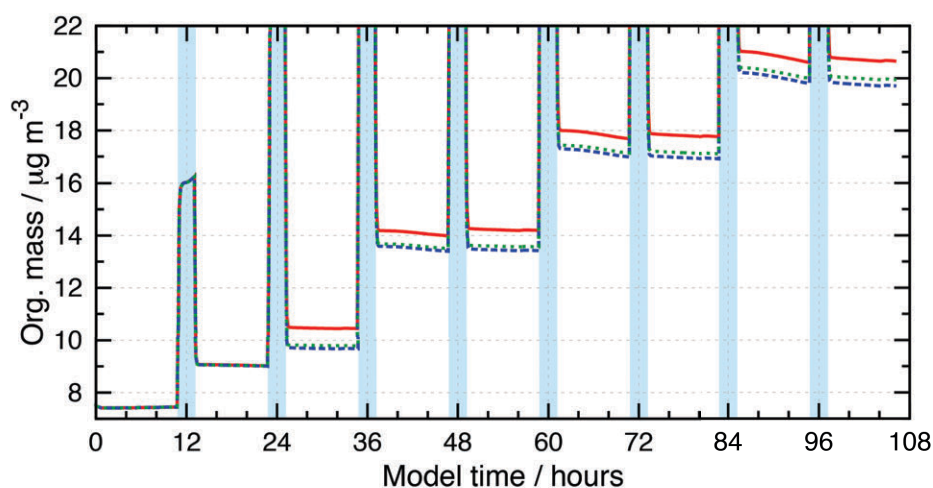
Another impact of the  $\alpha$  runs is the production of organic nitrates, which was therefore investigated in these sensitivity runs. For the first generation stable product in the oxidation chain of butenedial, 1,4-dioxo-2-hydroxy-butyl-3-nitrate ( $\text{O}=\text{CHCH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}=\text{O}$ ) and its hydrated forms, no significant accumulation is seen (see Figure 5.18e). After a build up, maximum concentrations of  $5\text{ }\mu\text{M}$  are observed at noon of the second model day. Thereafter, maximum concentrations decline to values below  $1.5\text{ }\mu\text{M}$  on the last model day. Formyl nitrate was chosen as another example as it is the smallest organic nitrate at the end of the oxidation chain of organic nitrates. Its concentration-time profile is depicted in Figure 5.18f. Concentrations are about a factor of three higher for formyl nitrate compared to 1,4-dioxo-2-hydroxy-butyl-3-nitrate with peak concentrations of  $14\text{ }\mu\text{M}$  at the third model day. Moreover, no significant decrease in the maximum concentrations is observed thereafter. However, although very slow, hydrolysis of organic nitrates seems to be a sufficient sink for this compound class. It must be concluded that the addition of nitrate radicals to double bonds under urban conditions is important and should not be neglected in the mechanism as it can lead to the formation of organic nitrates in the  $\mu\text{M}$  range. Therefore, it is recommended to use the full  $\alpha$  version for model scenarios under urban conditions.

For a complete evaluation, the sensitivity study has also been performed under winter conditions, where less solar radiation is available. Results for the same selected organic compounds as for the summer runs are given in Appendix E.6, Figure E.8. In general, the same explanations apply as under summer conditions. However, due to a decreased availability of solar radiation, the influence of nitrate radical chemistry increases and differences between the different subversions of CAPRAM 4.0 increase for very oxidised dicarboxylic acids due to the importance of the electron transfer channel for nitrate radical reactions. Moreover, 1,4-dioxo-2-hydroxy-butyl-3-nitrate concentrations increase to about  $19\text{ }\mu\text{M}$  while formyl nitrate concentrations decrease to about  $5\text{ }\mu\text{M}$ . More detailed analysis including the analysis of the chemical fluxes would be needed to fully understand this

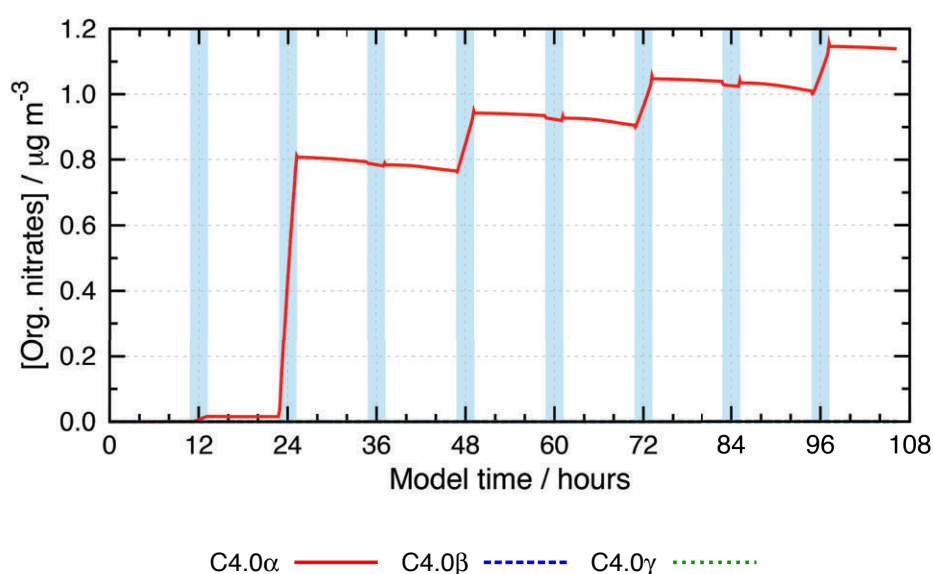
behaviour, which is beyond the scope of this simple sensitivity study. Yet, it shows that nitrate radical chemistry is important, while results are not always predictable. Therefore, it is advisable to do model simulations under urban conditions with the full  $\alpha$ -mechanism.

Investigations of the total organic mass and the organic nitrate fraction in Figure 5.19 show an increasing influence of organic nitrates under winter conditions. While the organic mass concentrations double to around  $20 \mu\text{g m}^{-3}$ , organic nitrate concentrations in the  $\alpha$ -run quadruple from about  $0.3 \mu\text{g m}^{-3}$  (compare subsection 5.5.1) to  $\sim 1.2 \mu\text{g m}^{-3}$  (see Figure 5.19b). The organic nitrate fraction increases from little over 1% to almost 6% of the total organic mass. The omission of parts or the total nitrate chemistry in the mechanism causes a decrease in the total organic mass by about  $1 \mu\text{g m}^{-3}$  at the end of

(a) Total organic mass



(b) Organic nitrate fraction



**Figure 5.19** Time-resolved evolution of the total organic mass (a) and the organic nitrate fraction (b) in the sensitivity runs investigating the nitrate radical chemistry under urban winter conditions. High organic mass concentration during cloud periods have been cut off in subfigure a.

the model run in the  $\beta$ - and  $\gamma$ -versions of CAPRAM 4.0. While high concentrations were cut off in Figure 5.19a to better distinguish the differences between the different model runs under non-cloud conditions, an overview of the total concentrations including high concentrations during cloud periods is given in Figure E.7.

Investigations have also been extended to remote continental environments under summer and winter conditions as  $\text{NO}_x$  concentrations are significantly decreased in remote areas and, hence, an influence from the mechanisms with the reduced  $\text{NO}_3$  radical chemistry is likely to be less. Results from the remote scenarios are shown in Figure E.9 and Figure E.10 in Appendix E.6 for summer and winter conditions, respectively, for the same species discussed above in the urban sensitivity runs. The concentration-time profiles of the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -run are indistinguishable from one another except for a slight deviation of the  $\gamma$ -run for the highly oxidised dicarboxylic acids towards the end of the summer run. Moreover, this effect is opposite for the two DCAs and causes decreased concentrations of mesoxalic acid and increased concentrations of oxalic acid in the  $\gamma$ -run. This suggests an increased oxidation of mesoxalic acid due to ETR by  $\text{NO}_3$  radicals and an increased formation of oxalic acid due to an increased oxidation of larger organic compounds such as mesoxalic acid by nitrate radicals. In both, the summer and the winter run, organic nitrate formation is small and concentrations of these compounds stay in the nM range. The overall organic nitrate production in both remote scenarios is less than  $5 \cdot 10^{-12} \text{ g m}^{-3}$  (see Figure E.11b and Figure E.12b in Appendix E.6 for remote summer and winter conditions, respectively). Organic mass production is generally low and an increase is seen only during cloud periods (see Figure E.11a and Figure E.12a in Appendix E.6 for remote summer and winter conditions, respectively). It is, therefore, possible to use the reduced  $\beta$ - or  $\gamma$ -mechanisms under these conditions.

## 5.7 The final protocol for aqueous phase mechanism self-generation

A protocol has been created for the the computerised mechanism self-generation with GECKO-A. The protocols defines the rules, with which GECKO-A estimates rate constants of reactions of organic compounds with hydroxyl and nitrate radicals as well as the decay of organic radical compounds when no experimental data in the kinetic database is available. The protocol relies on structure-activity relationships due to their many advantages discussed in section 3.6 and section 4.3. The new protocol has already been outlined in section 3.7, where an overview is given in Table 3.8, page 70. Moreover, the protocol and its processing in the mechanism generator GECKO-A is illustrated in Figure 4.1, page 74.

The final revised protocol as a result of the evaluation of prediction methods described in chapter 3 and the sensitivity studies presented in this chapter is as follows:

- Phase transfer is described using the SAR GROMHE (*Raventos-Duran et al.*, 2010) for the prediction of Henry's Law constants, the FSG method(*Fuller*, 1986) for the prediction of gas phase diffusion coefficients, and a constant value of 0.1 for the mass accommodation coefficient (see section 4.2 and section 5.2).
- Hydrations are predicted with GROMHE (see section 4.5).
- Dissociations are predicted using Taft parameters according to *Perrin et al.* (1981) (see section 4.7).
- SARs have been used to describe the oxidation of stable organic compounds by hydroxyl radicals. The determination of the rate constants is performed group-wise for every carbon atom bearing group (see section 4.3).
- The SAR of *Monod and Doussin* (2008)/*Doussin and Monod* (2013) is preferred over the SAR by *Minakata et al.* (2009), even if that means that the rate constant for a compound is calculated with a mixture of the SARs by both authors (see section 4.3).
- Rate constants of hydroxyl reactions with organic nitrates are calculated estimating the same  $\alpha$ - and  $\beta$ -parameters used for the hydroxyl group in the SAR by *Monod and Doussin* (2008) (see section 4.3).
- The oxidation of neutral saturated organic compounds by nitrate radicals is described with the advanced Evans-Polanyi-type correlations (see section 4.4).
- Nitrate radical reactions with unsaturated organic compounds are described with fixed rate constant of  $1 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$  using the branching ratios of the respective hydroxyl radical reactions (see section 4.4 and subsection 5.5.2).
- Nitrate radical reactions with dissociated carboxylic acids are described with fixed rate constants assuming ETR as the only reaction pathway (see section 4.4).
- A monomolecular decay of polycarbonyl compounds has been estimated with a fixed rate constant of  $0.1 \text{ s}^{-1}$  to decrease the concentration of this compound class to realistic values (see section 5.1).
- Hydrolysis of carbonyl nitrates has been estimated with a fixed value of  $7.5 \cdot 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$  and a temperature dependency of 6600 K (see section 4.6).
- Radical decomposition is based on the mechanism suggested by *von Sonntag and Schuchmann* (1991) and *von Sonntag et al.* (1997) and experimental data, e.g., by *Schaefer et al.* (2012) using fixed estimates for rate constants and branching ratios (see section 4.8). The following radical degradation processes are implemented in the protocol:
  - Peroxy radical recombinations and cross-reactions (see subsection 4.8.1)
  - $\text{HO}_2$  elimination of peroxy radical with a hydroxyl group in  $\alpha$ -position (see subsection 4.8.2)
  - Hydration and immediate  $\text{HO}_2$  elimination of acylperoxy radicals (see subsection 4.8.3)



- Decarboxylation of peroxy radicals with a carboxyl group in  $\beta$ -position (see subsection 4.8.4)
- Reactions of alkoxy radicals with oxygen (see subsection 4.8.5)
- Monomolecular decomposition of alkoxy radicals (see subsection 4.8.5 and 5.5.4)
- Decarboxylation by C–C bond breaking of acyloxy radicals (see subsection 4.8.6 and 5.5.4)

Moreover, for every CAPRAM version, three subversions are produced with different levels of detail concerning the nitrate radical chemistry ranging from a full consideration of the nitrate radical chemistry to no consideration of the nitrate radical chemistry except for the reactions already implemented in CAPRAM 3.0n (see also section 4.4). Based on the sensitivity studies in section 5.6, it is recommended to use the full  $\alpha$  subversion in urban environments, while the reduced  $\gamma$  subversion may be used for remote environments. However, to have equal chemical mechanisms for the comparison of the two meteorological scenarios, the full  $\alpha$  subversion has been used in either the urban or remote scenario in this study.

The generator is able to omit minor pathways of chemical reactions and equilibria with an adjustable threshold according to the explanations in subsections 4.3, 4.5, and 4.7. Based on the discussions in these subsections and the sensitivity study in section 5.3, a standard cut-off parameter of 3% for hydroxyl and nitrate radical reaction pathways and 5% for hydrations have been implemented in GECKO-A. No cut-off is used for dissociations at the current state (see discussion in section 4.7). The cut-off parameter for chemical reactions might be further reduced for a single reaction, if the omission of minor branches would result in a loss of more than 20% of the mass. Moreover, phase transfer is treated only for species with an HLC between  $10^2$  and  $10^{12} \text{ M atm}^{-1}$  to reduce the number of compounds and reactions. Phase transfer of dissociated carboxylic acids and hydrated carbonyl compounds is always prohibited regardless of the Henry's Law constant.

Although not directly part of the protocol, the mechanism extension has caused further adjustments to the CAPRAM mechanism. Due to the oxidative nature of the mechanism with currently no description of non-oxidative processes, parameterisations for the reactions of hydroxyl and nitrate radicals with WSOC and HULIS species has been implemented according to Table G.12, page 395, to adjust hydroxyl and nitrate radical concentrations and decrease the oxidative capacity in the aqueous phase. Furthermore, complexation of iron species with HULIS and photolysis of the Fe(III)–HULIS complex to transform Fe(III) into Fe(II) (see Table G.12) was added to all CAPRAM versions.

## 5.8 CAPRAM mechanism development

The extended and revised generator was used to create new CAPRAM versions, which are introduced in this section. Moreover, the extension of CAPRAM by means of automated mechanism self-generation and particularly the introduction of peroxy radical cross-



reactions demanded several changes in the original CAPRAM 3.0n mechanism, which are described in subsection 5.8.1. After these adaptations, two levels of extensions were performed to the new CAPRAM 3.0p version. In CAPRAM 3.5 branching ratios were introduced to CAPRAM 3.0p and resulting intermediate compounds were oxidised according to the generator protocol (see subsection 5.8.2). The chemistry of organic compounds with up to four carbon atoms has been extended in CAPRAM 4.0 using phase transfer from the gas phase as source for the aqueous phase chemistry (see subsection 5.8.3).

### 5.8.1 CAPRAM 3.0

In the course of the extension of CAPRAM 3.0n, a revision of the mechanism has been performed. In a first step, all kinetic data has been revised and updated to values from the kinetic database introduced in section 3.1 and provided Appendix C, page 275. Moreover, the ideas from the protocol have been taken over and applied to the original CAPRAM 3.0n version. Several nitrate radical reactions with organic compounds are estimated in CAPRAM. In the previous 3.0n version, these reactions were estimated with Evans-Polanyi-type correlations using the method by *Benson* (1976) for the estimation of the *BDEs*. This estimation method was advanced to the improved Evans-Polanyi-type correlation, which correlates the second order rate constant to the overall *BDE* of all bonds connected to an hydrogen atom.

Besides the revision of the rate constants, the reaction mechanism has been evaluated as well. In the new aqueous phase protocol for the generator, recombination and cross-reactions are used for peroxy radicals, which are implemented as pseudo first order reactions. In CAPRAM 3.0n, only recombination reactions are used and described explicitly. Moreover, the different channels of the peroxy radical reactions (see, Reaction R13, page 85) were previously implemented as separate reactions. In the revised CAPRAM version, the ideas from the protocol were taken over and peroxy radical reactions were extended to cross-reactions. The decay is implemented as pseudo first order reaction and all possible reaction channels are combined in an overall reaction using the respective stoichiometric indices. With these changes, a new subversion has been created, which is addressed as CAPRAM 3.0o in the following.

Finally, the parameterisations concerning the processing of WSOC and HULIS species as discussed in subsection 5.5.1 and given in Table G.12 have also been added to CAPRAM 3.0o. A new subversion labelled with CAPRAM 3.0p has been created.

Although the description in CAPRAM 3.0o and p is more detailed allowing peroxy radical cross-reactions, the number of reactions could be reduced due to the accumulation of different peroxy radical decay channels in one overall reaction. The revised CAPRAM 3.0p mechanism comprises 393 aqueous phase compounds and 759 aqueous phase processes. Among these processes are 159 temperature-dependent and 649 temperature-independent irreversible reactions, 94 equilibria, and 16 photolysis processes. Moreover, the number of uptake processes has increased to 66 in CAPRAM 3.0p due to the coupling to MCMv3.1 instead of RACM as in the previous version (see *Tilgner and Herrmann, 2010*). An overview

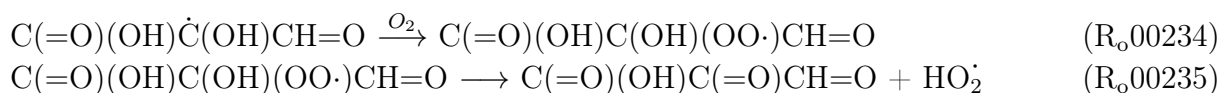
of the number of species and processes in comparison to the new CAPRAM versions is given in Table 5.3 at the end of this section. Tables of all reactions, which are part of CAPRAM 3.0p are provided in Tables G.1 – G.7 and G.10 – G.12 in Appendix G.

### 5.8.2 CAPRAM 3.5

A major achievement of the protocol for automated mechanism construction is the introduction of branching ratios to aqueous phase reactions. In CAPRAM 3.5, this issue is addressed to all organic compounds of the original CAPRAM 3.0n mechanism with up to four carbon atoms, which are handled in the protocol. This excludes the heterocyclic compound pyrrolidinone and the ester ethyl formate as well as their oxidation products.

The generator was used to extend CAPRAM 3.0p by means of automated mechanism construction. For every stable organic compound, reactions were regenerated by GECKO-A introducing branching ratios to these reactions. Resulting intermediates were checked by the generator for their presents in CAPRAM 3.0p. New compounds were oxidised according to the protocol introduced in chapter 4 and section 5.7. The routines were continuously applied until all intermediates were oxidised to compounds already present in CAPRAM 3.0p. For the first time in the CAPRAM history, the NO<sub>3</sub> reduction scheme has been used to deliver three subversion CAPRAM 3.5 $\alpha$ ,  $\beta$ , and  $\gamma$ . Details about the differences of these subversions are described in detail in section 4.4.

To create the mechanisms, the generator was used with standard threshold parameters, i.e. 3% for the cut-off of minor branches, 5% for the cut-off of minor hydration forms, no cut-off of dissociations, and uptake allowed only for compounds with an effective HLC between 10<sup>2</sup> and 10<sup>12</sup> M atm<sup>-1</sup>. 37 compounds were used as input for the primary stack (compare also Figure 4.1, page 74). The whole set of input species can be found in Appendix F.1, page 325. In the full  $\alpha$  subversion of CAPRAM 3.5, 2405 compounds and 4187 reactions have been implemented in addition to CAPRAM 3.0p. Moreover, two reactions from the 3.0p version have become obsolete in CAPRAM 3.5. These two reactions are:



The reason for the omission of these reactions in CAPRAM 3.5 is the introduction of branching ratios. Previously, the main abstraction site in the reaction of oxo-lactic acid with hydroxyl radicals has been identified at the methine group. However, SARs suggest the dominant H-abstraction site at the aldehyde group, where 90.9% of the H-atoms are abstracted. This fact is also supported by the *BDEs* of that molecules. The lowest *BDE* with 375 kJ mol<sup>-1</sup> is found at the aldehyde group compared to 390 kJ mol<sup>-1</sup> at the methine group, 439 kJ mol<sup>-1</sup> at the hydroxyl group, and 443 kJ mol<sup>-1</sup> at the carboxyl group. Only 2.2% of all H-atoms are abstracted at the methine group, which falls below the standard threshold for the cut-off parameter of minor branches. Therefore, this reaction channel is omitted in CAPRAM 3.5. As the resulting intermediate alkyl and alkoxy radicals are not produced in further reactions, these two reactions have become obsolete in the current

CAPRAM versions. However, another minor channel with contributions of 6.9% is found in the mechanism. This is the H-abstraction at the hydroxyl group despite the higher *BDE* compared to the methine group. The most likely explanation for this behaviour are steric effects (see, e.g., *Monod and Doussin*, 2008). After the omission of minor branches below the threshold and rescaling the branching ratios to the remaining reaction pathways the oxidation of oxo-lactic acid has been implemented with the branching ratios of 92.9% for the abstraction channel at the aldehyde group and 7.1% for the abstraction channel at the hydroxyl group. Reactions R<sub>o</sub>00234 and R<sub>o</sub>00235 are omitted in CAPRAM 3.5 and future CAPRAM versions.

Moreover, for a few organic compounds, simple attempts have been made to consider several reaction pathways. For methyl ethyl ketone (MEK) two H-atom abstraction pathways have been implemented for the reactions with OH and NO<sub>3</sub> in CAPRAM 3.0p, one at the methyl group and one at the ethyl group (see reactions R<sub>o</sub>02803, R<sub>o</sub>00179, R<sub>o</sub>02804, and R<sub>o</sub>00180 in Table G.10, page 365). The reaction pathways have been implemented as separate reactions. With the mechanism extension in CAPRAM 3.5, these branches have been revised and a new pathway was added. All pathways have been implemented as overall reaction. Therefore, the second reaction pathway in CAPRAM 3.0p of MEK with OH and NO<sub>3</sub> (reactions R<sub>o</sub>00179 and R<sub>o</sub>00180 in Table G.10) becomes obsolete from CAPRAM 3.5 on.

An overview of the total number of compounds, reactions, and uptake processes in comparison to the other CAPRAM versions is given in Table 5.3. Moreover, the complete CAPRAM 3.5 reaction mechanism is given in Table G.8 and Table G.13 in Appendix G.3.

### 5.8.3 CAPRAM 4.0

The introduction of branching ratios to CAPRAM 3.0p led to a significant number of new intermediate radical and stable organic compounds in CAPRAM 3.5, which can be seen from Table 5.3. However, there is still a significant number of semi-volatile organic compounds present in the gas phase mechanism MCMv3.1, which is not yet treated in CAPRAM 3.5. Therefore, these species have been added to the stack of primary compounds in the generator (compare Figure 4.1) and their uptake to the aqueous phase and further aqueous phase degradation has been treated based on the protocol described in chapter 4 and section 5.7. In total, 92 compounds have been added to the primary stack of the generator (see section F.2, page 325). With the aid of GECKO-A under standard conditions (3% cut-off for minor branches, 5% cut-off for minor hydration forms, no cut-off of dissociations, and uptake allowed only for compounds with an effective HLC between 10<sup>2</sup> and 10<sup>12</sup> M atm<sup>-1</sup>), three new subversions with different levels of detail concerning the nitrate radical chemistry have been created. These versions are addressed as CAPRAM 4.0 $\alpha$ ,  $\beta$ , and  $\gamma$ . The full version comprises 4174 aqueous compounds and 7145 aqueous phase reactions. 134 species undergo phase transfer. More details are given in Table 5.3. Tables of the full mechanism are provided in the Appendix G.3 (Table G.9 and G.14).

**Table 5.3** Overview of the number of species and processes implemented in the various new CAPRAM versions.

	CAPRAM 3.0		CAPRAM 3.5			CAPRAM 4.0		
	o	p	$\alpha$	$\beta$	$\gamma$	$\alpha$	$\beta$	$\gamma$
# Compounds	390	393	2405	1985	1891	4174	2518	2386
# Aqueous phase processes (total)	748	759	4187	3477	3014	7145	4321	3712
# Irreversible reactions	642	649	3680	3043	2580	6331	3790	3181
# Equilibria	91	94	491	418	418	798	515	515
# Photolysis processes	15	16	16	16	16	16	16	16
# Phase transfers	66	66	101	82	82	134	115	115

The protocol of the generator as given in section 5.7 and schematically shown in Figure 4.1 has been applied for primary and intermediate compounds not yet covered by CAPRAM 3.5. New compounds were mainly unsaturated organic compounds and organic nitrates. Furthermore, several branched C<sub>4</sub> compounds have been added in CAPRAM 4.0. The list of primary input compounds contains also few organic compounds with an expected low solubility. The solubility is evaluated by the generator and only compounds with a HLC larger than 10<sup>2</sup> M atm<sup>-1</sup> are considered in the new CAPRAM version.

## 6 Model results and discussion

Special emphasis was placed on the further validation of the generated mechanisms. To test their plausibility, aerosol chamber experiments have been performed at the aerosol chamber LEAK (LEipziger Aerosol-Kammer; see *Iinuma et al.*, 2009, *Kahnt*, 2012, *Mutzel*, 2014) of the TROPOS. GECKO-A has been applied to generate mechanisms especially designed for the comparison with the aerosol chamber experiments. These mechanisms, the design of the chamber experiments, and results from the evaluation process are presented in section 6.1.

To assess the atmospheric implications of the organic multiphase chemistry, the newly generated CAPRAM mechanisms introduced in section 5.8 have been applied in box model studies simulating real tropospheric environments under urban and remote conditions. A key feature in these ‘real atmosphere’ scenarios are non-permanent clouds. Eight cloud passages are performed to investigate the particle-cloud interactions and the influence of clouds on the tropospheric multiphase chemistry, the processing of the organic mass fraction and SOA formation. Results from these studies are discussed in section 6.2. Furthermore, a brief introduction to the basic concepts of the meteorological scenario and the data of the model initialisation is provided.

### 6.1 Comparisons of model results with aerosol chamber experiments

Great effort has been undertaken to validate the generated mechanisms. Chamber experiments are an adequate technique for mechanism evaluation as they provide a closed reaction cell with known microphysical conditions. An ideally simple system with well-investigated multiphase chemistry can be set up for study. Measured concentration-time profiles can then serve as a reference for the quality of the model results. Two different experiments have been performed by the team of the aerosol chamber LEAK to validate the generator protocol. The experimental setup is introduced in subsection 6.1.1. GECKO-A was used to generate new mechanisms, especially designed for these experiments. In subsection 6.1.2, details about the parameters for mechanism generation and the mechanisms created are explained. Results from the chamber and model experiments and their comparison to validate the quality of the generated mechanisms are discussed in subsection 6.1.3.

### 6.1.1 Design of the aerosol chamber experiments

The aerosol chamber LEAK used in these experiments is an indoor chamber that consists of a 19 m<sup>3</sup> teflon bag with a surface-to-volume ratio of 2 m<sup>-1</sup> (*Iinuma et al.*, 2009). The chamber is equipped with UV-C lamps ( $\lambda = 254$  nm) and several instrumentation to measure the concentration-time profiles of inorganic and organic gas phase compounds and the size distribution and composition of aerosol particles. Furthermore, gas phase compounds can be collected on Tenax cartridges and denuders and particles can be collected on polytetrafluoroethylene (PTFE) filters (Pallflex Membran; QTY: 50, MM: 47; Type: Fibrefilm T60A20) for offline analysis. A complete description can be found elsewhere (*Iinuma et al.*, 2009, *Kahnt*, 2012, *Mutzel*, 2014).

Two different sets of experiments were performed to evaluate the precision and quality of the generated mechanisms. In both experiments, a primary organic gas phase compound was oxidised by OH radicals leading to semi-volatile organic compounds that can partition into the aqueous phase (deliquescent seed particles), where they are further degraded, e.g. by aqueous phase hydroxyl radical reactions. The experiments differed by the primary gas phase compounds (hexane and 1,3,5-trimethylbenzene) used for the oxidation experiment and the experimental setup. The most important differences in the experimental setup were the generation of hydroxyl radicals in the gas phase (under dark conditions or with ozone photolysis by UV-C lamps) and the aqueous hydroxyl radical source (uptake from the gas phase only or an additional aqueous phase in-situ source from sodium peroxide in the seed particles).

#### 6.1.1.1 Hexane oxidation experiment

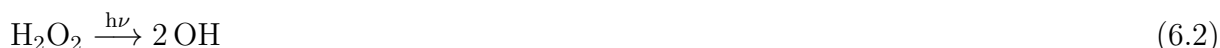
For the first experiment, a compound with a very simple structure with well investigated degradation chemistry was chosen. N-hexane is a linear C<sub>6</sub> hydrocarbon. Although the parent compound is very volatile, its oxidation leads to highly functionalised and, therefore, highly water-soluble oxidation products (compare MCMv3.1, <http://mcm.leeds.ac.uk/MCM/>). Moreover, a complete and validated gas phase oxidation scheme exists in the MCMv3.1. Therefore, it was chosen as primary compound for the chamber oxidation experiment to evaluate the aqueous phase mechanism generated by GECKO-A. As the UV lamps in the chamber do not reflect the solar spectrum, an experiment under dark conditions was chosen to minimise errors introduced by a parameterisation derived for tropospheric photolysis by sunlight in the model. Hexane was oxidised by OH radicals in the experiment. Hydroxyl radicals were produced by a dark reaction of tetramethylethylene (TME) with ozone, in which a Criegee intermediate is formed, whose further decay leads to OH radicals (see *Berndt and Böge*, 2006). Hydroxyl radical production from TME oxidation is also part of the MCMv3.1. All necessary reactions are available at the MCM website (<http://mcm.leeds.ac.uk/MCM/>) and the reader is referred to this page for more details of the mechanism. To guarantee a constant OH radical source, TME was injected with a flow rate of  $\approx 6.3$  ppb min<sup>-1</sup> and ozone with a flow rate of  $\approx 2.8$  ppb min<sup>-1</sup> throughout the whole experiment.

Prior to each experiment, the aerosol chamber was flushed with air until the ambient conditions were stable at a relative humidity level of 75%. The relative humidity level was chosen as a compromise between the guarantee of a high LWC in the seed particles and a proper functioning of all instruments and measuring techniques. Afterwards, seed particles were generated by nebulising an aqueous solution of sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) to account for aqueous phase chemistry. The only aqueous phase OH radical source in the experiment was uptake of hydroxyl radicals into the seed particles from the gas phase.

After the conditions in the chamber were stable, 50  $\mu\text{l}$  (500 ppb) hexane were introduced into the chamber. The experiment was started with the injection of TME and ozone and allowed to continue for 2.5 hours. During the experiment, the evolution of VOCs was monitored with a proton-transfer-reaction mass spectrometer (PTR-MS). However, concentration-time profiles can be determined only qualitatively and no reliable absolute concentration values are provided by the instrument. Moreover, the PTR-MS only provides mass-to-charge ratios ( $m/z$ ). Therefore, the molecular structure cannot precisely be determined and it is not possible to distinguish between different isomers. The compounds do not even have to belong to the same compound class. Therefore, samples were taken on Tenax cartridges throughout the experiment. Gas phase samples were analysed offline with thermo desorption gas chromatography to gain information about the structure of the gas phase intermediates and their turnovers. Moreover, the decay of hexane could be determined with the latter method, but not by the PTR-MS as hexane cannot be protonated. Furthermore, the size-resolved particle number and mass distribution was monitored throughout the experiment by a scanning mobility particle sizer (SMPS). An aerosol mass spectrometer (AMS) monitored the increase in particle mass and the variation in the particle phase composition. At the end of each experiment, 1.8  $\text{m}^3$  chamber air were collected on PTFE filters for offline analysis of particulate products using high pressure liquid chromatography electrospray ionisation time of flight mass spectrometry (HPLC/(-)ESI-TOFMS). Denuders (five-channel annular denuder tubes, see *Kahnt*, 2012) were used to reduce artifacts from semi-volatile compounds.

#### 6.1.1.2 Trimethylbenzene oxidation experiment

For a more thorough validation of the generator protocol, a second set of experiments was performed. However, several assumptions had to be made to keep the model framework simple as will be explained in subsection 6.1.2. In the second experiment, 1,3,5-trimethylbenzene (TMB) was oxidised by OH radicals with UV-C lights turned on. The chamber was flushed with humid air until a stable relative humidity level of 75% was reached. Seed particles were introduced by nebulising an aqueous solution of sodium sulfate (10 mM) and sodium peroxide (77 mM). The additional sodium peroxide in the solution served as an in-situ OH radical source in the seed particles according to the following equations:



In the gas phase, ozone photolysis served as OH radical source. Therefore, after the injection of 9.3  $\mu\text{l}$  (100 ppb) TMB, the experiment was started by a continuous introduction of 3 l  $\text{min}^{-1}$  ozone and switching on the UV-C lamps. The system was allowed to react for about 2.5 hours. As in the hexane oxidation experiment, PTR-MS measurements were used to analyse the degradation of gas phase organic compounds, the AMS monitored the particle mass and composition, and the SMPS monitored the particle mass and size distribution. Besides aerosol sampling on filters at the end of the experiment, a Condensational-Growth and Impaction System (C-GIS; *Sierau et al.*, 2003, *Mutzel*, 2014) was used to sample particles about every 15 min throughout the experiment. Both, filter and C-GIS samples were analysed offline by capillary electrophoresis (CE) and mass spectroscopy.

## 6.1.2 Mechanism generation and model setup

### 6.1.2.1 Hexane oxidation experiment

For the chamber runs, special mechanisms have been generated designed to describe the oxidation of the possible aqueous phase oxidation products from the primary compounds with which the chamber was initialised. A list with possible oxidation products was derived from the gas phase mechanism MCMv3.1. The generator was applied to the list and the uptake to the aqueous phase and the aqueous phase degradation of all soluble stable intermediates (with an HLC between  $10^2$  and  $10^{12}$   $\text{M atm}^{-1}$ ) has been generated. As the aim of the chamber runs is to solely test the generator protocol and the complex chemistry of CAPRAM 3.0p is not necessary for the modelling of the chamber experiments, the generator was used in a different mode. In this mode, only the inorganic section of CAPRAM 3.0n is considered, whereas the organic part of CAPRAM 3.0p bearing additional radical oxidants such as  $\text{SO}_4^-$  is neglected. The organic scheme is generated completely by GECKO-A up to  $\text{C}_1$  organic compounds. The degradation of  $\text{C}_1$  compounds is described in the generator protocol according to CAPRAM 3.0n.

A fully explicit description of  $\text{C}_6$  oxidation products would lead to an extraordinary large number of reactions in the order of  $10^6$  (compare Figure 2.2, page 16). Such large reaction mechanisms are not only impractical for the analysis of the results, they also demand high computational costs. Therefore, a reduction scheme developed for the gas phase, has also been applied to the aqueous phase in GECKO-A, where different isomers of molecules are lumped to an overall model compound. This procedure could reduce the number of reactions to about  $10^4$ .

With the aid of GECKO-A, a comprehensive aqueous phase oxidation scheme was generated that was coupled to MCMv3.1. The list of soluble MCM intermediates with which the generator was initialised is given in Appendix H.1, page 889. The generated aqueous phase mechanism includes 6406 species and 9451 reactions. 427 Phase transfers are described in



the mechanism for the hexane oxidation experiment. Together with the MCM, the number of processes totals to 21 259 including overall 11 310 species.

The model was initialised with the same microphysical and chemical conditions as adjusted in the aerosol chamber LEAK. The initial temperature was set to 25°C, the pressure to 1000 hPa (as no measurements were taken for this parameter), and the relative humidity was initialised with 75%. Furthermore, the model was set to dark conditions. According to the chamber experiment, the model was initialised with 500 ppb hexane and 30 ppb ozone. To account for any background concentrations of NO<sub>x</sub> in the chamber, the model was initiated with 0.5 ppb NO and NO<sub>2</sub>, respectively. Throughout the model run, constant emission fluxes of  $2.1 \cdot 10^9$  molecules cm<sup>-3</sup> s<sup>-1</sup> TME and  $1.8 \cdot 10^9$  molecules cm<sup>-3</sup> s<sup>-1</sup> ozone were used. Seed particles were described as pure sodium sulfate particles. The model was initialised with a spectral particle distribution of 18 669 particles cm<sup>-3</sup> with a mean diameter of 79.6 nm according to the SMPS measurements.

#### 6.1.2.2 Trimethylbenzene oxidation experiment

A special mechanism has also been generated for the second experiment. The oxidation of 1,3,5-trimethylbenzene (TMB) leads to methylglyoxal (MGLY) with yields close to 1. Therefore, only the uptake of methylglyoxal is considered in the mechanism development. The generator has been used to design an aqueous phase mechanism for the oxidation of methylglyoxal in the seed particles and the description of phase transfers of possible MGLY oxidation products. As for the other experiment, the generator was used to describe the oxidation up to C<sub>1</sub> compounds. The degradation of C<sub>1</sub> compounds was described according to CAPRAM 3.0p. Significant background concentrations of malic acid, succinic acid, malonic acid, oxalic acid, acetic acid, and formic acid were measured in the C-GIS samples prior to each experiment. Test runs have been performed, where the initial concentrations of these compounds have not been subtracted as blind values, but were initialised and explicitly calculated in the model runs. Therefore, GECKO-A has been applied to generate an aqueous oxidation scheme for these compounds as well. Overall, an aqueous phase mechanism with 264 species and 596 reactions has been created, which was coupled to MCMv3.1.

As the analysis of the model results given in subsection 6.1.3.2 will show, methylglyoxal is the first compound in the oxidation chain of TMB with significant concentrations in the gas phase. However, there are several stable intermediates in the oxidation chain prior to methylglyoxal, which are potentially water-soluble. The degradation of these compounds is fast so that no significant increase in the concentrations of these compounds is seen. For simplicity and to be able to generate mechanisms without having to apply the lumping routine as for the hexane oxidation experiment, these intermediates have been omitted in the aqueous phase oxidation scheme. To investigate their contributions to SOA mass, additional model runs have been performed, where the uptake of these intermediates to the aqueous phase has been considered. Further aqueous phase degradation is either totally omitted (sensitivity run ‘UPT’) or the first reaction steps are described

leading to WSOC, which is not further specified (sensitivity run ‘RXN’). For polycarbonyl compounds, mono-molecular degradation is described as well in the sensitivity run RXN. When the decay leads to fragments already part of the original mechanism (labelled ‘TMB’ in the following), these products are treated explicitly, otherwise fragments are not further specified and treated as WSOC. As WSOC is a pure aqueous phase model species, this implementation would imply that all organic matter produced in aqueous phase reactions will remain in the aqueous phase. To investigate the fraction of highly water-soluble OM that will predominantly be found in the aqueous phase, further sensitivity studies have been performed, where the yields of the WSOC formed in the initial aqueous phase reactions have been downscaled to simulate a release back to the gas phase of the reaction products of either the first generation or later in the oxidation chain. The additional reactions of the sensitivity runs UPT and RXN are given in Table H.1, page 891. In total, 20 phase transfers and 77 reactions have been added to the scenario TMB.

The microphysical and chemical model initialisation in all three scenarios was adjusted to the initial condition of the aerosol chamber LEAK. A constant temperature of 25°C and a constant pressure of 1000 hPa were used throughout the model runs. The relative humidity was held at 75%. A mono-disperse particle population of 30 000 particles cm<sup>-3</sup> with a diameter of 45 nm was used, which reflects the particle number and mass distribution of the SMPS measurements in a simplified way. Seed particles consisted of 70% sodium sulfate and 30% sodium peroxide. In the test scenario explicitly calculating the organic impurities, seed particles were initialised with additional concentrations of organic compounds as observed in the first C-GIS measurement A00 (given in the Appendix in Table H.2, page 897) prior to the experiment.

The model was initialised with 100 ppb TMB and traces of NO and NO<sub>2</sub> ( $1.5 \cdot 10^{10}$  and  $2.0 \cdot 10^{10}$  molecules cm<sup>-3</sup>, respectively). The production of OH radicals from ozone photolysis in the gas phase and sodium peroxide degradation in the aqueous phase has not been described explicitly. This is due to the different spectrum of the UV-C lights compared to tropospheric sunlight on the one hand. On the other hand, the photon flux is constant in the chamber whereas a sine-shaped parameterisation is used in the model to account for the diurnal variation of radiation. To simulate a constant OH radical source, OH concentrations are prescribed in the model with a fixed value of  $5 \cdot 10^6$  molecules cm<sup>-3</sup> in the gas phase and  $1 \cdot 10^{-11}$  M in the aqueous phase.

### 6.1.3 Evaluation of the model versus aerosol chamber results

#### 6.1.3.1 Hexane oxidation experiment

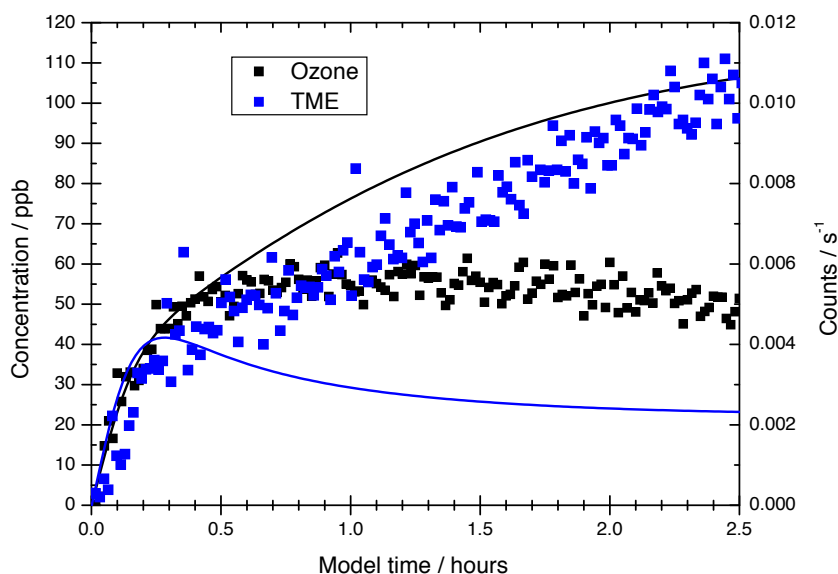
In regard to the aqueous phase, little information was gleaned from the hexane oxidation experiment. Despite a predicted uptake of several gas phase intermediates of the hexane oxidation (see Figure H.1a, page 889, for a selection) and a mass increase of a few  $\mu\text{g m}^{-3}$  (Figure H.1b) by the model, no particle mass increase was observed in the chamber. Hence, no organic compounds were found in the experimental analysis of the particle phase.

However, predicted concentrations by the model were close to the detection limit of the instrumentation used. In the experiment, only wall losses were seen; a process that is not implemented in the air parcel model SPACCIM as it was designed for the simulation of atmospheric processes.

Nevertheless, the experiment contributed significantly to the development process of the generator protocol and helped to increase the quality of the mechanisms created. The generation of long-chained  $C_6$  organic compounds led to a number of highly functionalised organic compounds. Model results showed significant concentrations of organic compounds with 4 or more carbonyl groups mostly in their hydrated forms. As the stability of such highly functionalised compounds is believed to be low, additional degradation processes for polycarbonyl compounds have been added to the protocol as described in section 5.1.

In regard to the gas phase, model and chamber results show a very good agreement in respect to many organic compounds. Difficulties are observed in the dark reaction for the generation of hydroxyl radicals. Model and chamber result agree in the first 20 to 30 minutes, where the injection of ozone and TME leads to an increase in both concentrations. Thereafter, stable ozone concentrations are monitored in the chamber, while there is still an increase in the TME concentrations, albeit at a lower rate. In the model, concentrations are predicted vice versa. An increase of ozone (at reduced rates especially towards the end of the experiment) leads to initially decreasing and afterwards stable TME concentrations. Results are shown in Figure 6.1. In this and the following plots, solid squares represent the experimentally detected concentrations in LEAK, while lines reflect the modelled concentration-time profiles.

Differences in the experimentally determined and modelled concentration-time profiles in Figure 6.1 indicate an overestimation of hydroxyl radicals in the model as more TME is oxidised by ozone. However, a verification is not possible as hydroxyl radicals are not monitored in the chamber. It should furthermore be noted that TME concentrations in



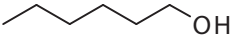
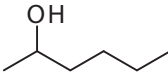
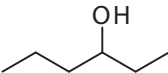
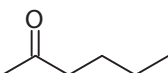
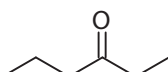
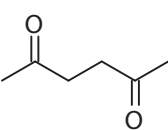
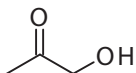
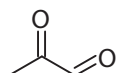
**Figure 6.1** Modelled (lines) and measured concentrations (squares) of ozone (black) and TME (blue).

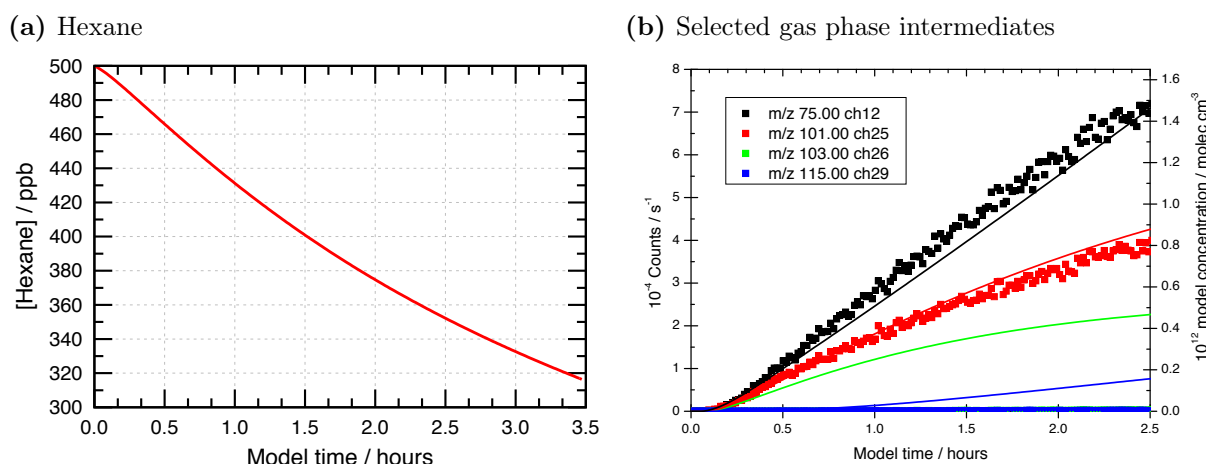
the chamber were monitored by PTR-MS, which determines only ratios for  $m/z$ . If in the oxidation of hexane a product with the same mass-to-charge ratio is formed, this product will interfere with TME measurements and cannot be distinguished. Therefore, the blue squares in Figure 6.1 represent the sum of all concentrations of compounds with an  $m/z$  of 85 and must be regarded as possible maximum concentrations of TME. However, the overestimation of ozone in the model suggests at least an underestimation of TME to some extent in the model.

A likely explanation for the deviations between the modelled and the experimental results are wall losses of ozone to the wetted chamber walls. These losses are currently not implemented in the model but could significantly reduced ozone concentrations and, consequently, increase TME concentrations as less TME is oxidised by ozone. If this explanation is valid, it seems to be significant for high ozone concentrations above 40 – 50 ppb only. This fact could also explain the overprediction of particle mass production in the model. As more TME is oxidised in the model, more semi-volatile organic compounds are formed, which are likely to enter the particle phase and contribute to mass production.

Nevertheless, the decay of  $\approx 200$  ppb hexane determined by the cartridge-denuder system was reflected by the model (see Figure 6.2a). Moreover, the concentration-time profiles of several gas phase oxidation products show a good agreement with model results, albeit only a qualitative analysis is provided by the PTR-MS measurements. Table 6.1 lists examples of compounds and possible isomers detected by gas chromatography mass spectrometry (GC-MS) and PTR-MS. Besides the products listed in Table 6.1, the PTR-MS

**Table 6.1** Gas phase oxidation products from the degradation of hexane identified by GC-MS and PTR-MS as well as the corresponding molecular weight ( $M_w$ ) and the mass-to-charge ratio ( $m/z$ ).

Compound tentatively identified by GC-MS	$M_w$ / g mol <sup>-1</sup>	Structure	$m/z$ detected by PTR-MS
1-Hexanol	102		☑ (103)
2-Hexanol	102		☑ (103)
3-Hexanol	102		☑ (103)
2-Hexanone	100		☑ (101)
3-Hexanone	100		☑ (101)
Hexanedione	114		☑ (115)
Hydroxyacetone	74		☑ (75)
Methylglyoxal	72		☒



**Figure 6.2** Modelled concentration-time profiles of hexane (a) and selected gas phase oxidation products (solid lines, b) as well as experimentally detected concentrations (solid squares, b) in the model run simulating the hexane oxidation experiment.

detected also  $m/z$  61, 63, 65, 67, 69, 71, 77, 79, 81, 83, 89, 91, 93, 95, 97, 99, 109, 117, 119, 121, and 123. The concentration-time profile is well captured by the model as can be seen from Figure 6.2b. To compare the model results to the PTR-MS measurements, all isomers of a certain mass were accumulated to an overall concentration and then compared to the corresponding  $m/z$ . While there is an excellent agreement of the model results (solid lines in Figure 6.2b) with hydroxy acetone ( $m/z = 75$ ) and  $C_6$  monocarbonyls ( $m/z = 101$ ), the model predicted a much higher concentration for  $C_6$  monoalcohols ( $m/z = 103$ ) and hexanedione ( $m/z = 115$ ) than the counts of the PTR-MS suggest. However, the shape of the concentration-time profile of the latter two compounds matches well, when rescaling the chamber analysis to the model results (graphic not shown).

Overall, the model shows a good performance in the gas phase, however, the experiment is not suitable to validate the aqueous phase mechanism and the generator protocol.

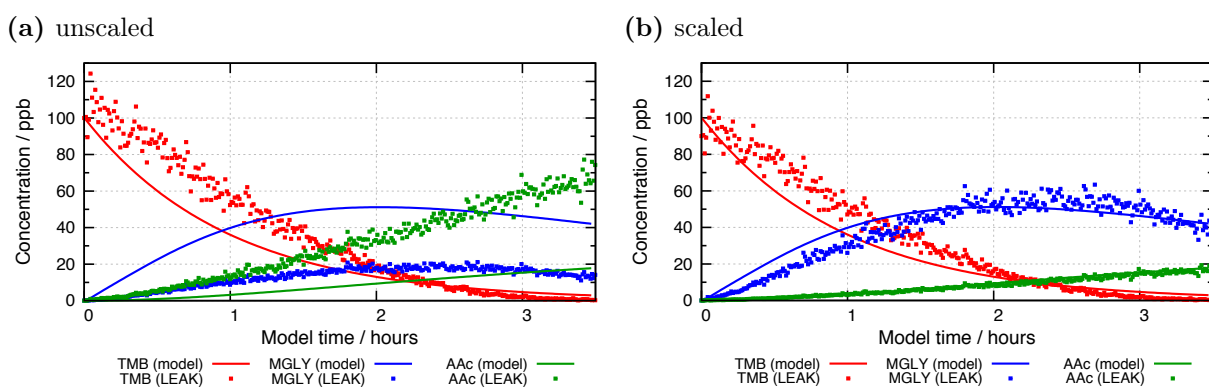
### 6.1.3.2 Trimethylbenzene oxidation experiment

Results of the second chamber experiment were much more revealing in regard to the evaluation of the multiphase chemistry mechanism. A large increase in particle mass was seen in the chamber (from  $\sim 24\ \mu g\ m^{-3}$  to  $60 - 70\ \mu g\ m^{-3}$ ) and several organic compounds have been identified in the aqueous phase, namely methylglyoxal, formate, acetate, pyrovalate, oxalate, malonate, succinate, and malate. Comparison with model results showed a good agreement for a wide range of the results and pointed out the most critical issues about the generator protocol.

### Gas phase concentration-time profiles of TMB and its main oxidation products

In the gas phase, the decay of 1,3,5-trimethylbenzene (TMB) was monitored. The initiated 100 ppb were degraded to concentrations close to zero within 3 hours. The only gas phase oxidation products with a significant increase in concentration were methylglyoxal (MGLY) and acetic acid (AAc). The decay of TMB and the build-up of MGLY and AAc concentrations as observed in the chamber by the PTR-MS are shown in Figure 6.3. Figure 6.3a shows the unadjusted concentrations as monitored by the PTR-MS. In this subfigure, the first data point of the PTR-MS measurements of TMB were set to 100 ppb, which was the initial concentration in the chamber. The counts of the other compounds were scaled accordingly to derive the gas phase concentrations of the further oxidation products. The model performs well on reproducing the measured TMB decay and only slight deviations are observed. In the model, a more exponential decay is observed with increased degradation rates at the beginning of the model run. In the chamber, a more gradual almost linear decay is observed, which slows down after 2 hours.

However, the model is not able to capture the concentrations of methylglyoxal and acetic acid as observed by the PTR-MS. MGLY concentration is overestimated by a factor of 3 in the model while AAc concentration is underestimated by a factor of 4. It should be noted, however, that there are known problems to derive a proper concentration with the PTR-MS, especially for small compounds. First of all, only the mass-to-charge ratio ( $m/z$ ) is determined, and another compound with the same mass, but a different structure could overlay the PTR-MS signal although model results did see no indications for significant concentrations of other isomers. Moreover, the efficiency of the protonation of the molecules, which allows the derivation of the  $m/z$  ratios with mass spectrometry, varies for different molecules. As a consequence, large errors are found in the PTR-MS measurements and a proper determination of the concentrations of the oxidation products, where the initial concentration is unknown, is not possible. Hence, only results of TMB, where the counts of the PTR-MS were fixed to known concentrations, show a good qualitative agreement between the model and the chamber. As mentioned before, PTR-MS measurements are



**Figure 6.3** Modelled and measured concentrations of gas phase TMB and the gas phase oxidation products methylglyoxal and acetic acid (a). In subfigure b, PTR-MS counts have been rescaled to match the model predictions.

suitable for a qualitative analysis of the profile of the observed concentrations only. Therefore, the experimentally determined concentrations have been rescaled to the results of the model run RXN<sub>0.25</sub> (described in subsection 6.1.2.2) using the above-mentioned factors of 3 and 1/4 for MGLY and AAc, respectively. Moreover, TMB concentrations were scaled with a factor of 0.9 as the initial count of the PTR-MS was on the lower edge of the measurement range and further measuring points in that time span (of up to 130 ppb) indicated slightly lower TMB concentrations.

The rescaled concentrations in Figure 6.3b show a very good agreement with model results. There is still ‘a somewhat more exponential’ behaviour of the modelled TMB concentrations than observed in LEAK. As a consequence, MGLY concentrations start to build up faster in the model causing a steeper initial increase of MGLY concentrations. With declining TMB concentrations, yet continuing efficient sinks of MGLY, a decrease of methylglyoxal concentrations is observed towards the end of the experiment in both, the model and chamber results. Due to the different shapes of the TMB concentration-time profiles in the chamber and model results, the concentration decrease is slightly weaker in the model. Moreover, peak concentrations are shifted from about 2 hours and 20 minutes after the start of the experiment in LEAK to little less than 2 hours in the model. For acetic acid, a perfect agreement between measured and modelled results is observed.

The slight variations in the concentration-time profiles of TMB and MGLY are likely to derive from the experimental conditions using photolysis as OH radical source. While deviations of the prescribed OH radical concentration levels in the model compared to the chamber are one possible source for errors, photolysis of further organic compounds produced from the oxidation of 1,3,5-trimethylbenzene is another more likely explanation for observed discrepancies.

### **Background concentrations and particle initialisation in the aerosol chamber**

In the chamber, significant concentrations of malic acid (hydroxy succinic acid) were monitored by the PTR-MS (see Figure H.3a, page 899, in the Appendix). These background concentrations may derive from contaminations on the chamber wall or on the seed particles itself as malic acid was already identified on the C-GIS samples prior to the experiment (see sample A00 in Table H.2, page 897). Moreover, background concentrations may be part of the ambient air in the chamber or attached to the inlets of the instrumentation, the sampling line or vials.

PTR-MS observations suggest an initial increase of malic acid in the gas phase from 0 to  $\approx 3.5$  ppb at 1.5 hours after the start of the experiment and a subsequent decrease to concentrations around zero in about two hours. A likely explanation for the concentration-time profile of malic acid in the gas phase is the multiphase oxidation of further background concentrations of compounds such as succinic acid to malic acid besides the direct release of particulate malic acid background concentrations. As all particulate background concentrations and background concentrations of precursor compounds are depleted, gas phase oxidation of malic acid leads to a gradual decrease in the concentration-time profile. More-

over, re-partitioning of the malic acid into the aqueous phase and subsequent degradation might lead to additional depletion of malic acid concentrations in the second half of the chamber experiment.

At the current state it remains unclear, whether malic acid concentrations derive from the background concentrations of the chamber or are part of an undetected reaction pathway in the TMB oxidation. In the study of *Fisseha et al.* (2004), concentrations of malic acid and further compounds, which were identified as background concentration in the first C-GIS sample of this study (e.g., succinic or malonic acid), were found. However, concentrations of these compounds are small compared to concentrations of further products such as formic, acetic, pyruvic, and lactic acid in the study of *Fisseha et al.* (2004). Furthermore, there is no statement about background concentrations in this publication. Other studies, e.g. by *Praplan et al.* (2014), did not see any of these products identified as background concentration in the C-GIS sample A00.

A model sensitivity study was performed, where the seed particles were initiated with the concentrations of the organic compounds found in the C-GIS samples prior to the experiment (A00, see Table H.2). However, there are constraints of the gas phase mechanism MCMv3.1, which does not include the description of the oxidation of dicarboxylic acids. Therefore, only the phase transfer of DCAs between the gas and the aqueous phase is described in these sensitivity runs, but no further gas phase oxidation. The model runs indicate a release of the particulate background concentrations. However, in the model, the release is prompt at the beginning of the experiment and immediate oxidation degrades all malic acid concentrations within an hour. Moreover, the same behaviour is seen for succinic acid, a potential precursor for malic acid. Both concentration-time profiles can be found in the Appendix in Figure H.3b, page 899.

These discrepancies confirm a likely underestimation of the Henry's Law constants in GROMHE as already discussed in section 5.5. The observed depletions of the DCA concentrations in the model runs have to occur in the aqueous phase as no gas phase reactions for dicarboxylic acids exist in MCMv3.1. Thus, after the release of the DCAs to the gas phase, the remaining small fractions in the aqueous phase are oxidised in the model. Due to the Henry's Law equilibrium, malic and succinic acid is taken up from the gas phase again as aqueous phase concentration decrease until all gaseous and aqueous sources are depleted. Further extensions of the gas phase mechanism MCMv3.1 to describe the oxidation of dicarboxylic acids would be needed to resolve discrepancies between modelled and measured concentration-time profiles. Moreover, an update of the Henry's Law constants should be performed as there seems to be a significant underestimation of the HLCs in the model. This is confirmed by further studies. *Healy et al.* (2008) showed an underestimation of up to 4 orders of magnitude of theoretical gas-particle partitioning coefficients of carbonyl compounds compared to experimental determinations. They argued that heterogenous reactions of carbonyl compounds might be important for particle growth besides partitioning alone. Thus, a critical review of the uptake processes is needed together with further mechanism development. The results strengthen the decision



in subsection 5.5.3 to prohibit phase transfer processes for compounds with an O:C ratio greater than or equal to one.

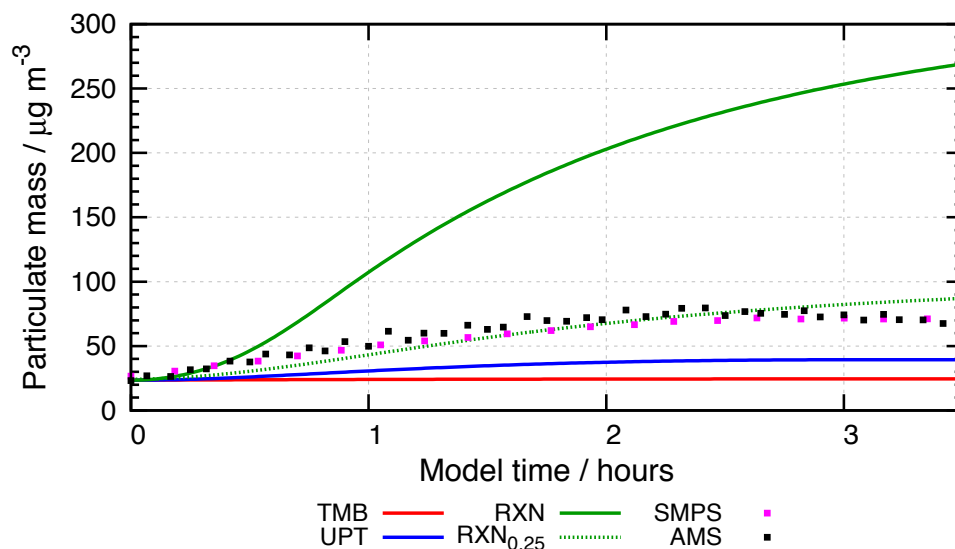
Oligomerisation in the aqueous phase as discussed in detail in the next paragraph is another possibility for the discrepancies observed between modelled and measured results. Oligomers could be formed in the aqueous phase and subsequent oxidation might produce malic acid, which is released to the gas phase. No non-oxidative processes are implemented in the current protocol and, hence, this possible formation process of malic acid would not be predicted by model simulations. There is also further need for model development to include chamber walls as a reactive medium for more realistic simulations under these distinct conditions.

Furthermore, maximum concentrations in the model are about a factor of 100 smaller compared to the unscaled raw data of the PTR-MS measurements. This very large factor cannot be explained by the inaccuracy of the PTR-MS instrument alone. Additional processes must occur in the chamber. A possibility is the release of these compounds from the chamber walls increasing the measured background concentrations. Due to the high relative humidity, chamber walls are moistened and chemistry is occurring on these large surfaces. Therefore, large amounts of malic acid might be produced on and/or released from the chamber walls. Chemistry on the walls might determine the concentration-time profile of malic acid in the gas phase.

### Particle mass increase

The most striking difference between modelled and experimental results in the TMB oxidation experiment is the increase in organic particle mass. In the chamber, the SMPS monitored a particle mass increase of a factor of 2.67 from 26.6 to maximum concentrations around  $71 \mu\text{g m}^{-3}$  (see Figure 6.4, magenta squares). The AMS showed an even larger increase from 24.2 to  $79.6 \mu\text{g m}^{-3}$ . At the end of the experiment a slight decrease in particle mass concentration to  $70.3 \mu\text{g m}^{-3}$  was observed (see black squares in Figure 6.4). It should be noted that the AMS data has been corrected for an unexplained time gap between AMS and SMPS data, probably due to different timer settings of the two instruments. In the base run (TMB), the model predicted only an insignificant increase in particle mass concentration of about  $1 \mu\text{g m}^{-3}$  with maximum concentrations at the end of the model run (red line in Figure 6.4).

A number of reasons exist for this huge underestimation of modelled particle mass concentrations. Discrepancies are likely to derive from assumptions made to keep the model framework simple or limitations of the current state of mechanism development. First of all, CAPRAM and the mechanisms generated by GECKO-A are pure oxidative descriptions. Non-oxidative processes such as accretion reactions are not part of currently published CAPRAM versions. However, several products measured in the C-GIS samples (see Table H.2) and especially the main gas phase oxidation product methylglyoxal have been suggested to take part in oligomerisation processes as described in subsection 2.1.3 (see also *Ervens and Volkamer, 2010*). In fact, oligomerisation has been suggested as an



**Figure 6.4** Modelled particle mass concentrations for the various sensitivity runs and measured particle concentrations as monitored by the SMPS and AMS.

important process in the degradation of TMB in several studies (see, e.g. *Kalberer et al.*, 2004, *Fisseha et al.*, 2004, *Healy et al.*, 2008, *Müller et al.*, 2012, *Im et al.*, 2014). *Kalberer et al.* (2004) suggested that oligomerisation processes account for more than half of the particle mass. Oligomerisation leads to high molecular weight organic compounds in the aqueous phase with molecular weights between 100 and 1000 g mol<sup>-1</sup> (*Kalberer et al.*, 2004). Thus, this process can cause a rapid increase in SOA mass.

Discrepancies between the model and the experiments might also derive from the simplistic assumption to include only the uptake of methylglyoxal and acetic acid into the aqueous phase to keep the model framework simple. The decision was supported by the fact that only for these compounds significant concentrations were monitored by the PTR-MS in the chamber. However, further MGLY precursor compounds might be taken up by the particles despite low concentrations due to a high water-solubility and, therefore, cause a relevant particle mass increase. Detailed flux analyses have shown that several further intermediates are formed in advance of the formation of methylglyoxal. Although their concentrations are insignificant, they have large turnovers. The analysis is shown in Figure H.2, page 898, in the Appendix. Further sensitivity studies as described in detail in subsection 6.1.2.2 have been performed to assess the impact of the uptake of these intermediate organic compounds.

### Analysis of TMB to MGLY turnovers and uptake sensitivity investigations

In a first study labelled UPT, the effective uptake of all intermediate compounds evolving prior to methylglyoxal in the TMB oxidation has been implemented additionally to the aqueous phase oxidation scheme of MGLY. No further oxidation of these compounds is treated in the aqueous phase and their aqueous concentrations are the consequence of the Henry's Law equilibrium. To account for reactive uptake of solvents with a high

reactivity, a second sensitivity study has been performed named RXN. In this model run, the uptake of these intermediates is described with the physical HLC and the formation of further aqueous forms by hydration or dissociation is described explicitly. Moreover, the degradation by OH to the first generation products is implemented in the mechanism. All reaction products are assumed to stay in the aqueous phase and are treated as WSOC. In addition, the monomolecular decay of polycarbonyl compounds is described. The chemistry of the fragments is treated explicitly, if they are already part of the original mechanism ‘TMB’. A more detailed description can be found in subsection 6.1.2.2 or in Appendix H.4, where the additional processes of both sensitivity runs are provided in Table H.1, page 891.

The assumption that all products formed in the aqueous phase oxidation chain of TMB oxidation products will remain in the aqueous phase is highly implausible. It is much more likely that a series of semi-volatile organic compounds are formed that are in equilibrium with the gas phase. Thus, parts of the WSOC formed in the sensitivity study RXN will be released back to the gas phase. To account for this fact, a series of sensitivity studies were performed, where the yield of WSOC has been reduced to simulate the loss to the gas phase. Results are shown only for the best fit of this series, where the yield was reduced to 25%. This sensitivity study is labelled with RXN<sub>0.25</sub> in the following.

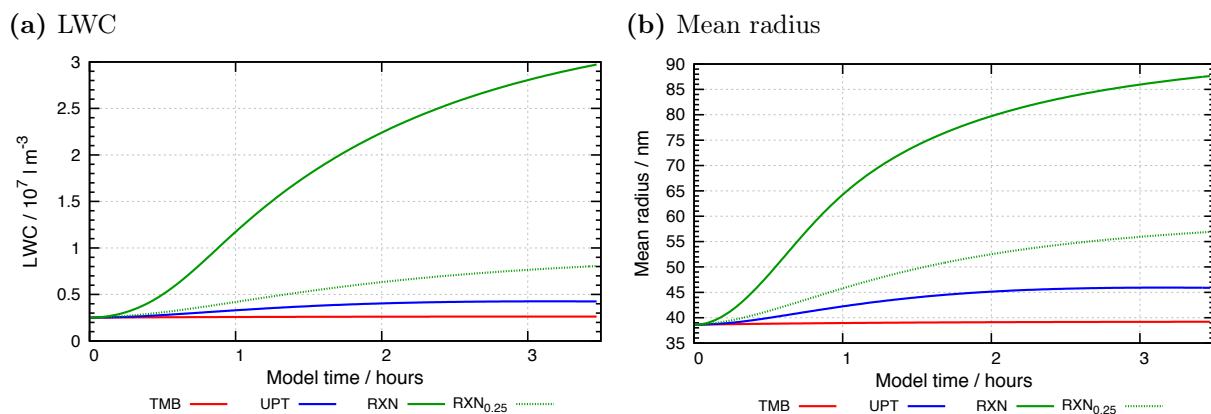
The necessity of such sensitivity studies and the plausibility of the above-mentioned assumptions is supported by further aerosol chamber studies reported in literature. Numerous studies detected particulate compounds with up to nine carbon atoms and molecular weights up to 250 g mol<sup>-1</sup> (Cocker III *et al.*, 2001, Fisseha *et al.*, 2004, Healy *et al.*, 2008, Sato *et al.*, 2012, Müller *et al.*, 2012, Praplan *et al.*, 2014). Moreover, the study of Müller *et al.* (2012) identified minor gas phase concentrations of large TMB oxidation products with more than 6 carbon atoms. Main concentrations were seen for C<sub>2</sub> and C<sub>3</sub> compounds, which is conform with the detected products methylglyoxal and acetic acid in this study. On the other hand, in the aqueous phase, C<sub>9</sub> compounds dominated the mass fraction, which supports the need for the sensitivity studies UPT, RXN, and RXN<sub>0.25</sub>. For many compounds detected, only molecular weights could be determined. Suggestions for a chemical formula were made, but no exact structure could be derived, see e.g. Müller *et al.* (2012) or Praplan *et al.* (2014). 2-methyl-4-oxo-2-pentenal as a fragment of the degradation of the ring-retaining ‘peroxide-bicyclic’ compounds (see Müller *et al.*, 2012) was found in the gas and the aqueous phase in the experiments performed by Healy *et al.* (2008). There is further evidence for aromatic compounds (benzene and furan derivatives) and epoxides from the oxidation of 1,3,5-trimethylbenzene in the aqueous phase (Fisseha *et al.*, 2004, Healy *et al.*, 2008, Müller *et al.*, 2012, Sato *et al.*, 2012), which manifest the importance for MGLY precursor compounds for the aqueous phase.

The model sensitivity studies in this dissertation showed significant improvements compared to the base scenario TMB. Missing uptake processes are a likely explanation for a wide range of the discrepancies between model and chamber results. Considering only the effective uptake of all TMB oxidation products in the sensitivity run UPT, increased the particle mass concentration to 39.4 µg m<sup>-3</sup> (see blue line in Figure 6.4). Including the

first degradation step in the aqueous phase (scenario RXN) resulted in a massive increase of the particle mass concentration to  $268.3 \mu\text{g m}^{-3}$  (green solid line in Figure 6.4). This concentration is a factor 3.8 higher than measured in LEAK. Thus, only about a quarter of the reaction products formed in the aqueous phase oxidation of TMB oxidation products will remain in the aqueous phase. The main fraction of the aqueous phase oxidation products are likely to be semi-volatile organic compounds that will partly or predominantly re-enter the gas phase and alter the gas phase chemical composition and multiphase chemistry. This fact is demonstrated by the sensitivity study  $\text{RXN}_{0.25}$  (green broken line in Figure 6.4), where the SOA yield of the aqueous phase oxidation has been reduced to 0.25. Apart from the small decrease in the particle mass concentration observed in LEAK at the end of the experiment, modelled and measured mass concentrations are in excellent agreement in this study (see Figure 6.4).

The discrepancies at the end of the experiment could be a consequence of the simplifications of the photolysis processes in the model runs. As shown above in the analysis of the gas phase products, LEAK measurements suggested a steeper decrease of methylglyoxal concentrations than the model. Thus, particle concentrations in the chamber might decrease due to the decrease in MGLY concentrations and less uptake or even release of particulate MGLY to the gas phase. The release of aqueous MGLY concentration products will further reduce particulate matter. In the model, the slight decrease in MGLY concentrations is not sufficient to show a decrease of particle mass and only slows down particle mass production.

It should furthermore be noted that the particle mass concentration is largely influenced by microphysics rather than chemistry. The particle mass increase as a consequence of uptake is heavily dependent on the liquid water content. The LWC is shown in Figure 6.5a for all sensitivity scenarios and the same behaviour is seen as for the particle mass. There is almost no increase in the original run, a moderate increase in the scenario UPT and a massive increase in the scenario RXN. Reducing the WSOC yield in the sensitivity run  $\text{RXN}_{0.25}$ , reduces the LWC by the same ratio. The LWC, in return, is influenced by the particle radius, which is given in Figure 6.5b. Again, the same trend of the sensitivity runs



**Figure 6.5** Modelled liquid water content (a) and mean particle radius (b) in the TMB oxidation experiment.

is observed for the particle radius, albeit the spread of the various scenarios is smaller. Thus, the increased particle mass in the sensitivity runs can be explained as a feedback of the multiphase chemistry of organic compounds with the microphysics of the particles. The increased uptake of additional organic compounds leads to particle growth. Increasing particle radii reduce the curvature effect that restricts the condensational growth. Hence, more water molecules adsorb to the particles with larger radii, which accelerates the growth further. Moreover, larger particles have a larger surface area, which increases uptake. This positive feedback causes the massive increase of the three closely linked quantities particle mass, radius, and LWC in the scenario RXN. Thus, small changes in particle radii due to the uptake of a few organic compounds can lead to a huge increase in LWC. Atmospheric chemistry is important to trigger microphysical processes, which then determine the particle growth by increased uptake of organic compounds. A model run with a more detailed microphysical scheme such as a fine resolved particle spectrum would be desirable to study these effects in more detail.

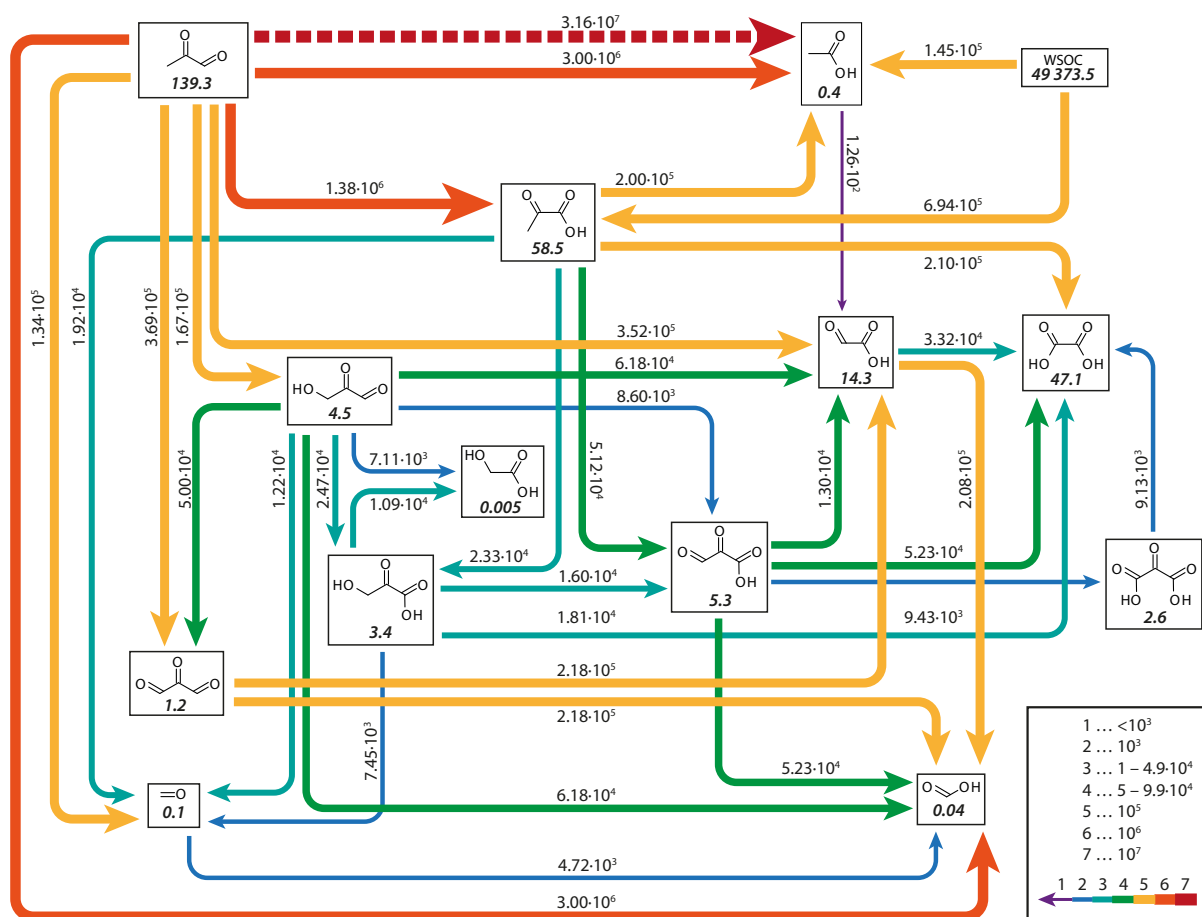
### Detailed investigations of aqueous concentrations and MGLY to AAc turnovers

For the experimental analysis of the particle, i.e. aqueous phase, composition, C-GIS samples have been taken every 15 min. Moreover, particles were collected on PTFE filters at the end of the experiment. All samples were analysed offline and the uncorrected values are given in Table H.2, page 897.

Particle phase chemistry is triggered by the uptake of methylglyoxal. Modelled MGLY concentrations of almost  $70 \text{ ng m}^{-3}$  in the scenario MGLY are a factor of 1.46 higher than experimental determinations from the filter samples ( $48 \text{ ng m}^{-3}$ ). Differences increase even further in the other scenarios. In RXN<sub>0.25</sub>, final concentrations of  $139 \text{ ng m}^{-3}$  are observed, which are a factor of 2 higher than in the base model scenario. To reveal discrepancies between measured and modelled results, a thorough multiphase chemical flux analysis of the fate of methylglyoxal has been performed.

Results from the flux analysis are shown in Figure 6.6. In this figure, the major turnovers in the gas phase (dashed arrow) and aqueous phase (solid arrows) of the fate of methylglyoxal are shown for the scenario RXN<sub>0.25</sub>. Moreover, the formation of further aqueous phase compounds from major MGLY degradation fluxes was investigated. Aqueous phase concentrations at the end of the experiment in the scenario RXN<sub>0.25</sub> are provided for completeness beneath the compound structure.

Under the conditions in the chamber, less than 10% of MGLY are processed in the aqueous phase, the main fraction is oxidised in the gas phase (see Figure 6.6). Main stable aqueous phase oxidation products with the largest turnovers are acetic acid and formic acid as well as pyruvic acid with production fluxes in the order of  $10^6 \text{ molecules cm}^{-3} \text{ s}^{-1}$ . Both, acetic and pyruvic acid concentrations, are increased by the decay of methylglyoxal precursor polycarbonyl compounds in the scenario RXN<sub>0.25</sub>. This is indicated by fluxes from WSOC in Figure 6.6. For acetic acid, fluxes from MGLY precursor compounds are a factor of 20 smaller than fluxes directly from methylglyoxal, while for pyruvic acid fluxes



**Figure 6.6** Multiphase flux analysis of major aqueous phase turnovers in the TMB oxidation experiment for the scenario RXN<sub>0.25</sub>. Gas phase turnovers are indicated by the dashed arrow, aqueous phase turnovers are represented by solid arrows with turnovers given in molecules cm<sup>-3</sup> s<sup>-1</sup> averaged over the whole experiment. Slanted numbers in the compound boxes denote aqueous phase concentrations in ng m<sup>-3</sup> at the end of the experiment.

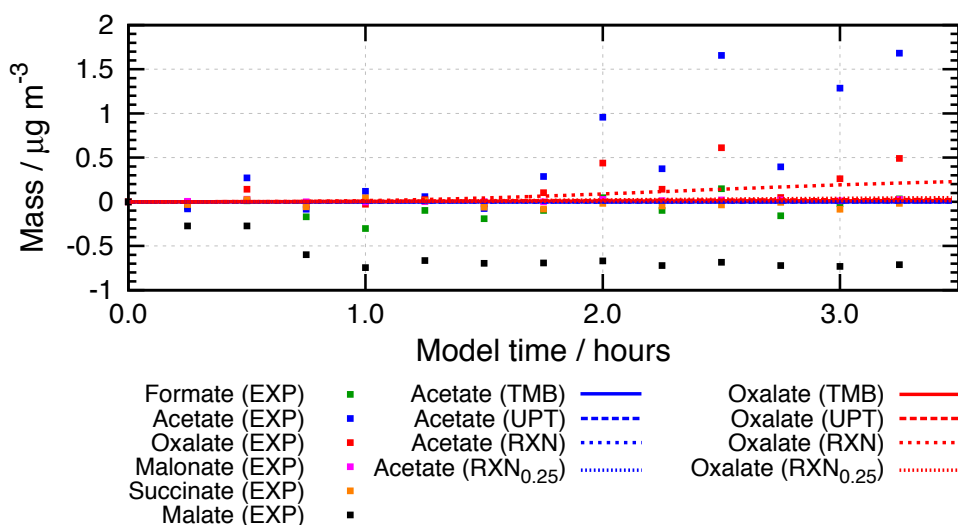
are decreased only by a factor of 2. Acetic and formic acid are in equilibrium with the gas phase. Further aqueous phase oxidation comprises chemical fluxes decreased by at least one order of magnitude (see Figure 6.6). Only 0.4 ng m<sup>-3</sup> acetate and 0.04 ng m<sup>-3</sup> formate are found in the scenario RXN<sub>0.25</sub>. Depending on the experimental method between 0.36 and 0.65 μg m<sup>-3</sup> formate and 0.81 and 2.2 μg m<sup>-3</sup> acetate were measured at the end of the chamber experiment. Thus, these acids are underestimated by three to four orders of magnitude in the model. For pyruvate the underprediction is much less with modelled concentrations of 58.5 ng m<sup>-3</sup> compared to measured concentrations of 280 ng m<sup>-3</sup>. Pyruvate is oxidised to oxalate, which accumulates to 47.1 ng m<sup>-3</sup> at the end of the experiment in the model. In the chamber, 0.7 μg m<sup>-3</sup> were measured in the last C-GIS sample and 6.8 μg m<sup>-3</sup> on the filter sample. Further sources for oxalate derive from the methylglyoxal oxidation to glycolate, hydroxy- and oxo-methylglyoxal, but are an order of magnitude lower than from the pyruvate oxidation. The latter compounds further produce hydroxy- and oxo-pyruvate as stable organic intermediates.

Discrepancies between modelled and measured concentrations are most likely the consequence of the missing explicit oxidation scheme of MGLY precursor compounds. Their

oxidation would increase aqueous phase concentrations of the compounds measured in the chamber. Further errors could be introduced from an imprecise description of phase transfer processes (see also discussion in section 5.5).

It should also be noted that large uncertainties in the measurements exist. C-GIS samples suggested acetate as the main oxidation product with concentrations of  $2.2 \mu\text{g m}^{-3}$ . Oxalate concentrations were determined more than a factor of 3 smaller ( $0.7 \mu\text{g m}^{-3}$ ). On the filter samples, oxalate is the main oxidation product. Moreover, oxalate concentrations are much higher with  $6.8 \mu\text{g m}^{-3}$ , while acetate concentrations are much smaller with  $0.8 \mu\text{g m}^{-3}$  on the filter samples. Thus, the ratio between the two species increases to 8.5. As the model suggests that both acids have negligible aqueous phase sinks, this ratio is determined either by the Henry's Law constant and, hence, the equilibrium with the gas phase of these acids or the branching ratios of the initial reaction of hydroxyl radicals with methylglyoxal. The latter aspect also includes the formation of different hydrated forms of MGLY and their different reactivities. With more conclusive measurements, this would have been an excellent opportunity to validate the determination of branching ratios with SARs.

For a better overview, a graphical output of the concentrations determined in the C-GIS samples is provided in Figure 6.7 (coloured squares, see figure legend for colour code). In Figure 6.7, the experimental values have been corrected for any particulate background concentrations. Therefore, the blind values of the sample A1 (beginning of the experiment) have been subtracted from the following samples A2 – A14. As can be seen from Figure 6.7, the concentrations of most aqueous phase compounds identified in the C-GIS samples vary around  $0 \mu\text{g m}^{-3}$ . The corrected malic acid concentrations show even values significantly below 0 ( $-0.27 \mu\text{g m}^{-3}$  in the first half hour of the experiment and around  $-0.7 \mu\text{g m}^{-3}$  thereafter). The significantly negative corrected concentrations are another indication for malic acid background concentrations rather than missing production pathways in



**Figure 6.7** Concentrations of organic constituents detected in the C-GIS samples corrected for the blind values at sampling point A1 and modelled concentrations of acetic and oxalic acid for the various sensitivity runs.

the mechanism. Malic acid is released from the aqueous phase at the beginning of the experiment and degraded in the gas phase as discussed above.

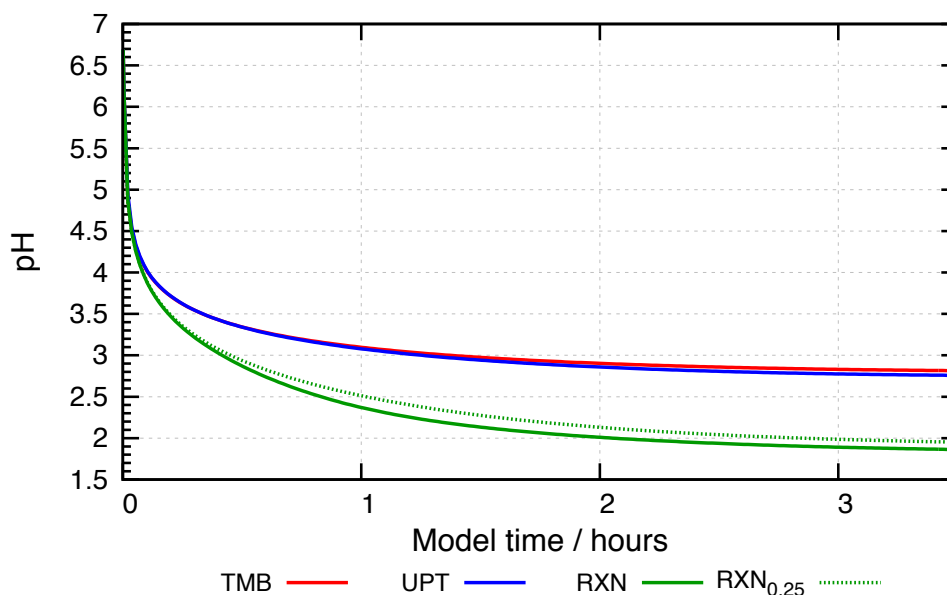
The only compounds, which show concentrations significantly above  $0\text{ }\mu\text{g m}^{-3}$  in the C-GIS samples, are oxalic acid with corrected concentrations of about  $0.5\text{ }\mu\text{g m}^{-3}$  and acetic acid with corrected concentrations around  $1.5\text{ }\mu\text{g m}^{-3}$ . For these two compounds, the modelled concentrations of the various sensitivity studies are provided in Figure 6.7 as well. The base run TMB (solid lines in the colour of the respective experimental data points in Figure 6.7) significantly underestimates both acids and concentrations indistinguishable from the zero-line are predicted by the model. Improvements in the UPT scenario are minor (dashed lines in Figure 6.7). In the scenario RXN (dotted lines in Figure 6.7), major improvements are seen for oxalic acid while still insignificant concentrations for acetic acid are predicted. The reduction of the WSOC yield in the scenario  $\text{RXN}_{0.25}$  also reduces the concentrations of both acids to negligible values (broken lines in Figure 6.7).

The improved oxalate values in the scenario RXN together with a poor agreement in the scenario  $\text{RXN}_{0.25}$  are an indication for the need of a more advanced explicit chemical oxidation scheme in the aqueous phase. With rising liquid water content in the scenario RXN, more acetic and oxalic acid remains in the aqueous phase due to the Henry's Law equilibrium. The reduction of the SOA yield in  $\text{RXN}_{0.25}$  also reduces the LWC and, thus, acetic acid and oxalate concentrations. However, more realistic particulate mass concentrations are achieved in the latter scenario. Moreover, in both scenarios, aqueous phase oxidation products from MGLY precursor compounds are described as WSOC. An explicit chemical oxidation scheme would lead to acetic and oxalic acid production, which could resolve the above discrepancies. The scenario RXN should be seen as a upper limit of the possible oxalic and acetic acid concentrations as a result of the Henry's Law equilibrium. Decreased concentrations in the scenario  $\text{RXN}_{0.25}$  are likely the consequence of the missing explicit description of the oxidation of aqueous phase MGLY precursor compounds to these acids.

## Particle acidity

The particle acidity is shown in Figure 6.8. The initial  $\text{Na}_2\text{SO}_4/\text{Na}_2\text{O}_2$  seed particles show only a weak acidity and near neutral conditions are found. The  $\text{H}^+$  concentration increases immediately in the first minutes by several orders of magnitude due to uptake of organic compounds and acid formation. The increase is enhanced in the scenario RXN as more organic compounds are dissolved in the aqueous phase. Within the first hour, the pH decreases to about 3 in the scenarios TMB and UPT and below 2.5 in the scenarios RXN and  $\text{RXN}_{0.25}$ . In the remaining 2.5 hours only a minor decrease in pH of about 0.3 units is seen for the first two sensitivity runs, while it takes longer to reach equilibrium in the scenario RXN/ $\text{RXN}_{0.25}$ . After 2 hours, the pH reaches a value of 2, thereafter only a weak decrease to the final value of 1.9 is seen. Despite large differences between the scenario RXN and  $\text{RXN}_{0.25}$ , e.g. in particle mass, differences in particle acidity are small.





**Figure 6.8** Modelled particle pH for the 3 sensitivity runs TMB, UPT, and RXN.

### Conclusions of chamber experiments

Overall, the second oxidation experiment of TMB in the aerosol chamber LEAK provided a good basis for a detailed evaluation of the GECKO-A protocol and the mechanisms created. Given the difficulties of such a complex experiment, the modelled results must be regarded as a success. Considering that the model SPACCIM was designed to simulate tropospheric processes and not for aerosol chamber studies, where additional processes such as wall losses or chemistry at the wetted walls have to be considered, excellent agreement was achieved between modelled and measured results. Deviations can be explained by the difficulties to simulate chamber conditions with the model SPACCIM as well as a missing explicit description in the oxidations schemes applied. Moreover, differences in experimentally determined and modelled results pointed at weaknesses in the GECKO-A protocol.

## 6.2 Simulations with a ‘real atmosphere’ scenario

Sophisticated box model simulations have been performed with the parcel model SPACCIM (Wolke *et al.*, 2005) and the new CAPRAM mechanisms 3.0o/p, 3.5 $\alpha$ , and 4.0 $\alpha$ . For the model simulations, a model scenario with non-permanent clouds has been chosen based on previous model runs. The scenario is described in detail in subsection 6.2.1. Furthermore, the initialisation of model runs is described in this section. An overview over meteorological and microphysical parameters in the model runs is given in subsection 6.2.2. Results are discussed in subsection 6.2.3 – 6.2.7 for various subsystems of interest.

### 6.2.1 Model setup

The meteorological scenario is based on previous CAPRAM model scenarios (see, e.g., *Tilgner and Herrmann, 2010, Tilgner et al., 2013*). The simulation are performed for urban and remote continental summer conditions. Model runs start at Jun 19th, midnight and last for 108 hours (4.5 days).

A special feature in the meteorological scenario are non-permanent cloud periods. Throughout the modelling period, every noon and midnight a cloud is formed for about 2 hours. Therefore, the air parcel is lifted from 850 to 800 hPa within 15 min starting at 10.45 am and pm, respectively. During the ascend, a cloud is formed and the particles get activated to cloud droplets. The parcel remains at the lower pressure level for 2 hours. During this time, the whole parcel volume is filled with a cloud. At 1am and 1pm of every day the parcel starts to descend for the next 15 min. During this time, the cloud evaporates leaving only aged aerosol particles behind. Altogether, 8 cloud passages are performed in the model run. Between cloud periods, relative humidity is adjusted to 90%. The high value was chosen to assure deliquescent particles, which are needed to apply the aqueous phase chemical scheme in the particles. When relative humidity decreases, solutes become more concentrated and non-ideal effects have to be considered such as ion–ion interactions. With a complex chemical scheme such as the ones applied in this dissertation the computational costs are too high to treat non-ideality. Therefore, the meteorological scenarios are adjusted to be able to neglect effects arising from non-ideal solutions.

The meteorological scenario was designed following the studies of *Pruppacher and Jaenicke (1995)*. These authors performed calculations and estimations about tropospheric clouds. According to their work, clouds in the lowermost 6 km of the atmosphere fill a volume of  $4.66 \cdot 10^{17} \text{ m}^3$ , which corresponds to 15.4% of the tropospheric volume (*Pruppacher and Jaenicke, 1995*). Therefore, for the model runs a trajectory was chosen, which has a in-cloud residence time of about 15%. This value corresponds to 3.7 hours a day, which was rounded to 4 hours. To distinguish between day- and night-time effects, cloud periods were split into 2 hours of in-cloud residence time during the day and 2 hours during the night, respectively. Moreover, splitting the in-cloud residence time into two periods per day results in cloud lifetimes, which are closer to the calculated ones. While *Pruppacher and Jaenicke (1995)* give a typical in-cloud residence time of about 3 hours of an air parcel, the achieved two hours of in-cloud residence time in the CAPRAM meteorological scenario agree with the value given by *Rodhe (1992)*.

In contrast to previous CAPRAM model studies, where a fine-resolved spectral aerosol distribution was applied, the model is initialised with a mono-disperse aerosol population in this work. The very complex chemical mechanisms demand high computational costs and, therefore, a more simplified microphysical description has to be used in the model. The particle number concentration is set to 100 particles per  $\text{cm}^{-3}$  for the remote case and  $300 \text{ cm}^{-3}$  for the urban case, which resembles typical values for these environments. In both scenarios, a particle radius of  $0.2 \mu\text{m}$  is used. The radius falls in the range of typical CCN radii (see, e.g. *Herrmann, 2003*). More importantly, with the chosen particle radius,

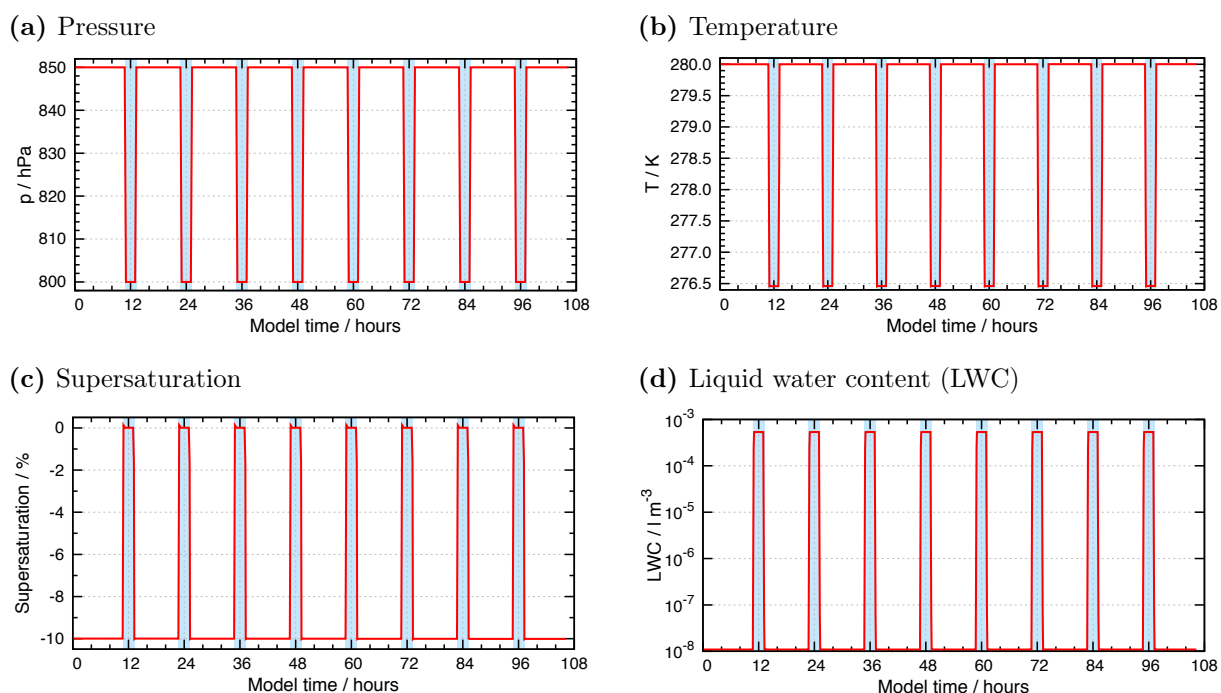
an aqueous phase volume is achieved, which leads to plausible mass concentrations of the particles and their constituents after the model initialisation. Furthermore, realistic aqueous phase concentrations and chemical fluxes of all aerosol constituents are achieved with the chosen particle initialisation throughout the whole model run. The initial aerosol population is processed throughout the model run. Particles may grow or shrink as gas phase trace compounds condense on the particle surface or evaporate from it. However, no emissions of fresh aerosols or depositions of aged aerosols are considered in the present version of SPACCIM. The missing particle emissions and depositions determined the length of the model run. 4.5 days are a typical residence time of aerosol particles (see, e.g., *Hobbs, 1993, Warneck, 1999*). Longer modeling times would lead to an inaccurate description of the chemistry and chemical composition in aged aerosol particles.

Furthermore, the model is provided with information about the initial composition of the aerosol particles. The data is provided in Table F.1, page 327, in the Appendix for the urban and the remote case, respectively. It is taken over from previous CAPRAM model studies (see, e.g., *Tilgner et al., 2013*) with typical values for urban and remote continental environments. Appendix F.3 also details the gas phase initialisation. Before the start of a model run, the initial gas phase concentrations of several important compounds are prescribed in the model. They can be found in Table F.2, page 328. Throughout the model runs, emissions and depositions exist for several important compounds. Data are provided for the emission and deposition rates in Table F.3, page 329, and Table F.4, page 330, respectively. Values of the gas phase initialisation have been taken over from previous CAPRAM studies as well (see *Tilgner et al., 2013*). However, the adoption to the new gas phase mechanism MCMv3.1 has made a few modifications necessary as can be seen from the tables in Appendix F.3. All data reflect typical conditions for polluted urban or remote continental environments.

At last it should be noted that for all calculations the full  $\alpha$  version has been used either in the urban or the remote continental case. Results of section 5.6 have shown that the nitrate radical chemistry has an influence at least on several subsystems in the urban case. As the study aims at a most detailed description and understanding of the organic multiphase chemistry, the most detailed mechanism subversion was chosen. For a better comparison, the  $\alpha$ -version was used in the remote case as well, albeit results of section 5.6 have shown that a more simplified description gives equally adequate results.

## 6.2.2 Meteorological and microphysical parameters

In the model, the trajectory determines the pressure, which is prescribed and can be found in Figure 6.9a. For the temperature, the starting value is provided in the model, while temperature changes are calculated according to the adiabatic ascent and descent of the air parcel. The resulting temperature profile can be found in Figure 6.9b. Moreover, the relative humidity and, hence, the liquid water content of the particles is influenced by these meteorological parameters, as can be seen in Figure 6.9c and Figure 6.9d, respectively. In Figure 6.9c, the relative humidity is shown in terms of supersaturation ranging from -10%,



**Figure 6.9** Overview of important meteorological and microphysical parameters in the ‘real atmosphere’ scenarios.

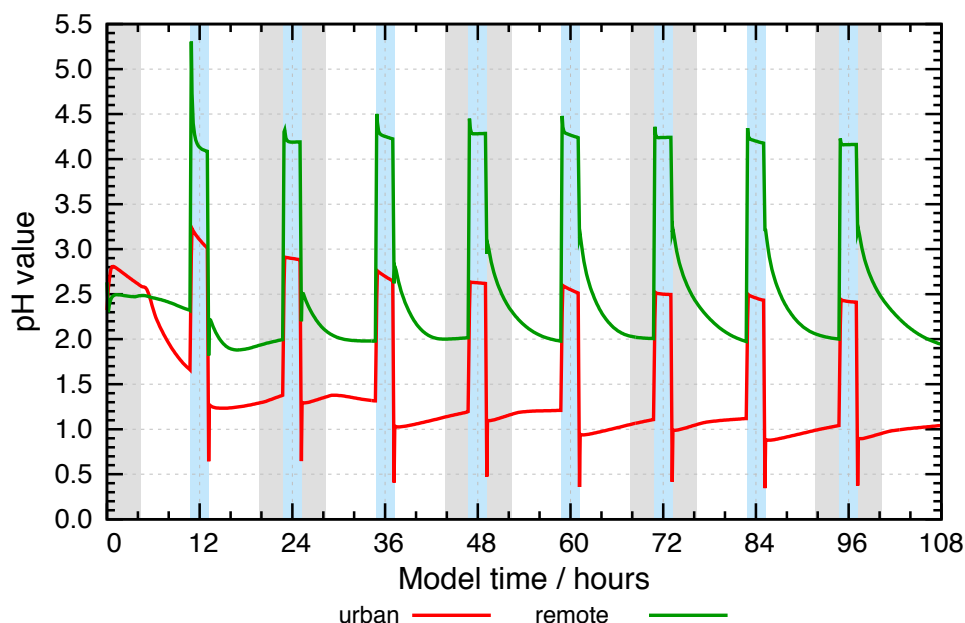
i.e. 90% rH, to a few tenth, i.e. a little over 100% rH. The parameters in Figure 6.9 are shown for the CAPRAM 3.0p mechanism only as any influences of the extended organic schemes in CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$  are indistinguishable from CAPRAM 3.0p.

### 6.2.3 Influence of the extended organic scheme on the particle acidity and SOA formation

Detailed investigations on the concentration-time profiles and the chemical fluxes have been performed to gain new insides on the organic multiphase chemistry. In the current section, details about general questions concerning particle acidity and SOA formation are discussed.

#### 6.2.3.1 Particle acidity

Figure 6.10 shows the modelled particle and cloud droplet acidity for the urban and remote case, respectively. From Figure 6.10 can be seen that the pH value is adjusted approximately within the first 12 model hours in both scenarios. Thereafter, only slight changes in the day-to-day variation are observed. Moreover, the particle acidification under urban conditions can be seen from Figure 6.10. This is most noticeable from the lower pH values under urban conditions (red line in Figure 6.10) than under remote conditions (green line).



**Figure 6.10** Time profile of the particle/cloud droplet pH for CAPRAM 4.0 $\alpha$  in the urban and remote scenario.

During cloud periods, the pH stays at levels between 4 and 4.5 in the remote case and between 3.3 and 2.4 in the urban scenario. For a better legibility, cloud periods are marked with blue bars in Figure 6.10 and the following graphs. Moreover, night-time periods are shaded with light grey. During non-cloud periods, the pH is significantly decreased. It is between 3 and 2 pH units in the remote scenario and between 0.9 and 1.4 in the urban case. In the urban scenario, the pH drops immediately to the lower values upon the evaporation of the cloud. In the remote scenario, it takes several hours to adjust to the lower values. In this scenario, an exponential decay is seen for every non-cloud period. This decay is faster during the day than during the night.

Reasons for the slower decay in the remote scenario could be the decreased emissions and consequently concentrations of sulfur dioxide. Decreased uptake will lead to decreased sulfuric acid production in either the gas or the aqueous phase, which means a slower acidification after cloud periods. The decreased  $\text{NO}_x$  level leads to less nitric acid formation and further decreased acidity in rural particles. Moreover, ammonia emissions might have a stronger effect on the less acidic particles in remote areas and buffer the acidification as ammonia acts as a base and will form ammonium ions in deliquescent particles.

Furthermore, particle acidification can be observed from a slight decrease in particle pH in the day-to-day variation in the urban scenario. This decrease occurs during cloud periods and is more pronounced during the day. During non-cloud periods, pH increases, but cannot compensate the decrease from the cloud periods.

The model results are in good agreement with previous CAPRAM model studies. *Tilgner et al.* (2013) found a pH value of 4.8 and 2.9 under cloud conditions and 2.3 and 1.3 under non-cloud conditions for the remote and urban scenario, respectively. Thus, in the present study, pH values have decreased slightly. Particle pH in CAPRAM 2.4 model

studies was even higher with values between 5 and 5.5 as well as 2 and 2.5 for remote and urban conditions, respectively (see *Ervens et al.*, 2003). However, the reason for this is not additional acidity produced by further carboxylic acids in the system. It is rather a combination of the additional parameterisations used for the reactions of hydroxyl and nitrate radicals with WSOC and HULIS compounds and the different microphysical model setup.

*Tilgner et al.* (2013) used a fine resolved particle and droplet spectrum while this study uses a mono-disperse particle population due to the complex chemistry. The pH in the CAPRAM 4.0 $\alpha$ , 3.5 $\alpha$ , and 3.0p model studies shows no significant differences between these runs. The comparison of the pH between the different CAPRAM versions is given in Appendix I.1 in Figure I.1, page 901. From this figure can also be seen that significant deviations are only observed in CAPRAM 3.0o, where the OH/NO<sub>3</sub> + WSOC/HULIS parameterisations are omitted. The increased pH is, however, only a indirect result of organic chemistry. The decreased hydroxyl and nitrate radical concentrations lead to changes in inorganic chemical cycles, which affect nitrate and sulfate production and, hence, particle acidity. These effects will be discussed in more detail in subsection 6.2.6.

The pH increase from the new parameterisations is, however, not enough to explain the differences to the model study by *Tilgner et al.* (2013). As CAPRAM 3.0o resembles the mechanism version used by *Tilgner et al.* (2013) apart from a few updates of rate constants and the introduction of peroxy radical recombinations, which do not affect particle acidity, the difference can be attributed to the different microphysical schemes used in the model studies.

Measured pH values from field experiments in urban areas are even below the modelled pH values of this study. *Li et al.* (1997) found particle pH values between -2.4 and 0.2 with an average value of -0.85 in Southern California. More recent measurements in the Hong Kong area derive a particle pH of 0.95 in average, which is in excellent agreement with the modelled pH value at the end of the scenario. In the latter study a brief period with pH values up to 4.5 was seen during spring-time measurements, when air was advected from remote north-north easterly continental regions (*Lee et al.*, 2013).

The very low pH values are at one hand the result of the very polluted urban regime of megacities. Both measurement sides bear megacities with extreme air pollution as the latter study was performed in the Hong Kong area and the first study in Southern California, where Los Angeles is situated. Moreover, the first study was performed over 15 years ago, when environmental protection methods were not as advanced as they are today and, therefore, particle acidification was more pronounced. *Tilgner et al.* (2013) give a lower relative humidity as another reason for the lower particle pH found in the field experiments. With the lower relative humidity, ionic strength increases and, hence, the pH decreases.

This explanation can only be applied to the dry regions of Southern California and, hence, the measurements performed by *Li et al.* (1997). The Hong Kong area, where the measurements by *Lee et al.* (2013) took place, is marine influenced with monthly average

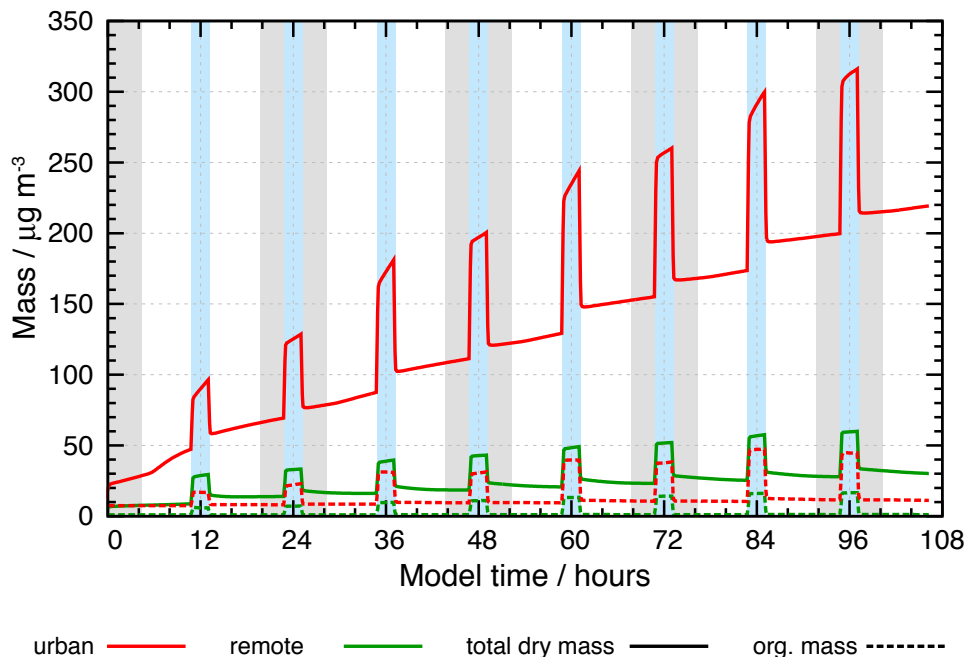
values of the relative humidity between 68 and 83% (*Hong Kong Observatory*, 2013). Values get close to the relative humidity of 90% used in this model study and the study by (*Tilgner et al.*, 2013). Therefore, the good agreement of the modelled pH values in this study with the measured pH values by *Lee et al.* (2013) confirms the importance of humidity for particle acidity. Moreover, the measured pH value of 4.5 (*Lee et al.*, 2013) in advected air masses from a remote continental sector in Hong Kong is in excellent agreement with the modelled pH value in the remote scenario.

Numerous determinations of aerosol particle and cloud droplet pH values exist. A good overview is given in the review by *Herrmann et al.* (2014). From the data, a wide spread in the range of measured pH values is observed. Modelled pH values during both, cloud and non-cloud conditions, fall well within this range. Hence, for a general model scenario as applied in this dissertation, simulated pH values can be considered as realistic under typical tropospheric conditions.

### 6.2.3.2 Particle mass

#### Overview

The particle mass (dry and organic) is plotted in Figure 6.11. In the remote case, significantly less particle mass is in the system compared to the urban case. At the end of the model run, particle mass is more than a factor 7 smaller in the remote scenario compared to the urban scenario. Particle mass increases throughout the model run. While there is a steady increase in the urban case, in the remote case, particle mass stays constant or



**Figure 6.11** Time profile of the organic and dry particulate mass for CAPRAM 4.0α in the urban and remote scenario.

even slightly decreases during non-cloud periods. The increase of particulate matter in the remote scenario derives from an increase during cloud periods, which overcompensates losses during non-cloud periods. Due to uptake of water-soluble material, particle mass is increased during cloud periods in both scenarios. The increases amount to about  $35 \mu\text{g m}^{-3}$  at the beginning of the urban case and little less than  $20 \mu\text{g m}^{-3}$  in the remote case for the total dry mass. Throughout the model runs, these values increase as more species are emitted into the air parcel and are oxidised and, thus, become more water-soluble. At the end of the model run, increase in particle mass during cloud periods compared to non-cloud periods is more than  $100 \mu\text{g m}^{-3}$  for the urban case and about  $30 \mu\text{g m}^{-3}$  for the remote case.

During cloud periods, a significant fraction of the particulate matter are organic compounds. In the urban case, at the beginning of the model run about 1/3 of the particulate matter is organic. The fraction decreases to about 1/5 as the increase of the organic mass fraction is not as strong as the increase of the inorganic mass. In the remote scenario, the percentage of the organic mass fraction is even higher although absolute values are less. At the end of the last cloud in the remote scenario,  $17 \mu\text{g m}^{-3}$  organic matter are found, which is about 30% of the dry particulate matter. During non-cloud periods, the organic fraction in particles is small. In the remote case, concentrations are indistinguishable from the zero-line. At the end of the model run,  $1 \mu\text{g m}^{-3}$  additional organic material is found in particles, which corresponds to 3.4% of the total dry particle mass. In the urban case, a few  $\mu\text{g}$  of particulate organic matter are produced in the 4.5 model days totalling to  $9.6 \mu\text{g m}^{-3}$  or 5.0% of the dry particulate matter at the end of the model run.

Various measurements of aerosol mass exist along the attempt to determine the aerosol composition. These measurements suggest, that the current mechanism and model is still not able to reproduce the organic aerosol production observed in the troposphere. For example, *Seinfeld and Pandis* (2006) compiled aerosol measurements from different sampling sites and grouped them into different classes. According to their compilation, the particle mass concentrations in remote areas is  $4.8 \mu\text{g m}^{-3}$  on average containing about 11% organic carbon. The concentrations increase to  $15 \mu\text{g m}^{-3}$  with 24% organic carbon in non-urban continental areas and reach  $32 \mu\text{g m}^{-3}$  with 31% organic carbon in urban areas (see *Seinfeld and Pandis*, 2006 and references therein). Comparing the model results in Figure 6.11 with the data of *Seinfeld and Pandis* (2006) shows a higher production of inorganic aerosol mass (mainly sulfate and nitrate, see subsection 6.2.6), but a lower organic fraction within the aerosol particles.

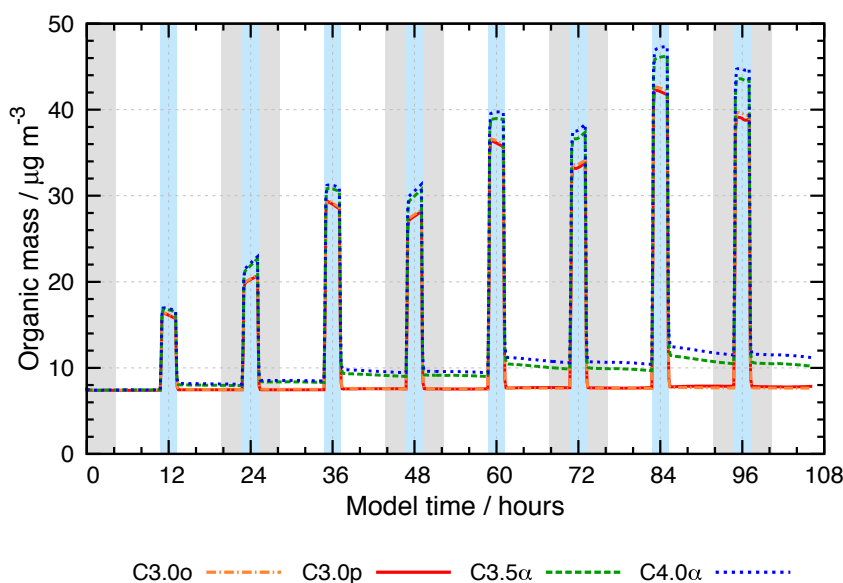
Reasons for the insufficient organic mass production could be missing organic sources, a regime that is too oxidative, thus too efficiently oxidising organic molecules to smaller fragments and ultimately  $\text{CO}_2$ , which do not remain in the aqueous phase, or a wrong product distribution leading to products, which are unreasonably volatile. The latter two aspects have already been addressed in comprehensive sensitivity studies as described in section 5.5. To adjust the oxidative capacity of the tropospheric aqueous phase and account for OH and nitrate radical scavengers from higher WSOC and HULIS compounds currently not resolved in the mechanism, parameterisations have been derived in subsection 5.5.1.



To evaluate the uncertainties in the product distribution, the alkoxy radical decay has been examined in subsection 5.5.4 and new rate constants have been estimated based on the results of the sensitivity studies. Moreover, reaction pathways between different radical oxidants have been adjusted by carefully revising the reaction rate constants of nitrate radicals with unsaturated compounds in subsection 5.5.2. Missing sources from further organic compounds not yet addressed in CAPRAM 4.0 $\alpha$  will be discussed later in this subsection. However, it should be noted that the data from global aerosol measurements comprises a large variability (see, e.g., *Jimenez et al.*, 2009) and caution should be taken when comparing and idealised model study as in this dissertation with any of these data.

As this dissertation focuses on the evolution of organic carbon in the tropospheric multiphase system, the organic particulate mass fraction shown in Figure 6.11 has been investigated in more detail for the urban scenario, where organic compounds are ubiquitously found. The level of detail in the organic scheme of the applied mechanisms has an influence on the organic particle mass. This fact is demonstrated in Figure 6.12, where the organic mass fraction is plotted over time for the urban scenario and the different mechanisms applied in this study. In general, the simulations of all four mechanisms show an increased organic particulate mass during cloud periods due to more dissolved organic matter in the dilute cloud droplets as a result of the Henry’s Law equilibrium with the gas phase. Moreover, a general increase in organic mass dissolved in cloud droplets is observed over time, which is delayed during the night, where concentration levels stay below the values of the preceding daytime cloud. Only the first night-time cloud forms an exception.

During night-time, organic mass increases during in-cloud residence times while at day, concentrations decrease. In contrast, comparing pre- and post-cloud concentrations in Figure 6.12, significant in-cloud organic mass production is found only during the day at least in the runs with the extended organic schemes. This points towards increased



**Figure 6.12** Time profile of the organic particulate mass for the different CAPRAM mechanisms in the urban scenario.

oxidation during the day. During cloud periods, organic matter is oxidised, which will produce organic compounds that are less water-soluble and will partition to the gas phase and decrease aqueous concentrations during cloud periods on the one hand. On the other hand, more soluble organic compounds are produced that stay in the aqueous phase even with a significantly decreased LWC after the evaporation of the cloud.

The complexity of the description of organic chemistry in CAPRAM has a large impact on the organic mass production. In the two CAPRAM 3.0 versions with restricted C<sub>3</sub> and C<sub>4</sub> chemistry, an increase in organic mass is seen only during cloud periods as a result of the gas phase oxidation of organic compounds and their equilibrium with the aqueous phase during high levels of liquid water content. In contrast to the particle acidity, the additional parameterisations of the reactions of OH and NO<sub>3</sub> with WSOC and HULIS compounds have no effect on organic particle mass production. Both scenarios show an insufficient mass production of about 0.5 µg m<sup>-3</sup> in 4.5 days. Thus, the effect of additional sinks for hydroxyl and nitrate radicals in CAPRAM 3.0p is restricted to inorganic particle mass production (see subsection 6.2.6).

With the introduction of branching ratios, the new CAPRAM 3.5α mechanism becomes much more detailed and comprehensive, which results in a different concentration-time profile of the organic mass fraction. In addition to the organic carbon, with which the particles were initialised in the model runs (compare Table F.1), an increase of almost 3 µg m<sup>-3</sup> is observed at the end of the model runs. Adding almost 1800 additional organic compounds with up to four carbon atoms and nearly 3000 additional reactions in CAPRAM 4.0α increases the organic mass production by another microgram per cubic meter at the end of the model run.

Particle mass is produced mainly during daytime clouds. During non-cloud periods, the OM fraction is oxidised during the day and stays at constants levels or only slightly decreases during night. The oxidation is, however, not sufficient to compensate for the large in-cloud productions.

To gain more insights into the evolution of the organic particulate mass, the organic mass fraction has been investigated more closely. On one hand, it is desired to have more information about the constituents of the organic mass fraction, however, on the other hand with such large mechanisms as CAPRAM 4.0α, it is infeasible to investigate each single compound. For the clarity of the evaluation process of the results, single compounds have been grouped under certain aspects. The categorisation should compromise between a detailed view on the organic matter and the feasibility to manage the discussion of such comprehensive mechanisms.

### **Investigation of organic particulate matter by compound classes**

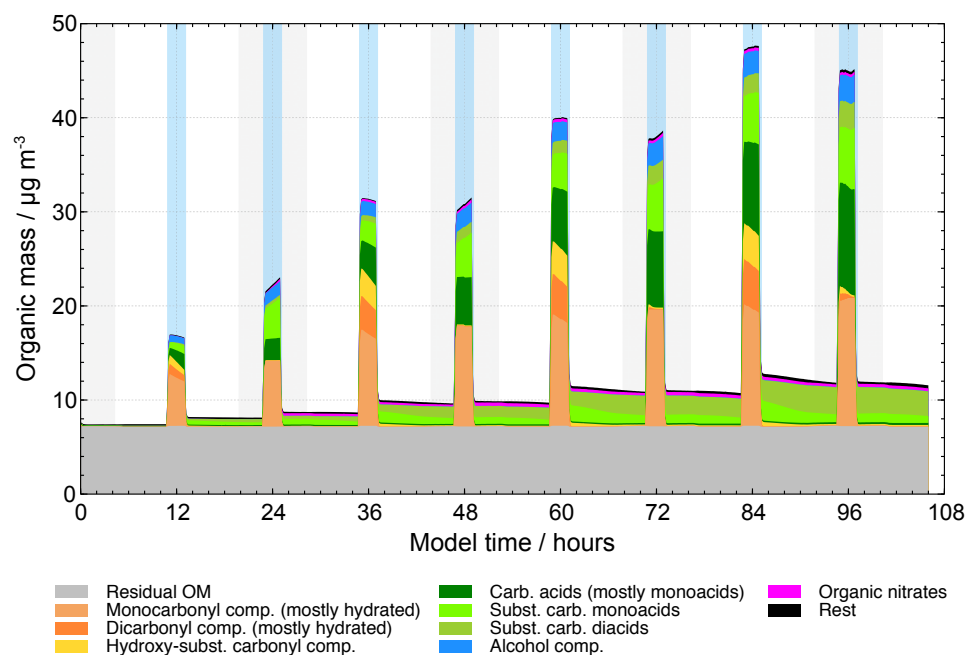
One aspect of categorisation has been the type of functional groups, a molecule bears. The following compound classes have been investigated (with the abbreviations used in the following given in parantheses):

- Monoalcohols (O1)
- Di- and polyols (O2)
- Functionalised organic nitrates (N1)
- Hydroperoxides (H1)
- Organic peracids (P1)
- Monocarbonyl compounds (C1)
- Di- and polycarbonyl compounds (C2)
- Carbonyl compounds and di-/polycarbonyl compounds with at least one hydrated carbonyl function (G1/2)
- Hydroxy-substituted carbonyl compounds or gem-diols (PF)
- Carboxylic monoacids (A1) and di-/polyacids (A2)
- Functionalised carboxylic monoacids (B1) and di-/polyacids (B2), except  $\text{NO}_3$ -substituted acids, which are counted as N1
- Iron complexes with organic ligands (FC)
- Sulphur containing organic compounds (SC),
- Organic C- and O-centered radicals (00)
- Residual organic matter including EC, WISOC, WSOC, and HULIS/HULIS<sup>-</sup> (XX)

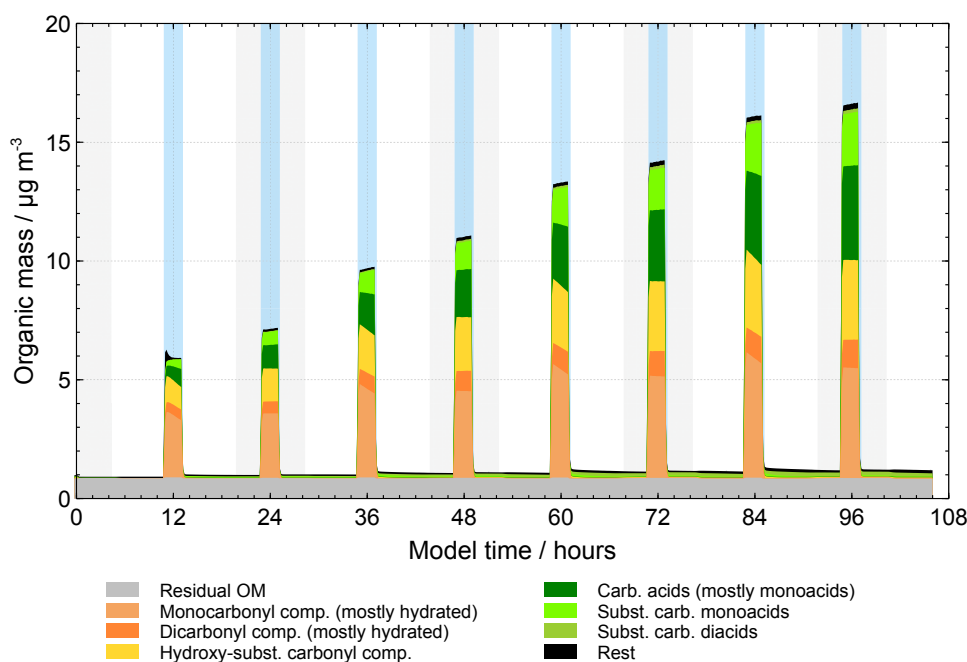
The derived concentration-time profile for the organic mass differentiated by compound classes is plotted in Figure 6.13. Results are shown for model runs with CAPRAM 4.0 $\alpha$  under urban and remote conditions. Moreover, the compound classes have been further grouped as appropriate according to the abundance in the model runs.

In both scenarios, the model has been initialised with a water-soluble and -insoluble organic fraction of the particulate mass. Compounds in this class are only converted to different forms within the class and the overall fraction does not change over time (see grey fraction in Figure 6.13). The initialised mass is about 8 times smaller in the remote scenario than in the urban scenario with  $0.9 \mu\text{g m}^{-3}$  compared to  $7.3 \mu\text{g m}^{-3}$ . Under non-cloud and remote conditions, negligible contributions of the explicit organic scheme to the organic mass of about  $0.2 \mu\text{g m}^{-3}$  at the end of the model run are found in particles (see Figure 6.13b). The additional content consists mainly of dicarboxylic acids. In the urban scenario (Figure 6.13a), additional organic matter is found, which consists mainly of substituted carboxylic acids and diacids. A small fraction can be attributed to substituted organic nitrates from the aqueous phase oxidation of unsaturated organic compounds by nitrate radicals. The additional organic content is produced during daytime clouds and degraded during non-cloud periods. From Figure 6.13a can be seen that during cloud periods carboxylic mono- and diacids are produced to about equal shares. During non-cloud periods monocarboxylic acids are further oxidised to dicarboxylic acids. Thus, monocarboxylic acid concentrations decrease during non-cloud periods, while dicarboxylic acid concentrations increase. Overall, only a small decrease in OM is seen during non-cloud periods.

(a) Urban scenario



(b) Remote scenario



**Figure 6.13** Evolution of the organic particulate mass differentiated by compound classes for the urban (a) and remote scenario (b) with CAPRAM 4.0 $\alpha$ .

An explanation for the additional organic mass during non-cloud periods in CAPRAM 4.0 $\alpha$  compared to CAPRAM 3.0n are most likely the introduction of branching ratios in the new versions. In the new mechanisms, the oxidation of organic compounds can lead to highly functionalised organic compounds as the molecule is attacked at several sites. Previously, only the weakest bound H-atom was abstracted in the mechanism and molecules were generally attacked at already functionalised sites. The oxidation led to molecules

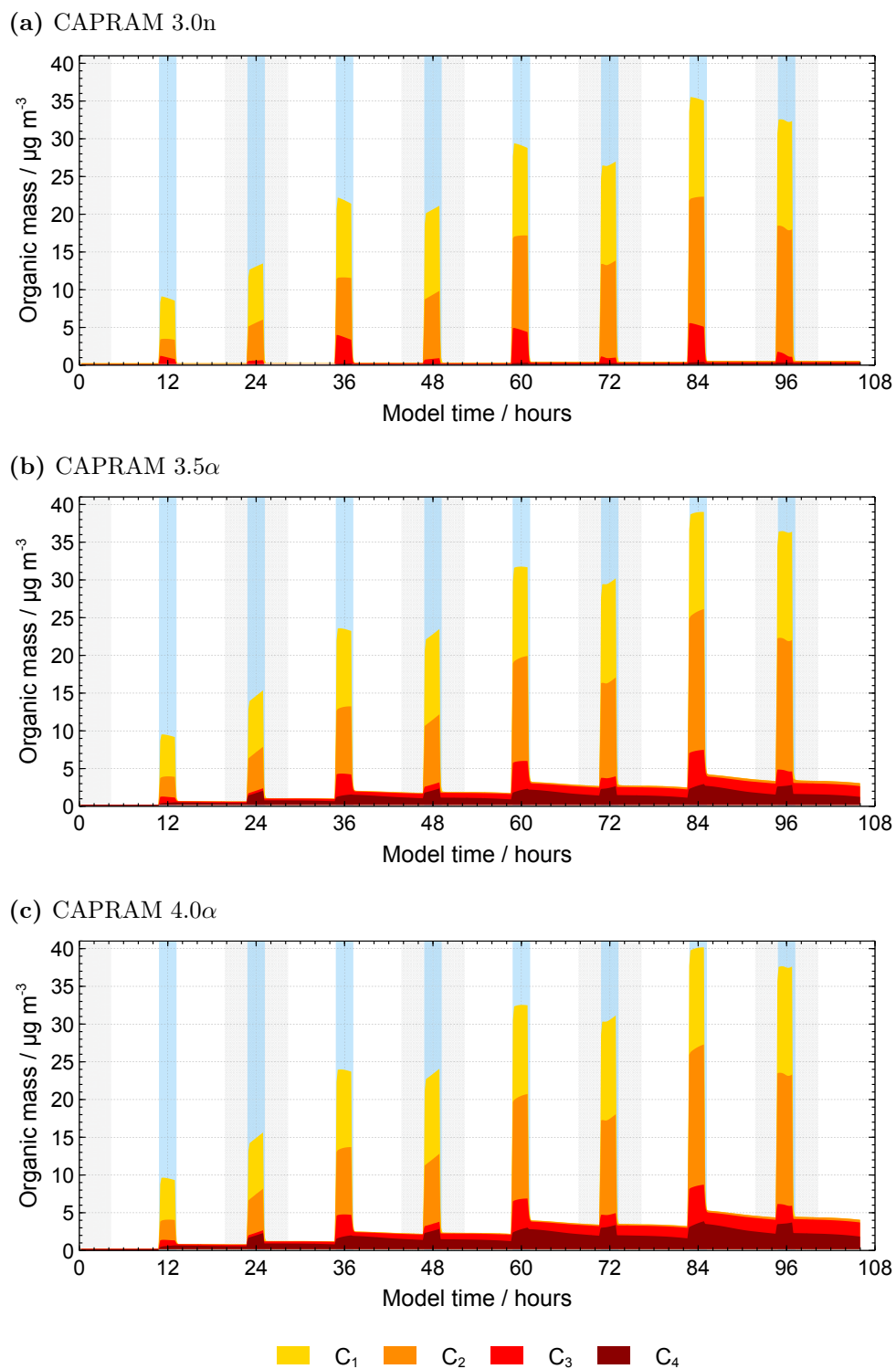
with less functional groups and thus a lower O:C ratio. Molecules have been less water-soluble. During non-cloud periods, the Henry’s Law constant was not high enough to allow significant mass increases at the lower relative humidity levels. In the new mechanisms, highly functionalised molecules with high O:C ratios are observed, which stay in the aqueous phase even at lower relative humidity values during non-cloud periods. Oxidation still most likely occurs at H-atoms with a low *BDE*, which is typically at functionalised carbon atoms. Thus, hydrocarbons are oxidised to alcohols, then carbonyl compounds, and finally carboxylic acids. Therefore, in most of the oxidised organic compounds a carboxyl group is found, which is resembled by the analysis of compound classes during non-cloud periods in Figure 6.13.

During cloud periods, carboxylic acids (functionalised or not) remain an important constituent of the aqueous phase. The relative fraction of di- and polycarboxylic acids is, however, significantly reduced (see Figure 6.13a). While the absolute concentrations of dicarboxylic acids stay the same as under non-cloud conditions, their relative contributions to organic mass decrease due to more uptake of monocarboxylic acids from the gas phase under high LWC conditions. Furthermore, a significant fraction of the organic mass contains carbonyl compounds under in-cloud conditions. It is the dominant fraction under daytime conditions and slightly smaller than the sum of all carboxylic acids under night-time conditions. The major fraction are mono gem-diols (G1). Hydrated di- and polycarbonyls (G2) and hydroxy-substituted carbonyl compounds (PF) are present in significant amounts only during daytime in-cloud periods. Both classes are equally abundant, but to a much smaller extent than monocarbonyl compounds (see Figure 6.13a). With decreasing LWC upon cloud evaporation, most carbonyl compounds are released to the gas phase. Under urban in-cloud conditions, a small but significant fraction can be attributed to alcohol compounds (classes O1 and O2, blue shade in Figure 6.13a). Organic nitrates concentrations do not significantly increase during cloud periods, thus their relative contributions are negligible during in-cloud residence times.

Under remote in-cloud conditions, similar to the urban scenario, organic mass composition is dominated by carbonyl compounds (see Figure 6.13b). In contrast to the urban scenario, no variation within the carbonyl compounds is seen during day- and night-time conditions. The major fraction are mono-functionalised gem-diols. Di- and polycarbonyl compounds exist to a much smaller extent than in the urban scenario, but the fraction of functionalised carbonyl compounds has increased. The other main organic constituents are monocarboxylic acids, which may or may not be functionalised. Other compound classes show only negligible contributions to the organic mass (see Figure 6.13b). Thus, the importance of alcohol compounds and dicarboxylic acids decreases in remote areas.

### Investigation of organic particulate matter by carbon number

Another aspect of categorisation has been the chain length of the organic molecule. The organic matter has been divided into the four categories  $C_1$  to  $C_4$  according to the number of carbon atoms born by a molecule. Figure 6.14 shows the results for the organic mass

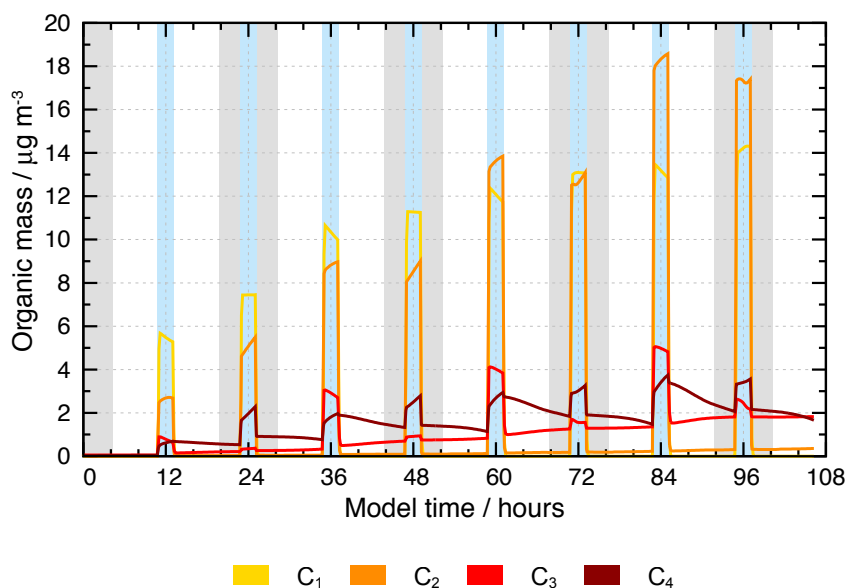


**Figure 6.14** Evolution of the organic particulate mass excluding the residual OM differentiated by chain length for the 3 different mechanisms CAPRAM 3.0p, 3.5 $\alpha$ , and 4.0 $\alpha$  under urban conditions.

fraction differentiated by chain length of the molecule excluding the residual organic mass fraction (class XX). The evolution of the organic mass is shown for CAPRAM 3.0p, 3.5 $\alpha$ , and 4.0 $\alpha$ . When comparing the three subfigures of Figure 6.14, an increased mass fraction of longer chained molecules can be observed for the more detailed chemical mechanisms. The organic mass fraction in CAPRAM 3.0p is dominated by C<sub>1</sub> and C<sub>2</sub> compounds (see Figure 6.14a). A small fraction can also be attributed to C<sub>3</sub> compounds. The C<sub>3</sub> mass is significantly larger during the day and almost negligible during night. The mass increases throughout the model run. Furthermore, it is important to notice that C<sub>4</sub> organic mass is completely negligible in the whole model runs calculated with CAPRAM 3.0p. Moreover, organic particulate mass concentrations are negligible in CAPRAM 3.0p with concentrations below 1  $\mu\text{g m}^{-3}$ .

The largest effect on the organic mass fraction is seen with the introduction of branching ratios in CAPRAM 3.5 $\alpha$ , while the extension of the C<sub>3</sub> and C<sub>4</sub> chemistry in CAPRAM 4.0 $\alpha$  causes only a small mass increase of about 1  $\mu\text{g m}^{-3}$  at the end of the model run under urban conditions (see Figure 6.14). The mass fraction of larger molecules gains importance. C<sub>4</sub> chemistry is no longer negligible in the advanced mechanisms in Figure 6.14b and 6.14c. In the middle of the last daytime cloud at model hour 84, 12.5% of the organic mass in CAPRAM 4.0 $\alpha$  belong to C<sub>3</sub> compounds and 8.5% to C<sub>4</sub> compounds. While the C<sub>3</sub> fraction is with 14% comparable in CAPRAM 3.0p to 4.0 $\alpha$ , the C<sub>4</sub> fraction is only about 1%. For night-time clouds, the contrast is even higher, with 6.7% of the organic mass being C<sub>3</sub> compounds in CAPRAM 4.0 $\alpha$  at the middle of the last cloud period at model hour 96 and 9% being C<sub>4</sub> compounds. In CAPRAM 3.0p, this fraction is only 3.4% for C<sub>3</sub> compounds and 1% for C<sub>4</sub> compounds. However, all mechanisms have in common that under in-cloud conditions organic mass is dominated by C<sub>1</sub> and C<sub>2</sub> compounds.

As already discussed, largest growth rates in particulate organic mass production are seen for CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$  with maximum concentrations of 4 and 5  $\mu\text{g m}^{-3}$  additional organic material, respectively. The maximum concentrations are directly after the last daytime cloud. In the values given, the residual organic mass of 7.3  $\mu\text{g m}^{-3}$  is excluded. In contrast to in-cloud residence times, organic matter is mainly composed of larger C<sub>3</sub> and C<sub>4</sub> molecules. For a better evaluation of the organic mass processing, the data in Figure 6.14 has been replotted as a line plot instead of a stacked area plot. From Figure 6.15 a major restriction of the current mechanism becomes clear, which is a general restriction for all modelling studies. Although very detailed, the chemical mechanism is restricted to compounds with no more than four carbon atoms. This restriction results in the degradation of organic matter during non-cloud periods due to missing input from oxidation products of higher molecular weight compounds. In Figure 6.15, no increase is seen during non-cloud periods for C<sub>1</sub> compounds. A constant but negligible increase of less than 0.5  $\mu\text{g m}^{-3}$  is observed for C<sub>2</sub> compounds. C<sub>3</sub> compounds increase constantly throughout the model run to final concentrations of about 2  $\mu\text{g m}^{-3}$ . C<sub>4</sub> compounds show the highest concentrations during non-cloud periods with up to 3.5  $\mu\text{g m}^{-3}$  directly after the cloud period. However, due to the missing input of C<sub>≥5</sub> chemistry, their production is restricted to cloud periods and concentrations decrease during non-cloud periods (see Figure 6.15.)



**Figure 6.15** Re-evaluation of the evolution of the organic particulate mass differentiated by chain length in CAPRAM 4.0 $\alpha$  under urban conditions.

More importantly, the larger  $C_4$  organic molecules produced in the model during cloud periods have the potential to remain in the aqueous after the evaporation of the cloud. In contrast, the smaller  $C_1$  to  $C_3$  compounds are predominantly released to the gas phase upon cloud evaporation as their HLC is not high enough for the remainder of these compounds in the aqueous phase under these low LWC conditions. During cloud periods between 1 and  $2 \mu\text{g m}^{-3}$  of  $C_4$  compounds are taken up at the beginning of the cloud period and further compounds are produced throughout the whole cloud period. During the day, almost all organic  $C_4$  compounds initially dissolved in cloud droplets remain in the particle phase upon cloud evaporation. On the contrary, at night most  $C_4$  compounds are released back to the gas phase right after the evaporation of the cloud. The different behaviour is likely to derive from the different radical regimes present under these distinct conditions. As given above, a large fraction of the organic matter are dicarboxylic acids. During the day, the dominant oxidant is the OH radical, which preferably reacts by H-atom abstraction at non-carboxyl groups in the organic rest of the DCAs. Subsequent reactions will lead to more oxygenated and thus water-soluble compounds, which remain in the aqueous phase even during times of low LWC. At night, the nitrate radicals is the predominant oxidant. For reactions of  $\text{NO}_3$  with dissociated carboxylic acids, electron transfer is preferred over H-atom abstraction. The resulting acyloxy radical will fragment to  $\text{CO}_2$  and an  $C_3$  alkyl radical. The data in Figure 6.15 suggests that the smaller fragments will not remain in the aqueous phase upon cloud evaporation.

Therefore, even larger mechanisms considering the chemistry of  $C \geq 5$  compounds are needed to adequately describe organic mass production in particles. Future studies should aim to apply GECKO-A to extent CAPRAM to higher carbon numbers and investigate trends of the discussed behaviours of organic compounds in this section.

In the remote scenario, differences between the various CAPRAM versions are substantially smaller. For comparison, results from the remote scenario are shown in the Appendix



in Figure I.2, page 902. In contrast to the urban scenario, negligible additional organic matter is found during non-cloud periods in either CAPRAM 3.5 $\alpha$  or CAPRAM 4.0 $\alpha$ . The amount of additional C<sub>3</sub> compounds in the 3.5 $\alpha$  and 4.0 $\alpha$  mechanisms is small. There is an additional organic mass fraction deriving from C<sub>4</sub> compounds, yet the concentration is below half a microgram per cubic meter even during cloud periods.

Explanations for the different behaviour are a decreased burden of organic trace gases in remote areas. Moreover, a different composition is found in both regimes. While in remote areas, isoprene and terpene are the main emitants, in urban areas the regime comprises a great variety of different organic compounds including aromatic compounds, alkanes and their oxidations products. The different composition affects the distribution of the oxidation products and different water-solubilities may lead to different SOA yields.

## 6.2.4 Influence of the extended organic scheme on inorganic radical oxidants

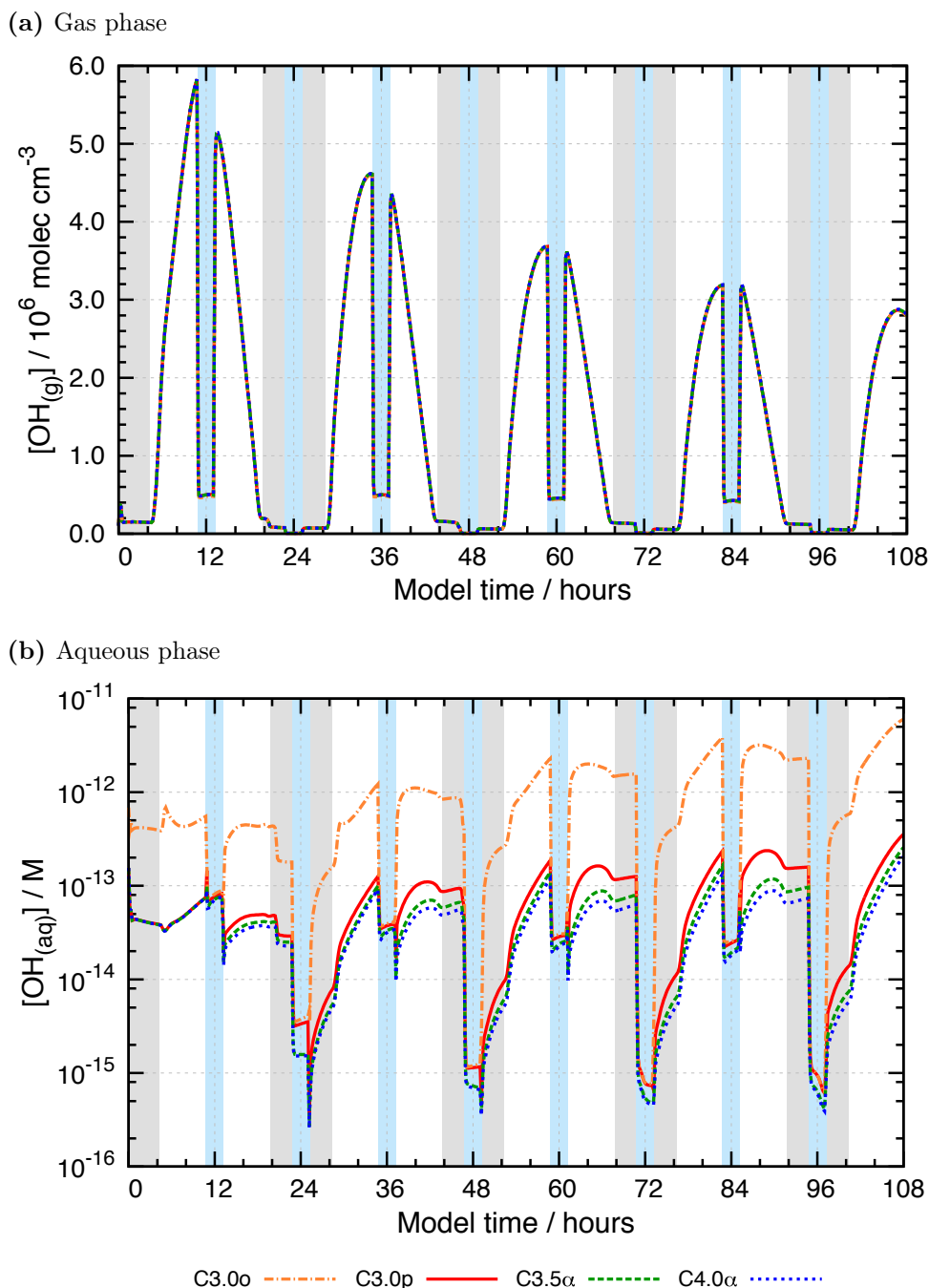
The major degradation pathway of organic compounds is initiated by inorganic radicals and particularly hydroxyl radicals. These radicals play an important role in both, the gas and the aqueous phase. Therefore, the current section investigates the budgets of the most important inorganic radical oxidants OH, NO<sub>3</sub> and HO<sub>2</sub>/O<sub>2</sub><sup>-</sup>.

### 6.2.4.1 OH chemistry

Figure 6.16 shows the concentration-time profiles of the hydroxyl radical in the gas and the aqueous phase for the four mechanisms CAPRAM 3.0o/p, 3.5 $\alpha$ , and 4.0 $\alpha$  under urban conditions. A diurnal variation with maximum concentrations right before each daytime cloud can be observed in either phase. During cloud periods concentrations are significantly decreased.

As already discussed in section 5.5, additional parameterisations for the reactions of hydroxyl radicals with dissolved organic compounds (WSOC and HULIS) led to a large decrease of aqueous phase hydroxyl concentrations of at least an order of magnitude during non-cloud periods in CAPRAM 3.0p compared to CAPRAM 3.0o (see Figure 6.16b).

The increased number of organic compounds in CAPRAM 3.5 $\alpha$  led to further decreased hydroxyl radical concentrations (mind the logarithmic scale in Figure 6.16b). Additional decreases in aqueous phase OH radical concentrations caused by additional organic compounds in CAPRAM 4.0 $\alpha$  are less pronounced, but still significant. The increase in reactions in CAPRAM 4.0 $\alpha$  totals to about 3000 compared to CAPRAM 3.5 $\alpha$ . The resulting hydroxyl radical concentrations are up to a factor 0.75 smaller. Therefore, there is a trend of reduced hydroxyl radical reactions with an increasing complexity of the organic description in the chemical scheme. This underlines the importance of organic compounds as a sink for tropospheric radicals and the influence on the atmospheric oxidation capacity.



**Figure 6.16** Concentration-time profiles of hydroxyl radicals in the gas (a) and the aqueous phase (b) for the different CAPRAM versions under urban conditions.

Hydroxyl radical concentrations in the aqueous phase vary largely over 3 to 4 orders of magnitude between  $\sim 10^{-16}$  M and  $10^{-11}$  M in the various CAPRAM versions. High concentrations are observed during the day, while night-time clouds cause a large decrease in concentrations of up to two orders of magnitude. Concentrations recover until the daytime cloud period, where the maximum concentrations are observed right before cloud formation. The largest growth rate in the radical concentrations is observed in the early morning hours upon sunrise (see Figure 6.16b).

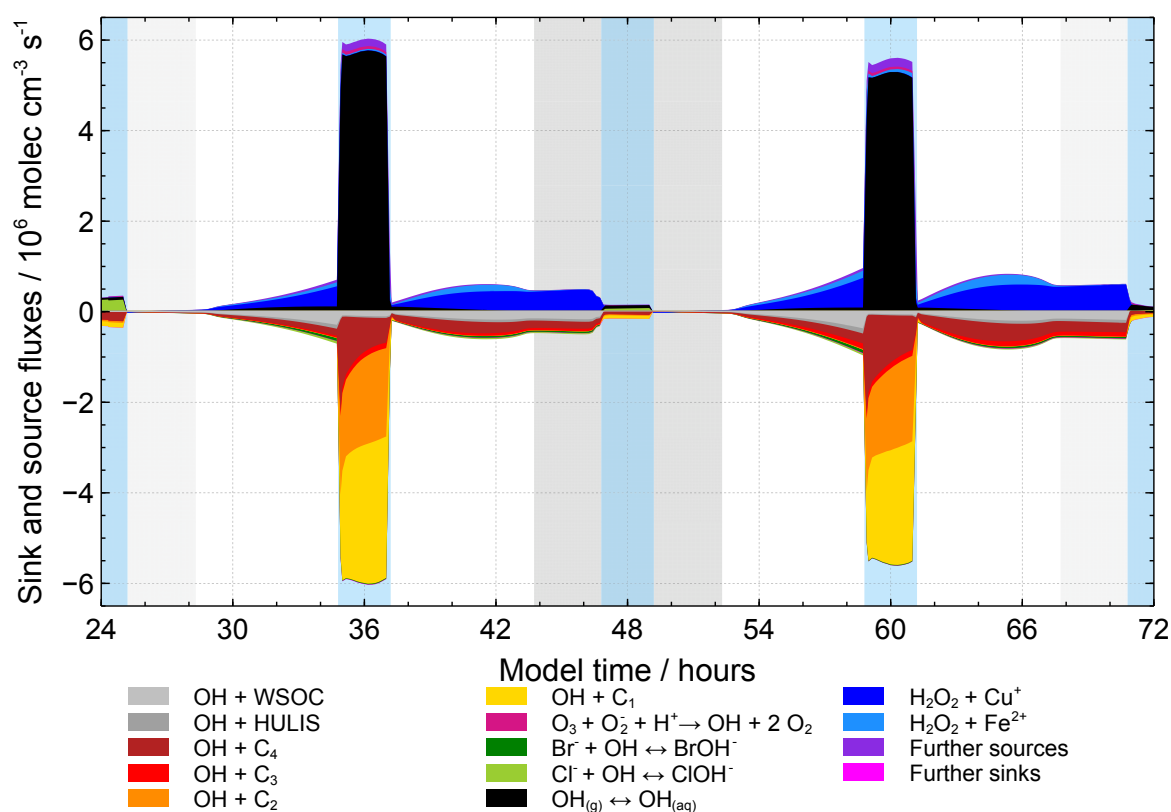
There is no feedback from the additional aqueous OH radical sinks by the extended aqueous phase organic scheme on the gas phase hydroxyl radical budget (see Figure 6.16a). The OH concentration-time profiles of all CAPRAM versions are indistinguishable from each other. The model results reflect the concentrations from previous model studies and measurements very well (see, e.g., the review of *Stone et al.*, 2012 for an overview and comparison), which reflects the high quality of the inorganic reaction scheme in CAPRAM and the MCM. Gas phase measurements in urban areas range from  $1.2 \cdot 10^6$  to  $2 \cdot 10^7$  molecules  $\text{cm}^{-3}$  (*Stone et al.*, 2012). More measured data in the same range can be found in the publications of *Lu et al.* (2013), *Ren et al.* (2013), *Worton et al.* (2013), and *Commane et al.* (2010). The modelled maximum concentrations of  $3 - 6 \cdot 10^6$  molecules  $\text{cm}^{-3}$  lie well within this range (see Figure 6.16a). Moreover, the diurnal variation matches well with the experimentally derived results.

Modelled hydroxyl radical concentrations compare well with previous CAPRAM studies. Urban aqueous phase non-cloud concentrations between  $10^{-14}$  and more than  $10^{-12}$  M in the study of *Tilgner et al.* (2013) are in the range of the CAPRAM 3.0 scenarios in this study. Cloud droplet concentrations of  $10^{-14}$  M or less during the day are smaller than in this study, but night-time in-cloud concentrations of less than  $10^{-15}$  M are in the same order in this study and the study of *Tilgner et al.* (2013). Hydroxyl radical concentrations inferred from simple box model studies with CAPRAM 2.4 and no cloud present by *Ervens et al.* (2003) gave maximum concentrations of  $1.1 \cdot 10^{-13}$  M, which compare well with the CAPRAM 3.0p scenario of this study.

For a more detailed investigation, time-resolved analyses of the chemical sink and source fluxes have been performed for the hydroxyl radical in the simulations with CAPRAM 4.0 $\alpha$ . These fluxes are shown in Figure 6.17 for the urban scenario. For clarity, only the second and third model days are shown as the chemical fluxes show a similar diurnal variation every model day with only a slightly varying strength. Moreover, single organic compounds have been grouped again according to the carbon number in each molecule.

Despite decreased concentrations of aqueous hydroxyl radicals during cloud periods, chemical fluxes in the aqueous phase are significantly increased during daytime clouds with values around  $6 \cdot 10^6$  molecules  $\text{cm}^{-3} \text{s}^{-1}$  (see Figure 6.17). The dominant source during this time is uptake from the gas phase. Degradation is solely caused by reaction with organic compounds with a relative contribution of more than 99.5% to the overall sinks. Smaller compounds show larger contributions to the OH degradation than larger organic compounds.  $\text{C}_3$  compounds form an exception as the analysis of their chemical fluxes shows only minor contributions to OH radical sinks compared to the organic compounds. During cloud periods, the effect of the additional WSOC and HULIS content in cloud droplets is negligible for the sinks of OH radicals.

During night-time clouds, the dominant sinks for OH radicals are the reactions with  $\text{C}_1$  and  $\text{C}_4$  compounds, so that a trend of an influence of the chain length of an organic molecule is not observed. Under night-time in-cloud conditions, the decay of the  $\text{ClOH}^-$  radical anion is another important source for aqueous hydroxyl radicals.



**Figure 6.17** Time-resolved production (positive values) and degradation fluxes (negative values) of aqueous phase hydroxyl radicals for the second model day in the simulation with CAPRAM 4.0 $\alpha$  under urban conditions.

Under non-cloud conditions, chemical fluxes are smaller. There is little variation in the content of day- and night-time sinks and source fluxes. Only the strength of the chemical fluxes changes. With sunrise, the fluxes increase up to their maximum value under non-cloud conditions right before the daytime cloud. After the cloud period, fluxes are significantly decreased (in the order of  $10^5 \text{ molecules cm}^{-3} \text{ s}^{-1}$ ) and have to recover again until they start to decrease in the late afternoon hours. After sunset, chemical fluxes stabilise and a very slight increase is observed. After the night-time cloud periods, fluxes are decreased again. Fluxes remain at negligible levels until sunrise.

The dominant source for aqueous hydroxyl radicals under non-cloud conditions is the Fenton-like reaction of copper(I) with hydrogen peroxide. Under daytime conditions, a significant contribution of the Fenton-reaction of iron(II) with hydrogen peroxide is observed. The major loss process is the reaction with organic compounds with a relative contribution of 89.2% to the overall sinks (see Figure 6.17). In contrast to in-cloud conditions, sinks for OH are dominated by large compounds, i.e. WSOC and HULIS species and C<sub>4</sub> compounds. To a smaller extend C<sub>3</sub> are a sink for hydroxyl radicals as well. Minor contributions are seen from inorganic halogen recycling, i.e. the reaction of OH with Br<sup>-</sup> to form the radical anion BrOH<sup>-</sup>.

Hydroxyl radicals are expected to react preferably with dissolved organic matter. The identification of C<sub>4</sub> and C<sub>3</sub> compounds as well as WSOC/HULIS species as the most

important organic reaction partners can be explained by the composition of the organic particulate matter during non-cloud periods. As already discussed in subsection 6.2.3.2, particulate matter during non-cloud periods is mainly composed of  $C_4$  compounds and to a smaller extend of  $C_3$  compounds (compare Figure 6.14). Hence, the availability of only  $C_4$  and  $C_3$  compounds as organic reaction partners is reflected in the chemical sink fluxes of aqueous hydroxyl radicals. As the chemical sink fluxes recover in the early afternoon hours, concentrations of the dissolved  $C_3$  and  $C_4$  compounds decrease. With smaller concentrations, sink fluxes begin to decrease in the late afternoon hours.

Due to the significance of the hydroxyl radical to the tropospheric oxidation capacity and the radical budget, a discussion for remote conditions shall be given in the following. Under remote conditions, OH radicals show a similar diurnal variation at slightly different concentration levels ( $1.5 - 4 \cdot 10^6$  molecules  $\text{cm}^{-3}$ , compare Figure I.3, page 903, in Appendix I.2). In the gas phase concentrations are about a factor of 2 smaller, due to the smaller burden of organic compounds and, hence, less HOx production and recycling.

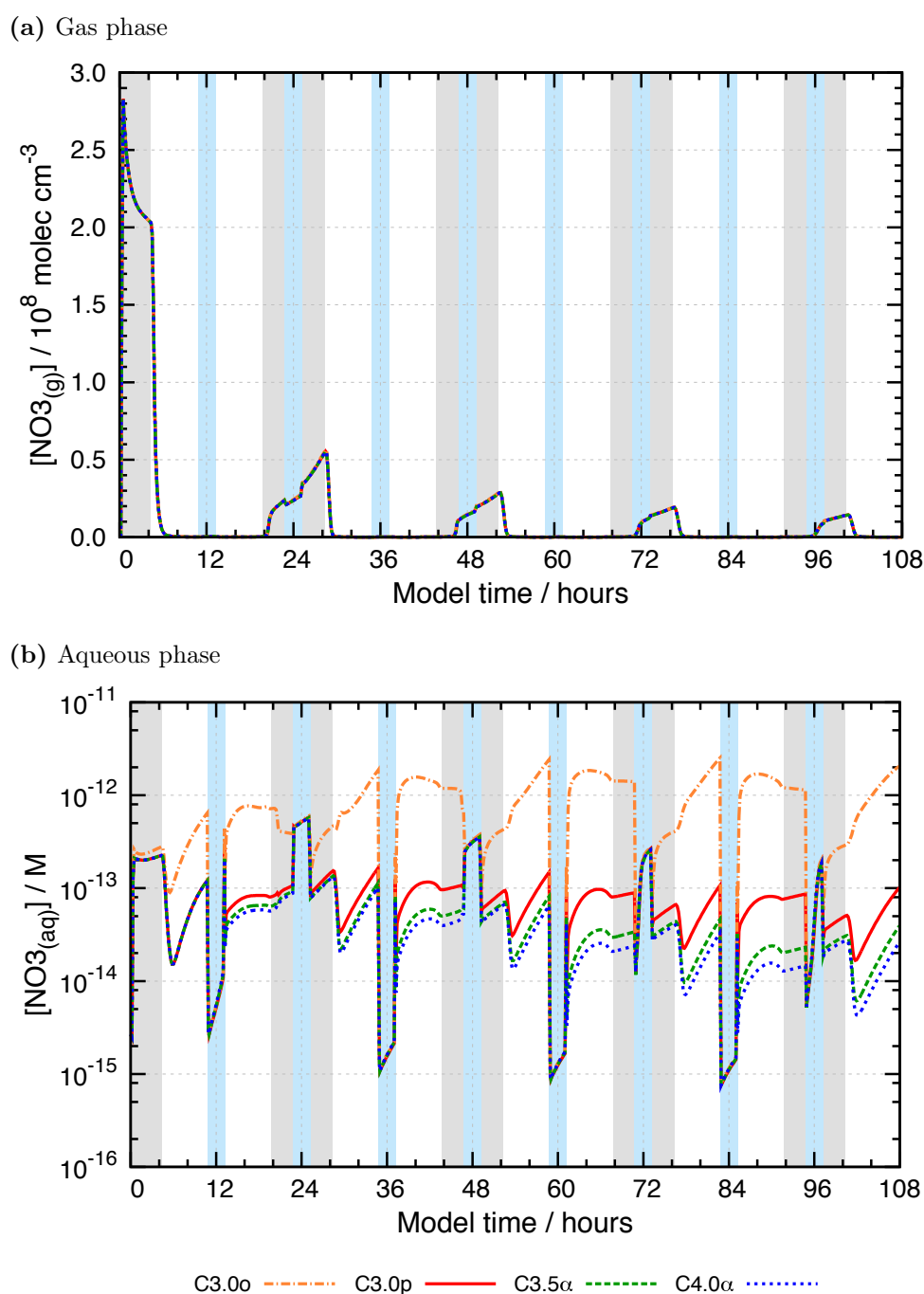
Aqueous phase concentrations are increased in the remote scenario compared to the urban case due to the smaller burden of dissolved organic material and therefore less sinks (compare Figure I.3b and 6.16b). The introduction of the OH/ $\text{NO}_3$  + WSOC/HULIS parameterisations has a similar effect than under urban conditions, but differences between the other CAPRAM versions are smaller due to the cleaner environment. They are most noticeable after daytime cloud periods.

Differences can also be observed in the composition and strength of the chemical sink and source fluxes. Fluxes, such as concentrations, are reduced by a factor of about 2. Organic compounds remain the predominant hydroxyl radical sink. During cloud periods, small organic compounds contribute even more to the chemical sink fluxes while large organic compounds dominate OH sinks during non-cloud periods

Under remote conditions, halogen recycling does not play a role for the formation or degradation of hydroxyl radicals. Main differences are observed for the chemical source fluxes of OH. During the day, the contributions of the Fenton reaction ( $\text{Fe}^{2+} + \text{H}_2\text{O}_2$ ) is smaller than under urban conditions. The most striking differences occur during cloud periods. Uptake is not the dominant source anymore. During the day, it remains the largest source contributing to about 40 to 60% of all sources. A large fraction of the hydroxyl radicals is generated by the Fenton reaction or the Fenton-like reaction of copper(I) with hydrogen peroxide. A significant fraction of hydroxyl radicals are directly generated from hydrogen peroxide photolysis. Another fraction is the indirect result of subsequent reactions from the reaction of ozone with the superoxide radical anion  $\text{O}_2^-$ . During the night, the main source is the reaction of iron(II) with  $\text{H}_2\text{O}_2$ . A large fraction of the hydroxyl radicals still derives from uptake from the gas phase.

6.2.4.2 NO<sub>3</sub> chemistry

The nitrate radical has been investigated as it is important for night-time chemistry and its chemistry with organic compounds is also part of protocol for mechanism generation. As a consequence of elevated NO<sub>x</sub> concentration and emission levels in urban areas, the importance of the nitrate radical is restricted mainly to these regions (see, e.g. *Tilgner and Herrmann, 2010, Tilgner et al., 2013*). Therefore, this subsection focuses on urban conditions only. The modelled concentration-time profiles are given in Figure 6.18 for the



**Figure 6.18** Concentration-time profiles of nitrate radicals in the gas (a) and the aqueous phase (b) for the different CAPRAM versions under urban conditions.

gas and the aqueous phase, respectively. Measurements observed night-time  $\text{NO}_3$  mixing ratios typically of a few tens of ppt (see, e.g., *Asaf et al.*, 2010, *Stutz et al.*, 2010, *Fry and Sackinger*, 2012, *Wang et al.*, 2013). This corresponds to nitrate radical concentrations in the order of mid to high  $10^7$  molecules  $\text{cm}^{-3}$  to low to mid  $10^8$  molecules  $\text{cm}^{-3}$ . Modelled concentrations meet this range during the first 1 to 2 nights. Thereafter, modelled concentrations are at the lower end or slightly below the measurements indicating a slight under-estimation of  $\text{NO}_3$  radical concentrations in the model. The diurnal variation of high concentrations during the night and low concentrations due to rapid photolysis during the day is captured well by the model.

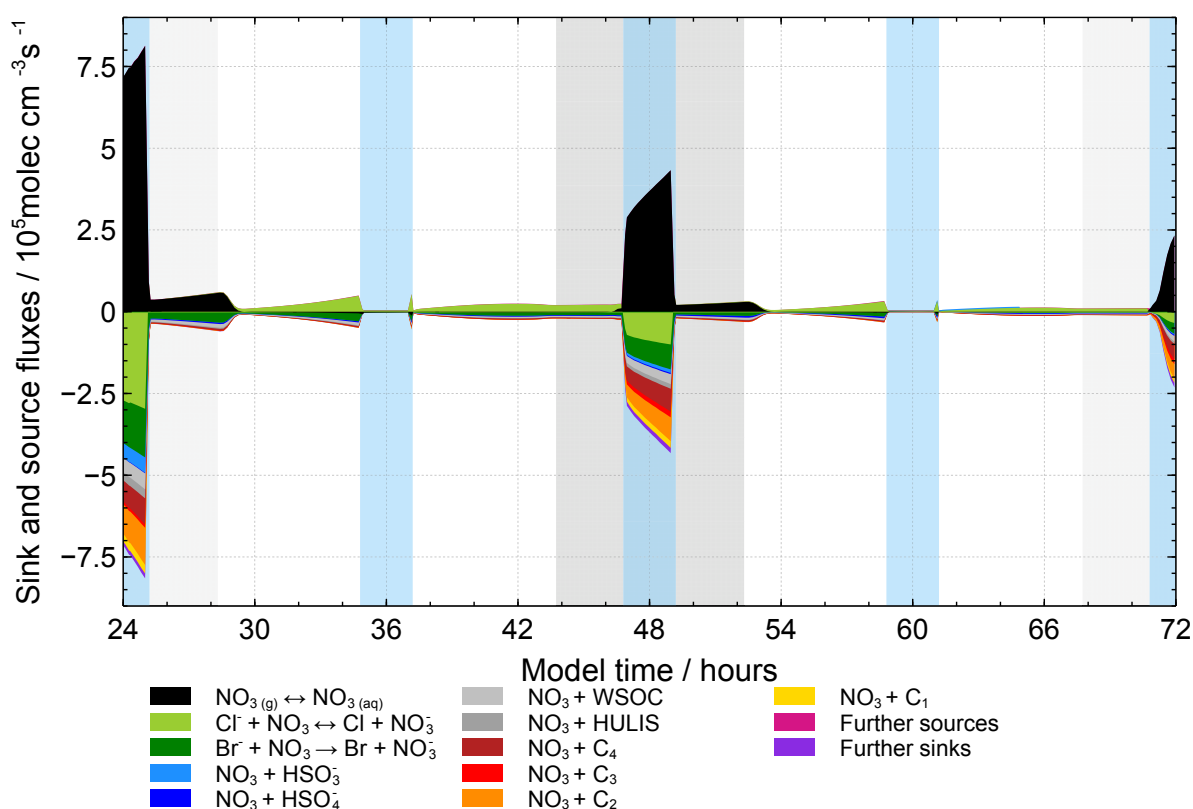
As for the OH radical, no effects of the new chemical schemes on the gas phase nitrate radical concentrations is seen, when comparing the different model runs in Figure 6.18a. For the aqueous phase, the largest effect comes again from the parameterisations of  $\text{NO}_3 + \text{WSOC}/\text{HULIS}$  in CAPRAM 3.0p, which reduces nitrate radical concentrations during non-clouds periods by over one order of magnitude. Further decreases in  $\text{NO}_3$  concentrations are seen in CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$ . As for the hydroxyl radical, differences are less pronounced in CAPRAM 4.0 $\alpha$ . Average concentrations range between  $10^{-14}$  and  $10^{-13}$  M during non-cloud periods for the runs with the additional  $\text{NO}_3 + \text{WSOC}/\text{HULIS}$  parameterisations.

Concentrations vary largely during cloud periods. During the first two night clouds, elevated concentration levels in the order of high  $10^{-13}$  M with a slight increase throughout the cloud period are observed. At the last two night-time cloud periods, initial concentrations are only about  $10^{-14}$  M but increase rapidly by over one order of magnitude. During daytime clouds,  $\text{NO}_3$  concentrations are decreased by up to two orders of magnitude to concentration levels around  $10^{-15}$  M.

It should be noted that the aqueous phase diurnal variation is contrary to the gas phase variation (compare Figure 6.18a with 6.18b). Due to a coupling of the nitrate radical chemistry to halogen chemistry, a daytime profile of the  $\text{NO}_3$  radical concentrations is found in the aqueous phase. The link to the halogen chemistry is given in Figure 6.19, where the chemical source and sink fluxes of the nitrate radical are analysed. In general, large differences between cloud periods and non-cloud periods can be seen from Figure 6.19. Chemical fluxes vary by composition and strength. Moreover, it has to be distinguished between daytime and night-time fluxes.

Chemical fluxes are negligible during night-time in-cloud conditions. On the other hand, turnovers are largely increased during day-time in-cloud periods. Fluxes decrease over time throughout the whole model run, which is most noticeable for night-time in-cloud conditions in Figure 6.19.

During cloud periods, the only source for aqueous phase nitrate radicals is uptake from the gas phase. This source remains dominant after night-time cloud periods until sunrise. Thereafter, the dominant source of  $\text{NO}_3$  under urban conditions during non-cloud periods is the reaction of chlorine atoms with particulate nitrate (equilibrium E<sub>i</sub>0044 in Appendix G.2.2). As chlorine atoms possess a daytime concentration-time profile, the



**Figure 6.19** Time-resolved production (positive values) and degradation fluxes (negative values) of aqueous phase nitrate radicals for the second and third model day in the simulations with CAPRAM 4.0 $\alpha$  under urban conditions.

link to halogen chemistry imposes a daytime profile on aqueous phase nitrate radical concentrations in Figure 6.18b and explains the difference to the gas phase.

Upon sunrise, source fluxes from gas phase nitrate radicals decrease rapidly and fluxes from nitrate particle chemistry with chlorine atoms begin to increase steadily until they are disturbed by the cloud period at noon, where they decrease to a negligible strength. Upon cloud evaporation, fluxes increase again until the late afternoon, when the influence of the solar radiation becomes weaker. After sunset, source fluxes from the equilibrium of nitrate with chlorine atoms is slightly decreased.

Throughout the whole model run, reactions with bromide are an important sink for nitrate radicals and are dominant throughout non-cloud periods stressing the importance of interactions with halogen chemistry for the  $\text{NO}_3$  budget. Reactions with organic compounds are far less important than for the hydroxyl radicals. Only 35% of the sink fluxes are due to reactions with organic compounds under non-cloud conditions and between 40 and 45% of the overall sinks can be attributed to organic compounds under in-cloud conditions. Again, only the chemistry of large organic compounds serves as a sink for nitrate radicals during non-cloud periods.

The chemical system is drastically changed during night-time clouds. Fluxes are significantly increased. The only source for nitrate radicals is the uptake from the gas phase. The



equilibrium between nitrate radicals, chloride and chlorine atoms and nitrate has become a sink for nitrate radicals rather than a source. In general, inorganic chemistry is much more important than for OH radicals. Besides the reaction with chloride, the reaction with bromide is another important sink for  $\text{NO}_3$ . Furthermore, reactions with sulfur species contribute to the loss fluxes. Reactions with organic compounds make up only about half of the loss fluxes during cloud periods. Main contributions derive from  $\text{C}_2$  and  $\text{C}_4$  compounds so that a clear trend of the influence of the size of a molecule on the degradation of nitrate radicals is not observable.

Previous CAPRAM model studies gave contradicting results. In the study of *Ervens et al.* (2003) with CAPRAM 2.4, an increase in nitrate radical aqueous phase concentrations were observed in the day-to-day variation throughout the model run. Maximum concentrations of  $2.5 \cdot 10^{-13} \text{ M}$  were found at the beginning of the last night. More importantly, the diurnal variation was linked to the gas phase concentrations and maximum concentrations were observed during night-time hours. During darkness a decrease in concentrations was observed, so that maximum concentrations were found at the beginning of each night. Compared to this study, results were in-between the scenarios CAPRAM 3.0o and p. An increase in concentrations was observed close to the 3.0o scenario, but with concentrations an order of magnitude smaller as in the 3.0p scenario. However, the most striking difference remains to be the different diurnal variation.

Later model studies by *Tilgner et al.* (2013) with an extended  $\text{C}_3$  and  $\text{C}_4$  chemistry in CAPRAM 3.0i gave results much closer to the current study. The diurnal variation with a daytime-profile and links to halogen chemistry in the aqueous phase was also observed in the study by *Tilgner et al.* (2013). Moreover, decreasing nitrate radical concentrations throughout the model runs were seen as in the scenarios with the WSOC/HULIS parameterisations in this study. Concentrations were initially higher in the order of  $10^{-12} \text{ M}$  and decreased to values around  $10^{-13} \text{ M}$  at the end of the model run (see *Tilgner et al.*, 2013). Thus, concentrations were about an order of magnitude higher in the study of *Tilgner et al.* (2013) than in this study, resembling concentrations in CAPRAM 3.0o without the WSOC/HULIS parameterisations, which were developed during this dissertation. However, the diurnal variation and the day-to-day variation in the study of *Tilgner et al.* (2013) is more similar to the scenarios with the WSOC/HULIS parameterisations in this study.

#### 6.2.4.3 Comparison of OH and $\text{NO}_3$ chemistry

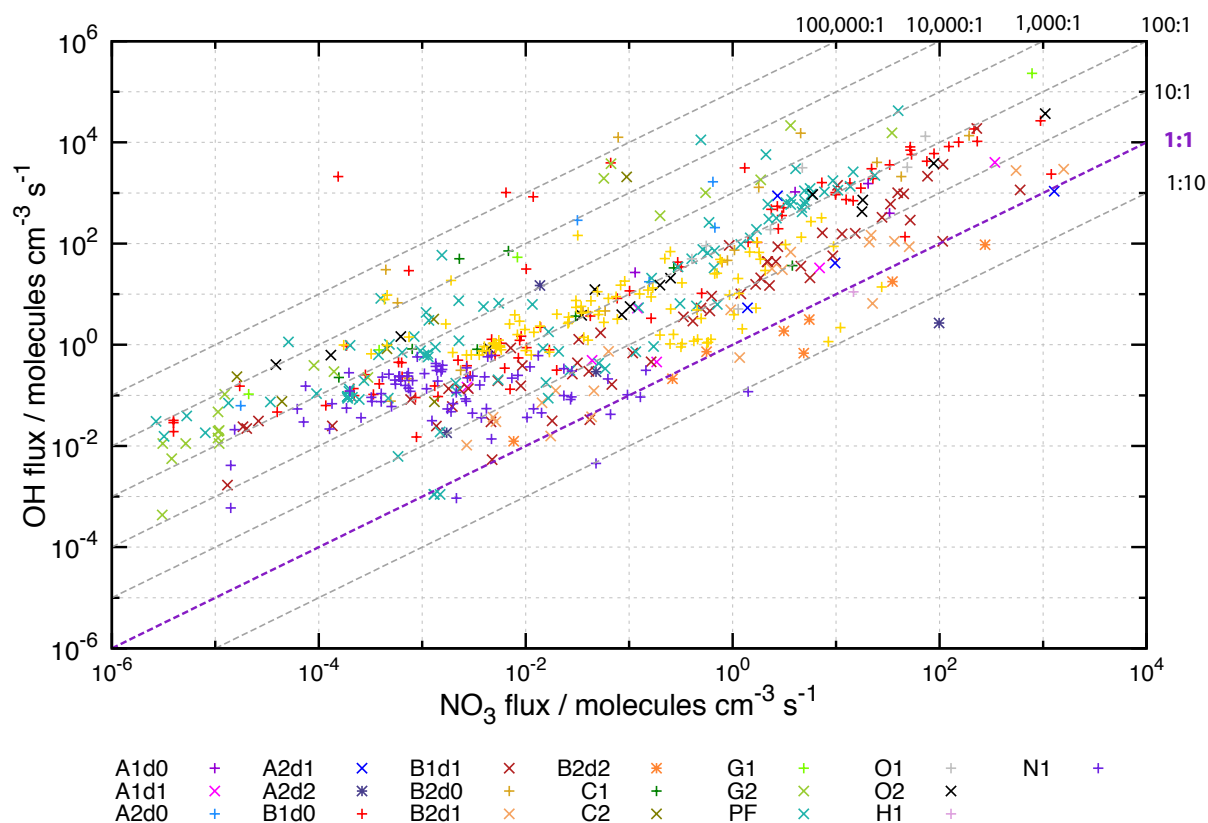
Hydroxyl and nitrate radicals are the two most important atmospheric radical oxidants and have consequently both been considered in the generator protocol. Due to their importance, a comparison of both radicals and their chemistry is performed in the current subsection.

Figure 6.20 shows the direct comparison of the chemical turnovers of the hydroxyl radical against the nitrate radical in reactions with organic compounds. In this figure, the various reactions are distinguished by compound class as it was performed previously in subsection 6.2.3.2 with slight modifications. For a more detailed evaluation, the dissociation

states of organic acids have been considered and added to the compound classes A1, A2, B1, and B2:

- A1d0: Protonated monocarboxylic acids
- A1d1: Deprotonated monocarboxylic acids
- A2d0: Protonated DCAs
- A2d1: DCA mono-anions
- A2d2: DCA di-anions
- B1d0/B1d1/B2d0/B2d1/B2d2: same as for the corresponding compound classes with ‘A’ instead of ‘B’, but for substituted carboxylic acids

It is most noticeable that there are much higher turnovers by the hydroxyl radical than by the nitrate radical. Most  $\text{NO}_3$  turnovers are between  $10^{-4}$  and  $10^2$  molecules  $\text{cm}^{-3} \text{s}^{-1}$ , while OH turnovers range between  $10^{-2}$  and  $10^5$  molecules  $\text{cm}^{-3} \text{s}^{-1}$ . Typically, OH fluxes exceed  $\text{NO}_3$  fluxes by a factor 10 to 1000 and for small turnovers even by a factor of 10 000. These results manifest previous findings from CAPRAM studies investigated by *Tilgner et al.* (2013). The major improvement of the current study is the much larger database and, therefore, a higher significance of the results.



**Figure 6.20** Comparison of the turnovers of reactions of organic compounds with hydroxyl versus nitrate radicals distinguished by compound classes as given in the legend and explained in the text.

In contrast to the previous study by *Tilgner et al.* (2013), there are several reactions where the OH turnovers drastically exceed the nitrate radical turnovers by several (occasionally more than 6) orders of magnitude. Additionally to the previous study, there are a number of nitrate radical reactions with organic compounds with very small turnovers significantly below  $10^{-3}$  molecules  $\text{cm}^{-3} \text{s}^{-1}$ . Hydroxyl radical turnovers are not significantly decreased and stay above levels of  $10^{-3}$  molecules  $\text{cm}^{-3} \text{s}^{-1}$ . Therefore, for these small  $\text{NO}_3$  turnovers, the ratio of OH versus  $\text{NO}_3$  turnovers is increased by about one order of magnitude.

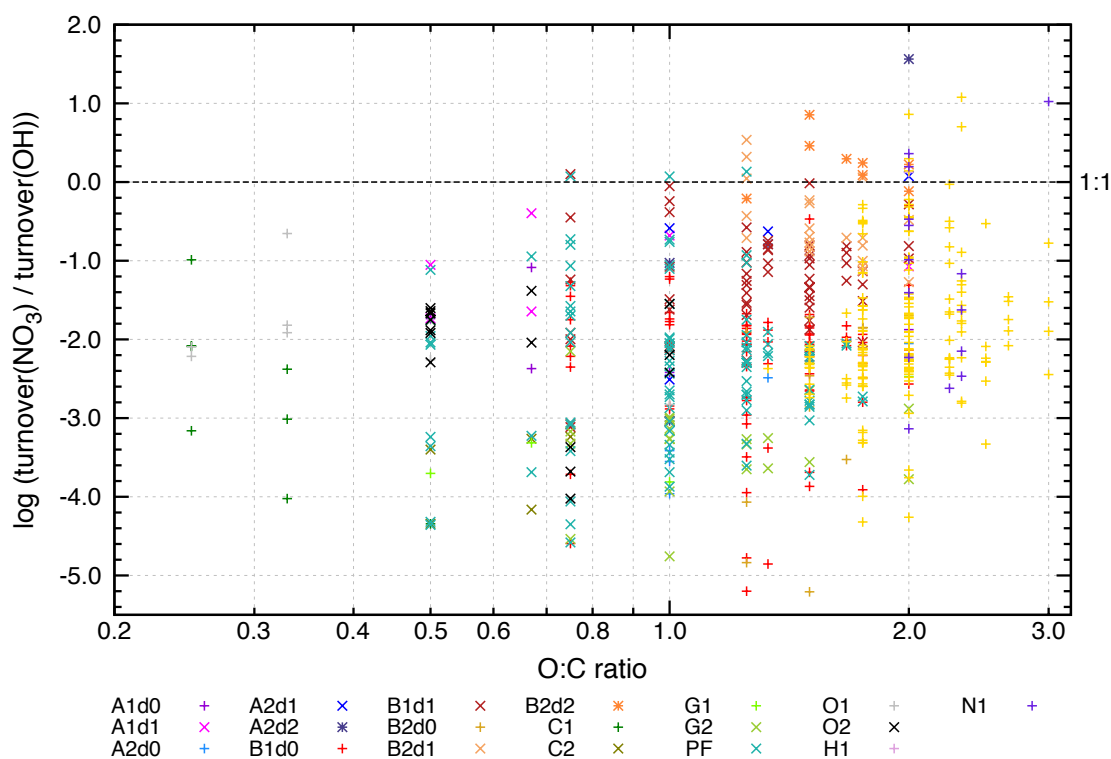
In conclusion, OH radical turnovers are significantly increased for small  $\text{NO}_3$  radical turnovers, while for larger  $\text{NO}_3$  turnovers the differences become smaller. This is due to a more rapid increase of the nitrate radical turnovers than the hydroxyl radical turnovers as the OH reactions for the larger turnovers are approaching the diffusion limit of the reaction.

Looking more detailed at the various compound classes, it can be seen from Figure 6.20 that the turnovers of carbonyl compounds (with one or more carbonyl functions in their hydrated or unhydrated form as well as hydroxy-substituted carbonyl compounds) are generally two to four orders of magnitude higher for the hydroxyl radical than for the nitrate radical. The same is true for fully protonated oxidised (hydroxy- or carbonyl-substituted) carboxylic acids and alcohol compounds including di- and polyols. Dissociated carboxylic acids and diacids can have comparable OH and  $\text{NO}_3$  radical turnovers. The range of nitrate radical turnovers compared to OH turnovers reaches from a factor of 0.01 decreased  $\text{NO}_3$  turnovers to slightly increased values of about a factor of 10 higher. Turnovers of organic nitrates show a large variability for nitrate radical reactions ranging from  $10^{-5}$  to  $10^0$  molecules  $\text{cm}^{-3} \text{s}^{-1}$ . For OH radicals, the variability is less with fluxes between  $10^{-3}$  and  $10^0$  molecules  $\text{cm}^{-3} \text{s}^{-1}$ . Hence, the ratios vary largely between 0.1 and 1000.

The decreased OH: $\text{NO}_3$  turnover ratio for dissociated carboxylic acids and diacids, especially when highly functionalised, is in agreement with the study by *Tilgner et al.* (2013). The explanation for these exceptions is a different reaction mechanism for nitrate radical reactions with dissociated carboxylic acids. For carboxylate ions, electron transfer reactions become important. This reaction type is faster than H-abstraction reactions. The electron transfer, however, is performed only by  $\text{NO}_3$  radicals and not by OH radicals. Therefore, the nitrate radical turnovers are increased for deprotonated carboxylic acids while hydroxyl radical turnovers stay at a lower level. Hence, nitrate radical turnovers can reach the same magnitude as OH radical turnovers. For highly oxidised carboxylates without a carbon bound H-atom, rate constants are significantly decreased for hydroxyl radical reactions. ETR is expected to be of minor importance and possible H-abstraction reactions at hydroxyl or carboxyl groups are slow due to the increased *BDE*. Therefore, nitrate radical turnovers, where ETR is possible, can even exceed hydroxyl radical turnovers for these highly oxidised compounds. In addition to previous CAPRAM model studies, carboxylic acids can also be substituted with nitrate functions in the new CAPRAM versions, in which case these acids count as organic nitrates. For highly oxidised organic nitrates with a carboxyl function, the same explanations apply. It should be noted, however, that due

to missing data, nitrate radical reactions with deprotonated carboxylic acids and organic nitrates with a carboxyl function have been estimated solely as electron transfer reaction. However, a fraction of these compounds might also react by H-atom abstraction and the magnitude of the turnover might therefore be overestimated. In conclusion, the reactions of nitrate radicals with deprotonated carboxylic acids must be regarded as an upper limit of this reaction type.

For a better illustration of the fact that mainly the turnovers of highly functionalised deprotonated acids in reaction with the nitrate radical exceed the OH radical turnovers, the logarithmised  $\text{NO}_3\text{:OH}$  turnover ratio has been plotted against the O:C ratio in Figure 6.21. In Figure 6.21, the O:C ratio reflects the progress of the oxidation of the organic compound as oxygen is added to the molecular structure throughout the oxidation process. Therefore, compounds to the right in Figure 6.21 with higher O:C ratios are typically higher functionalised and thus more oxidised compounds. Compared to previous CAPRAM studies by *Tilgner et al.* (2013), not only the number of data points in the plot has increased, there is also a shift to higher O:C ratios up to  $\text{O:C} = 3$ . This increase derives from the addition of nitrate radicals to double bonds, which significantly increases the O:C ratio at once. Although there is a large scatter in the data, a trend is visible of



**Figure 6.21** Comparison of the logarithmised hydroxyl radical versus nitrate radical turnovers of reactions with organic compounds against the O:C ratio distinguished by compound classes as given in the legend and explained in the text.

increasing  $\text{NO}_3\text{:OH}$  turnover ratios with an increasing O:C ratio with the exception of very low O:C ratios below 0.4. Therefore, nitrate radical reactions become especially important for highly oxidised compounds. Moreover, compounds exceeding a logarithmised  $\text{NO}_3\text{:OH}$  turnover ratio of 0 are predominantly dissociated and functionalised carboxylic acids and diacids. The high O:C ratios of mostly more than one indicate a high functionalisation. Therefore, no carbon bound hydrogen atoms might be available in these compounds.

As the many data points allow no plotting without overlap in Figure 6.21, the data has been replotted in Figure I.5 in the Appendix on page 905 for clarification, where the data was zoomed in to a  $\log(\text{NO}_3\text{:OH turnover})$  ratio from -4 to 1. Moreover, unsaturated compounds have been indicated by a box around the compound class symbol. From Figure I.5 can be seen that with the reduced nitrate radical addition rate constants derived in subsection 5.5.2, turnovers of unsaturated compounds reacting with  $\text{NO}_3$  are generally small compared to the turnovers by hydroxyl radicals. The logarithmised  $\text{NO}_3\text{:OH}$  ratio is below -1 except for one monoalcohol compound and ranges to values close to -4. Furthermore, Figure I.5 shows valuable insights on the oxidation of unsaturated compounds. For these compounds, O:C ratios of no higher than one are found. This fact underlines the importance of the addition pathway of reactions of unsaturated organic compounds with radical oxidants. The low O:C ratios of unsaturated organic compounds imply a low oxidation by H-atom abstraction as the only way to increase the O:C ratio of this compound class.

Further analysis has been performed to evaluate the importance of nitrate radical chemistry. Sink fluxes of reactions of hydroxyl and nitrate radicals with the various organic compounds in CAPRAM 4.0 $\alpha$  including WSOC and HULIS have been accumulated averaged over the whole model run, non-cloud and in-cloud periods, respectively, to identify the contributions of nitrate radicals to the oxidation of organic compounds in the aqueous phase. On average, nitrate radical chemistry accounts for about 2% of the oxidation of organic compounds in the aqueous phase under the simulated (urban) conditions. Little variation is seen between non-cloud periods (1.9%) or in-cloud periods (2.5%). The significance of nitrate radical chemistry rises during periods of darkness due to the different diurnal variations of the concentration-time profiles of both radical compounds. Under day-time in-cloud conditions, only 0.02% of the organic compounds are oxidised by nitrate due to the rapid photolytic loss of  $\text{NO}_3$ . During night-time, hydroxyl radical concentrations are low due to the missing source from ozone photolysis. Nitrate radical chemistry becomes competitive with hydroxyl radical chemistry, yet contributions to the oxidation of organic compounds in the aqueous phase are still somewhat lower from nitrate radicals (41.6%) than from hydroxyl radicals (58.4%). Thus, the significance of nitrate radical chemistry could potentially increase in winter month or higher latitudes, where solar radiation is less available.

#### 6.2.4.4 $\text{HO}_2/\text{O}_2^-$ chemistry

Another very important tropospheric radical is the hydroperoxyl radical  $\text{HO}_2$ , which is equilibrium with the superoxide radical  $\text{O}_2^-$  in the aqueous phase. Gas phase concentrations

of HO<sub>2</sub> are shown in Figure 6.22a. Again, no big differences of the extended organic schemes in CAPRAM 3.0n, 3.5 $\alpha$  and 4.0 $\alpha$  are seen compared to the CAPRAM 3.0o mechanism. The model results compare well to recent measurements; see e.g. the review of *Stone et al.* (2012), who give a concentration range in urban areas of  $2 \cdot 10^7$  to  $2 \cdot 10^9$  molecules cm<sup>-3</sup>. Further publications confirm the quality of the modelled HO<sub>2</sub> concentrations. The modelled values are within the range of measured data by *Ren et al.* (2013) and *Commane et al.* (2010). Compared to the data of the BEARPEX field campaign, the modelled data is at the upper end of the measured values. On the other hand, compared to measurements in the very polluted Beijing suburban region during the CAREBeijing 2006 field campaign, modelled values are at the very low end compared to the measurements.

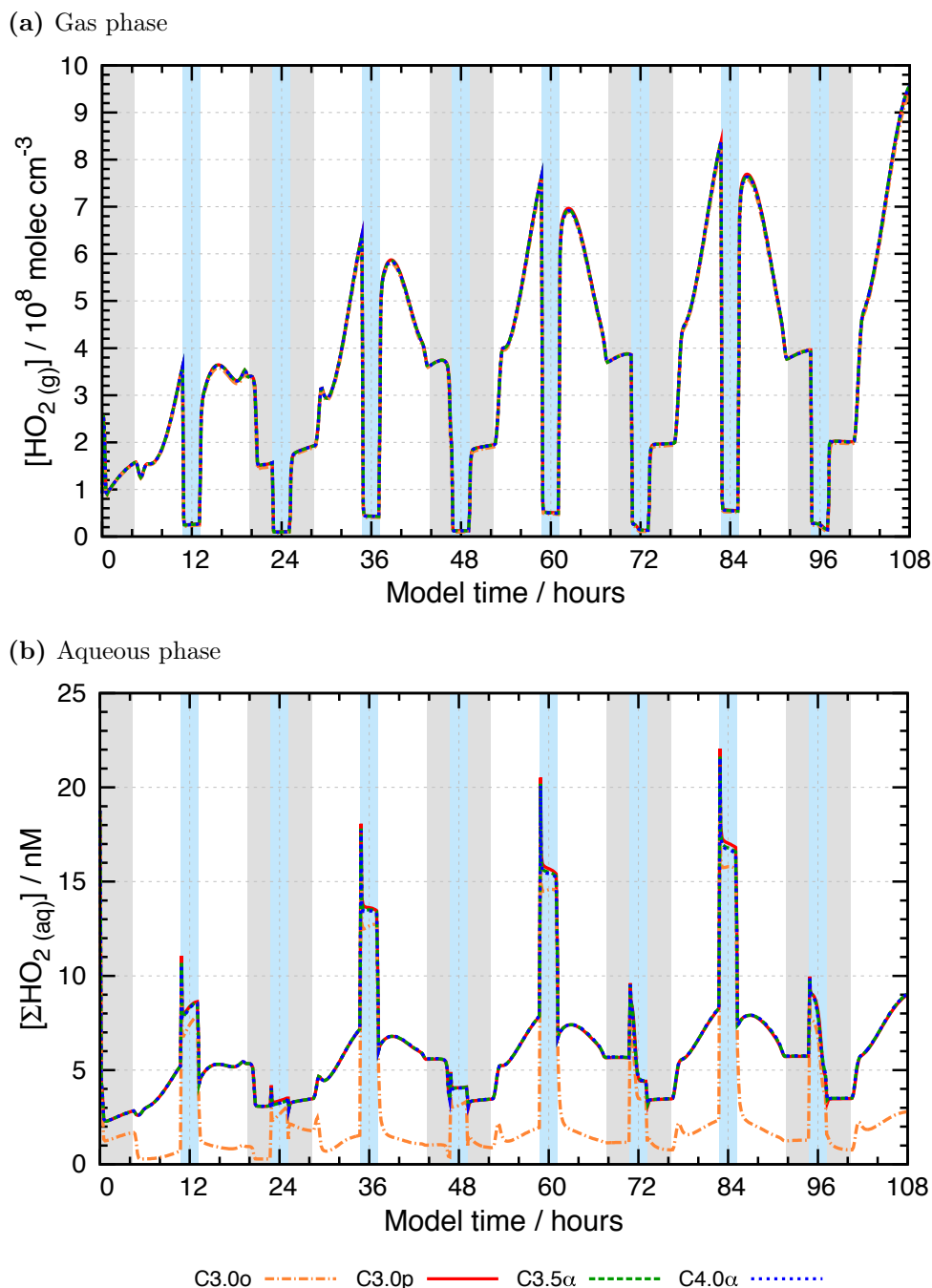
In the aqueous phase, significant differences are observed. As can be seen in Figure 6.22b, the parameterisations of hydroxyl and nitrate radical reactions with WSOC and HULIS species increase aqueous phase hydroperoxyl radical concentrations significantly especially during non-cloud periods. However, no influence from the extended explicit organic scheme is observed on concentrations of the simulations with CAPRAM 3.0p, 3.5 $\alpha$  and 4.0 $\alpha$  (see Figure 6.22b).

It should be noted that concentrations in Figure 6.22b combine the accumulated hydroxyl and superoxide radical concentrations, which is indicated by the ‘ $\Sigma$ ’ in the ordinate label. This nomenclature is used throughout this section for species, where the different dissociation and/or hydration states are combined to an overall concentration

Moreover, a pronounced diurnal variation of hydroperoxyl and superoxide radicals is observed in the runs with the WSOC/HULIS parameterisations, which is only disturbed by the cloud periods. In CAPRAM 3.0o, the typical daytime concentration profile is missing, albeit there is an expected pattern of maximum concentrations around noon and lower concentrations in the evening and during night.

In general, the sum of aqueous phase hydroperoxyl radical and superoxide concentrations are increasing with time throughout the model run. Concentrations increase from 2 to 9 nM during non-cloud periods for the mechanisms CAPRAM 3.0p, 3.5 $\alpha$  and 4.0 $\alpha$  and stay at constant levels around 2 nM for CAPRAM 3.0o. For the extended schemes, night-time in-cloud concentrations are on the same level as during non-cloud periods, while night-time in-cloud concentrations in CAPRAM 3.0o are increased and do not differ significantly from the other scenarios. During daytime cloud periods, concentrations are increased in all scenarios with increasing values throughout the model runs from about 8 to 17 nM. To understand the behaviour of the concentration-time profiles, detailed time-resolved flux analyses are necessary.

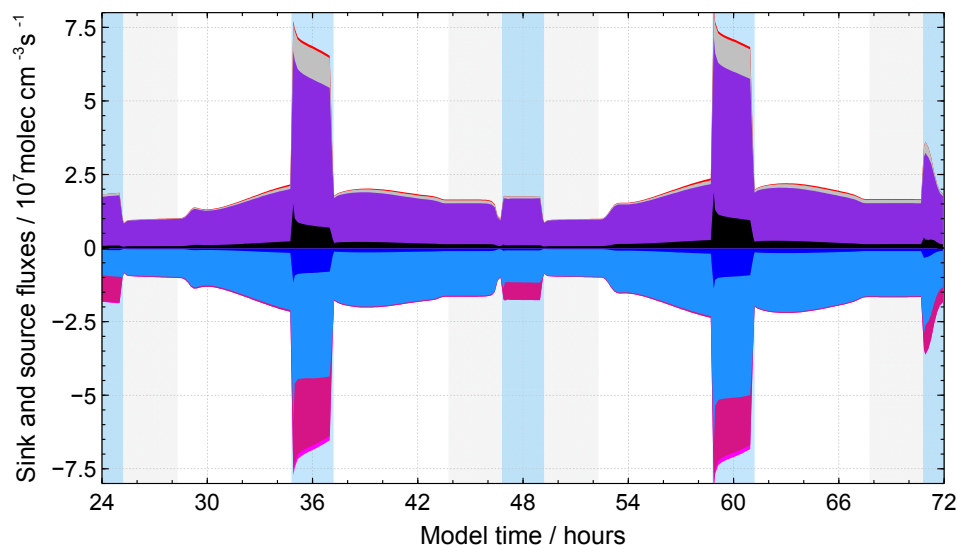
Figure 6.23 shows the evolution of the combined chemical source and sink fluxes for HO<sub>2</sub> and O<sub>2</sub><sup>-</sup> for the scenario without the WSOC/HULIS parameterisations (CAPRAM 3.0o) and the most extended organic scheme CAPRAM 4.0 $\alpha$ . It can be seen that the fluxes in both scenarios vary rather by strength than by compositions. In CAPRAM 4.0 $\alpha$ , fluxes vary between 1 and  $2.5 \cdot 10^7$  molecules cm<sup>-3</sup> s<sup>-1</sup> and have increased values between 7 and  $7.5 \cdot 10^7$  molecules cm<sup>-3</sup> s<sup>-1</sup> during daytime cloud periods. In CAPRAM 3.0o, similar fluxes



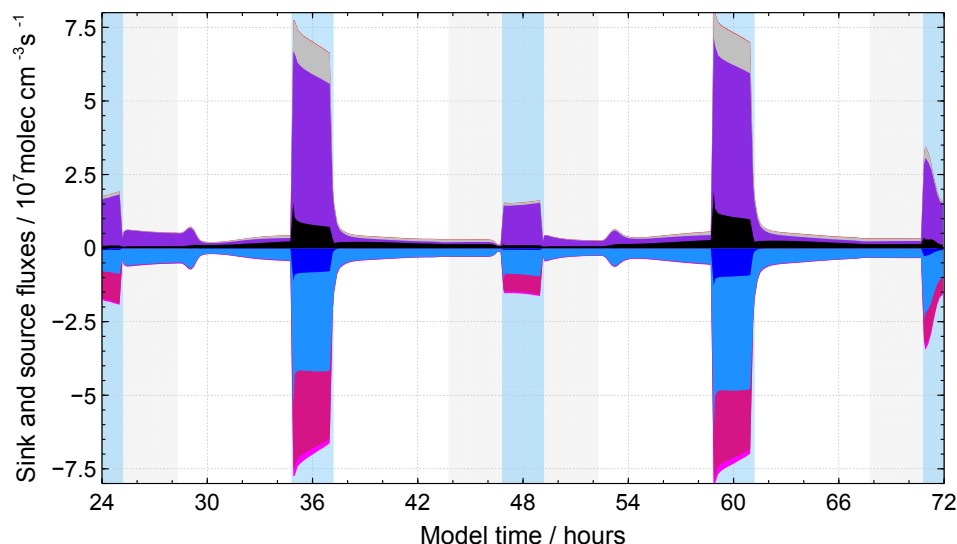
**Figure 6.22** Concentration-time profiles of the sum of hydroperoxyl and superoxide radicals in the gas (a) and the aqueous phase (b) for the different CAPRAM versions under urban conditions.

are observed during cloud periods, but during non-cloud periods fluxes are significantly decreased with values below  $5 \cdot 10^6 \text{ molecules cm}^{-3} \text{ s}^{-1}$ .

The dominant source and sink fluxes derive from the copper(I/II) recycling and overlay all other sources. Only during cloud periods, further sources from the organic chemistry and gas phase uptake are observed. To identify the real sources and sinks of  $\text{HO}_2$  and  $\text{O}_2^-$ , a net flux has to be determined for the fast and dominant copper recycling system as described in *Tilgner et al. (2013)*. The refined flux analysis is given in Figure 6.24, page 180.

(a) CAPRAM 4.0 $\alpha$ 

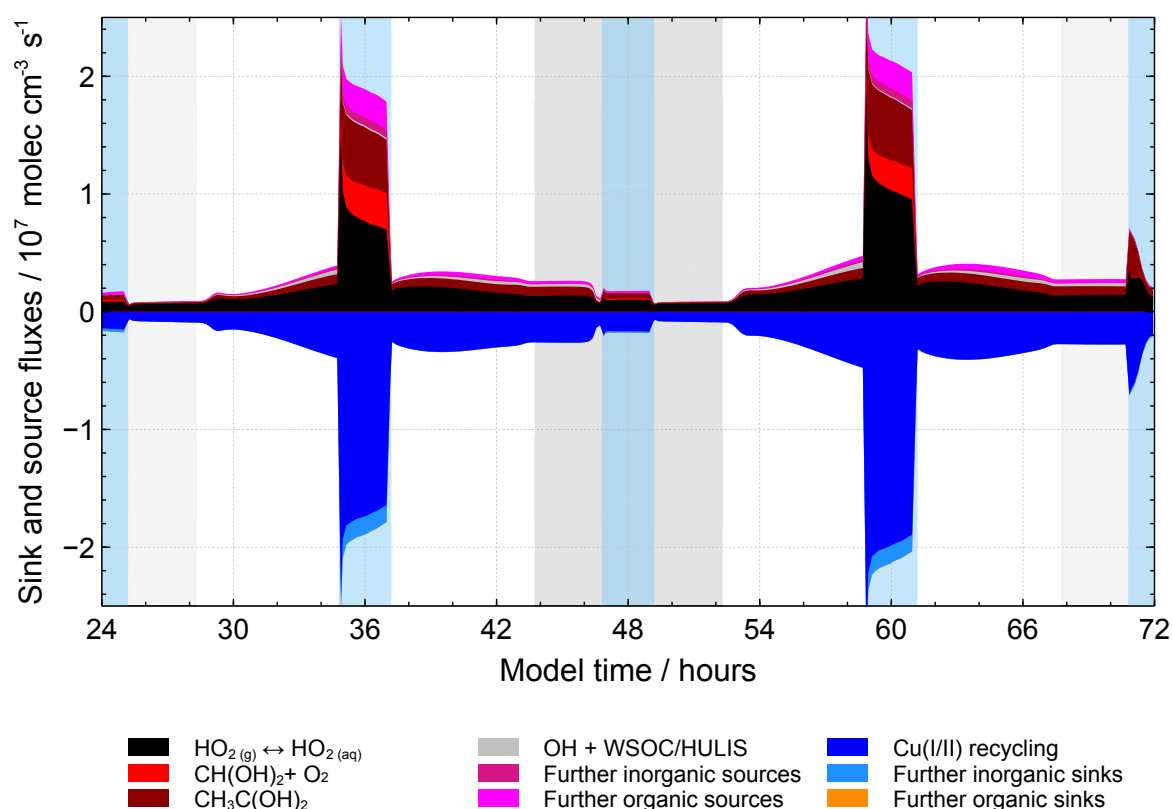
(b) CAPRAM 3.0o



**Figure 6.23** Time-resolved total production (positive values) and degradation fluxes (negative values) of hydroperoxyl and superoxide radicals in the CAPRAM 4.0 $\alpha$  (a) and 3.0o (b) simulations for the second and third model day under urban conditions.

Copper(I/II) recycling remains important. After the calculation of the net fluxes, reactions with copper are the dominant sink throughout the whole model run with only small further sinks from inorganic reactions during daytime cloud periods (see Figure 6.24). The major single source in the refined flux analysis is now uptake from the gas phase. Further source fluxes derive mainly from organic peroxy radical chemistry, where the peroxy radicals formed from the formaldehyde and acetaldehyde oxidation are the major contributors to the organic source fluxes. Source fluxes from the additional parameterisations account for only 4% of the total fluxes on average with main contribution of about 7% of the





**Figure 6.24** Refined time-resolved total production (positive values) and degradation fluxes (negative values) of hydroperoxyl and superoxide radicals in CAPRAM 4.0 $\alpha$  for the second and third model day under urban conditions.

total fluxes during non-cloud periods. WSOC is the most important parameterisation with contributions of 5.7% of the total source fluxes during non-cloud periods compared to 1.6% of the HULIS parameterisation. HULIS<sup>-</sup> shows negligible contributions. Further organic compounds contribute with about 10% on average to the total source fluxes of HO<sub>2</sub>/O<sub>2</sub><sup>-</sup>. Out of these 10%, 3.5% of the species were already incorporated in CAPRAM 3.0 $\alpha$ , 3% are part of the extended organic scheme in CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$  and 3.5% can be attributed to species with negligible single contributions of less than 0.1%.

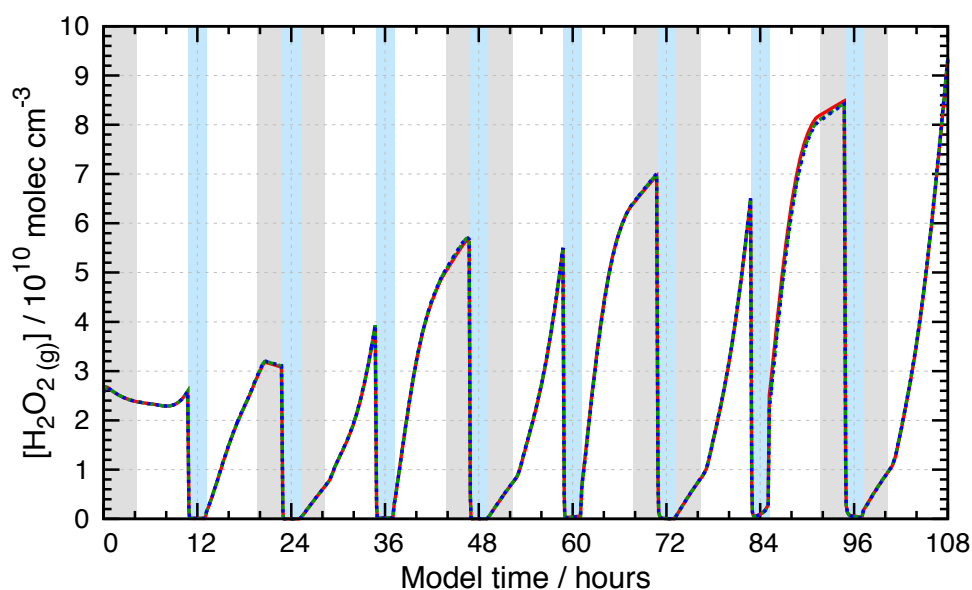
Although contributing with only 4% to the total source fluxes averaged over the whole model run, the new parameterisations have a large impact on the modelled HO<sub>2</sub>/O<sub>2</sub><sup>-</sup> concentrations. The main sources and sinks have already been described in CAPRAM 3.0 $\alpha$ . However, chemical fluxes from additional sources of the extended scheme are, with about 3%, in the order of the source fluxes from the WSOC/HULIS parameterisations. Yet, no effect on the HO<sub>2</sub>/O<sub>2</sub><sup>-</sup> concentration profile is seen in the runs with CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$ . Therefore, effects of the additional parameterisations must to a large part be indirect. As can be seen from Figure 6.17, page 168, the reaction of copper(I) with hydrogen peroxide is the main source for hydroxyl radicals during non-cloud periods. Decreased aqueous phase hydroxyl radical concentrations from the parameterisations impact the copper recycling and thus the formation and destruction of hydroperoxyl and superoxide radical concentrations.

## 6.2.5 Influence of the extended organic scheme on inorganic non-radical oxidants

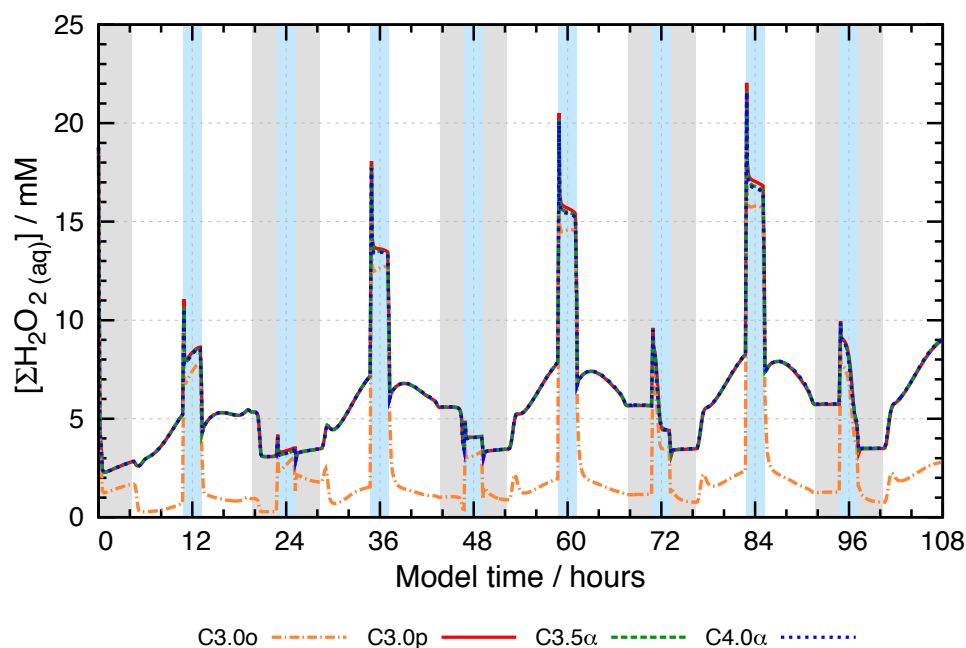
### 6.2.5.1 $\text{H}_2\text{O}_2$ chemistry

Hydrogen peroxide plays an important role in the aqueous phase. It is an essential non-radical oxidant, contributing substantially to the sulfur(IV) to sulfur(VI) conversion or the redox cycling of transition metal ions. Moreover, its reactions with iron(II) or copper(I)

(a) Gas phase



(b) Aqueous phase

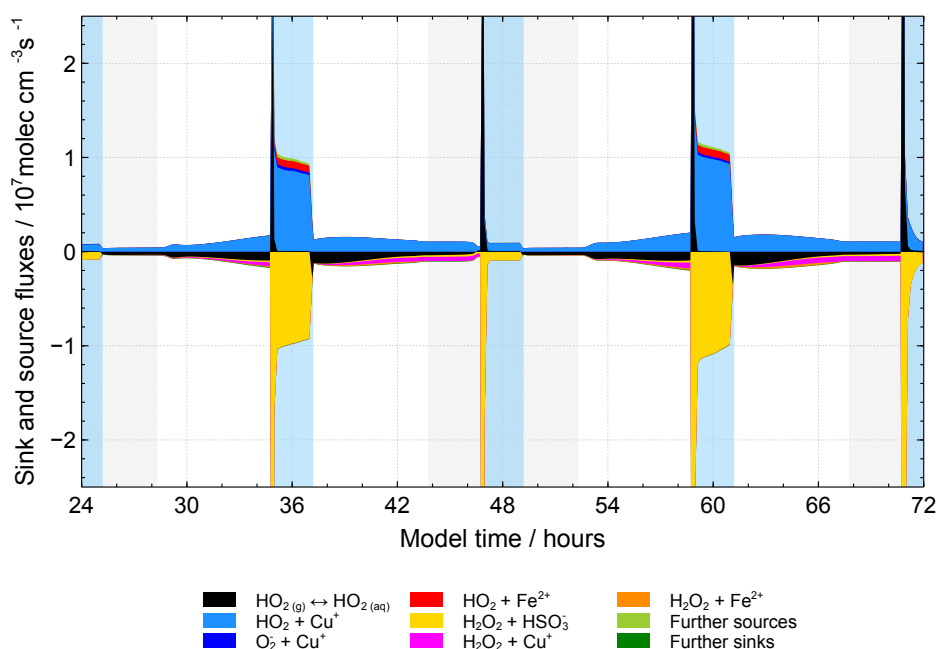


**Figure 6.25** Concentration-time profiles of hydrogen peroxide in the gas (a) and the aqueous phase (b) for the various CAPRAM versions under urban conditions.

are the most important aqueous phase in-situ source of hydroxyl radicals (see Figure 6.17, page 168), which further increases the importance of  $\text{H}_2\text{O}_2$  for tropospheric aqueous phase oxidation processes.

In Figure 6.25, the gas and aqueous phase concentration-time profiles of hydrogen peroxide in the urban scenario are shown. Again, significant differences are only seen for CAPRAM 3.0o in the aqueous phase, where concentrations are significantly reduced. This is most pronounced during non-cloud periods. As for  $\text{HO}_2$  and  $\text{O}_2^-$  radicals, the introduction of the WSOC/HULIS parameterisations causes a more pronounced diurnal variation. Both species are very closely linked in reaction cycles such as the redox cycles of transition metal ions and explanations for the decreased concentrations of  $\text{H}_2\text{O}_2$  in CAPRAM 3.0o are closely related to the explanations given in subsection 6.2.4.4.

The redox cycling of copper transforms  $\text{HO}_2$  into  $\text{H}_2\text{O}_2$ . This reaction is the dominant source for hydrogen peroxide in the aqueous except for short peaks of uptake from the gas phase during cloud formation periods (see Figure 6.26). On the other hand, the reaction of copper(I) with hydrogen peroxide is an important sink during non-cloud period besides release to the gas phase. During cloud periods, the oxidation of sulfur(IV) dominates the sinks of hydrogen peroxide as can be seen from Figure 6.26. The reaction of  $\text{HO}_2$  with iron(II) shows contributions to the sources of hydrogen peroxide during cloud periods as well, albeit to a much smaller extent than the reaction with Cu(I). In conclusion, the perturbed redox cycling of TMIs and the increased hydroperoxyl and superoxide radical concentrations in the CAPRAM runs with the WSOC/HULIS parameterisations is the most likely cause for the differences in the aqueous phase  $\text{H}_2\text{O}_2$  concentrations seen in Figure 6.25b.

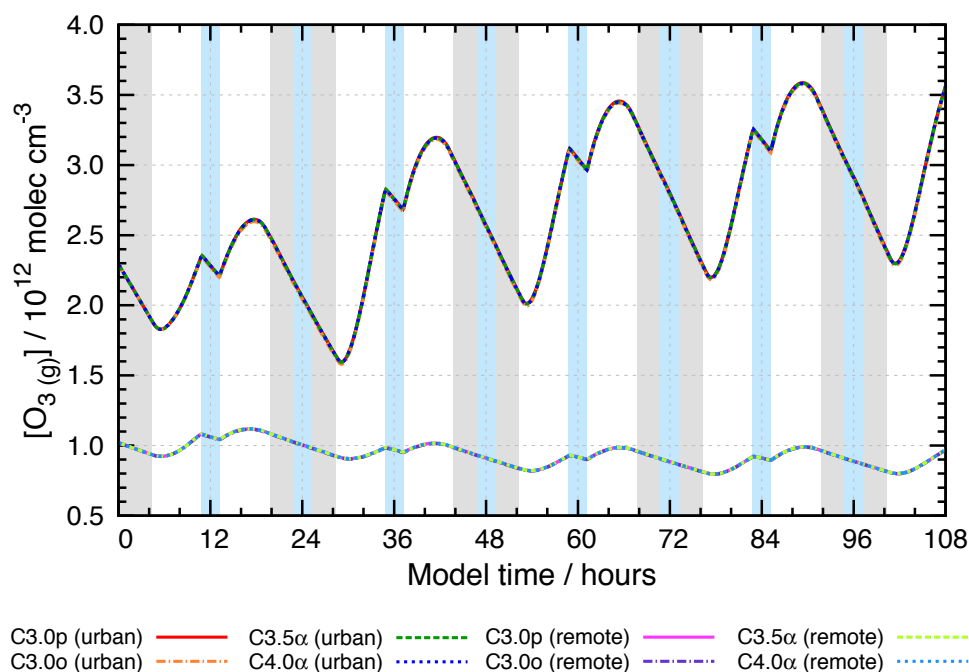


**Figure 6.26** Time-resolved total production (positive values) and degradation fluxes (negative values) of hydrogen peroxide for the second and third model day in CAPRAM 4.0α under urban conditions.

### 6.2.5.2 O<sub>3</sub> chemistry

As ozone has a low water-solubility, its chemistry is dominated by gas phase processes. Therefore, changes to the aqueous phase mechanism do not affect the concentration-time profiles of ozone (see Figure 6.27). However, for completion and proof of the plausibility of the modelled results, gas phase ozone concentration-time profiles are provided in Figure 6.27 for the urban and remote scenario.

Ozone concentrations show the typical diurnal variation with lowest values in the morning hours at sunrise and highest values in the afternoon. In the urban scenario, concentrations range between  $1.6 \cdot 10^{12}$  and  $3.6 \cdot 10^{12}$  molecules  $\text{cm}^{-3}$  with a steady increase of the daily maxima and minima throughout the model run. In the remote scenario, concentrations are lower with values between  $6 \cdot 10^{11}$  and  $1.2 \cdot 10^{12}$  molecules  $\text{cm}^{-3}$ . Moreover, concentrations decrease throughout the model run. Model values are in good agreement with field measurements for both, the concentration and the diurnal variation (compare, e.g., *Lu et al.*, 2013, *Worton et al.*, 2013, and *Han et al.*, 2013).



**Figure 6.27** Concentration-time profiles of ozone in the gas phase for the various CAPRAM versions under urban and remote conditions.

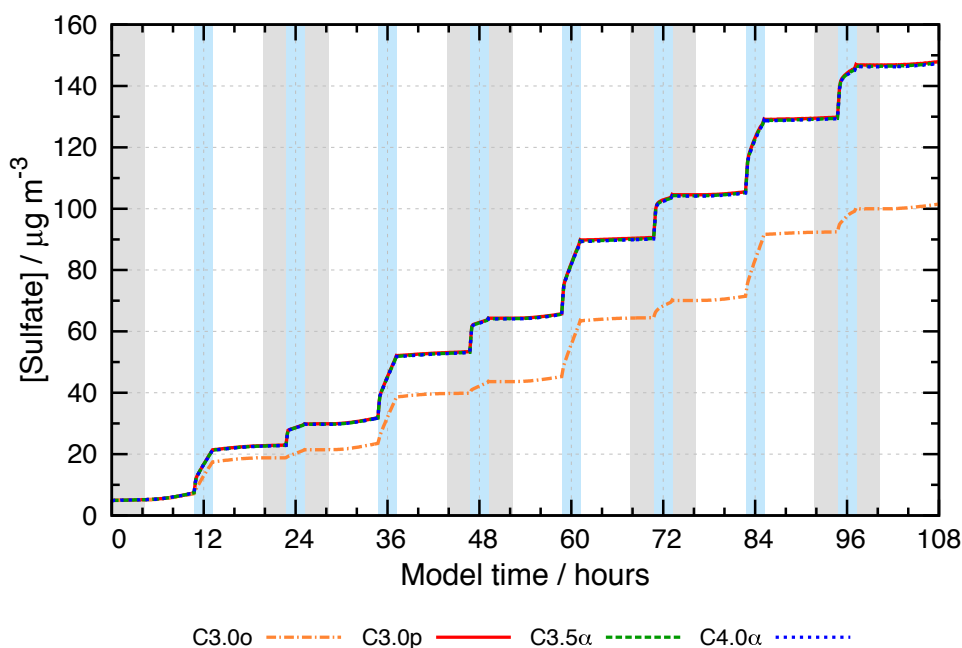
## 6.2.6 Influence of the extended organic scheme on inorganic particulate matter

In the current subsection, the most important contributors to inorganic particle mass, sulfate and nitrate, are discussed. The discussion is followed by an investigation of the iron(II) chemistry as most important representative of transition metal ions, which substantially influence the tropospheric aqueous phase chemistry.

### 6.2.6.1 Sulfate chemistry

Sulfate is the largest contributor to particle mass and the main reason for the increase in particulate matter. The main increase is observed during cloud periods as can be seen from Figure 6.28, where the concentration-time profiles of the sum of all sulfate forms (sulfate =  $\text{H}_2\text{SO}_4 + \text{HSO}_4^- + \text{SO}_4^{2-}$ ) are plotted for the different mechanisms. At the end of the model runs with the WSOC/HULIS parameters almost  $150 \mu\text{g m}^{-3}$  sulfate are found in particles.

Again, no significant differences are seen between the runs with the WSOC/HULIS parameterisations. A huge impact of the parameterisations is observed, when comparing the concentrations of CAPRAM 3.0p, 3.5 $\alpha$ , and 4.0 $\alpha$  with CAPRAM 3.0o. Without the reactions of OH and NO<sub>3</sub> with WSOC and HULIS compounds, the increase in particulate sulfate concentrations at the end of the model run is only about 2/3 compared to the other scenarios totalling to  $\sim 100 \mu\text{g m}^{-3}$ . The discussion of subsection 6.2.5 can help to understand the behaviour of the different concentration-time profiles in Figure 6.28.



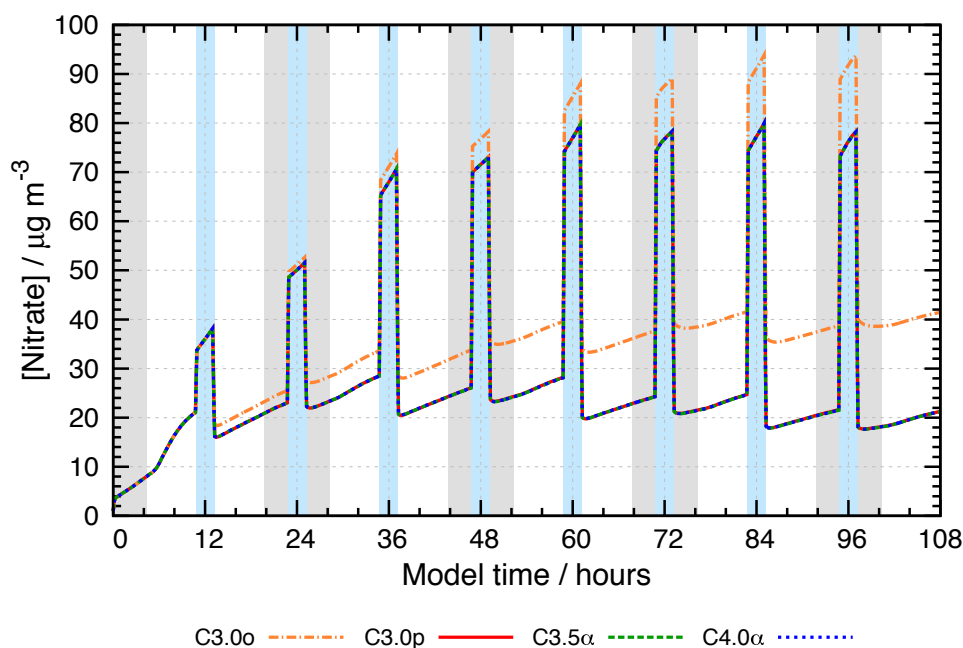
**Figure 6.28** Concentration-time profiles of aqueous phase sulfate for the various CAPRAM mechanisms under urban conditions.

It was shown that the reduced hydroxyl radical concentrations from the parameterisations of reactions with WSOC and HULIS/HULIS<sup>-</sup> have a large impact on the recycling of HO<sub>x</sub> species and the redox cycling of transition metal ions. Moreover, from Figure 6.26 can be seen that the reaction of hydrogen peroxide with the sulfite monoanion is a large sink for sulfur(IV) during cloud periods. In this reaction, sulfate is produced causing the large increase in S(VI) concentrations during cloud periods in Figure 6.28. With increased H<sub>2</sub>O<sub>2</sub> concentrations in the model runs with the WSOC/HULIS parameterisations (see Figure 6.25b), more sulfite is converted to sulfate and sulfate concentrations and consequently inorganic particle mass increase in these runs.

Sulfuric acid is a very strong acid with a  $pK_a$  of -3 and 2 for the first and second dissociation step, respectively (see *Seinfeld and Pandis*, 2006 and CAPRAM database in *Ervens et al.*, 2003). Therefore, the pH is decreased by more than 0.3 pH units in the runs with the increased sulfate concentrations caused by the WSOC/HULIS parameterisations (see Figure I.1, page 901, in Appendix I.1). Moreover, additional carboxylic acids do not influence particle acidity as these acids are generally weak with  $pK_a$  values between 4.7 and 5. Thus, as already implied in subsection 6.2.3, changes in pH in the CAPRAM versions 3.0p, 3.5 $\alpha$ , and 4.0 $\alpha$  derive almost exclusively from inorganic chemistry.

#### 6.2.6.2 Nitrate chemistry

Nitrate is the second most important contributor to particle mass as can be seen from Figure 6.29. During cloud periods, nitrate concentrations are with up to 97  $\mu\text{g m}^{-3}$  in CAPRAM 3.0o in the order of sulfate concentrations and even succeed them at the beginning of the model runs. During non-cloud periods, concentrations are significantly



**Figure 6.29** Concentration-time profiles of aqueous nitrate for the various CAPRAM mechanisms under urban conditions.

decreased with maximum concentrations of about  $30 \mu\text{g m}^{-3}$ . In contrast to sulfate, nitrate concentrations increase during non-cloud periods. After cloud periods, a decrease in  $\text{NO}_3^-$  concentrations is observed compared to pre-cloud concentration levels. From the third model day on, production during non-cloud periods cannot compensate for that loss in the runs with the WSOC/HULIS parameterisations so that a general decrease in particulate nitrate is observed in these scenarios (see Figure 6.29).

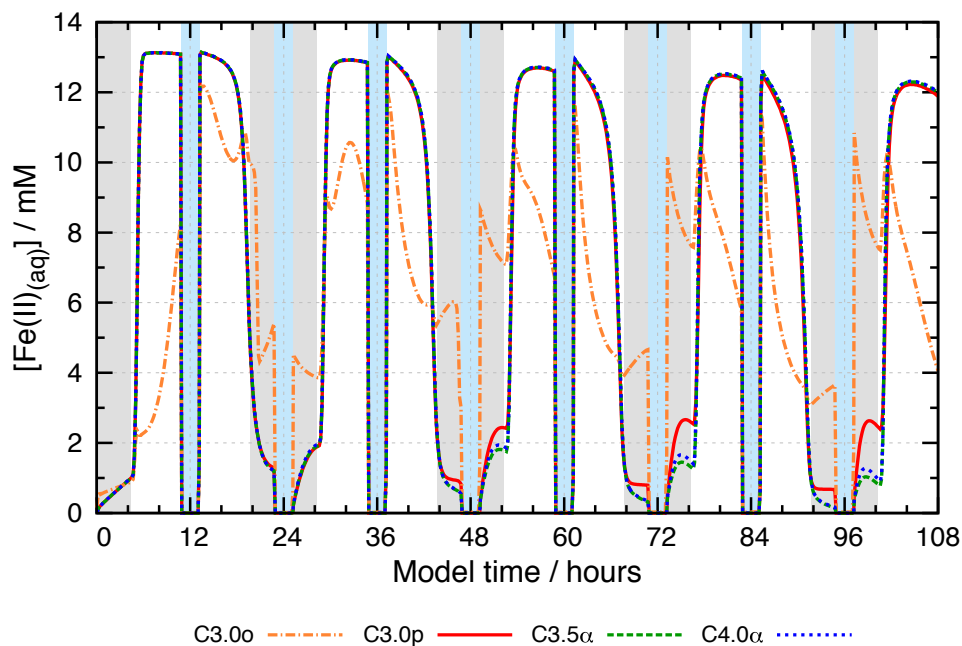
Overall, nitrate concentrations are strongly decreased in the model runs using the parameterisations. Nitrate depletion is not directly caused by the WSOC/HULIS parameterisations as  $\text{NO}_3^-$  is formed in these reactions. It is the consequence of inorganic acid base equilibria. As more sulfate is produced and pH is decreased (see discussion in subsection 6.2.6.1 and Figure 6.28, page 185, as well as Figure I.1, page 901), more nitrate is transformed into nitric acid. With a  $pK_a$  of -1.34 (*Redlich*, 1946, *Redlich and Hood*, 1957, and CAPRAM database as presented in *Ervens et al.*, 2003), nitric acid is weaker than sulfuric acid. Thus, with a decreasing pH value, nitrate gets protonated rather than sulfate. The effective Henry’s Law equilibrium causes a release to the gas phase. Hence, nitrate is replaced by sulfate in the CAPRAM runs with the WSOC/HULIS parameterisations causing a nitrate depletion of about  $20 \mu\text{g m}^{-3}$  in these scenarios.

### 6.2.6.3 TMI chemistry

Although present only in trace concentrations, transition metal ions have a large impact on the multiphase chemistry and composition of the troposphere as already outlined in previous discussions. Subsection 6.2.4 and 6.2.5 demonstrated the impact of TMI redox cycling on the  $\text{HO}_x$  budget in the aqueous phase. Especially copper contributed to a large extent to the formation and degradation processes in the  $\text{HO}_x$  cycle.

Iron is the most important transition metal ion as it is most abundant.  $\text{Fe}^{2+}$  concentrations are shown in Figure 6.30. Huge deviations are seen between the original CAPRAM 3.0o mechanism and the mechanisms with the WSOC/HULIS parameterisations. These deviations partly derive from the links of the  $\text{HO}_x$  cycle and the redox cycling of TMIs. The major impact, however, is seen from the newly implemented formation of iron-HULIS complexes and the photolysis of the iron(III)-HULIS complex, which liberates the HULIS bound in the complex and transforms Fe(III) into Fe(II) (see Table G.12, page 395).

In Figure 6.31, sink and source fluxes of the basic CAPRAM 3.0o version are compared to the fully extended CAPRAM 4.0 $\alpha$  mechanism. It can be seen that the turnovers in the extended scheme are reduced by about an order of magnitude during non-cloud periods as iron(II) is bound in the non-reactive iron-HULIS-complex. Chemical source and sink fluxes are of the same magnitude during in-cloud residence times of the air parcel. Moreover, the composition of the chemical fluxes has completely changed. In CAPRAM 3.0o, interactions with copper are the main source during non-cloud periods with fluxes up to  $4 \cdot 10^7 \text{ molecules cm}^{-3} \text{ s}^{-1}$ . During cloud periods, interactions with the  $\text{HO}_x$  cycle become more important. The introduction of the HULIS chemistry completely changes the iron recycling and the photolysis of the iron-HULIS complex is the dominant



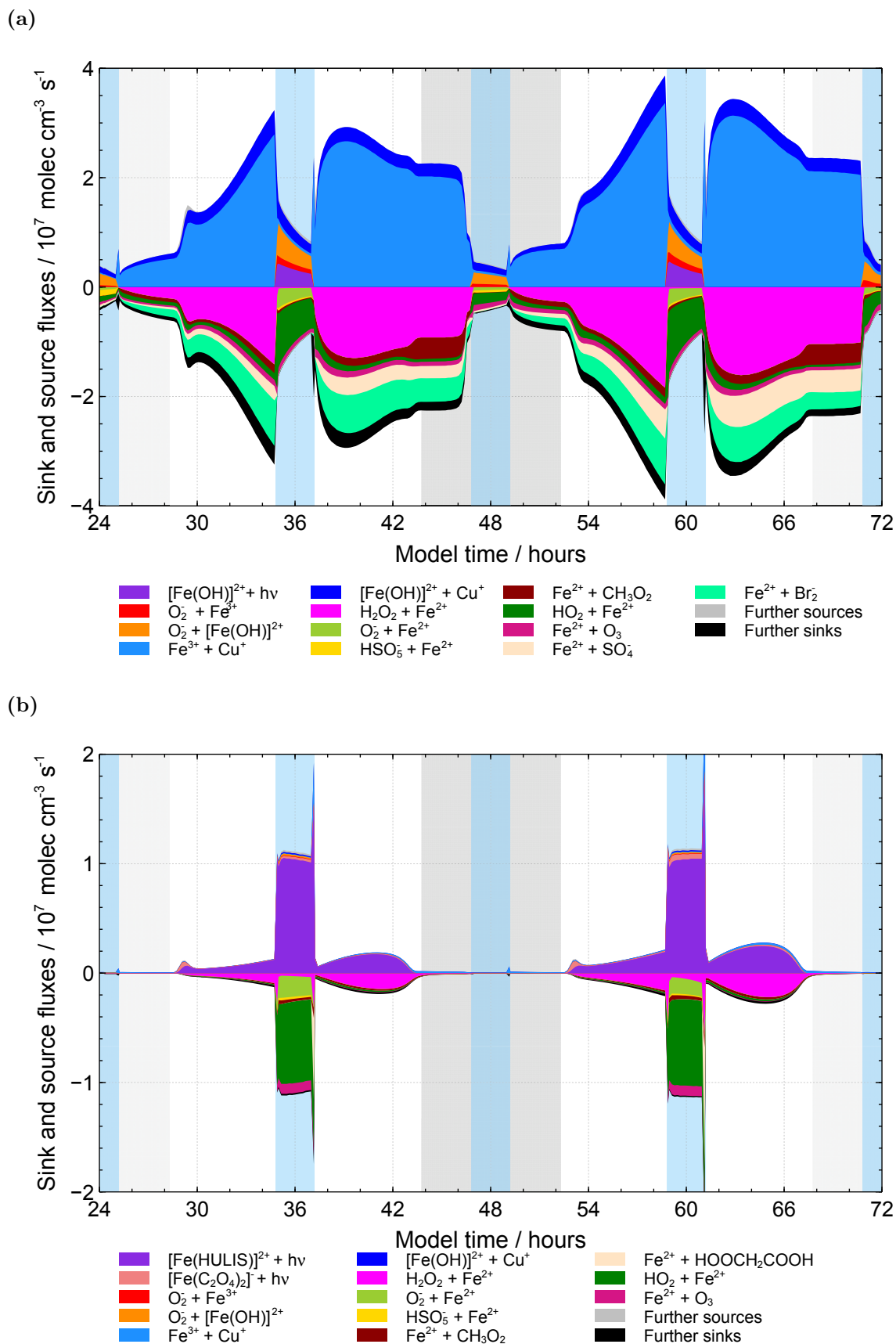
**Figure 6.30** Concentration-time profiles of aqueous phase iron(II) for the various CAPRAM mechanisms under urban conditions.

source of iron(II) throughout the whole model run. With photolysis processes as the dominant source, the diurnal variation of the concentration-time profile changes. In the runs with the parameterisation, high concentrations of Fe(II) of about 13 mM are found immediately after sunrise. Concentrations begin to decrease in the afternoon to concentration levels below 2 mM at night. In CAPRAM 3.0o, varying concentrations are found with a much more complex diurnal variation. It should be noted that all kinetic data concerning iron-HULIS complexation and the photolysis of the iron(III)-HULIS complex are estimates (see Table G.12). As the quality of the estimates is not validated, more laboratory data is desirable for a more precise description of the interactions of transition metal ions with HULIS.

For all scenarios, reactions of  $\text{Fe}^{2+}$  with  $\text{HO}_2$  and  $\text{O}_2^-$  is the dominant sink under in-cloud conditions. Under non-cloud conditions, the reaction with hydrogen peroxide is the dominant sink in CAPRAM 4.0α. In CAPRAM 3.0o, it is the main sink as well, but other sinks are important, too. Further important sinks are the reaction with the sulfate radical anion, the dibromine radical anion and to a smaller extent the formation of the iron-methyl peroxide complex, the reaction with ozone and hydroperoxyl radicals (see Figure 6.31).

From Figure 6.30 can be seen, that the extended explicit organic oxidation scheme in CAPRAM 3.5α and 4.0α has a small impact on night-time iron(II) concentrations. In the extended schemes, iron concentrations are decreased. The first extension step in CAPRAM 3.5α shows the largest impact and further iron(II) depletion in CAPRAM 4.0α is minor. Moreover, the effect is more pronounced after the cloud periods in the second half of the night and increases over time from negligible concentration differences to differences of over 1 mM. Although contributions to the overall sink fluxes are small, the formation of the  $[\text{Fe}(\text{CH}_3\text{O}_2)]^{2+}$  complex is a likely explanation of the decreased iron(II) concentrations





**Figure 6.31** Time-resolved production (positive values) and degradation fluxes (negative values) of aqueous phase iron(II) for the second and third model day under urban conditions in the scenarios with CAPRAM 3.0o (a) and 4.0a (b).

in CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$ . As more methyl peroxy radicals are produced in the extended CAPRAM versions, more Fe(II) is bound in the complex or transformed into Fe<sup>3+</sup> with the decomposition of the complex.

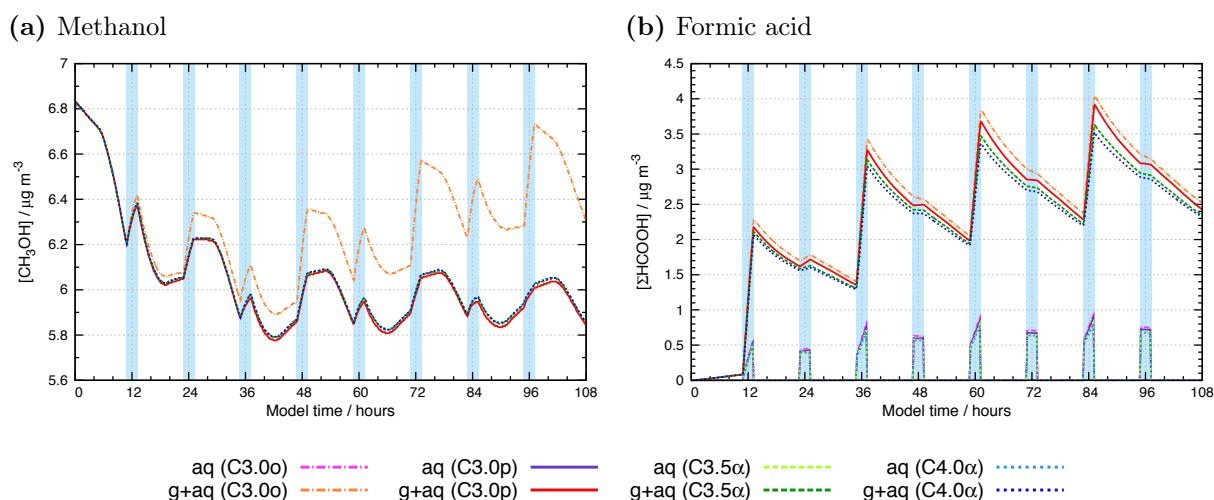
### 6.2.7 Detailed investigations of selected organic subsystems

The current subsection provides a detailed investigation of the influence of the extended organic scheme on the concentration-time profiles of important organic compounds in either the gas or the aqueous phase. The subsection highlights the major achievements of the extended mechanisms and gives details about the major uncertainties that remain due to the many estimations and the limitations that derive from the automated mechanism construction.

#### 6.2.7.1 Monofunctional organic compounds

The multiphase composition of several organic compounds is not or only slightly affected by the mechanism extension of the explicit organic scheme. A large portion of these unaffected compounds belongs to monofunctional organic compounds that are emitted in large quantities into the atmosphere. Their concentration-time profiles are dominated by the emissions rather than the atmospheric chemistry. For these compounds, the initialisation of the scenario plays a much greater role than the level of detail in the chemical scheme. Moreover, Henry's Law constants of monofunctional compounds are widely insufficient to generate sufficient concentrations of these compounds in the aqueous phase. These facts are demonstrated for a number of selected compounds in Figure I.6 in Appendix I.3, page 906, where the total aqueous phase concentrations including all possible hydration and dissociation states and overall gas and aqueous phase concentrations are plotted. From Figure I.6 can be seen, that significant concentrations of constituents of this compound class exist only for few compounds and only during cloud periods. Thus, as these compounds exist primarily in the gas phase, the extension of the aqueous phase chemical mechanism shows no effect.

Two exceptions are given in Figure 6.32 – methanol and formic acid. For methanol, the introduction of the WSOC and HULIS parameterisations show a big impact on the concentration-time profiles. Time-resolved flux analyses (not depicted) have shown that the decreased concentrations in the runs with the parameterisations derive from decreased source fluxes. The major source of methanol is the oxidation of hydrogen sulfite by methyl hydroperoxide leading to sulfate and methanol. In CAPRAM 3.0o, there is a source flux of  $1.3 \cdot 10^5 \text{ molecules cm}^{-3} \text{ s}^{-1}$  making up 98% of all source fluxes averaged over the model run. Contributions are mainly during cloud periods, where fluxes are increased to  $7.7 \cdot 10^5 \text{ molecules cm}^{-3} \text{ s}^{-1}$  on average. During non-cloud periods, only  $49 \text{ molecules cm}^{-3} \text{ s}^{-1}$  or about 27% of the total source fluxes are formed. In CAPRAM 3.0p, source fluxes decrease during cloud periods to  $2.9 \cdot 10^5 \text{ molecules cm}^{-3} \text{ s}^{-1}$ , but increase during non-cloud periods to  $3.2 \cdot 10^3 \text{ molecules cm}^{-3} \text{ s}^{-1}$ . Fluxes from the  $\text{HSO}_3^- + \text{CH}_3\text{OOH}$



**Figure 6.32** Concentration-time profiles of methanol (a) and formic acid (b) in the aqueous phase (including all dissociation states for formic acid) and overall gas and aqueous phase concentrations for the various CAPRAM versions under urban conditions.

reaction in CAPRAM 3.0p contribute with 90% to the total source fluxes during non-cloud and night-time cloud periods and about 70% during daytime cloud periods. As fluxes during cloud periods are by several orders of magnitude higher, their changes have a larger influence as the fluxes during non-cloud periods despite the much shorter residence time of the air parcel in clouds. On average, fluxes are reduced to  $5.1 \cdot 10^4 \text{ molecules cm}^{-3} \text{ s}^{-1}$ .

Changes in the source fluxes are caused by the formation of iron complexes with HULIS in the parameterisations. An important source for methyl hydroperoxide is the rapid decay of the iron-methylperoxy complex. From Figure 6.31 can be seen that in CAPRAM 3.0o, this decay is an important sink for iron(II) and, hence, important source for  $\text{CH}_3\text{OOH}$  with fluxes up to almost  $1 \cdot 10^6 \text{ molecules cm}^{-3} \text{ s}^{-1}$  during non-cloud periods. With the introduction of the iron-HULIS complexation, fluxes are generally reduced and this reaction pathways becomes negligible leaving the Fenton reaction of Fe(II) with  $\text{H}_2\text{O}_2$  as only important sink. Thus, with the parameterisations, less methyl hydroperoxide is produced and concentrations of methanol decrease as a consequence. The reduced concentrations also impact the gas phase concentrations, which can be seen in Figure 6.32a. Decrease occurs mainly during cloud periods, where larger fluxes with more pronounced changes occur and show little effect during non-cloud periods, where source fluxes in the aqueous phase from the reaction of hydrogen sulfite with methyl hydroperoxide are too small to show an influence compared to the large emissions of methanol. With the further extension of the explicit organic scheme in CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$ , minor increases in methanol concentrations caused by the oxidation of larger organic compounds can be observed in Figure 6.32a.

Formic acid is another compound, where differences between the various CAPRAM versions are seen, albeit on a much smaller scale than for methanol. The introduction of the WSOC/HULIS parameterisations causes a small decrease in aqueous phase concentrations during daytime cloud periods, which feeds back on the gas phase as can be seen from

Figure 6.32b. During night-time clouds, concentrations recover, but not to a full extent. No significant changes are observed during non-cloud periods.

Changes result, again, from interactions with the iron chemistry. An important sink for formate is the reaction with iron oxide ( $\text{FeO}^{2+}$ ). In CAPRAM 3.0o, this reaction contributes with 54% to the overall sink fluxes of formic acid and formate averaged over the whole model run and has a strength of  $1.24 \text{ molecules cm}^{-3} \text{ s}^{-1}$ . In CAPRAM 3.0p, this sink flux is reduced to  $5.2 \cdot 10^3 \text{ molecules cm}^{-3} \text{ s}^{-1}$  totalling to 40% of all sinks averaged over the whole model run. Further decreases in formic acid concentrations in the extended CAPRAM mechanisms may result from reduced hydroxyl radical concentrations and thus less formation of formic acid.

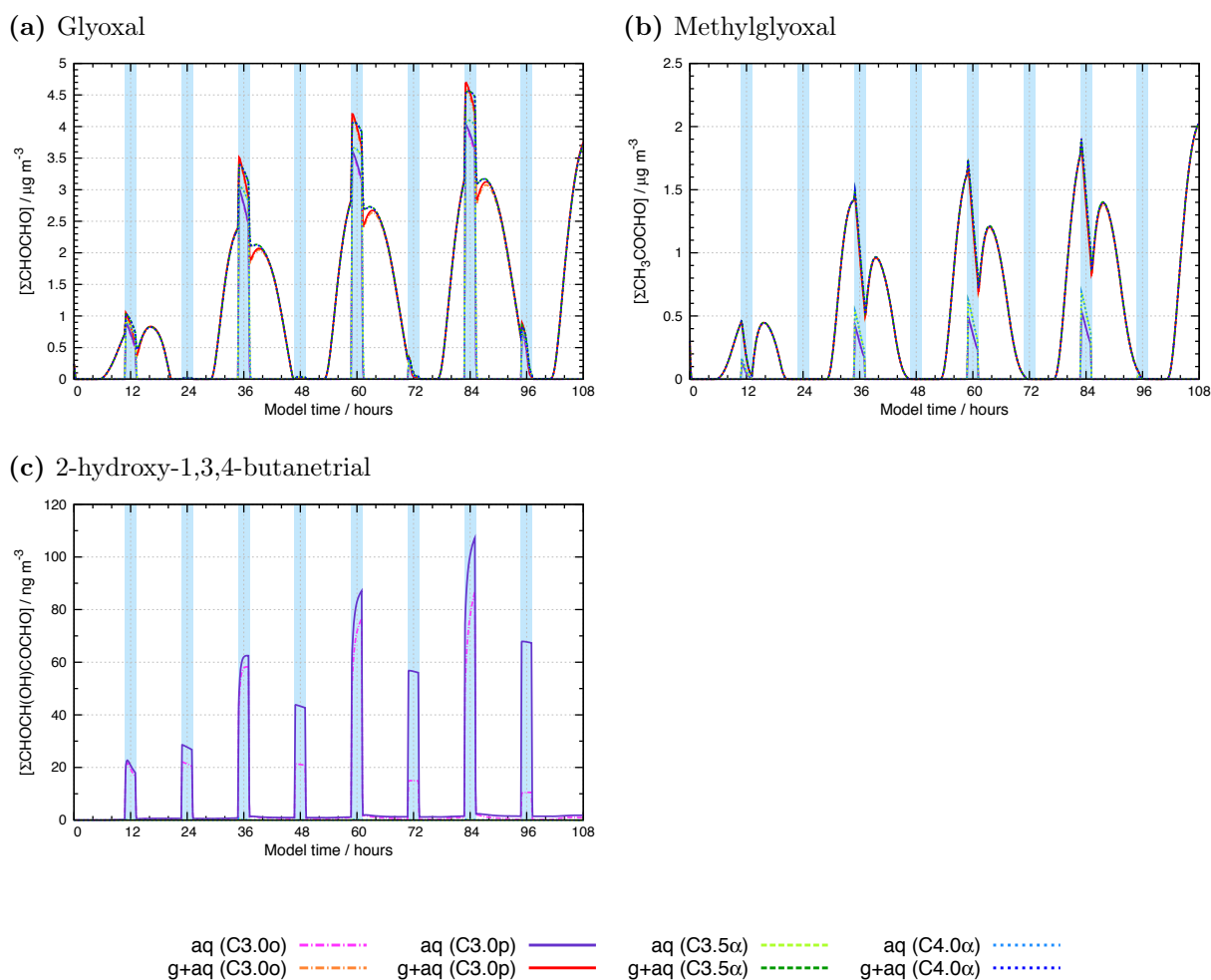
### 6.2.7.2 Carbonyl compounds

Carbonyl compounds play an important role in the atmospheric multiphase chemistry of organic compounds and comprise a large fraction of the organic particle mass during in-cloud residence times of the air parcel. Additional equilibria with water in the aqueous phase to form gem-diols increase the importance of particle and cloud droplet chemistry as the effective Henry's Law constant is increased and as a consequence partitioning to the aqueous phase as well. Therefore, carbonyl compounds are investigated in more depth in the current subsection.

Figure 6.33 shows a selection of important di- and polycarbonyl compounds – the abundant and widely studied  $\alpha$ -dicarbonyls glyoxal and methylglyoxal (Figure 6.33a and 6.33b), and, due to important differences in the chemistry and major changes in the concentration-time profiles in the new extended CAPRAM versions, the concentration of 2-hydroxy-1,3,4-butanetriol is shown in Figure 6.33c.

Glyoxal and methylglyoxal have gained considerable attention in the scientific community over the last decade. They are main oxidation products of either anthropogenically emitted organic compounds (e.g., aromatic compound) or naturally emitted sources such as isoprene. Therefore, they are very abundant  $\alpha$ -dicarbonyls and widely found in the troposphere. However, most measurements of particles glyoxal and methylglyoxal found these compounds at trace concentrations in the ng range (see, e.g., *Li and Yu*, 2010, *Wang et al.*, 2012, *Kawamura et al.*, 2013).

The model predicts total (gas and aqueous) glyoxal and methylglyoxal concentrations for all four mechanisms CAPRAM 3.0o/n, 3.5 $\alpha$ , and 4.0 $\alpha$  in the  $\mu\text{g}$ -range with significant partitioning to the aqueous phase only during cloud periods (see Figure 6.33). A diurnal variation is observed with maximum concentrations at noon. During cloud periods, glyoxal concentrations are increased, while methylglyoxal is degraded during cloud periods. Both compounds are found predominantly in their hydrated form, which increases the effective Henry's Law constant and makes uptake very efficient. Therefore, both compounds are found mostly in the aqueous phase during cloud periods.



**Figure 6.33** Profiles of the overall aqueous phase concentrations (including all hydrated forms) and the sum of the gas and overall aqueous phase concentration of selected carbonyl compounds for the various CAPRAM mechanisms under urban conditions.

The parameterisations of WSOC and HULIS have no effect on the two  $\alpha$ -dicarbonyls. During cloud periods, where glyoxal and methylglyoxal are predominantly present in the aqueous phase, the extended organic schemes of CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$  cause an increased production of these carbonyl compounds. As uptake is suppressed for  $C_3$  compounds with an O:C ratio greater or equal 1, this effect is restricted to the aqueous phase for methylglyoxal, which falls under that rule. Therefore, these decoupled species cannot be regarded as an overall system compound and the interpretation of accumulated concentration has to be treated with caution. For glyoxal, gas phase concentrations are affected and an initial increase in the total gas and aqueous phase concentrations is observed at the beginning of every daytime cloud period. Towards the end of the cloud periods, concentrations start to decrease, however, the initial production causes increase concentrations in CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$  compared to CAPRAM 3.0o/p. After cloud periods, concentrations increase more rapidly in CAPRAM 3.0o/p and concentration-time profiles are indistinguishable from the other scenarios from the afternoon onwards.

During non-cloud periods, glyoxal and methylglyoxal is found mainly in the gas phase. Aqueous concentrations decrease to a few  $\text{ng m}^{-3}$ , which is in very good agreement with

measurements of, e.g., *Li and Yu* (2010), *Wang et al.* (2012), and *Kawamura et al.* (2013). Moreover, *Kawamura et al.* (2013) measured gas phase glyoxal and methylglyoxal concentrations besides particle concentrations. On average,  $0.49 \mu\text{g m}^{-3}$  glyoxal and  $0.97 \mu\text{g m}^{-3}$  methylglyoxal were found in the gas phase by *Kawamura et al.* (2013) at Mt. Tai in China. Concentrations are lower than the modelled results, which predicted up to  $3.5 \mu\text{g m}^{-3}$  for glyoxal and  $1.8 \mu\text{g m}^{-3}$  for methylglyoxal during non-cloud periods. Discrepancies could derive from the sampling site. With an elevation of 1534 m (*Kawamura et al.*, 2013), there is a possibility that the top of Mt. Tai is above the boundary layer. Therefore, concentrations of organic compounds are further away from sources. An inversion at the top of the boundary layer makes mixing of air masses and thus pollutants more difficult. Moreover, with a larger volume of the free troposphere compared to the boundary layer, concentrations are more diluted. Therefore, concentrations are likely to be decreased in the free troposphere, which could explain the differences between modelled and measured concentrations. Maximum gas phase concentrations at Mt. Tai measured by *Kawamura et al.* (2013) were  $1.2 \mu\text{g m}^{-3}$  for glyoxal and  $2.7 \mu\text{g m}^{-3}$  for methylglyoxal, which is in much better agreement with the model results. These concentrations could possibly derive from periods, where the mountain's top was within the planetary boundary layer.

Comparing the different model scenarios, major differences between the original and the extended CAPRAM versions are seen for the highly oxidised compound 2-hydroxy-1,3,4-butanetriol (Figure 6.33c). Previously, up to  $110 \text{ ng m}^{-3}$  were found in the aqueous phase during cloud periods. During non-cloud periods, the tricarbonyl was found mostly in the gas phase. In the extended CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$  versions, the concentrations decrease to negligible concentrations. As the stability of such highly oxidised compounds is believed to be low, a mono-molecular decay has been implemented in the new CAPRAM versions as described in section 5.1. From the concentration-time profile in Figure 6.33c can be seen that the decay effectively decreases the concentrations of such highly oxidised compounds without increasing the oxidation capacity of the troposphere unrealistically or affecting the concentrations of other organic compounds in an unrealistic manner.

A new feature in the multiphase mechanism generator GECKO-A is the automated prediction of the hydration of carbonyl compounds (see *Raventos-Duran et al.*, 2010). As its influence on the effective Henry's Law constant is a crucial factor, which is important for an accurate description of phase transfer processes and thus the multiphase composition and chemistry of organic compounds, more detailed investigations have been performed. Interesting effects in CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$  derive from the newly implemented hydration scheme, which is part of the GECKO-A protocol. While the overall compound concentrations can be similar as for glyoxal and methylglyoxal in Figure 6.33, substantial differences are found in the speciation of the hydrated forms for many of the carbonyl compounds. In CAPRAM 3.0n, no hydration was used for keto-groups. In the extended organic schemes, the hydration routine GROMHE is used to calculate the hydration constants, which determines the speciation of unhydrated and hydrated keto-groups.

Simpler hydroxy-substituted ketones are still present mainly in their unhydrated forms in the new CAPRAM versions. While no gem-diol form is predicted for hydroxy-acetone,

the hydration of dihydroxy acetone is minor with only 0.3% (see Table 6.2). For higher oxidised ketones, hydration increases and 2.7% of pyruvic acid hydrate. For mesoxalic acid the hydrated fraction is already 22.1%. Moreover, the distance of a functionalised group to the carbonyl group in a molecule is an important aspect for hydration. Highly oxidised carbon atoms close to carbonyl groups seem to encourage hydration as can be seen from the example of oxo-butyric acid. While no hydration occurs for 3-oxo butyric acid, 2-oxo butyric acid hydrolyses to more than a half (see Table 6.2). The effect is less obvious for hydroxy-substituted carbonyl compounds with 1,4-dihydroxy-MEK being present only in the unhydrated form and dihydroxy acetone forming gem-diols to only 0.3%.

For di- and polycarbonyl compounds, the effect of the estimation of hydration constants with GROMHE (*Raventos-Duran et al.*, 2010) is even stronger. A strong tendency to at least partly hydrate is observed in Table 6.3. Except for 1,3-butanedial, the unhydrated state forms a minority. Moreover, besides the aldehyde groups in these polycarbonyl compounds, keto groups show an increased tendency to hydrate. Thus, the current assumption in previous CAPRAM studies of unhydrated keto functions (see, e.g., *Tilgner and Herrmann*, 2010, *Tilgner et al.*, 2013) seems invalid from the current calculations.

Hydration is not only important to describe the speciation of carbonyl compounds correctly, it also influences the oxidation capacity. Different forms of the same compound may react with different rate constants. Typically, gem-diols react much faster (in the order  $10^9$  to  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ ) than the carbonyl forms (in the order  $10^8 \text{ M}^{-1} \text{ s}^{-1}$ ). Typical rate constants of the hydrated and unhydrated forms can also be found in the Appendix C in Table C.1 and Table C.2 for OH and  $\text{NO}_3$  radicals, respectively, or in the reaction mechanism given in Appendix G.3. The implemented hydration of several of the carbonyl compounds increases the oxidation capacity and causes a faster degradation of larger compounds and, in return, a faster increase of the concentrations of smaller oxidation products. Moreover, hydration increases the number of abstractable H-atoms. While no H-atoms are available

**Table 6.2** Hydration states of various carbonyl compounds. Given are the percentages of the carbonyl and gem-diol form to the overall concentration in  $\text{mol l}^{-1}$ . The percentages were derived as average values over the whole model run as well as non-cloud or cloud periods only. For carboxylic acids and diacids the protonated and deprotonated forms have been accumulated and only the overall compounds are considered.

Compound	Overall		Non-cloud periods		Cloud periods	
	carbonyl	gem-diol	carbonyl	gem-diol	carbonyl	gem-diol
Acetone	100.0%	—	100.0%	—	100.0%	—
Hydroxyacetone	100.0%	—	100.0%	—	100.0%	—
Dihydroxyacetone	99.7%	0.3%	99.7%	0.3%	99.7%	0.3%
Pyruvic acid	97.3%	2.7%	97.3%	2.7%	98.6%	1.4%
Mesoxalic acid	77.9%	22.1%	77.9%	22.1%	78.9%	21.1%
1-Hydroxy MEK	100.0%	—	100.0%	—	100.0%	—
4-Hydroxy MEK	100.0%	—	100.0%	—	100.0%	—
1,4-Dihydroxy MEK	100.0%	—	100.0%	—	100.0%	—
2-Oxo butyric acid	47.4%	52.6%	100.0%	0.0%	46.0%	54.0%
3-Oxo butyric acid	100.0%	—	100.0%	—	100.0%	—
Oxaloacetic acid	84.8%	15.2%	98.4%	1.6%	84.8%	15.2%

\*MEK = methyl ethyl ketone (labelling of the carbon atoms starts at the methyl group)

**Table 6.3** Hydration states of various di- and polycarbonyl compounds as average over the whole model run. Given are the percentages averaged over the whole model run of the various hydration states to the overall concentration in  $\text{mol l}^{-1}$ . The following labels are used: unhyd = unhydrated form; hydALD = the aldehyde group is hydrated; hydKET = the keto group is hydrated; hydFULL = the compound is fully hydrated at every carbonyl group; hydXXALD = the outer aldehyde groups are hydrated (the carbon number is given for completeness indicated by XX); XXhyd = hydration occurs both at a aldehyde and a carbonyl group and the carbon number of the carbonyl group is given (indicated by XX).

Compound	Speciation averaged over whole model run in %			
	unhyd	hydALD	hydKET	hydFULL
Methylglyoxal	0.0	68.8	24.0	7.2
1,2-Butanedial	24.0	21.6	—	14.3
1,3-Butanedial	86.0	14.0	—	—
	see footnote (a)	hyd13ALD	hydFULL	REST
Propanetrial	10.6	5.2	12.6	50.3
	see footnote (b)	unhyd	12hyd	hydFULL
1,2,3-Butanetrial	10.1	38.0	6.6	4.9
	see footnote (c)	see footnote (d)	unhyd	12hyd
1,2,4-Butanetrial	13.7	15.7	24.8	2.8
	see footnote (e)	see footnote (f)	hyd14ALD	hydFULL
2-Hydroxy butanetrial	12.2	14.0	3.3	19.9

<sup>(a)</sup>for a better legibility, the average fraction of the following forms is listed in the table (exact fractions are given in parantheses): unhyd (10.6%), hydALD (10.9%), and hydKET (10.4%); <sup>(b)</sup>the following forms have the same fraction (the number in the table applies to each form): hydALD, hyd2KET, hyd3KET, hyd23KET, and 13hyd; <sup>(c)</sup>average of hyd4ALD (13.8%), hyd14ALD (13.5%), and 24hyd (13.8%); <sup>(d)</sup>average of hyd1ALD (15.3%) and hydFULL (16.1%); <sup>(e)</sup>average of hyd1ALD (12.3%), hyd4ALD (12.1%), 13hyd (11.5%), and hydKET (12.9%); <sup>(f)</sup>average of unhyd (13.6%) and 34hyd (14.4%)

in a keto group, 2 H-atoms are present in the respective gem-diol form, albeit high *BDEs* in oxygen-bound H-atoms suggest low reaction rate constants.

However, measured data on the speciation of the hydration state of carbonyl compounds is sparse (see *Raventos-Duran et al.*, 2010). More experimental data is desirable to evaluate the hydration estimations and subsequently improve the predictions. Currently, GROMHE is the most accurate prediction method to the best of our knowledge. However, the uncertainty of hydration is critical as it can have a large impact on the tropospheric oxidation.

Moreover, hydration affects dissociation. For the estimation of the dissociation of carboxylic acids, the method after *Perrin et al.* (1981) has been implemented into the GECKO-A protocol. The method is a group contribution method, which uses Taft parameters to estimate the  $pK_a$  of the carboxylic acids. Neighbouring groups affect the  $pK_a$ . Thus, gem-diols adjacent to carboxyl groups will result in a different  $pK_a$  than with a carbonyl group instead. From Table 6.4 can be seen that hydration of keto-carboxylic acids shifts the speciation towards the protonated forms. Although the effect is small, it might be important in different regime with different pH values. Moreover, there is a potential to affect particle acidity. Yet, the effect is expected to be small due to a small shift in the speciation only and the weak acidity of carboxylic acids.



**Table 6.4** Influence of the state of hydration on the dissociation state of oxo-substituted carboxylic acids. The given speciation of the dissociation state (in %) is the average over the whole model run and is calculated separately for the hydrated and unhydrated forms. The following labels are used: 0h = unhydrated and fully protonated form; 0h1d = unhydrated form with one carboxyl group deprotonated; 0h2d = unhydrated and fully deprotonated form; 1h/1h1d/1h2d = same as for 0h, but with an hydrated carbonyl function.

Compound	Speciation in % of unhydrated forms			Speciation in % of hydrated forms		
	0h	0h1d	0h2d	1h	1h1d	1h2d
Pyruvic acid	96.1	3.9	—	99.9	0.1	—
2-Oxo butyric acid	93.9	6.1	—	98.1	1.9	—
Mesoxalic acid	96.7	3.3	0.0	96.3	3.7	0.0
Oxaloacetic acid	53.9	46.1	0.0	99.8	0.2	0.0

### 6.2.7.3 Dicarboxylic acids and functionalised monocarboxylic acids

In subsection 6.2.3.2 it was shown that a substantial fraction of the organic mass are carboxylic acids and diacids (see Figure 6.13, page 160). Therefore, these compound classes are given special attention and a detailed discussion of selected representatives is given in the following.

#### Monocarboxylic acids

A large influence of the extended organic scheme in the new CAPRAM versions on the organic mass fraction was shown in subsection 6.2.3.2. As the organic mass is composed to a major fraction of organic acid, the extended organic schemes have a big impact on concentration-time profiles of single organic constituents as shown in Figure 6.34. Three typical representatives of this compound class have been chosen and the influence of the extended scheme on their aqueous phase composition and chemistry is discussed in this subsection.

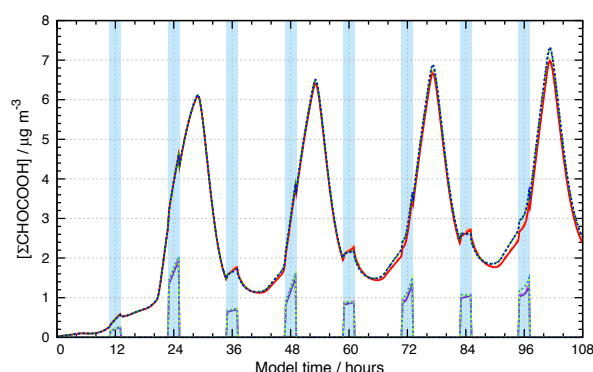
**Glyoxalic acid.** Glyoxalic acid is an important oxo-substituted C<sub>2</sub> carboxylic acid. Despite major changes in the extended CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$  only minor variations in the concentration-time profiles of the extended schemes are seen (see Figure 6.34a). Despite the extension of higher organic chemistry in the new CAPRAM versions, the oxidation of the unhydrated forms is treated besides the oxidation of the hydrated forms. Moreover, all possible equilibria between every hydration and dissociation state is treated explicitly from CAPRAM 3.5 $\alpha$  on.

In general, concentrations increase during the night. During the day, destruction exceeds formation processes and concentrations decrease from 6.2 – 8.4  $\mu\text{g m}^{-3}$  to 1 – 2  $\mu\text{g m}^{-3}$  in Figure 6.34a. With declining availability of radiation and, therefore, oxidant radicals, too, concentrations begin to rise in the evening hours. After sunset, a rapid increase in glyoxalic acid concentrations is observed. The increase is due to the gas phase formation of glyoxalic acid formed from oxidation products of aromatic compounds (mostly phenols and catechols) and missing sink processes for glyoxalic acid during night-time hours. There is a

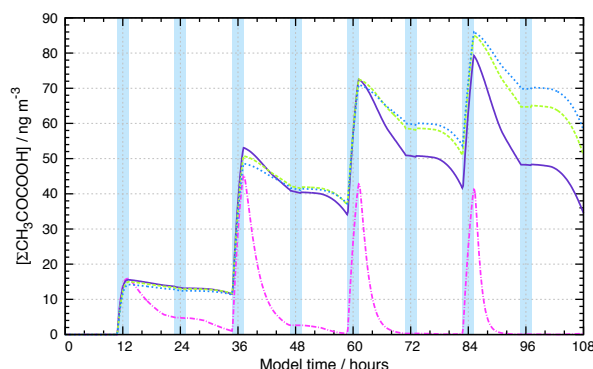
shift in the beginning of the enhanced increase to later hours, which remains unclear. At the second model day, the increase starts right before the night-time cloud, while it is shifted towards the middle and the second half of the cloud period on the third and fourth night, respectively. Moreover, no effect on the concentration-time profiles is seen by night-time clouds while daytime clouds slow down the degradation of the total gas and aqueous phase glyoxalic acid concentrations in CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$ . In CAPRAM 3.0n, even slight production periods can be observed. During cloud periods, a substantial fraction of glyoxalic acid is dissolved in cloud droplets while it is almost exclusively in the gas phase during non-cloud periods (see Figure 6.34a).

A minor concentration increase from the extended schemes in CAPRAM 3.5 $\alpha$  and 4.0  $\alpha$  is observed during night-time hours. During the day, differences between the various scenarios vanish. Therefore, the extended organic chemistry does not lead to an increased production of glyoxalic acid. Moreover, the description of the oxidation of only the hydrated forms of glyoxalic acid is sufficient to model realistic concentrations of this compound as the speciation and reactivity of the unhydrated forms is too low to influence oxidation.

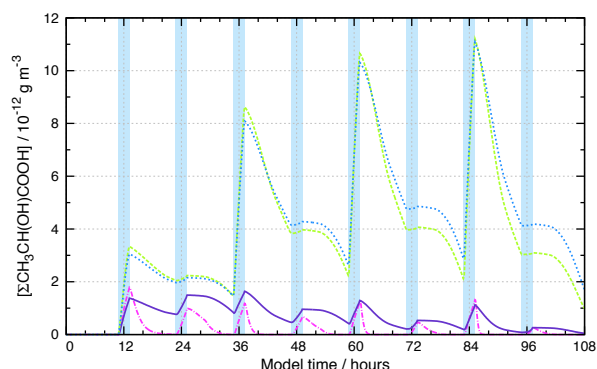
(a) Glyoxalic acid



(b) Pyruvic acid



(c) Lactic acid



aq (C3.0o)    aq (C3.0p)    aq (C3.5 $\alpha$ )    aq (C4.0 $\alpha$ )  
g+aq (C3.0o)    g+aq (C3.0p)    g+aq (C3.5 $\alpha$ )    g+aq (C4.0 $\alpha$ )

**Figure 6.34** Profiles of the overall aqueous phase concentration (including all hydrated or dissociated forms) and, for glyoxalic acid, the sum of the gas and overall aqueous phase concentrations of selected monocarboxylic acids for the various CAPRAM mechanisms under urban conditions.

Compared to field measurements by *Souza et al.* (1999), *Sun and Ariya* (2006), *Ho et al.* (2006, 2007), *Bao et al.* (2012), and *He et al.* (2014), the model severely underpredicts aqueous phase concentrations and overpredicts gas phase concentrations. Particulate concentrations in the studies of these authors measure particulate concentrations in the ng range from  $18.5 \text{ ng m}^{-3}$  in Hongkong (*Ho et al.*, 2006) to  $174 \text{ ng m}^{-3}$  in Tokio (*Sun and Ariya*, 2006). The dataset presented by *Li and Yu* (2010) confirms the large variability in the measurements. These authors found glyoxalic acid concentrations between 11 and  $588 \text{ ng m}^{-3}$  in Hongkong, with mean summer concentrations of  $15 \text{ ng m}^{-3}$  and mean roadside concentrations of  $59 \text{ ng m}^{-3}$ . The model predicts negligible particulate concentrations with less than  $0.26 \text{ ng m}^{-3}$  and an average of  $0.1 \text{ ng m}^{-3}$ . Only during cloud periods, significant aqueous phase concentrations are found with up to  $2 \mu\text{g m}^{-3}$ , which is significantly higher than in the above-mentioned measurements of urban particles.

*Bao et al.* (2012) simultaneously determined gas and aqueous phase concentrations of glyoxalic acid and found  $29.4 \pm 17.9 \text{ ng m}^{-3}$  in the gas phase and  $56.5 \pm 44.7 \text{ ng m}^{-3}$  in the aqueous phase. This contradicts the model results, which predicts glyoxalic acid predominantly in the gas phase. These discrepancies are another indication for severely underpredicted Henry’s Law constants in the model.

**Pyruvic acid.** Another atmospherically relevant oxo-substituted carboxylic acid is pyruvic acid. In contrast to glyoxalic acid, the extension of the organic scheme in CAPRAM has a big influence on the concentration-time profiles of this compound. As phase transfer was suppressed in the current model runs and the species is decoupled from the gas phase, only the aqueous phase concentrations are shown in Figure 6.34b. It can be seen that the introduction of the WSOC/HULIS parameterisations in CAPRAM 3.0p causes a large increase in pyruvate concentrations mainly due to the decreased hydroxyl radical concentrations and, hence, decreased oxidation of this acid. A more complex organic scheme further increases the concentrations in CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$  due to further aqueous phase sources from other  $\text{C}_3$  and  $\text{C}_4$  organic compounds.

Major production occurs during daytime cloud periods, where up to  $40 \text{ ng m}^{-3}$  pyruvate are produced. No production occurs during night-time cloud periods. During non-cloud periods, oxidation outweighs production and pyruvic acid is degraded. However, oxidation cannot compensate for the large in-cloud production during the day in the runs with the WSOC/HULIS parameterisations leading to an accumulation of pyruvate. At the end of the last daytime cloud, between  $80$  and  $90 \text{ ng m}^{-3}$  pyruvate are found in these model runs.

Modelled concentrations compare well with concentrations determined in field measurements in urban sampling sights. Measurements in North and South American, Asian, and European megacities span a range from  $1$  to  $410 \text{ ng m}^{-3}$  (*Souza et al.*, 1999, *Sun and Ariya*, 2006, *Ho et al.*, 2006, 2007, *Li and Yu*, 2010, *He et al.*, 2014). The oldest measurements in São Paulo, Brazil by *Souza et al.* (1999) show the highest concentrations ranging from  $60 \text{ ng m}^{-3}$  to  $1.15 \mu\text{g m}^{-3}$  with a mean of  $410 \pm 280 \text{ ng m}^{-3}$ . Modelled results are at the very low end of the measurements indicating recent advancements in air pollution control

measures. Measurements presented by *Sun and Ariya* (2006) in New York, USA, Tokio, Japan, and Vienna, Austria are in excellent agreement with modelled results as are the measurements by *Bao et al.* (2012) in a suburban site of Saitama, Japan. Compared to measurements by *He et al.* (2014), modelled results are at the high end of the determined concentrations. These authors also distinguished between day- and night-time concentrations with slightly higher concentrations during the day. This is in good agreement with the model as mass increase is seen only during day-time cloud periods, while pyruvic acid is decreased in the remaining model time. This behaviour causes higher concentrations during the day than during night.

**Lactic acid.** Large differences between the various CAPRAM runs are seen for lactic acid in Figure 6.34c. In the original CAPRAM 3.0o mechanism, up to  $2 \cdot 10^{-12} \text{ g m}^{-3}$  lactic acid are produced during cloud periods. Production is somewhat enhanced during daytime clouds. During non-cloud periods, lactic acid is degraded to negligible concentrations. The degradation is faster during the day than during night. With the introduction of the WSOC/HULIS parameterisations, oxidations is suppressed due to the decreased hydroxyl radical concentrations and lactic acid concentration levels between 1 and  $2 \cdot 10^{-12} \text{ g m}^{-3}$  are maintained for the first two days until concentrations start to decrease again.

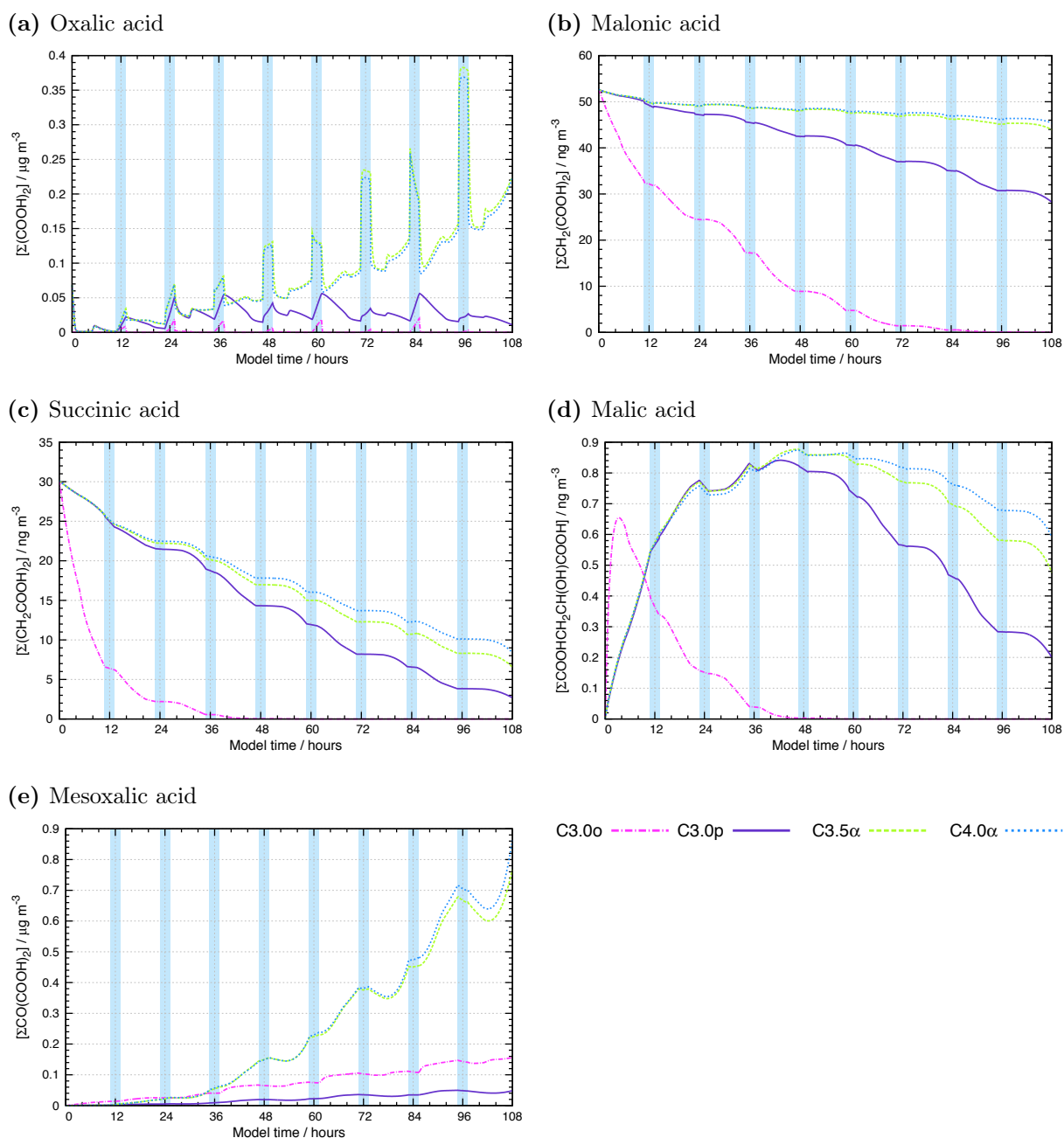
With the extension of the explicit organic scheme in CAPRAM 3.5 $\alpha$  a large increase in the production during daytime clouds is observed. Further increases in CAPRAM 4.0 $\alpha$  are small compared to the changes in CAPRAM 3.5 $\alpha$ . Most of the produced lactate is oxidised during non-cloud periods, but a small fraction of about  $2 \cdot 10^{-12} \text{ g m}^{-3}$  remains in the aqueous phase. Compared to other organic constituents, these traces are, however, negligible.

## Dicarboxylic acids

In Figure 6.35, important representatives of dicarboxylic acids are shown, which are discussed in detail in this paragraph.

**Oxalic acid.** The simplest, yet most abundant and, therefore, very important dicarboxylic acid is oxalic acid ( $\text{C}_2\text{H}_2\text{O}_4$ ). Its concentration-time profile under urban conditions is shown in Figure 6.35a. A large impact from the chemical scheme applied can be observed. In the original CAPRAM 3.0o mechanism, oxalic acid is present in noticeable concentration only during cloud periods with higher concentrations up to  $20 \text{ ng m}^{-3}$  during night-time clouds and less than  $10 \text{ ng m}^{-3}$  during the day.

The parameterisations of hydroxyl and nitrate radical reactions with WSOC and HULIS compounds and the formation of iron-HULIS complexes in CAPRAM 3.0p have a big impact on the concentration-time profile of oxalate. Due to decreased radical concentrations, less oxalate is oxidised. The major effect, however, derives from the formation of iron-HULIS complexes. With the new parameterisations, more free iron is bound in complexes



**Figure 6.35** Overall aqueous phase concentration-time profiles (including all dissociation states) of selected dicarboxylic acids for the various CAPRAM mechanisms under urban conditions.

and, hence, not available for the formation of iron-oxalate complexes. The photolysis of these complexes is a very effective sink for oxalate. Thus, with reduced iron-oxalate complexes, formation processes are able to compete with degradation processes and oxalate is present in concentrations up to  $50 \text{ ng m}^{-3}$ . Cloud periods remain most important for oxalate production, especially during the night. Oxalate is degraded during non-cloud periods, yet concentrations remain above the pre-cloud concentration level of the last cloud period.

Large sources for oxalic acid derive from the extended explicit organic chemical scheme in CAPRAM 3.5α, while insignificant additional sources are observed in CAPRAM 4.0α. In

the new schemes a constant increase in concentrations during non-cloud daytime periods is observed and a slight decrease during night-time non-cloud periods. Concentrations increase to more than  $0.2 \mu\text{g m}^{-3}$  at the end of the model run. A different behaviour is also observed during cloud periods in the extended CAPRAM versions. Except for the first cloud period, concentrations at the beginning of each cloud period adjust much fast to higher concentration levels. During cloud periods, concentrations are increased to values up to  $0.38 \mu\text{g m}^{-3}$ . However, at the end of the model runs, concentrations are immediately decreased again. During the day, clouds can act as sink for oxalate and concentrations are decreased by almost half a microgram after the last daytime cloud compared to pre-cloud concentration levels. The effect of daytime clouds acting as a sink for oxalate increases throughout the model run. While clouds produce oxalate in the first two days, degradation starts during the third daytime cloud period and increases in the fourth daytime cloud.

Due to its abundance, many measurements exist for oxalic acid. Typical particulate concentrations range from  $0.02 \mu\text{g m}^{-3}$  in Europe to about  $0.2 \mu\text{g m}^{-3}$  in South-East Asia (see, e.g., *Zhang et al.*, 2012, *Laongsri and Harrison*, 2013 and references therein). Therefore, with the WSOC/HULIS parameterisations, results are at the lower end of the measurements in CAPRAM 3.0p. The additional oxalate production from the extended explicit organic scheme in CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$  produces results that are in excellent agreement with field measurements. Moreover, rising concentrations throughout the model run in the extended CAPRAM versions reflect the organic particle growth observed in the field. Currently, only models excluding iron complex photolysis such as the one by *Ervens et al.* (2008) seemed to capture the daytime oxalate concentrations right. The additional parameterisation of the formation of iron-HULIS complexes helped to increase our understanding of iron recycling in the aqueous phase and the influence on the organic multiphase chemistry. While previous CAPRAM studies (see *Tilgner et al.*, 2013) overestimated the sinks from the photolysis of iron-oxalato complexes, it was possible to model realistic oxalate concentrations throughout the model run with the new parameterisations. Thus, this dissertation helped to resolve previous discrepancies from overpredicted sink processes from the iron-oxalato complex photolysis or their complete omission to obtain plausible daytime oxalate concentrations.

**Malonic and succinic acid.** Major changes are also observed for the higher unsubstituted carboxylic acids malonic acid and succinic acid (see Figure 6.35b and 6.35c). Both acids are initialised at the beginning of the model run with concentrations of  $52.3$  and  $30 \text{ ng m}^{-3}$  for malonic and succinic acid, respectively. While both acids are decreased rapidly in CAPRAM 3.0o, decreased radical concentrations due to the additional reactions with WSOC and HULIS compounds in CAPRAM 3.0p increase the lifetime of malonic and succinic acid significantly. In CAPRAM 3.0o, succinic acid is oxidised to negligible concentrations within one and a half days, while it takes about 3.5 days for malonic acid to be oxidised to negligible concentrations due to the higher initial concentrations of malonic acid. With the decreased radical concentrations in CAPRAM 3.0p, about  $28 \text{ ng m}^{-3}$  malonate and  $3 \text{ ng m}^{-3}$  succinate remain in the aqueous phase at the end of the model run under urban conditions (see Figure 6.35).

Further increases in DCA concentrations are observed for CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$ . Increases result from an enhanced formation of the DCAs in the extended organic scheme, but also from reduced radical concentrations due to the additional organic content acting as hydroxyl and nitrate radical scavenger. Again, changes in CAPRAM 3.5 $\alpha$  are much greater than in CAPRAM 4.0 $\alpha$ . Furthermore, production for malonic acid is much greater than for succinic acid and the initial concentrations are almost maintained throughout the model run. Only a slight decrease to 44 and 46 ng m<sup>-3</sup> at the end of the model run in CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$ , respectively, is observed. For succinic acid, there is still a significant decrease throughout the model run with final concentrations of 6.5 and 8.5 ng m<sup>-3</sup> in CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$ , respectively (see Figure 6.35).

The main reason for the insufficient description of succinate production derives from the extension process of the explicit organic scheme in CAPRAM 3.5 $\alpha$ /4.0 $\alpha$ . Only compounds with up to four carbon atoms were considered in the extension process. This is sufficient for malonic acid and new production pathways lead from succinic acid to oxaloacetic acid, its subsequent hydration, oxidation at the gem-diol group and the mono-molecular decay of the alkoxy radical to malonic acid. Thus, the oxidation of the C<sub>4</sub> dicarboxylic acid leads to the formation of the C<sub>3</sub> DCA. For succinic acid, input from higher organic compounds are missing and the oxidation scheme is not sufficient to describe the formation of succinic acid adequately.

Comparing the model results to field measurements, malonic acid is in excellent agreement with numerous field experiments. Most measurements range between 60 and 70 ng m<sup>-3</sup> (see, e.g., *Yang and Yu*, 2008, *Hsieh et al.*, 2009, *Wang et al.*, 2012). However, it should be kept in mind that phase transfer was suppressed in the current study in order to model a realistic processing of the organic mass fraction. Partitioning has been shown a crucial parameter in the generator protocol, which needs future revision.

Succinic acid is found in field measurements in concentrations between 70 and 100 ng m<sup>-3</sup> (*Hsieh et al.*, 2009, *Wang et al.*, 2012, *Bao et al.*, 2012) in Asian regions. Therefore, the initialised concentration as taken over from previous studies (*Tilgner and Herrmann*, 2010, *Tilgner et al.*, 2013) has already been too low in the CAPRAM scenario for these regions. Due to missing sources for succinic acid in a mechanism focused on compounds up to four carbon atoms, succinic acid concentrations are heavily underestimated at the current state. This fact stresses the importance for further mechanism development and extensions of the mechanism to higher carbon numbers.

**Malic acid.** Another interesting example is malic acid, a hydroxy-substituted C<sub>4</sub> dicarboxylic acid (see Figure 6.35d). Substantial differences can be seen in Figure 6.35d between the various CAPRAM versions. Generally, in all scenarios malic acid is initially produced in the model runs before concentrations start to decline again. Maximum concentrations range from 0.65  $\mu\text{g m}^{-3}$  in CAPRAM 3.0o to almost 0.9  $\mu\text{g m}^{-3}$  in CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$ .

There is a relatively narrow peak in maximum malic acid concentrations during the first night in CAPRAM 3.0o. The produced malic acid during that period is degraded within the first two model days. With the introduction of the WSOC/HULIS parameterisations in CAPRAM 3.0p maximum concentrations increase to about  $0.85 \mu\text{g m}^{-3}$ . Moreover, the peak concentrations are shifted to much later model towards the end of the second model day. The peak is widened and a period with high concentrations is observed rather than a distinct peak. A likely explanation for this shift in maximum concentrations are the decreased hydroxyl and nitrate radical concentrations from the WSOC/HULIS reactions. Malic acid is not initialised in the aqueous phase in the model runs. Its concentrations derived solely from the in-situ aqueous phase production throughout the simulation time. Thus, decreased radical oxidant concentrations cause a delay in the production. On the other hand, oxidation of malic acid is reduced. Thus, maximum concentrations are delayed and increase due to less oxidation by OH and  $\text{NO}_3$  radicals.

This effect can also be observed in CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$  to a smaller extent. Decreased radical oxidant concentrations further slow down the initial production of malic acid and cause slightly decreased concentrations on the first and second model day. Peak concentrations are further delayed towards the end of the second model day and are slightly higher than in CAPRAM 3.0p (see Figure 6.35d). Increased sources from the extended organic scheme in CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$  cause a slower decrease in malic acid concentrations and  $\sim 0.6$  and  $0.48 \mu\text{g m}^{-3}$  in CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$ , respectively, remain in the aqueous phase at the end of the model run compared to  $0.2 \mu\text{g m}^{-3}$  in CAPRAM 3.0p.

**Mesoxalic acid.** The last dicarboxylic acid discussed in this context is the highly oxidised DCA mesoxalic acid (Figure 6.35e). Again, substantial differences are found between the various CAPRAM versions. Mesoxalic acid increases throughout the whole model. The increase varies between  $50 \text{ ng m}^{-3}$  and  $0.9 \mu\text{g m}^{-3}$  depending on the mechanism.

A moderate decrease is observed in CAPRAM 3.0o up to almost  $0.16 \mu\text{g m}^{-3}$  at the end of the model run. The increase is slightly enhance after daytime clouds. During night-time clouds and in the second half of the night, a slight decrease in concentrations is observed. Reduced radical oxidant concentrations in CAPRAM 3.0p reduce mesoxalic acid production to about  $50 \text{ ng m}^{-3}$  at the end of the model run.

Substantial advancements have been introduced in the chemical schemes of CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$ . Besides a much more comprehensive scheme with a great variety of sources for mesoxalic acid, the chemistry of this oxo-substituted DCA has been extended. Hydration at the carbonyl group was introduced for every dissociation state. With the introduction of the hydration of the keto group, further sink processes are possible in CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$ . Previously, decarboxylation was the only loss process for mesoxalic acid in the CAPRAM 3.0 versions. From CAPRAM 3.5 on, oxidation by H-atom abstraction is possible at the gem-diol group as well.



Decarboxylation is a rather slow first order process with an implemented rate constant of  $1 \cdot 10^{-5} \text{ s}^{-1}$ . Additional sink processes in CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$  of H-atom abstraction by hydroxyl radicals at the gem-diol group with estimated rate constants between  $1.6$  and  $4.9 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for the different protonated forms and ETR by nitrate radicals with second order rate constants up to  $7.75 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$  are competitive with the decarboxylation. Despite this additional sink processes, production from further sources of the extended organic scheme in CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$  outweigh loss processes and a steady increase is observed in both model runs leading to final mesoxalic acid concentrations of  $0.76$  and  $0.86 \mu\text{g m}^{-3}$  in CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$ , respectively.

In the extended CAPRAM 3.5 $\alpha$  and 4.0 $\alpha$  versions, periods of substantial mesoxalic acid degradation are observed in Figure 6.35e. After night-time cloud periods, concentrations decrease until sunrise. The decrease starts after the second night-time cloud, where only a few nanogram of mesoxalic acid are degraded. The effect increases in magnitude over time and after the last cloud period, almost  $0.1 \text{ ng m}^{-3}$  are lost. It is, however, unlikely that the effect is caused by the additional sink processes in CAPRAM. As hydroxyl radicals show a diurnal variation with significant concentrations only during the night, they cannot account for these night-time losses. A small fraction of the mesoxalic loss might be attributed to additional sinks by ETR with the nitrate radical. The main fraction of the loss, however, is most likely due to decreased sources from the oxidation of further organic compounds in the extended schemes and, thus, increased relative importance of the oxidation of mesoxalic acid.

**Comparison with field measurements.** Compared to field measurements, modelled dicarboxylic acid concentrations are mostly at the lower end of the range of measurements (see, e.g., data presented by *Sun and Ariya*, 2006, *Ho et al.*, 2006, 2007, *Wang et al.*, 2011, *He et al.*, 2014 and references therein). All unsubstituted DCAs oxalic, malonic, and succinic acid and the hydroxy-substituted C<sub>4</sub> DCA malic acid are below the very high concentrations in Asian megacities (compare data in Figure 6.35 with literature data, e.g., by *Ho et al.*, 2006, 2007, and *He et al.*, 2014. Modelled concentrations fall in the range of concentrations measured in American cities such as New York, Las Vegas, or Houston, or European cities such as Leipzig (see, e.g., *Sun and Ariya*, 2006 or references within *Ho et al.*, 2006). One reason for the low concentrations in the model is the rather conservative model initialisation with initial concentrations below most Asian megacities, where a lot of the measurements are performed.

The only exception forms mesoxalic acid (keto-malonic acid), for which significantly higher concentrations were modelled than measured in the field. In the extended mechanisms, mesoxalic acid constantly increases to concentrations of about  $0.8 \mu\text{g m}^{-3}$ . Even in very polluted Chinese cities, concentrations of only a few  $\text{ng m}^{-3}$  were measured range from concentrations below the detection limit up to  $7.43 \text{ ng m}^{-3}$  (*Ho et al.*, 2007, *He et al.*, 2014). This indicates currently missing degradation processes in the model. Additional sinks such as photolysis, complexation and subsequent photolysis of the complex need to be considered in future CAPRAM versions for a more accurate description. Moreover, more

experimental data such as equilibrium constants for complexation processes or extinction coefficients and quantum yields for photolysis processes are needed to design more accurate protocols for mechanism self-generations and consequently chemical oxidation schemes.

# 7 Conclusions

## Aim of the dissertation

Recent research led to a considerable number of large chemical mechanisms to describe the atmospheric fate of a multitude of compounds of environmental interest. However, the description of the atmospheric aqueous phase, i.e. cloud and fog droplets or deliquescent particles, is still lagging behind the gas phase. A more detailed aqueous phase mechanism developed over the last decades is CAPRAM, which latest published version 3.0 comprises 777 aqueous phase processes. The aim of the present study was to advance this mechanism to investigate still pressing unresolved issues concerning the role of the aqueous phase in tropospheric multiphase chemistry. In particular, this dissertation tried to give specific answers about the composition of cloud droplets and deliquescent particles with a focus on the organic content. It further aimed at a clarification of the formation and destruction pathways of the constituents (single compounds and compound classes) and, therefore, one of the goals of this dissertation is a more accurate description of aqueous SOA formation processes.

However, advancements in the developed mechanisms have led to large oxidation schemes and further manual extensions have become unfeasible. Therefore, preceding work focused on the automation of the mechanism development process. The work included the evaluation of kinetic data and methods to predict missing kinetic data, which were then incorporated into an expert system. As the group of Bernard Aumont at the LISA in Paris, France, has already the expertise in self-generating gas phase chemical mechanisms, the work was performed in close cooperation with the LISA. The expert system GECKO-A (*Aumont et al.*, 2005) was extended from the gas to the aqueous phase and then used for the mechanism self-generation.

## Evaluation of kinetic data and prediction methods for missing data

The construction of chemical mechanisms heavily relies on experimental data. The data is needed either directly to assign rate constants to the reactions considered in the mechanism or indirectly to use the data to derive correlations or further methods for the prediction of any missing data. Therefore, preliminary work included the collection and evaluation of kinetic and thermodynamic data for organic compounds of potential importance for tropospheric aqueous phase chemistry. A database with 465 OH and 129 NO<sub>3</sub> radical reactions with organic compounds was the result of an comprehensive literature review.

The data was applied to validate existing methods for the prediction of kinetic data for reactions of organic compounds with the hydroxyl and nitrate radical. The following methods have been reviewed and evaluated:

- Prediction of aqueous phase rate constants by correlation to gas phase rate constants
- Extrapolation of homologous series of kinetic data of several compound classes
- Comparison of OH and NO<sub>3</sub> radical reactivities
- Evans-Polanyi-type correlations including the prediction of *BDEs* with the method by *Benson* (1976)
- Structure-activity relationships

The evaluation showed that even simple correlations are capable to produce appreciable results, which will at least predict the correct order of magnitude of the considered reaction rate constant. It was shown, however, that the precision of the predictions can be significantly increased by relating the kinetic data to properties of fractional parts of a molecule rather than the molecule as a whole.

The highest precision in prediction was reached with structure-activity relationships (SARs). A very detailed and thorough evaluation has been performed using scatter and box plots for the statistical analysis of the comparison of predicted and experimental rate constants. Box plots directly show the fraction of reactions predicted within a certain absolute error. A linear regression of the experimental over predicted data in a scatter plot delivers further valuable information. From the slope and the y-intercept of the regression line, biases of the prediction method can be evaluated, while the standard deviation of the correlation coefficients  $R^2$  provide information about the quality of a single prediction of a certain rate constant.

It was shown that the accuracy of SARs depends on the complexity of the molecular structure. Both SARs investigated, i.e. the SAR by *Monod and Doussin* (2008)/*Doussin and Monod* (2013) and the one by *Minakata et al.* (2009), showed high correlation coefficients of around 0.9 for the simple structure of pure hydrocarbons and little deviations of the regression line from the 1:1 line. By adding only one functional group of either an alcohol ( $-\text{OH}$ ), a carbonyl ( $-\text{CH}=\text{O}/>\text{C}=\text{O}$ ), or a carboxyl/carboxylate ( $-\text{C}(=\text{O})\text{OH}/-\text{C}(=\text{O})\text{O}^-$ ) function, the correlation coefficients decreased slightly to 0.8 – 0.9 for the SAR of *Monod and Doussin* and to values around 0.7 for the SAR by *Minakata et al.*. The addition of two or more functional groups of the same kind further decreased the accuracy for di- and polyols to  $R^2 = 0.7$  and even 0.2 for the SARs by *Monod and Doussin* and *Minakata et al.*, respectively. On the other hand, the SARs worked equally well for dicarboxylic acids as for hydrocarbons. Worst agreement between experimental and predicted results was seen for polyfunctional compounds with different functional groups and correlation coefficients of less than 0.33 were achieved as well as a slope of the regression line of the predicted versus experimental data points significantly below 1. Nevertheless, the analysis of the box plots showed the highest precision for this estimation method with more than half of the data being predicted within a factor of 2 and almost all data within the correct order of magnitude.

---

More importantly, the method is easy to use and can be instantly adapted in computer assisted prediction tools such as the expert system GECKO-A. The application of molecular increments for the prediction of the rate constants allows furthermore the prediction of the reaction products and their branching ratios. A weakness of the method is the large number of descriptors needed for the predictions. Therefore, SARs rely on a large experimental database and, consequently, current predictions of rate constants with this method exist only for hydroxyl radical reactions, for which rate constants are determined most abundantly.

The prediction of nitrate radical reactions had to be achieved with another prediction method. Evans-Polanyi-type correlations relate the bond dissociation energy (BDE) of the weakest bound H-atom to the second order rate constant of that molecule with  $\text{NO}_3$ . However, this approach assumes, that OH predominantly attacks the weakest bound H-atom, which is not true, especially for larger compounds at which this study aims. Therefore, a new approach was introduced in this dissertation, where the second order rate constant is correlated to the sum of all *BDEs* of chemical bonds of hydrogen atoms with carbon or oxygen atoms. The precision of the predicted rate constants significantly improved although information about the reaction products cannot be retrieved.

Moreover, differences in the correlation of hydroxyl and nitrate radical rate constants of organic compounds were seen. While a linear correlation was seen for the nitrate radical, hydroxyl radical reactions showed a quadratic relationship. A possible explanation for this behaviour is the circumstance that hydroxyl radical reactions are faster than nitrate radical reactions and can even become diffusion controlled. Therefore, the increase in the second order rate constants with increasing *BDE* slows down for high *BDEs* and a quadratic equation is better capable of describing this behaviour.

### **Designing a protocol for automated mechanism construction with GECKO-A and extension of the CAPRAM mechanism**

Based on the results of the evaluation process, a protocol for automated mechanism construction was designed and implemented as FORTRAN routines in the expert system GECKO-A. The programming was mainly performed at the LISA with several adoptions according to the need of the box model SPACCIM at the TROPOS. SARs were used for the prediction of hydroxyl radical reactions, while nitrate radical reactions were predicted with the advanced Evans-Polanyi-type correlations. The decay of organic radical compounds had to be estimated with fixed rate constants and branching ratios.

GECKO-A was used to extend the current version 3.0 of the CAPRAM mechanism. Besides the update of the kinetic data, major advancements were the introduction of radical cross reactions in CAPRAM 3.0o, parameterisations for hydroxyl and nitrate radical reactions with WSOC and HULIS compounds as well as the formation and degradation of iron-HULIS complexes in CAPRAM 3.0p, the introduction of branching ratios and the description of the oxidation of new intermediate organic compounds in CAPRAM 3.5, and the extension of the organic chemistry of compounds with up to four carbon atoms in

CAPRAM 4.0. Moreover, three levels of detail were used for the description of the nitrate radical chemistry from CAPRAM 3.5 on. Besides the complete oxidation scheme, reactions with unsaturated compounds were omitted to suppress organic nitrate formation, which significantly reduces the mechanism size. In a third version, no nitrate radical chemistry is treated at all besides the chemistry already present in CAPRAM 3.0.

Sensitivity studies were carried out to investigate the most crucial parameters in the protocol. As model studies encountered a formation of unrealistically high concentrations of highly functionalised polycarbonyl compounds (mostly in their hydrated forms), their decay was investigated and added to the protocol. Moreover, it was found that it is important to include the complete nitrate radical chemistry. Even though, contributions of the nitrate radical addition to double bonds are minor for the oxidation of unsaturated compounds, they lead to the formation of organic nitrates, which cannot be neglected. Further sensitivity studies aimed at discrepancies of an insufficient organic particle mass production and an overprediction of the organic nitrate fraction. As a consequence of these studies, new parameterisations of reactions and equilibria of WSOC and HULIS compounds were parameterised and a new CAPRAM subversion 3.0p was created.

Furthermore, the sensitivity studies pointed at the importance of organic radical chemistry. Currently, only very few measurements of the kinetics of organic radicals exist. However, the distribution of the products from the radical decay can have a substantial influence on particulate organic mass production. New estimations of the alkoxy radical decay increase organic mass production by a couple of nanogram to more realistic production rates. Further sensitivity studies pointed at lack of understanding in tropospheric multiphase chemistry. Sufficient organic mass production was only seen, when phase transfer processes of species with more than two carbon atoms and an O:C ratio greater or equal one were omitted. This fact indicates a lack of knowledge, which could derive from insufficient estimations of the Henry's Law constants in GROMHE (*Raventos-Duran et al.*, 2010) as recent literature pointed to higher HLCs for example for dicarboxylic acids. The problems could also derive from missing or poorly estimated aqueous phase equilibria affecting the effective Henry's Law constant. Therefore, more measurements need to be performed to investigate important aqueous phase processes. Measurement techniques need to be refined for a higher accuracy and a better resolution of fast processes such as organic radical reactions.

### Mechanism validation against chamber experiments

For a further evaluation of the plausibility and quality of the generated mechanisms by the expert system GECKO-A, chamber experiments were performed by the LEAK team at the aerosol chamber LEAK of the Leibniz Institute for Tropospheric Research. Two different experiments were performed. GECKO-A was used to generate mechanisms especially designed to simulate the chamber experiments.

In a first attempt, gas phase hexane was oxidised. While the model predicted the formation of a number of highly oxidised and, hence, soluble compounds, this was not observed in

---

the chamber. However, uptake led to only a small increase in particle mass and most of the predicted compounds were close to the detection limit of the instruments used at LEAK. Nevertheless, the experiment showed good agreement in the gas phase concentration profiles of the organic trace gases monitored in LEAK and pointed at weaknesses in the predicted aqueous phase mechanism, which led to improvements in the description of the degradation of polycarbonyl compounds.

The second experiment was much more conclusive. In the experiment, 1,3,5-trimethylbenzene (TMB) was oxidised in the gas phase, which led to the formation of mainly methylglyoxal and acetic acid, both interacting with the aqueous phase. Despite difficulties to reflect the complex conditions in the chamber, good agreement was achieved between model and experimental results for most of the compounds.

The experiment also showed that it is important to consider the chemistry of larger compounds and representation of only a number of small aqueous phase sample compounds is not sufficient to reflect the complex multiphase chemical processes in the atmosphere or even under chamber conditions. Moreover, it was shown that a detailed microphysical scheme is equally important as the atmospheric composition and chemistry can have a profound impact on the microphysical parameters such as the liquid water content and particle radius, which in return influences the atmospheric chemistry leading to a positive feedback. Sensitivity runs performed pointed out differences in the LWC of one order of magnitude due to different complexities of the chemical schemes.

### **Model simulations with an ‘real atmosphere’ scenario**

The advanced CAPRAM versions were applied in parcel model scenarios with non-permanent clouds simulating remote continental and urban conditions and compared to the CAPRAM 3.0o/p versions. Due to the complexity of the chemical mechanisms, simulations were performed with a restricted microphysical scheme for a mono-disperse particle population.

Detailed investigations were performed on the processing of the particulate mass with a focus on organic matter. In addition to previous CAPRAM studies, more advanced investigations on the compound classes and the size of the molecules present in the aerosol particles were performed. During non-cloud periods, significant contributions of the organic scheme to the particulate matter is found only under urban conditions and in the extended CAPRAM versions. However, production of SOA mass is outweighed by loss processes and stagnant or slightly declining organic aerosol mass is observed during non-cloud periods in the current model run. An overall particle mass increase of about  $5 \mu\text{g m}^{-3}$  was observed due to mass increase during cloud periods. It was shown that organic particulate matter mainly consists of functionalised dicarboxylic acids and monocarboxylic acid. Only a small fraction can be attributed to organic nitrates. During cloud periods carbonyl compounds form another important constituent.

Looking at the chain length of the organic constituents, substantial differences were observed during non- and in-cloud conditions. While organic matter is mainly composed of smaller molecules with one or two carbon atoms only during in-cloud conditions, during non-cloud conditions C<sub>3</sub> and C<sub>4</sub> compounds dominate. It was shown that missing input from higher weight organic compounds is a likely cause for an underpredicted SOA production.

Further investigations showed a big impact of the new parameterisations of WSOC and HULIS compounds reacting with OH and NO<sub>3</sub> radicals or the formation of iron-HULIS complexes. The parameterisations widely affected the redox cycling of transition metal ions, decreased the radical oxidant concentrations, had an impact on the sulfur(IV) to sulfur(VI) conversion, inorganic particulate sulfate and nitrate formation and particle acidity. With the parameterisations, the particle pH decreased by more than 0.3 pH units due to different inorganic reaction cycles.

Detailed investigations of the concentration-time profiles of single compounds showed improvements for a great variety of compounds with increased and plausible aqueous phase concentrations. Comparisons to field measurements showed a good agreement with the model results over a wide range of organic compounds investigated. Furthermore, it was shown that nitrate radical chemistry becomes more important for highly functionalised acids and diacids and can even exceed hydroxyl radical oxidation as electron transfer reactions dominate over H-abstraction reactions for these specific compounds. However, overall contributions of the nitrate radical to the oxidation of organic compounds are with 2% small.

### Final conclusions and outlook

With the mechanism generator GECKO-A, a powerful tool has been generated to quickly develop large oxidation schemes for organic compounds of interest. Validation against chamber experiments and first applications in the CAPRAM mechanism extension have proven the plausibility of the generated mechanisms. However, some critical issues remain and need further testing such as the phase transfer of highly oxidised organic compounds or the degradation of organic radical compounds. Besides further model studies and the development of better prediction methods, it is necessary to measure a wider range of reactions of organic compounds with dissolved radical oxidants. While a sufficient database for hydroxyl radical reactions exists, kinetics of further radicals such as the nitrate radical or the sulfate radical anion with organic compounds are currently still not well investigated. Further experimental determinations are needed to develop reliable prediction methods.

Furthermore, advances in the generator protocol are needed. Currently a description of the chemistry of many atmospherically relevant compounds are missing. Further studies should aim at the advancement of the protocol to compound classes such as organic hydroperoxides, ethers, esters or aromatic compounds. Moreover, currently only oxidative processes are described in the generator protocol. With the current description, a prediction of particulate mass increase as observed in the field was impossible. Therefore, non-oxidative



---

processes such as accretion reactions (see, e.g., *Hallquist et al.*, 2009, *Ervens and Volkamer*, 2010) should be considered in future versions of GECKO-A.

Besides the advancements of the protocol for automated mechanism construction, the chemical mechanism CAPRAM itself should be further developed. Most importantly, the mechanism should be extended to compounds with higher carbon numbers ( $\geq C_5$ ). Even with the current version of GECKO-A, significant improvements can be expected as the current work pointed at a potential missing source from the aqueous phase oxidation of larger organic compounds.

Moreover, further model development is needed for a more accurate description of the degradation of organic compounds. Past studies have shown that organic compounds can form an ‘organic phase’, which can be externally or internally mixed (*Song et al.*, 2012). Liquid-liquid phase separation between organic and inorganic particulate components can increase particle mass formation by up to 50% (see *Song et al.*, 2012 and references therein). The organic phase can have a liquid to glassy state, which impacts the particle properties and most likely chemistry. Model development should focus on an adequate description of the organic phase and partitioning between liquid and gas phase.

It can be concluded that the advancement of the expert system GECKO-A to the aqueous phase has been proven of great scientific value. Further development of the protocol and applications in model studies should be undertaken to foster the research and help understanding the complex multiphase processing of organic compounds in different environments and contributions to SOA formation, particle acidification and further important processes concerning particle composition and chemistry.



# References

- Alfassi, Z.B., Padmaja, S., Neta, P., and Huie, R.E. Rate constants for reactions of nitrate ( $\text{NO}_3$ ) radicals with organic compounds in water and acetonitrile. *The Journal of Physical Chemistry*, **97**(15), 3780 – 3782, 1993. doi:10.1021/j100117a025.
- Altieri, K., Seitzinger, S., Carlton, A., Turpin, B., Klein, G., and Marshall, A. Oligomers formed through in-cloud methylglyoxal reactions: Chemical composition, properties, and mechanisms investigated by ultra-high resolution FT-ICR mass spectrometry. *Atmospheric Environment*, **42**(7), 1476 – 1490, 2008. ISSN 1352-2310. doi:10.1016/j.atmosenv.2007.11.015.
- Amels, P., Elias, H., Götz, U., Steinges, U., and Wannowius, K.J. Kinetic investigation of the stability of peroxonitric acid and of its reaction with sulfur (IV) in aqueous solution. In *Heterogenous and Liquid Phase Processes*, edited by P. Warneck, *Transport and Chemical Transformation of Pollutants in the Troposphere*, volume 2, 77 – 78. Springer, Berlin, Germany, 1996.
- Ammann, M., Cox, R.A., Crowley, J.N., Jenkin, M.E., Mellouki, A., Rossi, M.J., Troe, J., and Wallington, T.J. Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VI – heterogeneous reactions with liquid substrates. *Atmospheric Chemistry and Physics*, **13**(16), 8045 – 8228, 2013. doi:10.5194/acp-13-8045-2013.
- Arakaki, T., Anastasio, C., Kuroki, Y., Nakajima, H., Okada, K., Kotani, Y., Handa, D., Azechi, S., Kimura, T., Tsuchioka, A., and Miyagi, Y. A general scavenging rate constant for reaction of hydroxyl radical with organic carbon in atmospheric waters. *Environmental Science & Technology*, **47**(15), 8196 – 8203, 2013. doi:10.1021/es401927b.
- Arakaki, T., Saito, K., Okada, K., Nakajima, H., and Hitomi, Y. Contribution of fulvic acid to the photochemical formation of Fe(II) in acidic Suwannee River fulvic acid solutions. *Chemosphere*, **78**(8), 1023 – 1027, 2010. ISSN 0045-6535. doi:http://dx.doi.org/10.1016/j.chemosphere.2009.11.035.
- Asaf, D., Tas, E., Pedersen, D., Peleg, M., and Luria, M. Long-Term Measurements of  $\text{NO}_3$  Radical at a Semiarid Urban Site: 2. Seasonal Trends and Loss Mechanisms. *Environmental Science & Technology*, **44**(15), 5901 – 5907, 2010. doi:10.1021/es100967z.
- Asmus, K.D., Möckel, H., and Henglein, A. Pulse radiolytic study of site of OH radical attack on aliphatic alcohols in aqueous solution. *Journal of Physical Chemistry*, **77**(10), 1218 – 1221, 1973. ISSN 0022-3654. doi:10.1021/j100629a007.

- Atkinson, R. A structure-activity relationship for the estimation of rate constants for the gas-phase reactions of OH radicals with organic compounds. *International Journal of Chemical Kinetics*, **19**(9), 799–828, 1987. ISSN 0538-8066. doi:10.1002/kin.550190903.
- Atkinson, R. and Arey, J. Atmospheric degradation of volatile organic compounds. *Chemical Reviews*, **103**(12), 4605 – 4638, 2003. ISSN 0009-2665. doi:10.1021/cr0206420.
- Atkinson, R., Baulch, D.L., Cox, R.A., Crowley, J.N., Hampson, R.F., Hynes, R.G., Jenkin, M.E., Rossi, M.J., and Troe, J. Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II – gas phase reactions of organic species. *Atmospheric Chemistry and Physics*, **6**(11), 3625 – 4055, 2006. ISSN 1680-7316.
- Atkinson, R., Calvert, J.G., Kerr, J.A., Madronich, S., Moortgat, G.K., Wallington, T.J., and G., Y. *The Mechanism of Atmospheric Oxidation of the Alkenes*. Oxford University Press, Oxford, Great Britain, 2000.
- Atkinson, R., Lloyd, A.C., and Wings, L. An updated chemical mechanism for hydrocarbon/NO<sub>x</sub>/SO<sub>2</sub> photooxidations suitable for inclusion in atmospheric simulation models. *Atmospheric Environment*, **16**(6), 1341 – 1355, 1982. ISSN 1352-2310. doi:10.1016/0004-6981(82)90055-5.
- Aumont, B., Szopa, S., and Madronich, S. Modelling the evolution of organic carbon during its gas-phase tropospheric oxidation: development of an explicit model based on a self generating approach. *Atmospheric Chemistry and Physics*, **5**(9), 2497 – 2517, 2005. doi:10.5194/acp-5-2497-2005.
- Aumont, B., Valorso, R., Mouchel-Vallon, C., Camredon, M., Lee-Taylor, J., and Madronich, S. Modeling SOA formation from the oxidation of intermediate volatility n-alkanes. *Atmospheric Chemistry and Physics*, **12**(16), 7577 – 7589, 2012. ISSN 1680-7316. doi:10.5194/acp-12-7577-2012.
- Bao, L., Matsumoto, M., Kubota, T., Sekiguchi, K., Wang, Q., and Sakamoto, K. Gas/particle partitioning of low-molecular-weight dicarboxylic acids at a suburban site in Saitama, Japan. *Atmospheric Environment*, **47**(0), 546 – 553, 2012. ISSN 1352-2310. doi:10.1016/j.atmosenv.2009.09.014.
- Benkelberg, H.-J., Schäfer, P., and Warneck, P. Product quantum yields for the photodecomposition of H<sub>2</sub>O<sub>2</sub> and Fe(III) complexes in aqueous solution. In *Air pollution research report 33: Atmospheric oxidation processes*, edited by K.-H.. Becker, pp. 130. CEC, Brussels, Belgium, 1991.
- Benkelberg, H.-J. and Warneck, P. Photodecomposition of Iron(III) Hydroxo and Sulfato Complexes in Aqueous Solution: Wavelength Dependence of OH and SO<sub>4</sub><sup>-</sup> Quantum Yields. *The Journal of Physical Chemistry*, **99**(14), 5214 – 5221, 1995. doi:10.1021/j100014a049.
- Benson, S.W. *Thermochemical kinetics: Methods for the estimation of thermochemical data and rate parameters*. John Wiley & Sons, Inc., New York/London/Sydney/Toronto, 2nd edition, 1976.

- Berglen, T.F., Berntsen, T.K., Isaksen, I.S.A., and Sundet, J.K. A global model of the coupled sulfur/oxidant chemistry in the troposphere: The sulfur cycle. *Journal of Geophysical Research – Atmospheres*, **109**(D19), 2004. ISSN 2156-2202. doi:10.1029/2003JD003948.
- Berndt, T. and Böge, O. Formation of phenol and carbonyls from the atmospheric reaction of OH radicals with benzene. *Physical Chemistry Chemical Physics*, **8**(10), 1205 – 1214, 2006. doi:10.1039/B514148F.
- Bräuer, P., Tilgner, A., Wolke, R., and Herrmann, H. Mechanism development and modelling of tropospheric multiphase halogen chemistry: The CAPRAM Halogen Module 2.0 (HM2). *Journal of Atmospheric Chemistry*, **70**(1), 19 – 52, 2013. ISSN 0167-7764. doi:10.1007/s10874-013-9249-6.
- Buxton, G.V., Greenstock, C.L., Helman, W.P., and Ross, A.B. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ( $\cdot\text{OH}/\cdot\text{O}^-$ ) in aqueous solution. *Journal of Physical and Chemical Reference Data*, **17**(2), 513 – 886, 1988. ISSN 0047-2689.
- Carlton, A.G., Bhave, P.V., Napelenok, S.L., Edney, E.O., Sarwar, G., Pinder, R.W., Pouliot, G.A., and Houyoux, M. Model Representation of Secondary Organic Aerosol in CMAQv4.7. *Environmental Science & Technology*, **44**(22), 8553 – 8560, 2010. doi:10.1021/es100636q.
- Carlton, A.G., Turpin, B.J., Lim, H.-J., Altieri, K.E., and Seitzinger, S. Link between isoprene and secondary organic aerosol (SOA): Pyruvic acid oxidation yields low volatility organic acids in clouds. *Geophysical Research Letters*, **33**(6), 2006. ISSN 1944-8007. doi:10.1029/2005GL025374.
- Carter, W.P.L. A detailed mechanism for the gas-phase atmospheric reactions of organic compounds. *Atmospheric Environment Part A – General Topics*, **24**(3), 481 – 518, 1990. ISSN 0960-1686. doi:10.1016/0960-1686(90)90005-8.
- Carter, W.P.L. Development of a condensed SAPRC-07 chemical mechanism. *Atmospheric Environment*, **44**(40), 5336 – 5345, 2010a. ISSN 1352-2310. doi:10.1016/j.atmosenv.2010.01.024. 2nd Biennial Conference on Atmospheric Chemistry Mechanisms, Air Quality Res Ctr, Davis, CA, DEC, 2008.
- Carter, W.P.L. Development of the SAPRC-07 chemical mechanism. *Atmospheric Environment*, **44**(40), 5324 – 5335, 2010b. ISSN 1352-2310. doi:10.1016/j.atmosenv.2010.01.026. 2nd Biennial Conference on Atmospheric Chemistry Mechanisms, Air Quality Res Ctr, Davis, CA, DEC, 2008.
- Carter, W.P.L. SAPRC Atmospheric Chemical Mechanisms and VOC Reactivity Scales. 2013. URL <http://www.cert.ucr.edu/~carter/SAPRC/>.
- Chameides, W.L. and Davis, D.D. The free radical chemistry of cloud droplets and its impact upon the composition of rain. *Journal of Geophysical Research – Oceans*, **87**(C7), 4863 – 4877, 1982. ISSN 2156-2202. doi:10.1029/JC087iC07p04863.

- Cocker III, D.R., Mader, B.T., Kalberer, M., Flagan, R.C., and Seinfeld, J.H. The effect of water on gas–particle partitioning of secondary organic aerosol: Part II. m-xylene and 1,3,5-trimethylbenzene photooxidation systems. *Atmospheric Environment*, **35**(35), 6073 – 6085, 2001. ISSN 1352-2310. doi:[http://dx.doi.org/10.1016/S1352-2310\(01\)00405-8](http://dx.doi.org/10.1016/S1352-2310(01)00405-8).
- Commane, R., Floquet, C.F.A., Ingham, T., Stone, D., Evans, M.J., and Heard, D.E. Observations of OH and HO<sub>2</sub> radicals over West Africa. *Atmospheric Chemistry and Physics*, **10**(18), 8783 – 8801, 2010. doi:[10.5194/acp-10-8783-2010](https://doi.org/10.5194/acp-10-8783-2010).
- Compernelle, S. and Müller, J. Henry’s law constants of diacids and hydroxy polyacids: Recommended values. *Atmospheric Chemistry and Physics*, **14**(5), 2699 – 2712, 2014a. doi:[10.5194/acp-14-2699-2014](https://doi.org/10.5194/acp-14-2699-2014).
- Compernelle, S. and Müller, J. Henry’s law constants of polyols. *Atmospheric Chemistry and Physics Discussions*, **14**(9), 13529 – 13559, 2014b. doi:[10.5194/acpd-14-13529-2014](https://doi.org/10.5194/acpd-14-13529-2014).
- Davidovits, P., Hu, J.H., Worsnop, D.R., Zahniser, M.S., and Kolb, C.E. Entry of gas molecules into liquids. *Faraday Discussions*, **100**, 6 5– 81, 1995. ISSN 0301-7249. doi:[10.1039/fd9950000065](https://doi.org/10.1039/fd9950000065). Faraday Discussions on Atmospheric Chemistry - Measurements, Mechanics and Models, UNIV E ANGLIA, E ANGLIA, ENGLAND, APR 19-21, 1995.
- Day, D.A., Liu, S., Russell, L.M., and Ziemann, P.J. Organonitrate group concentrations in submicron particles with high nitrate and organic fractions in coastal southern California. *Atmospheric Environment*, **44**(16), 1970 – 1979, 2010. ISSN 1352-2310. doi:<http://dx.doi.org/10.1016/j.atmosenv.2010.02.045>.
- Deguillaume, L., Leriche, M., Monod, A., and Chaumerliac, N. The role of transition metal ions on HO<sub>x</sub> radicals in clouds: a numerical evaluation of its impact on multiphase chemistry. *Atmospheric Chemistry and Physics*, **4**(1), 95 – 110, 2004. doi:[10.5194/acp-4-95-2004](https://doi.org/10.5194/acp-4-95-2004).
- Deguillaume, L., Tilgner, A., Schrödner, R., Wolke, R., Chaumerliac, N., and Herrmann, H. Towards an operational aqueous phase chemistry mechanism for regional chemistry-transport models: CAPRAM-RED and its application to the COSMO-MUSCAT model. *Journal of Atmospheric Chemistry*, **64**(1), 1 – 35, 2009. ISSN 0167-7764. doi:[10.1007/s10874-010-9168-8](https://doi.org/10.1007/s10874-010-9168-8).
- Dentener, F.J. and Crutzen, P.J. A three-dimensional model of the global ammonia cycle. *Journal of Atmospheric Chemistry*, **19**(4), 331 – 369, 1994. ISSN 0167-7764. doi:[10.1007/BF00694492](https://doi.org/10.1007/BF00694492).
- Dodge, M.C. Combined use of modeling techniques and smog chamber data to derive ozone-precursor relationships. In *Report EPA-600/3-77-001a*, 881 – 889. US Environmental Protection Agency, Research Triangle Park, N.C., 1977. URL <http://www.epa.gov/nscep/index.html>.
- Doussin, J.F. and Monod, A. Structure–activity relationship for the estimation of OH-oxidation rate constants of carbonyl compounds in the aqueous phase. *Atmospheric Chemistry and Physics*, **13**(23), 11625 – 11641, 2013. doi:[10.5194/acp-13-11625-2013](https://doi.org/10.5194/acp-13-11625-2013).

- Drozd, G., Woo, J., Häkkinen, S.A.K., Nenes, A., and McNeill, V.F. Inorganic salts interact with oxalic acid in submicron particles to form material with low hygroscopicity and volatility. *Atmospheric Chemistry and Physics*, **14**(10), 5205 – 5215, 2014.
- Durham Environment Watch. 2014. URL [http://www.durhamenvironmentwatch.org/incineration\\_health.htm](http://www.durhamenvironmentwatch.org/incineration_health.htm). Last checked: Feb 2014.
- Ervens, B., Carlton, A.G., Turpin, B.J., Altieri, K.E., Kreidenweis, S.M., and Feingold, G. Secondary organic aerosol yields from cloud-processing of isoprene oxidation products. *Geophysical Research Letters*, **35**(2), 2008. ISSN 1944-8007. doi:10.1029/2007GL031828.
- Ervens, B., Feingold, G., Frost, G.J., and Kreidenweis, S.M. A modeling study of aqueous production of dicarboxylic acids: 1. Chemical pathways and speciated organic mass production. *Journal of Geophysical Research – Atmospheres*, **109**(D15), 2004. ISSN 2156-2202. doi:10.1029/2003JD004387.
- Ervens, B., George, C., Williams, J.E., Buxton, G.V., Salmon, G.A., Bydder, M., Wilkinson, F., Dentener, F., Mirabel, P., Wolke, R., and Herrmann, H. CAPRAM 2.4 (MODAC mechanism): An extended and condensed tropospheric aqueous phase mechanism and its application. *Journal of Geophysical Research – Atmospheres*, **108**(D14), 2003. ISSN 2156-2202. doi:10.1029/2002JD002202.
- Ervens, B. and Volkamer, R. Glyoxal processing by aerosol multiphase chemistry: towards a kinetic modeling framework of secondary organic aerosol formation in aqueous particles. *Atmospheric Chemistry and Physics*, **10**(17), 8219 – 8244, 2010. doi:10.5194/acp-10-8219-2010.
- Evans, M.G. Thermodynamical treatment of transition state. *Transactions of the Faraday Society*, **34**, 49 – 57, 1938. doi:10.1039/TF9383400049.
- Evans, M.G. and Polanyi, M. Inertia and driving force of chemical reactions. *Transactions of the Faraday Society*, **34**, 11 – 24, 1938. doi:10.1039/TF9383400011.
- Faust, B.C. and Zepp, R.G. Photochemistry of aqueous iron(III)-polycarboxylate complexes: roles in the chemistry of atmospheric and surface waters. *Environmental Science & Technology*, **27**(12), 2517 – 2522, 1993. doi:10.1021/es00048a032.
- Fisseha, R., Dommen, J., Sax, M., Paulsen, D., Kalberer, M., Maurer, R., Höfler, F., Weingartner, E., and Baltensperger, U. Identification of organic acids in secondary organic aerosol and the corresponding gas phase from chamber experiments. *Analytical Chemistry*, **76**(22), 6535 – 6540, 2004. doi:10.1021/ac048975f.
- Fry, J.L., Draper, D.C., Zarzana, K.J., Campuzano-Jost, P., Day, D.A., Jimenez, J.L., Brown, S.S., Cohen, R.C., Kaser, L., Hansel, A., Cappellin, L., Karl, T., Hodzic Roux, A., Turnipseed, A., Cantrell, C., Lefer, B.L., and Grossberg, N. Observations of gas- and aerosol-phase organic nitrates at BEACHON-RoMBAS 2011. *Atmospheric Chemistry and Physics*, **13**(17), 8585 – 8605, 2013. doi:10.5194/acp-13-8585-2013. URL <http://www.atmos-chem-phys.net/13/8585/2013/>.

- Fry, J.L., Kiendler-Scharr, A., Rollins, A.W., Wooldridge, P.J., Brown, S.S., Fuchs, H., Dubé, W., Mensah, A., dal Maso, M., Tillmann, R., Dorn, H.P., Brauers, T., and Cohen, R.C. Organic nitrate and secondary organic aerosol yield from NO<sub>3</sub> oxidation of  $\beta$ -pinene evaluated using a gas-phase kinetics/aerosol partitioning model. *Atmospheric Chemistry and Physics*, **9**(4), 1431 – 1449, 2009. doi:10.5194/acp-9-1431-2009.
- Fry, J.L. and Sackinger, K. Model investigation of NO<sub>3</sub> secondary organic aerosol (SOA) source and heterogeneous organic aerosol (OA) sink in the western United States. *Atmospheric Chemistry and Physics*, **12**(18), 8797 – 8811, 2012. doi:10.5194/acp-12-8797-2012.
- Fuller, E.N. Diffusion coefficients for binary gas systems at low pressures: Empirical correlations. In *Properties of Gases and Liquids*, edited by R. et al., 587. McGraw Hill, New York, 1986.
- George, C., Strekowski, R.S., Kleffmann, J., Stemmler, K., and Ammann, M. Photoenhanced uptake of gaseous NO<sub>2</sub> on solid organic compounds: a photochemical source of HONO? *Faraday Discussions*, **130**, 195 – 210, 2005. doi:10.1039/B417888M.
- George et al. *Final report (sections 1 – 6)*. Fifth Framework Programme 1998 – 2002, Thematic Programme: Environment and Sustainable Development, Project number EVK2-CT-2001-00114, 2005.
- Ginnebaugh, D.L. and Jacobson, M.Z. Coupling of highly explicit gas and aqueous chemistry mechanisms for use in 3-D. *Atmospheric Environment*, **62**, 408 – 415, 2012. ISSN 1352-2310. doi:10.1016/j.atmosenv.2012.08.057.
- Goldstein, A.H. and Galbally, I.E. Known and unexplored organic constituents in the earth's atmosphere. *Environmental Science & Technology*, **41**(5), 1514 – 1521, 2007. ISSN 0013-936X. doi:10.1021/es072476p.
- Goliff, W.S., Stockwell, W.R., and Lawson, C.V. The regional atmospheric chemistry mechanism, version 2. *Atmospheric Environment*, **68**, 174 – 185, 2013. ISSN 1352-2310. doi:{10.1016/j.atmosenv.2012.11.038}.
- Graedel, T.E. and Goldberg, K.I. Kinetic studies of raindrop chemistry: 1. Inorganic and organic processes. *Journal of Geophysical Research – Oceans*, **88**(C15), 10865 – 10882, 1983. ISSN 2156-2202. doi:10.1029/JC088iC15p10865.
- Graedel, T.E., Mandich, M.L., and Weschler, C.J. Kinetic model studies of atmospheric droplet chemistry: 2. Homogeneous transition metal chemistry in raindrops. *Journal of Geophysical Research – Atmospheres*, **91**(D4), 5205 – 5221, 1986. ISSN 2156-2202. doi:10.1029/JD091iD04p05205.
- Graedel, T.E. and Weschler, C.J. Chemistry within aqueous atmospheric aerosols and raindrops. *Reviews of Geophysics and Space Physics*, **19**(4), 505 – 539, 1981. ISSN 8755-1209. doi:10.1029/RG019i004p00505.
- Griffin, R.J., Dabdub, D., and Seinfeld, J.H. Secondary organic aerosol - 1. Atmospheric chemical mechanism for production of molecular constituents. *Journal of Geophysical*



- Research – Atmospheres*, **107**(D17), 4332 – 4357, 2002. ISSN 0747-7309. doi:{10.1029/2001JD000541}.
- Haag, W. and Yao, C. Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. *Environmental Science & Technology*, **26**(5), 1005 – 1013, 1992. ISSN 0013-936X. doi:10.1021/es00029a021.
- Hallquist, M., Wenger, J.C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N.M., George, C., Goldstein, A.H., Hamilton, J.F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M.E., Jimenez, J.L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T.F., Monod, A., Prevot, A.S.H., Seinfeld, J.H., Surratt, J.D., Szmigielski, R., and Wildt, J. The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmospheric Chemistry and Physics*, **9**(14), 5155 – 5236, 2009. ISSN 1680-7316.
- Han, S.-Q., Zhang, M., Zhao, C.-S., Lu, X.-Q., Ran, L., Han, M., Li, P.-Y., and Li, X.-J. Differences in ozone photochemical characteristics between the megacity Tianjin and its rural surroundings. *Atmospheric Environment*, **79**(0), 209 – 216, 2013. ISSN 1352-2310. doi:http://dx.doi.org/10.1016/j.atmosenv.2013.06.045.
- Hazarika, P., Sarma, R.L., Karim, M., Bezbaruah, B., Kalita, R., and Medhi, C. Prediction of  $pK_a$  from basic principles: *Ab initio* and DFT studies on some molecules. *Indian Journal of Chemistry*, **48A**, 520 – 525, 2009.
- He, C., Liu, J., Carlton, A.G., Fan, S., Horowitz, L.W., Levy II, H., and Tao, S. Evaluation of factors controlling global secondary organic aerosol production from cloud processes. *Atmospheric Chemistry and Physics*, **13**(4), 1913 – 1926, 2013. doi:10.5194/acp-13-1913-2013.
- He, N., Kawamura, K., Okuzawa, K., Pochanart, P., Liu, Y., Kanaya, Y., and Wang, Z. Diurnal and temporal variations of water-soluble dicarboxylic acids and related compounds in aerosols from the northern vicinity of Beijing: Implication for photochemical aging during atmospheric transport. *Science of the Total Environment*, **499**, 154 – 165, 2014. ISSN 0048-9697. doi:http://dx.doi.org/10.1016/j.scitotenv.2014.08.050.
- Healy, R.M., Wenger, J.C., Metzger, A., Duplissy, J., Kalberer, M., and Dommen, J. Gas/particle partitioning of carbonyls in the photooxidation of isoprene and 1,3,5-trimethylbenzene. *Atmospheric Chemistry and Physics*, **8**(12), 3215 – 3230, 2008. doi:10.5194/acp-8-3215-2008.
- Herckes, P., Valsaraj, K.T., and Collett, Jr., J.L. A review of observations of organic matter in fogs and clouds: Origin, processing and fate. *Atmospheric Research*, **132**, 434 – 449, 2013. ISSN 0169-8095. doi:10.1016/j.atmosres.2013.06.005.
- Herrmann, H. Kinetics of aqueous phase reactions relevant for atmospheric chemistry. *Chemical Reviews*, **103**(12), 4691–4716, 2003. ISSN 0009-2665. doi:10.1021/cr020658q.
- Herrmann, H. On the photolysis of simple anions and neutral molecules as sources of  $O^-/OH$ ,  $SO_3^-$  and  $Cl$  in aqueous solution. *Physical Chemistry Chemical Physics*, **9**(30),

- 3935 – 3964, 2007. doi:10.1039/B618565G.
- Herrmann, H., Ervens, B., Jacobi, H.-W., Wolke, R., Nowacki, P., and Zellner, R. CAPRAM2.3: A Chemical Aqueous Phase Radical Mechanism for Tropospheric Chemistry. *Journal of Atmospheric Chemistry*, **36**(3), 231–284, 2000. ISSN 0167-7764. doi:10.1023/A:1006318622743.
- Herrmann, H., Ervens, B., Nowacki, P., Wolke, R., and Zellner, R. A chemical aqueous phase radical mechanism for tropospheric chemistry. *Chemosphere*, **38**(6), 1223 – 1232, 1999. ISSN 0045-6535. doi:10.1016/S0045-6535(98)00520-7.
- Herrmann, H., Hoffmann, D., Schaefer, T., Bräuer, P., and Tilgner, A. Tropospheric aqueous-phase free-radical chemistry: radical sources, spectra, reaction kinetics and prediction tools. *ChemPhysChem*, **11**(18), 3796 – 3822, 2010. ISSN 1439-4235. doi:10.1002/cphc.201000533.
- Herrmann, H., Jacobi, H.-W., Raabe, G., Reese, A., Umschlag, T., and Zellner, R. Free radical reactions in the tropospheric aqueous phase. In *The oxidizing capacity of the troposphere*, 503 – 512. Proceedings of the seventh European symposium on physico-chemical behaviour of atmospheric pollutants, Venice, Italy, 1996.
- Herrmann, H., Majdik, Z., Ervens, B., and Weise, D. Halogen production from aqueous tropospheric particles. *Chemosphere*, **52**(2), 485 – 502, 2003. ISSN 0045-6535. doi: {10.1016/S0045-6535(03)00202-9}.
- Herrmann, H., Schaefer, T., Tilgner, A., Weller, C., Teich, M., and Styler, S. Tropospheric aqueous phase chemistry: Kinetics, mechanisms and its coupling to a changing gas phase, 2014. Submitted to Chemical Reviews.
- Herrmann, H., Tilgner, A., Barzaghi, P., Majdik, Z., Gligorovski, S., Poulain, L., and Monod, A. Towards a more detailed description of tropospheric aqueous phase organic chemistry: CAPRAM 3.0. *Atmospheric Environment*, **39**(23–24), 4351 – 4363, 2005. ISSN 1352-2310. doi:10.1016/j.atmosenv.2005.02.016.
- Herrmann, H., Weller, C., and Tilgner, A. *Atmospheric Chemistry — Aqueous Phase Chemistry, Multiphase Modelling — Final report*. TelTek report no. 2211030ZAQ05, 2011.
- Herrmann, H. and Zellner, R. Reactions of NO<sub>3</sub>-radicals in aqueous solution. In *N-Centered Radicals*, edited by Z. Alfassi, 291 – 343. Wiley, New York, 1998.
- Ho, K., Cao, J., Lee, S., Kawamura, K., Zhang, R., Chow, J., and Watson, J. Dicarboxylic acids, ketocarboxylic acids, and dicarbonyls in the urban atmosphere of China. *Journal of Geophysical Research – Atmospheres*, **112**, D22S27, 2007.
- Ho, K., Lee, S., Cao, J., Kawamura, K., Watanabe, T., Cheng, Y., and Chow, J.C. Dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban roadside area of Hong Kong. *Atmospheric Environment*, **40**(17), 3030 – 3040, 2006. ISSN 1352-2310. doi:http://dx.doi.org/10.1016/j.atmosenv.2005.11.069.

- Hobbs, P.V. *Aerosol-Cloud-Climate Interactions*, *International Geophysics*, volume 54. Academic Press, London, UK, 1993. ISBN 0-12-350725-1.
- Hoffmann, D. *Multiphasenchemie substituierter Phenole: Analytik und Prozessstudien*. Dissertation, University of Leipzig, Leipzig, Germany, 2007.
- Hoffmann, D., Weigert, B., Barzaghi, P., and Herrmann, H. Reactivity of poly-alcohols towards OH, NO<sub>3</sub> and SO<sub>4</sub><sup>-</sup> in aqueous solution. *Physical Chemistry Chemical Physics*, **11**(41), 9351 – 9363, 2009. ISSN 1463-9076. doi:10.1039/b908459b.
- Hoffmann, M.R. On the kinetics and mechanism of oxidation of aquated sulfur dioxide by ozone. *Atmospheric Environment*, **20**(6), 1145 – 1154, 1986. ISSN 0004-6981. doi:10.1016/0004-6981(86)90147-2.
- Hoffmann, T. and Warnke, J. Organic Aerosols. In *Volatile Organic Compounds in the Atmosphere*, edited by R. Koppmann, chapter 9, 342 – 387. Blackwell Publishing Ltd, Oxford, Great Britain, 2007. ISBN 978-1-4051-3115-5.
- Hong Kong Observatory. 2013. URL <http://www.weather.gov.hk/wxinfo/climat/normals.htm#table5>. Last checked: Nov 2013.
- Hsieh, L.Y., Kuo, S.C., Chen, C.L., and Tsai, Y.I. Size distributions of nanomicon dicarboxylic acids and inorganic ions in suburban PM episode and non-episodic aerosol. *Atmospheric Environment*, **43**(29), 4396 – 4406, 2009. ISSN 1352-2310. doi:<http://dx.doi.org/10.1016/j.atmosenv.2009.04.034>.
- Iinuma, Y., , Keywood, M., Gnauk, T., and Herrmann, H. Diaterebic Acid Acetate and Diaterpenylic Acid Acetate: Atmospheric Tracers for Secondary Organic Aerosol Formation from 1,8-Cineole Oxidation. *Environmental Science & Technology*, **43**(2), 280 – 285, 2009. doi:10.1021/es802141v.
- Im, Y., Jang, M., and Beardsley, R.L. Simulation of aromatic SOA formation using the lumping model integrated with explicit gas-phase kinetic mechanisms and aerosol-phase reactions. *Atmospheric Chemistry and Physics*, **14**(8), 4013 – 4027, 2014. doi:10.5194/acp-14-4013-2014.
- IUPAC. *Compendium of Chemical Terminology (the "Gold Book")*. Compiled by A. D. McNaught and A. Wilkinson. XML on-line corrected version: <http://goldbook.iupac.org> (2006-) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins. Blackwell Scientific Publications, Oxford, Great Britain, 2nd edition, 1997.
- Jacob, D.J. Chemistry of OH in remote clouds and its role in the production of formic acid and peroxymonosulfate. *Journal of Geophysical Research – Atmospheres*, **91**(D9), 9807 – 9826, 1986. ISSN 2156-2202. doi:10.1029/JD091iD09p09807.
- Jacob, D.J. *Introduction to Atmospheric Chemistry*. Princeton University Press, Chichester, New Jersey, USA, 1999. ISBN 0-691-00185-5.
- Jacob, D.J. and Hoffmann, M.R. A dynamic model for the production of H<sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> in urban fog. *Journal of Geophysical Research – Oceans*, **88**(C11), 6611 – 6621,

1983. ISSN 2156-2202. doi:10.1029/JC088iC11p06611.
- Jacobson, M. Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols. *Nature*, **409**(6821), 695 – 697, 2001. ISSN 0028-0836. doi:10.1038/35055518.
- Jacobson, M.Z. A Solution to the problem of nonequilibrium acid/base gas-particle transfer at long time step. *Aerosol Science and Technology*, **39**(2), 92 – 103, 2005. doi:10.1080/027868290904546.
- Jenkin, M., Watson, L., Utembe, S., and Shallcross, D. A Common Representative Intermediates (CRI) mechanism for VOC degradation. Part 1: Gas phase mechanism development. *Atmospheric Environment*, **42**(31), 7185 – 7195, 2008. ISSN 1352-2310. doi:10.1016/j.atmosenv.2008.07.028.
- Jenkin, M.E., Saunders, S.M., and Pilling, M.J. The tropospheric degradation of volatile organic compounds: A protocol for mechanism development. *Atmospheric Environment*, **31**(1), 81 – 104, 1997. ISSN 1352-2310. doi:{10.1016/S1352-2310(96)00105-7}.
- Jenkin, M.E., Saunders, S.M., Wagner, V., and Pilling, M.J. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds. *Atmospheric Chemistry and Physics*, **3**(1), 181 – 193, 2003. ISSN 1680-7324.
- Jimenez, J.L., Canagaratna, M.R., Donahue, N.M., Prevot, A.S.H., Zhang, Q., Kroll, J.H., DeCarlo, P.F., Allan, J.D., Coe, H., Ng, N.L., Aiken, A.C., Docherty, K.S., Ulbrich, I.M., Grieshop, A.P., Robinson, A.L., Duplissy, J., Smith, J.D., Wilson, K.R., Lanz, V.A., Hueglin, C., Sun, Y.L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J.M., Collins, D.R., Cubison, M.J., Dunlea, E.J., Huffman, J.A., Onasch, T.B., Alfarra, M.R., Williams, P.I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimojo, A., Sun, J.Y., Zhang, Y.M., Dzepina, K., Kimmel, J.R., Sueper, D., Jayne, J.T., Herndon, S.C., Trimborn, A.M., Williams, L.R., Wood, E.C., Middlebrook, A.M., Kolb, C.E., Baltensperger, U., and Worsnop, D.R. Evolution of organic aerosols in the atmosphere. *Science*, **326**(5959), 1525 – 1529, 2009. ISSN 0036-8075. doi:10.1126/science.1180353.
- Jin, S., Liu, H., Gao, X.J., Lin, Z., Chen, G., and Wang, D. Seven organic salts assembled from hydrogen-bonds of N–H···O, O–H···O, and C–H···O between acidic compounds and bis(benzimidazole). *Journal of Molecular Structure*, **1075**, 124 – 138, 2014. ISSN 0022-2860. doi:http://dx.doi.org/10.1016/j.molstruc.2014.06.077.
- Kahnt, A. *Semivolatile compounds from atmospheric monoterpene oxidation*. Ph.D. thesis, University of Leipzig, 2012.
- Kalberer, M., Paulsen, D., Sax, M., Steinbacher, M., Dommen, J., Prevot, A.S.H., Fisseha, R., Weingartner, E., Frankevich, V., Zenobi, R., and Baltensperger, U. Identification of polymers as major components of atmospheric organic aerosols. *Science*, **303**(5664),

- 1659 – 1662, 2004. doi:10.1126/science.1092185.
- Kames, J. and Schurath, U. Henry’s Law and hydrolysis-rate constants for peroxyacyl nitrates (PANS) using a homogeneous gas-phase source. *Journal of Atmospheric Chemistry*, **21**(2), 151 – 164, 1995. ISSN 0167-7764. doi:10.1007/BF00696578.
- Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C.J., Swietlicki, E., Putaud, J.P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G.K., Winterhalter, R., Myhre, C.E.L., Tsigaridis, K., Vignati, E., Stephanou, E.G., and Wilson, J. Organic aerosol and global climate modelling: a review. *Atmospheric Chemistry and Physics*, **5**(4), 1053 – 1123, 2005. ISSN 1680-7316.
- Kawamura, K., Okuzawa, K., Aggarwal, S.G., Irie, H., Kanaya, Y., and Wang, Z. Determination of gaseous and particulate carbonyls (glycolaldehyde, hydroxyacetone, glyoxal, methylglyoxal, nonanal and decanal) in the atmosphere at Mt. Tai. *Atmospheric Chemistry and Physics*, **13**(10), 5369 – 5380, 2013. doi:10.5194/acp-13-5369-2013.
- Kolesar, K., Buffaloe, G., Wilson, J., and Cappa, C. OH-initiated heterogeneous oxidation of internally-mixed squalane and secondary organic aerosol. *Environmental Science & Technology*, 2014. doi:10.1021/es405177d. Just accepted.
- Koop, T., Bookhold, J., Shiraiwa, M., and Poschl, U. Glass transition and phase state of organic compounds: dependency on molecular properties and implications for secondary organic aerosols in the atmosphere. *Physical Chemistry Chemical Physics*, **13**(43), 19238 – 19255, 2011. doi:10.1039/C1CP22617G.
- Kumar, P., Morawska, L., Birmili, W., Paasonen, P., Hu, M., Kulmala, M., Harrison, R.M., Norford, L., and Britter, R. Ultrafine particles in cities. *Environment International*, **66**, 1 – 10, 2014. ISSN 0160-4120. doi:http://dx.doi.org/10.1016/j.envint.2014.01.013.
- Kwok, E.S.C. and Atkinson, R. Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship – an update. *Atmospheric Environment*, **29**(14), 1685 – 1695, 1995. ISSN 1352-2310. doi:10.1016/1352-2310(95)00069-B.
- Lahoutifard, N., Ammann, M., Gutzwiller, L., Ervens, B., and George, C. The impact of multiphase reactions of NO<sub>2</sub> with aromatics: a modelling approach. *Atmospheric Chemistry and Physics*, **2**(3), 215–226, 2002. doi:10.5194/acp-2-215-2002.
- Laongsri, B. and Harrison, R.M. Atmospheric behaviour of particulate oxalate at UK urban background and rural sites. *Atmospheric Environment*, **71**(0), 319 – 326, 2013. ISSN 1352-2310. doi:http://dx.doi.org/10.1016/j.atmosenv.2013.02.015.
- Lawrence, J.R., Glass, S.V., Park, S.C., and Nathanson, G.M. Surfactant control of gas uptake: Effect of butanol films on HCl and HBr entry into supercooled sulfuric acid. *The Journal of Physical Chemistry A*, **109**(33), 7458 – 7465, 2005. doi:10.1021/jp0500438.

- Lee, B.P., Li, Y.J., Yu, J.Z., Louie, P.K.K., and Chan, C.K. Physical and chemical characterization of ambient aerosol by HR-ToF-AMS at a suburban site in Hong Kong during springtime 2011. *Journal of Geophysical Research – Atmospheres*, **118**(15), 8625 – 8639, 2013. ISSN 2169-8996. doi:10.1002/jgrd.50658.
- Lelieveld, J. and Crutzen, P. The role of clouds in tropospheric photochemistry. *Journal of Atmospheric Chemistry*, **12**(3), 229 – 267, 1991. ISSN 0167-7764. doi:10.1007/BF00048075.
- Leriche, M., Chaumerliac, N., and Monod, A. Coupling quasi-spectral microphysics with multiphase chemistry: a case study of a polluted air mass at the top of the Puy de Dôme mountain (France). *Atmospheric Environment*, **35**(32), 5411 – 5423, 2001. ISSN 1352-2310. doi:http://dx.doi.org/10.1016/S1352-2310(01)00300-4.
- Leriche, M., Deguillaume, L., and Chaumerliac, N. Modeling study of strong acids formation and partitioning in a polluted cloud during wintertime. *Journal of Geophysical Research – Atmospheres*, **108**(D14), 2003. ISSN 2156-2202. doi:10.1029/2002JD002950.
- Leriche, M., Voisin, D., Chaumerliac, N., Monod, A., and Aumont, B. A model for tropospheric multiphase chemistry: application to one cloudy event during the CIME experiment. *Atmospheric Environment*, **34**(29-30), 5015 – 5036, 2000. ISSN 1352-2310. doi:10.1016/S1352-2310(00)00329-0.
- Li, K. and Crittenden, J. Computerized pathway elucidation for hydroxyl radical-induced chain reaction mechanisms in aqueous phase advanced oxidation processes. *Environmental Science & Technology*, **43**(8), 2831 – 2837, 2009. ISSN 0013-936X. doi:10.1021/es802039y.
- Li, S.M., Macdonald, A.M., Strapp, J.W., Lee, Y.N., and Zhou, X.L. Chemical and physical characterizations of atmospheric aerosols over southern California. *Journal of Geophysical Research – Atmospheres*, **102**(D17), 21341 – 21353, 1997. ISSN 2156-2202. doi:10.1029/97JD01310.
- Li, Y.C. and Yu, J.Z. Composition profile of oxygenated organic compounds and inorganic ions in PM<sub>2.5</sub> in Hong Kong. *Environmental Chemistry*, **7**(4), 338 – 349, 2010. ISSN 1448-2517. doi:{10.1071/EN09167}.
- Li, Y.M. and Francisco, J.S. An ab initio molecular orbital study of the mechanism for the gas-phase water-mediated decomposition and the formation of hydrates of peroxyacetyl nitrate (PAN). *Journal of the American Chemical Society*, **127**(34), 12144 – 12146, 2005. ISSN 0002-7863. doi:10.1021/ja053916k.
- Lim, H.-J., Carlton, A.G., and Turpin, B.J. Isoprene forms secondary organic aerosol through cloud processing – model simulations. *Environmental Science & Technology*, **39**(12), 4441 – 4446, 2005. doi:10.1021/es048039h.
- Lim, Y.B., Tan, Y., Perri, M.J., Seitzinger, S.P., and Turpin, B.J. Aqueous chemistry and its role in secondary organic aerosol (SOA) formation. *Atmospheric Chemistry and Physics*, **10**(21), 10521 – 10539, 2010. doi:10.5194/acp-10-10521-2010.

- Lind, J.A., Lazrus, A.L., and Kok, G.L. Aqueous phase oxidation of sulfur(IV) by hydrogen peroxide, methylhydroperoxide, and peroxyacetic acid. *Journal of Geophysical Research – Atmospheres*, **92**(D4), 4171 – 4177, 1987. ISSN 2156-2202. doi:10.1029/JD092iD04p04171.
- Lu, K.D., Hofzumahaus, A., Holland, F., Bohn, B., Brauers, T., Fuchs, H., Hu, M., Häsel, R., Kita, K., Kondo, Y., Li, X., Lou, S.R., Oebel, A., Shao, M., Zeng, L.M., Wahner, A., Zhu, T., Zhang, Y.H., and Rohrer, F. Missing OH source in a suburban environment near Beijing: observed and modelled OH and HO<sub>2</sub> concentrations in summer 2006. *Atmospheric Chemistry and Physics*, **13**(2), 1057 – 1080, 2013. doi:10.5194/acp-13-1057-2013.
- Luo, Y.-R. *Handbook of Bond Dissociation Energies in Organic Compounds*. CRC Press, Boca Raton, FL, USA, 2003.
- Madronich, S. Photodissociation in the atmosphere: 1. Actinic flux and the effects of ground reflections and clouds. *Journal of Geophysical Research – Atmospheres*, **92**(D8), 9740 – 9752, 1987. ISSN 2156-2202. doi:10.1029/JD092iD08p09740.
- Madronich, S. Chemical evolution of gaseous air pollutants down-wind of tropical megacities: Mexico City case study. *Atmospheric Environment*, **40**(31), 6012 – 6018, 2006. ISSN 1352-2310. doi:10.1016/j.atmosenv.2005.08.047.
- Matthijssen, J., Builtjes, P., and Sedlak, D. Cloud model experiments of the effect of iron and copper on tropospheric ozone under marine and continental conditions. *Meteorology and Atmospheric Physics*, **57**(1-4), 43 – 60, 1995. ISSN 0177-7971. doi:10.1007/BF01044153.
- McNeill, V.F., Woo, J.L., Kim, D.D., Schwier, A.N., Wannell, N.J., Sumner, A.J., and Barakat, J.M. Aqueous-phase secondary organic aerosol and organosulfate formation in atmospheric aerosols: A modeling study. *Environmental Science & Technology*, **46**(15), 8075 – 8081, 2012. doi:10.1021/es3002986.
- Middleton, P., Stockwell, W.R., and Carter, W.P.L. Aggregation and analysis of volatile organic compound emissions for regional modelling. *Atmospheric Environment Part A – General Topics*, **24**(5), 1107 – 1133, 1990. ISSN 0004-6981. doi:10.1016/0960-1686(90)90077-Z.
- Minakata, D., Li, K., Westerhoff, P., and Crittenden, J. Development of a group contribution method to predict aqueous phase hydroxyl radical (HO) reaction rate constants. *Environmental Science & Technology*, **43**(16), 6220 – 6227, 2009. ISSN 0013-936X. doi:10.1021/es900956c.
- Monod, A. and Doussin, J.F. Structure-activity relationship for the estimation of OH-oxidation rate constants of aliphatic organic compounds in the aqueous phase: alkanes, alcohols, organic acids and bases. *Atmospheric Environment*, **42**(33), 7611 – 7622, 2008. ISSN 1352-2310. doi:10.1016/j.atmosenv.2008.06.005.
- Monod, A., Poulain, L., Grubert, S., Voisin, D., and Wortham, H. Kinetics of OH-initiated oxidation of oxygenated organic compounds in the aqueous phase: new rate constants, structure-activity relationships and atmospheric implications. *Atmospheric Environment*,

- 39**(40), 7667 – 7688, 2005.
- Mouchel-Vallon, C. *La chimie des composés organiques dans les nuages: Modélisation explicite multiphasique*. Ph.D. thesis, University Paris Est Créteil – Val de Marne, Créteil, 2013.
- Mouchel-Vallon, C., Bräuer, P., Camredon, M., Valorso, R., Madronich, S., Herrmann, H., and Aumont, B. Explicit modeling of volatile organic compounds partitioning in the atmospheric aqueous phase. *Atmospheric Chemistry and Physics*, **13**(2), 1023 – 1037, 2013. ISSN 1680-7316. doi:10.5194/acp-13-1023-2013.
- Müller, M., Graus, M., Wisthaler, A., Hansel, A., Metzger, A., Dommen, J., and Baltensperger, U. Analysis of high mass resolution PTR-TOF mass spectra from 1,3,5-trimethylbenzene (TMB) environmental chamber experiments. *Atmospheric Chemistry and Physics*, **12**(2), 829 – 843, 2012. doi:10.5194/acp-12-829-2012.
- Mutzel, A. *Influence of the reaction conditions on the oxidation of atmospheric first-generation monoterpene oxidation products*. Dissertation, Universität Leipzig, Leipzig, Germany, 2014.
- Nozière, B. and Chabert, P. Abiotic C–C bond formation under environmental conditions: Kinetics of the aldol condensation of acetaldehyde in water catalyzed by carbonate Ions ( $\text{CO}_3^{2-}$ ). *International Journal of Chemical Kinetics*, **42**(11), 676 – 686, 2010. ISSN 0538-8066. doi:10.1002/kin.20518.
- Paglione, M., Kiendler-Scharr, A., Mensah, A.A., Finessi, E., Giulianelli, L., Sandrini, S., Facchini, M.C., Fuzzi, S., Schlag, P., Piazzalunga, A., Tagliavini, E., Henzing, J.S., and Decesari, S. Identification of humic-like substances (HULIS) in oxygenated organic aerosols using NMR and AMS factor analyses and liquid chromatographic techniques. *Atmospheric Chemistry and Physics*, **14**(1), 25 – 45, 2014. doi:10.5194/acp-14-25-2014.
- Pandis, S.N. and Seinfeld, J.H. Sensitivity analysis of a chemical mechanism for aqueous-phase atmospheric chemistry. *Journal of Geophysical Research – Atmospheres*, **94**(D1), 1105 – 1126, 1989. ISSN 2156-2202. doi:10.1029/JD094iD01p01105.
- Panteliadis, P., Strak, M., Hoek, G., Weijers, E., van der Zee, S., and Dijkema, M. Implementation of a low emission zone and evaluation of effects on air quality by long-term monitoring. *Atmospheric Environment*, **86**(0), 113 – 119, 2014. ISSN 1352-2310. doi:http://dx.doi.org/10.1016/j.atmosenv.2013.12.035.
- Perrin, D.D., Dempsey, B., and Serjeant, E.P. *pKa prediction for organic acids and bases*. Chapman and Hall, London, Great Britain, 1981.
- Perring, A.E., Bertram, T.H., Wooldridge, P.J., Fried, A., Heikes, B.G., Dibb, J., Crounse, J.D., Wennberg, P.O., Blake, N.J., Blake, D.R., Brune, W.H., Singh, H.B., and Cohen, R.C. Airborne observations of total  $\text{RONO}_2$ : New constraints on the yield and lifetime of isoprene nitrates. *Atmospheric Chemistry and Physics*, **9**(4), 1451 – 1463, 2009. doi:10.5194/acp-9-1451-2009.



- Po, H.N. and Senozan, N.M. The Henderson-Hasselbalch equation: Its history and limitations. *Journal of Chemical Education*, **78**(11), 1499 – 1503, 2001. ISSN 0021-9584.
- Praplan, A.P., Hegyi-Gaeggeler, K., Barmet, P., Pfaffenberger, L., Dommen, J., and Baltensperger, U. Online measurements of water-soluble organic acids in the gas and aerosol phase from the photooxidation of 1,3,5-trimethylbenzene. *Atmospheric Chemistry and Physics*, **14**(16), 8665 – 8677, 2014. doi:10.5194/acp-14-8665-2014.
- Pruppacher, H.R. and Jaenicke, R. The processing of water-vapor and aerosols by atmospheric clouds, a global estimate. *Atmospheric Research*, **38**(1 - 4), 283 – 295, 1995. ISSN 0169-8095. doi:10.1016/0169-8095(94)00098-X.
- Pruppacher, H.R. and Klett, J.D. *Microphysics of Clouds and Precipitation*. Kluwer Academic Publishers, Dordrecht/Boston/London, 1997.
- Raventos-Duran, T., Camredon, M., Valorso, R., Mouchel-Vallon, C., and Aumont, B. Structure-activity relationships to estimate the effective Henry's law constants of organics of atmospheric interest. *Atmospheric Chemistry and Physics*, **10**(16), 7643 – 7654, 2010. ISSN 1680-7316. doi:10.5194/acp-10-7643-2010.
- Redlich, O. The Dissociation of Strong Electrolytes. *Chemical Reviews*, **39**(2), 333–356, 1946. ISSN 0009-2665. doi:10.1021/cr60123a005.
- Redlich, O. and Hood, G.C. Ionic interaction, dissociation and molecular structure. *Discussions of the Faraday Society*, **24**, 87–93, 1957.
- Reimann, S. and Lewis, A.C. Anthropogenic VOCs. In *Volatile Organic Compounds in the Atmosphere*, edited by R. Koppmann, chapter 2, 342 – 387. Blackwell Publishing Ltd, Oxford, Great Britain, 2007. ISBN 978-1-4051-3115-5.
- Ren, X., Brune, W.H., Cantrell, C.A., Edwards, G.D., Shirley, T., Metcalf, A.R., and Leshner, R.L. Hydroxyl and Peroxy Radical Chemistry in a Rural Area of Central Pennsylvania: Observations and Model Comparisons. *Journal of Atmospheric Chemistry*, **52**(3), 231 – 257, 2005. ISSN 0167-7764. doi:10.1007/s10874-005-3651-7.
- Ren, X., van Duin, D., Cazorla, M., Chen, S., Mao, J., Zhang, L., Brune, W.H., Flynn, J.H., Grossberg, N., Lefer, B.L., Rappenglück, B., Wong, K.W., Tsai, C., Stutz, J., Dibb, J.E., Thomas Jobson, B., Luke, W.T., and Kelley, P. Atmospheric oxidation chemistry and ozone production: Results from SHARP 2009 in Houston, Texas. *Journal of Geophysical Research – Atmospheres*, **118**(11), 5770 – 5780, 2013. ISSN 2169-8996. doi:10.1002/jgrd.50342.
- Renard, P., Siekmann, F., Gandolfo, A., Socorro, J., Salque, G., Ravier, S., Quivet, E., Clément, J.L., Traikia, M., Delort, A.M., Voisin, D., Vuitton, V., Thissen, R., and Monod, A. Radical mechanisms of methyl vinyl ketone oligomerization through aqueous phase OH-oxidation: on the paradoxical role of dissolved molecular oxygen. *Atmospheric Chemistry and Physics*, **13**(13), 6473 – 6491, 2013. doi:10.5194/acp-13-6473-2013.

- Rodhe, H. *Time scales characterizing the processing of water and cloud condensation nuclei by clouds*. Dep. Meteorol., Stockholm University, Rep. CM 80 edition, 1992.
- Ross, A.B., Bielski, B.H.J., Buxton, G.V., Cabelli, D.E., Helman, W.P., Huie, R.E., Grodkovski, J., Neta, P., Mulazzani, Q.G., and Wilkinson, F. *NIST standard reference database 40: NDRL/NIST solution kinetics database vers. 3.0*. Gaithersburg, MD, USA, 1998.
- Salma, I. and Lång, G.G. How many carboxyl groups does an average molecule of humic-like substances contain? *Atmospheric Chemistry and Physics*, **8**(20), 5997 – 6002, 2008. doi:10.5194/acp-8-5997-2008.
- Sander, R. Compilation of Henry's law constants, version 3.99. *Atmospheric Chemistry and Physics Discussions*, **14**(21), 29615 – 30521, 2014. doi:10.5194/acpd-14-29615-2014.
- Sander, S.P., Abbatt, J., Barker, J.R., Burkholder, J.B., Friedl, R.R., Golden, D.M., Huie, R.E., Kolb, C.E., Kurylo, M.J., Moortgat, G.K., Orkin, V.L., and Wine, P.H. *Chemical kinetics and photochemical data for use in atmospheric studies, Evaluation No. 17*. JPL Publication 10-6, Jet Propulsion Laboratory, Pasadena, CA, USA, 2011. URL <http://jpldataeval.jpl.nasa.gov>.
- Sato, K., Takami, A., Kato, Y., Seta, T., Fujitani, Y., Hikida, T., Shimono, A., and Imamura, T. AMS and LC/MS analyses of SOA from the photooxidation of benzene and 1,3,5-trimethylbenzene in the presence of NO<sub>x</sub>: Effects of chemical structure on SOA aging. *Atmospheric Chemistry and Physics*, **12**(10), 4667 – 4682, 2012. doi:10.5194/acp-12-4667-2012.
- Satterfield, C.N. and Case, L.C. Reaction of Aldehyde and hydrogen peroxide in aqueous solution – Kinetics of the initial reaction. *Industrial and Engineering Chemistry*, **46**(5), 998 – 1001, 1954. ISSN 0019-7866. doi:10.1021/ie50533a049.
- Saunders, S.M., Jenkin, M.E., Derwent, R.G., and Pilling, M.J. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds. *Atmospheric Chemistry and Physics*, **3**(1), 161 – 180, 2003. ISSN 1680-7324.
- Schaefer, T., Schindelka, J., Hoffmann, D., and Herrmann, H. Laboratory kinetic and mechanistic studies on the OH-initiated oxidation of acetone in aqueous solution. *Journal of Physical Chemistry A*, **116**(24), 6317 – 6326, 2012. ISSN 1089-5639. doi:10.1021/jp2120753.
- Scheinhardt, S., Müller, K., Spindler, G., and Herrmann, H. Complexation of trace metals in size-segregated aerosol particles at nine sites in Germany. *Atmospheric Environment*, **74**, 102 – 109, 2013. ISSN 1352-2310. doi:<http://dx.doi.org/10.1016/j.atmosenv.2013.03.023>.
- Scholes, G. and Willson, R.L.  $\gamma$ -Radiolysis of aqueous thymine solutions. Determination of relative reaction rates of OH radicals. *Transactions of the Faraday Society*, **63**(540P), 2983, 1967. doi:10.1039/tf9676302983.

- Schöne, L., Schindelka, J., Szeremeta, E., Schaefer, T., Hoffmann, D., Rudzinski, K.J., Szmigielski, R., and Herrmann, H. Atmospheric aqueous phase radical chemistry of the isoprene oxidation products methacrolein, methyl vinyl ketone, methacrylic acid and acrylic acid - kinetics and product studies. *Physical Chemistry Chemical Physics*, **16**(13), 6257 – 6272, 2014. doi:10.1039/C3CP54859G.
- Schuchmann, M., Zegota, H., and von Sonntag, C. Acetate peroxy radicals,  $\text{O}_2\text{CH}_2\text{CO}_2^-$  – A study on the gamma radiolysis and pulse-radiolysis of acetate in oxygenated aqueous solutions. *Zeitschrift für Naturforschung Section B – A Journal of Chemical Sciences*, **40**(2), 215 – 221, 1985. ISSN 0932-0776.
- Schwartz, S.E. Gas- and aqueous-phase chemistry of  $\text{HO}_2$  in liquid water clouds. *Journal of Geophysical Research – Atmospheres*, **89**(D7), 11589 – 11598, 1984. ISSN 2156-2202. doi:10.1029/JD089iD07p11589.
- Schwartz, S.E. Mass transport considerations pertinent to aqueous phase reactions of gases in liquid water clouds. In *Chemistry of Multiphase Atmospheric Systems*, edited by W. Jaeschke, 415 – 471. Springer, Berlin, Germany, 1986.
- Sedlak, D.L. and Hoigné, J. The role of copper and oxalate in the redox cycling of iron in atmospheric waters. *Atmospheric Environment Part A – General Topics*, **27**(14), 2173 – 2185, 1993. ISSN 0960-1686. doi:10.1016/0960-1686(93)90047-3.
- Seinfeld, J.H. and Pandis, S.N. *Atmospheric Chemistry and Physics – From Air Pollution to Climate Change*. John Wiley & Sons, Inc., Hoboken, New Jersey, USA, 2nd edition, 2006. ISBN 0-0471-72018-6.
- Sharkey, T.D., Wiberley, A.E., and Donohue, A.R. Isoprene emission from plants: Why and how. *Annals of Botany*, **101**(1), 5 – 18, 2008. ISSN 0305-7364. doi:10.1093/aob/mcm240.
- Sierau, B., Stratmann, F., Pelzing, M., Neususs, C., Hofmann, D., and Wilck, M. A condensation-growth and impaction method for rapid off-line chemical-characterization of organic submicrometer atmospheric aerosol particles. *Journal of Aerosol Science*, **34**(2), 225 – 242, 2003. ISSN 0021-8502. doi:10.1016/S0021-8502(02)00159-3.
- Simmel, M., Diehl, K., and Wurzler, S. Numerical simulation of the microphysics of an orographic cloud: Comparison with measurements and sensitivity studies. *Atmospheric Environment*, **39**(23–24), 4365 – 4373, 2005. ISSN 1352-2310. doi:10.1016/j.atmosenv.2005.02.017.
- Simmel, M., Trautmann, T., and Tetzlaff, G. Numerical solution of the stochastic collection equation – comparison of the Linear Discrete Method with other methods. *Atmospheric Research*, **61**(2), 135 – 148, 2002. ISSN 0169-8095. doi:10.1016/S0169-8095(01)00131-4.
- Simmel, M. and Wurzler, S. Condensation and activation in sectional cloud microphysical models. *Atmospheric Research*, **80**(2–3), 218 – 236, 2006. ISSN 0169-8095. doi:10.1016/j.atmosres.2005.08.002.

- Skogerboe, R.K. and Wilson, S.A. Reduction of ionic species by fulvic acid. *Analytical Chemistry*, **53**(2), 228 – 232, 1981. doi:10.1021/ac00225a023.
- Smith, J.D., Sio, V., Yu, L., Zhang, Q., and Anastasio, C. Secondary Organic Aerosol Production from Aqueous Reactions of atmospheric phenols with an organic triplet excited state. *Environmental Science & Technology*, **48**(2), 1049 – 1057, 2014. doi:10.1021/es4045715.
- Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K., Tignor, M., and Miller, H. (eds.). *Climate Change 2007: The Physical Science Basis. Contribution of working group I to the fourth assessment report of the IPCC*. Cambridge University Press, Cambridge, UK and New York, NY, USA, 2007.
- Song, M., Marcolli, C., Krieger, U.K., Zuend, A., and Peter, T. Liquid-liquid phase separation and morphology of internally mixed dicarboxylic acids/ammonium sulfate/water particles. *Atmospheric Chemistry and Physics*, **12**(5), 2691 – 2712, 2012. doi:10.5194/acp-12-2691-2012.
- Souza, S.R., Vasconcellos, P.C., and Carvalho, L.R. Low molecular weight carboxylic acids in an urban atmosphere: Winter measurements in São Paulo City, Brazil. *Atmospheric Environment*, **33**(16), 2563 – 2574, 1999. ISSN 1352-2310. doi:http://dx.doi.org/10.1016/S1352-2310(98)00383-5.
- Stefan, M. and Bolton, J. Reinvestigation of the acetone degradation mechanism in dilute aqueous solution by the UV/H<sub>2</sub>O<sub>2</sub> process. *Environmental Science & Technology*, **33**(6), 870 – 873, 1999. ISSN 0013-936X. doi:10.1021/es9808548.
- Stemmler, K., Ammann, M., Donders, C., Kleffmann, J., and George, C. Photosensitized reduction of nitrogen dioxide on humic acid as a source of nitrous acid. *Nature*, **440**(7081), 195 – 198, 2006. ISSN 0028-0836. doi:10.1038/nature04603.
- Stockwell, W.R. A homogeneous gas phase mechanism for use in a regional acid deposition model. *Atmospheric Environment*, **20**(8), 1615 – 1632, 1986. ISSN 1352-2310. doi:10.1016/0004-6981(86)90251-9.
- Stockwell, W.R., Kirchner, F., Kuhn, M., and Seefeld, S. A new mechanism for regional atmospheric chemistry modeling. *Journal of Geophysical Research – Atmospheres*, **102**(D22), 25847 – 25879, 1997. doi:10.1029/97JD00849.
- Stockwell, W.R., Lawson, C.V., Saunders, E., and Goliff, W.S. A Review of Tropospheric Atmospheric Chemistry and Gas-Phase Chemical Mechanisms for Air Quality Modeling. *Atmosphere*, **3**(1), 1 – 32, 2011. ISSN 2073-4433. doi:10.3390/atmos3010001.
- Stockwell, W.R., Middleton, P., Chang, J.S., and Tang, X.Y. The 2nd generation Regional Acid Deposition Model chemical mechanism for regional air quality modelling. *Journal of Geophysical Research – Atmospheres*, **95**(D10), 16343 – 16367, 1990. ISSN 0148-0227. doi:10.1029/JD095iD10p16343.

- Stone, D., Whalley, L.K., and Heard, D.E. Tropospheric OH and HO<sub>2</sub> radicals: field measurements and model comparisons. *Chemical Society Reviews*, **41**, 6348 – 6404, 2012. doi:10.1039/C2CS35140D.
- Stutz, J., Wong, K.W., Lawrence, L., Ziemba, L., Flynn, J.H., Rappenglück, B., and Lefer, B. Nocturnal NO<sub>3</sub> radical chemistry in Houston, TX. *Atmospheric Environment*, **44**(33), 4099 – 4106, 2010. ISSN 1352-2310. doi:http://dx.doi.org/10.1016/j.atmosenv.2009.03.004. URL http://www.sciencedirect.com/science/article/pii/S1352231009002052.
- Sun, J. and Ariya, P.A. Atmospheric organic and bio-aerosols as cloud condensation nuclei (CCN): A review. *Atmospheric Environment*, **40**(5), 795 – 820, 2006. ISSN 1352-2310. doi:http://dx.doi.org/10.1016/j.atmosenv.2005.05.052.
- Tan, Y., Lim, Y.B., Altieri, K.E., Seitzinger, S.P., and Turpin, B.J. Mechanisms leading to oligomers and SOA through aqueous photooxidation: insights from OH radical oxidation of acetic acid and methylglyoxal. *Atmospheric Chemistry and Physics*, **12**(2), 801 – 813, 2012. doi:10.5194/acp-12-801-2012.
- Tilgner, A. *Modelling of the physico-chemical multiphase processing of tropospheric aerosols*. Dissertation, University of Leipzig, Leipzig, Germany, 2009.
- Tilgner, A., Bräuer, P., Wolke, R., and Herrmann, H. Modelling multiphase chemistry in deliquescent aerosols and clouds using CAPRAM3.0i. *Journal of Atmospheric Chemistry*, 1 – 36, 2013. ISSN 0167-7764. doi:10.1007/s10874-013-9267-4.
- Tilgner, A. and Herrmann, H. Radical-driven carbonyl-to-acid conversion and acid degradation in tropospheric aqueous systems studied by CAPRAM. *Atmospheric Environment*, **44**(40), 5415 – 5422, 2010.
- Valorso, R., Aumont, B., Camredon, M., Raventos-Duran, T., Mouchel-Vallon, C., Ng, N.L., Seinfeld, J.H., Lee-Taylor, J., and Madronich, S. Explicit modelling of SOA formation from  $\alpha$ -pinene photooxidation: sensitivity to vapour pressure estimation. *Atmospheric Chemistry and Physics*, **11**(14), 6895 – 6910, 2011. ISSN 1680-7316. doi:10.5194/acp-11-6895-2011.
- Vereecken, L. and Francisco, J.S. Theoretical studies of atmospheric reaction mechanisms in the troposphere. *Chemical Society Reviews*, **41**, 6259 – 6293, 2012. doi:10.1039/C2CS35070J.
- Vione, D., Merlo, F., Maurino, V., and Minero, C. Effect of humic acids on the Fenton degradation of phenol. *Environmental Chemistry Letters*, **2**(3), 129 – 133, 2004. ISSN 1610-3653. doi:10.1007/s10311-004-0086-3.
- von Sonntag, C. *The chemical basis of radiation biology*. Taylor and Francis, London, Great Britain., 1987.
- von Sonntag, C., Döwdeit, P., Fang, X., Mertens, R., Pan, X., Schuchmann, M., and Schuchmann, H. The fate of peroxy radicals in aqueous solution. *Water Science and*

- Technology*, **35**(4), 9 – 15, 1997. ISSN 0273-1223. doi:10.1016/S0273-1223(97)00003-6.
- von Sonntag, C. and Schuchmann, H.P. The elucidation of peroxy radical reactions in aqueous solution with the help of radiation chemical methods. *Angewandte Chemie – International Edition in English*, **30**(10), 1229 – 1253, 1991. ISSN 0570-0833. doi: 10.1002/anie.199112291.
- Walcek, C.J., Yuan, H.-H., and Stockwell, W.R. The influence of aqueous-phase chemical reactions on ozone formation in polluted and nonpolluted clouds. *Atmospheric Environment*, **31**(8), 1221 – 1237, 1997. ISSN 1352-2310. doi:10.1016/S1352-2310(96)00257-9.
- Wang, G., Chen, C., Li, J., Zhou, B., Xie, M., Hu, S., Kawamura, K., and Chen, Y. Molecular composition and size distribution of sugars, sugar-alcohols and carboxylic acids in airborne particles during a severe urban haze event caused by wheat straw burning. *Atmospheric Environment*, **45**(15), 2473 – 2479, 2011. ISSN 1352-2310. doi: <http://dx.doi.org/10.1016/j.atmosenv.2011.02.045>.
- Wang, G., Kawamura, K., Cheng, C., Li, J., Cao, J., Zhang, R., Zhang, T., Liu, S., and Zhao, Z. Molecular Distribution and Stable Carbon Isotopic Composition of Dicarboxylic Acids, Ketocarboxylic Acids, and  $\alpha$ -Dicarbonyls in Size-Resolved Atmospheric Particles From Xi'an City, China. *Environmental Science & Technology*, **46**(9), 4783 – 4791, 2012. doi:10.1021/es204322c.
- Wang, S., Shi, C., Zhou, B., Zhao, H., Wang, Z., Yang, S., and Chen, L. Observation of NO<sub>3</sub> radicals over Shanghai, China. *Atmospheric Environment*, **70**, 401 – 409, 2013. doi:<http://dx.doi.org/10.1016/j.atmosenv.2013.01.022>.
- Warneck, P. The relative importance of various pathways for the oxidation of sulfur dioxide and nitrogen dioxide in sunlit continental fair weather clouds. *Physical Chemistry Chemical Physics*, **1**, 5471 – 5483, 1999. doi:10.1039/A906558J.
- Watson, L., Shallcross, D., Utembe, S., and Jenkin, M. A Common Representative Intermediates (CRI) mechanism for VOC degradation. Part 2: Gas phase mechanism reduction. *Atmospheric Environment*, **42**(31), 7196 – 7204, 2008. ISSN 1352-2310. doi:10.1016/j.atmosenv.2008.07.034.
- Weschler, C.J., Mandich, M.L., and Graedel, T.E. Speciation, photosensitivity, and reactions of transition metal ions in atmospheric droplets. *Journal of Geophysical Research – Atmospheres*, **91**(D4), 5189 – 5204, 1986. ISSN 2156-2202. doi:10.1029/JD091iD04p05189.
- Whitten, G.Z., Heo, G., Kimura, Y., McDonald-Buller, E., Allen, D.T., Carter, W.P.L., and Yarwood, G. A new condensed toluene mechanism for Carbon Bond CB05-TU. *Atmospheric Environment*, **44**(40), 5346 – 5355, 2010. ISSN 1352-2310. doi:10.1016/j.atmosenv.2009.12.029. 2nd Biennial Conference on Atmospheric Chemistry Mechanisms, Air Quality Res Ctr, Davis, CA, DEC, 2008.
- Whitten, G.Z., Hogo, H., and Killus, J.P. The Carbon-Bond Mechanisms: A condensed kinetic mechanism for photochemical smog. *Environmental Science & Technology*, **14**(6),

- 690 – 700, 1980. ISSN 0013-936X. doi:10.1021/es60166a008.
- Wolke, R., Sehili, A., Simmel, M., Knoth, O., Tilgner, A., and Herrmann, H. SPACCIM: A parcel model with detailed microphysics and complex multiphase chemistry. *Atmospheric Environment*, **39**(23–24), 4375 – 4388, 2005. ISSN 1352-2310. doi:10.1016/j.atmosenv.2005.02.038.
- Worton, D.R., Surratt, J.D., LaFranchi, B.W., Chan, A.W.H., Zhao, Y., Weber, R.J., Park, J.H., Gilman, J.B., de Gouw, J., Park, C., Schade, G., Beaver, M., Clair, J.M.S., Crounse, J., Wennberg, P., Wolfe, G.M., Harrold, S., Thornton, J.A., Farmer, D.K., Docherty, K.S., Cubison, M.J., Jimenez, J.L., Frossard, A.A., Russell, L.M., Kristensen, K., Glasius, M., Mao, J., Ren, X., Brune, W., Browne, E.C., Pusede, S.E., Cohen, R.C., Seinfeld, J.H., and Goldstein, A.H. Observational Insights into Aerosol Formation from Isoprene. *Environmental Science & Technology*, **47**(20), 11403 – 11413, 2013. doi:10.1021/es4011064.
- Yang, L. and Yu, L.E. Measurements of Oxalic Acid, Oxalates, Malonic Acid, and Malonates in Atmospheric Particulates. *Environmental Science & Technology*, **42**(24), 9268 – 9275, 2008. doi:10.1021/es801820z.
- Yarwood, G., Rao, S., Yocke, M., and Whitten, G.Z. *Updates to the carbon bond chemical mechanism: CB05*. Final report to the US EPA, RT-04-005675, 2005. URL <http://www.camx.com>.
- Zepp, R.G., Faust, B.C., and Hoigné, J. Hydroxyl radical formation in aqueous reactions (pH 3–8) of iron(II) with hydrogen peroxide: the photo-Fenton reaction. *Environmental Science & Technology*, **26**(2), 313 – 319, 1992. doi:10.1021/es00026a011.
- Zhang, X., Liu, J., Parker, E.T., Hayes, P.L., Jimenez, J.L., de Gouw, J.A., Flynn, J.H., Grossberg, N., Lefer, B.L., and Weber, R.J. On the gas-particle partitioning of soluble organic aerosol in two urban atmospheres with contrasting emissions: 1. Bulk water-soluble organic carbon. *Journal of Geophysical Research – Atmospheres*, **117**(D21), 2012. ISSN 2156-2202. doi:10.1029/2012JD017908.
- Zhao, R., Lee, A.K.Y., and Abbatt, J.P.D. Investigation of aqueous-phase photooxidation of glyoxal and methylglyoxal by aerosol chemical ionization mass spectrometry: observation of hydroxyhydroperoxide formation. *Journal of Physical Chemistry A*, **116**(24), 6253 – 6263, 2012. ISSN 1089-5639. doi:10.1021/jp211528d.
- Zhao, R., Lee, A.K.Y., Soong, R., Simpson, A.J., and Abbatt, J.P.D. Formation of aqueous-phase  $\alpha$ -hydroxyhydroperoxides ( $\alpha$ -HHP): potential atmospheric impacts. *Atmospheric Chemistry and Physics Discussions*, **13**(2), 5509 – 5552, 2013. doi:10.5194/acpd-13-5509-2013.
- Zuo, Y. and Hoigné, J. Formation of hydrogen peroxide and depletion of oxalic acid in atmospheric water by photolysis of iron(III)-oxalato complexes. *Environmental Science & Technology*, **26**(5), 1014 – 1022, 1992. doi:10.1021/es00029a022.





# Glossary

## **(Aerosol) particles**

Particles or aerosol particles are fine solid or liquid parts dispersed in the ambient air. In contrast to the phrase 'aerosols', the surrounding air shell is not considered in this context.

## **Aerosol**

Aerosols are a suspension of solid or liquid particles and the ambient gas (commonly air) (*Solomon et al.*, 2007).

## **Albedo**

*'The fraction of solar radiation reflected by a surface or object'* (*Solomon et al.*, 2007).

## **Anthropogenic**

*'Resulting from or produced by human beings'* (*Solomon et al.*, 2007).

## **Bond dissociation energy/enthalpy**

Bond dissociation energy or bond dissociation enthalpy (short *BDE*) is a measure of the strength of a chemical bond, which is defined by the change of the standard enthalpy  $\Delta H$  after a homolytic bond cleavage at 0°C.

## **Cloud condensation nuclei**

Cloud condensation nuclei or CCN are *'airborne particles that serve as an initial site for the condensation of liquid water, which can lead to the formation of cloud droplets'* (*Solomon et al.*, 2007).

## **Deliquescent**

Deliquescent particles attract moisture from the ambient air. They form a solution of the absorbed water molecules and the constituents of the particle (including salts, inorganic and organic trace compounds).

## **Greenhouse gas**

Greenhouse gases (GHGs) are trace gases, which absorb and emit radiation in the thermal infrared range causing a warming of the troposphere (*Solomon et al.*, 2007).

**HCCT-2010**

The Hill Cloud Cap Thuringia 2010 (HCCT-2010) field campaign was a sophisticated international cloud passage experiment at the Mount Schmücke in Thuringia, Germany. It took place in autumn 2010 (Sept. 14<sup>th</sup> – Oct. 24<sup>th</sup>) with measurements conducted at the summit of the mountain in an altitude of 937 m and two valley stations (Gehlberg and Goldlauter).

**HO<sub>x</sub>**

The sum of ·OH and HO<sub>2</sub>· radicals.

**Ionic strength**

Measure for the concentration of ions in a solution. The ionic strength  $I$  can be calculated as a function of the concentration of all ions ( $c_i$ ) and their charge ( $z_i$ ):

$$I = \frac{1}{2} \sum_i c_i z_i^2$$

(IUPAC, 1997)

**Isoprene**

Trivial name for 2-methyl-1,3-butadien ( $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$ ). A volatile organic compound emitted by deciduous trees with the largest non-methane volatile organic compound emission rate.

**Liquid water content**

Liquid water content or LWC is the amount of liquid water per volume of ambient air, given in g/kg, g/m<sub>air</sub><sup>3</sup>, or l/m<sub>air</sub><sup>3</sup>.

**NO<sub>x</sub>**

The sum of the nitrogen oxides NO· and NO<sub>2</sub>·.

**NO<sub>y</sub>**

NO<sub>y</sub> species are reactive odd nitrogen species. NO<sub>y</sub> is defined as the sum of NO<sub>x</sub> and NO<sub>x</sub> oxidation products including nitric acid.

**Oligomer**

Molecules that bear several basic units of the same or similar structure (monomers). The simplest oligomer is a dimer, however, typically oligomers consist of many monomers leading to high molecular-weight compounds. The number of monomers in an oligomer is limited in contrast to polymers.

**Oligomerisation**

Chemical process forming oligomers.

**Organic aerosol**

Organic aerosols or OAs are 'aerosol particles consisting predominantly of organic compounds, mainly carbon, hydrogen, oxygen and lesser amounts of other elements' (Solomon *et al.*, 2007).

**Part per million**

Part per million or ppm is a measure for the mixing ratio of trace gases in the troposphere. 1 ppm equals to 1 molecule of the trace compound per 1 million molecules of the ambient air or 1  $\mu\text{mol/mol}$ .

**pH**

Measure of acidity defined as the negative decimal logarithm of the proton concentration in  $\text{mol l}^{-1}$  of an aqueous solution:  $pH = -\log([H^+])$ .

**pK<sub>a</sub>**

Negative decimal logarithm of the dissociation constant  $K_a$  (in  $\text{mol l}^{-1}$ ) to determine the speciation of the protonated and deprotonated forms of an acid in a more convenient way:  $pK_a = -\log([K_a])$ .

**Primary organic aerosol**

Primary organic aerosol or POA is organic aerosol that is directly emitted into the atmosphere (Jimenez *et al.*, 2009).

**Secondary organic aerosol**

Secondary organic aerosol or SOA is organic aerosol formed by gas-to-particle conversions due to the oxidation of gas phase compounds (Seinfeld and Pandis, 2006, Jimenez *et al.*, 2009).

**Sulphur(IV)**

Four-valent sulphur (with the oxidation state +IV) mainly composed of sulphurous acid ( $\text{H}_2\text{SO}_3$ ,  $\text{HSO}_3^-$ , and  $\text{SO}_3^{2-}$ ) and sulphur dioxide ( $\text{SO}_2$ ). Often abbreviated with S(IV).

**Sulphur(VI)**

Six-valent sulphur (with the oxidation state +VI) mainly composed of sulphuric acid ( $\text{H}_2\text{SO}_4$ ,  $\text{HSO}_4^-$ , and  $\text{SO}_4^{2-}$ ). Often abbreviated with S(VI).

**Terpenes**

Class of organic compounds produced by a number of conifer trees. Terpenes are derived from units of isoprene having a chemical formula  $[\text{C}_5\text{H}_8]_n$  ( $n$  = number of isoprene units).

### **Transition metal ion**

A transition metal ions or TMI is '*an element whose atom has an incomplete d sub-shell, or which can give rise to cations with an incomplete d sub-shell*' (IUPAC, 1997).

### **Troposphere**

The lowermost part of the atmosphere with a mean height of 12 km in midlatitudes and minimum height of 8 km at the poles and 18 km at the equator (*Seinfeld and Pandis*, 2006).

# Acronyms

<b>AAc</b>	acetic acid
<b>AMS</b>	aerosol mass spectrometer
<b>BDE</b>	bond dissociation energy or bond dissociation enthalpy
<b>CACM</b>	Caltech Atmospheric Chemistry Mechanism (see <i>Griffin et al.</i> , 2002)
<b>CAPRAM</b>	Chemical Aqueous Phase RAdical Mechanism (see <i>Herrmann et al.</i> , 2005, <i>Tilgner and Herrmann</i> , 2010, <i>Bräuer et al.</i> , 2013)
<b>CCN</b>	cloud condensation nuclei
<b>CE</b>	capillary electrophoresis
<b>C-GIS</b>	Condensational-Growth and Impaction System (see <i>Sierau et al.</i> , 2003)
<b>CRI</b>	Common Representative Intermediates mechanism (see <i>Jenkin et al.</i> , 2008, <i>Watson et al.</i> , 2008)
<b>DCA</b>	dicarboxylic acid
<b>EC</b>	elemental carbon
<b>ELVOC</b>	extremely low-volatility organic compound
<b>ETR</b>	electron transfer reaction
<b>FSG</b>	Fuller-Schettler-Giddings method (see <i>Fuller</i> , 1986)
<b>GC-MS</b>	gas chromatography mass spectrometry
<b>GECKO-A</b>	Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere (see <i>Aumont et al.</i> , 2005)
<b>GROMHE</b>	GRoup contribution Method for Henry's law Estimate (see <i>Raventos-Duran et al.</i> , 2010)
<b>HLC</b>	Henry's Law constant, also denoted with $K_H$
<b>HPLC/(-)ESI-TOFMS</b>	high pressure liquid chromatography electrospray ionisation time of flight mass spectrometry
<b>HULIS</b>	humic-like substances (see, e.g., <i>Paglione et al.</i> , 2014)

<b>IUPAC</b>	International Union of Pure and Applied Chemistry ( <a href="http://www.iupac.org/">http://www.iupac.org/</a> )
<b>JPL</b>	Jet Propulsion Laboratory ( <i>Sander et al.</i> , 2011)
<b>LEAK</b>	LEipziger Aerosol-Kammer (Leipzig aerosol chamber, see <i>Iinuma et al.</i> , 2009, <i>Kahnt</i> , 2012)
<b>LISA</b>	Laboratoire Inter-universitaire des Systèmes Atmosphériques
<b>LWC</b>	liquid water content
<b>MCM</b>	Master Chemical Mechanism (see <i>Saunders et al.</i> , 2003, <i>Jenkin et al.</i> , 2003)
<b>MEK</b>	methyl ethyl ketone
<b>MGLY</b>	methylglyoxal
<b>MOST</b>	Multiphase chemistry of Oxygenated Species in the Troposphere (see <i>George et al.</i> , 2005)
<b>NASA</b>	National Aeronautics and Space Administration
<b>NCAR</b>	National Center for Atmospheric Research
<b>NIST</b>	National Institute of Standards and Technology
<b>NMVOC</b>	non-methane volatile organic compound
<b>OA</b>	organic aerosol
<b>OM</b>	organic matter
<b>PAN</b>	peroxyacyl nitrate
<b>POA</b>	primary organic aerosol
<b>PTFE</b>	polytetrafluoroethylene
<b>PTR-MS</b>	proton-transfer-reaction mass spectrometer
<b>RADM</b>	Regional Acid Deposition Model (see <i>Stockwell</i> , 1986, <i>Stockwell et al.</i> , 1990)
<b>RACM</b>	Regional Atmospheric Chemistry Mechanism (see <i>Stockwell et al.</i> , 1997, <i>Goliff et al.</i> , 2013)
<b>SAPRC</b>	Statewide Air Pollution Research Center mechanism (see <i>Carter</i> , 2010a,b, 2013)
<b>SAR</b>	structure-activity relationship
<b>SMPS</b>	scanning mobility particle sizer
<b>SOA</b>	secondary organic aerosol
<b>SPACCIM</b>	Spectral Aerosol Cloud Chemistry Interaction Model

(see *Wolke et al.*, 2005)

<b>TMB</b>	1,3,5-trimethylbenzene
<b>TME</b>	tetramethylethylene
<b>TMI</b>	transition metal ion
<b>TROPOS</b>	Leibniz Institute for Tropospheric Research
<b>VOC</b>	volatile organic compound
<b>WSOC</b>	water-soluble organic carbon
<b>WISOC</b>	water-insoluble organic carbon





# List of symbols

$\alpha$	mass accommodation coefficient
$D_g$	gas phase diffusion coefficient
$K_{diss}$	dissociation constant
$K_H$	Henry's Law constant
$K_{H,eff}$	effective Henry's Law constant
$K_{hyd}$	hydration constant
$k_T$	mass transfer function
$R^2$	correlation coefficient
$\sigma$	standard deviation
$v_d$	deposition velocity



# List of Figures

(2.1)	Overview of the resistance model by <i>Schwartz</i> (1986) as implemented in SPACCIM. . . . .	10
(2.2)	Number of species and reactions created by GECKO-A for different oxidation series using a 5% threshold for branching. . . . .	16
(2.3)	Overview of the version history of CAPRAM and CAPRAM special modules.	17
(2.4)	Schematic representation of the multiphase chemical mechanism MCMv.3.1-CAPRAM 3.0n. . . . .	22
(2.5)	Principles of the oxidation scheme of organic compounds in CAPRAM 3.0n.	24
(2.6)	Overview of the most important microphysical processes along with the multiphase chemical processes implemented in SPACCIM. . . . .	26
(2.7)	Coupling scheme of the microphysics and chemistry module in SPACCIM. .	28
(2.8)	Progress of the potential energy $U$ during a chemical reaction along a reaction coordinate $\ell$ after <i>Evans</i> (1938). . . . .	31
(2.9)	Simplified representation of the gas phase protocol for the VOC oxidation in GECKO-A (a) and its processing in the generator (b) according to <i>Aumont et al.</i> (2005). . . . .	36
(3.1)	Regression lines derived from the correlation of gas and aqueous phase kinetic data of hydroxyl radical reactions with organic compounds for the various compound classes. . . . .	41
(3.2)	Box plots of the absolute errors of the correlation of gas and aqueous phase rate constants of hydroxyl radical reactions with organic compounds. . . .	43
(3.3)	Correlation of hydroxyl radical reaction rate constants with the respective compound classes against the carbon number. . . . .	44
(3.4)	Box plots of the absolute errors of the correlation of hydroxyl radical reactions with organic compounds versus the carbon number. . . . .	47
(3.5)	Correlation of the OH versus NO <sub>3</sub> radical rate constants in the aqueous phase for the respective compound classes and the overall data. Regression lines for the various compound classes are shown in the same colour as the respective data points. The grey line represents the correlation of the overall data, the black dashed dotted line is the line of same reactivity. . . . .	48
(3.6)	Box plots of the absolute errors of the correlation of hydroxyl and nitrate radical aqueous phase rate constants of reactions with organic compounds. .	49
(3.7)	Evans-Polanyi-type correlations of hydroxyl radical reactions with the respective compound classes. . . . .	51

(3.8)	Box plots of the absolute errors of the Evans-Polanyi-type correlation of hydroxyl radical reactions with the respective compound classes. . . . .	53
(3.9)	Plot of predicted versus experimental data for hydroxyl radical reactions predicted with Evans-Polanyi-type correlations. . . . .	54
(3.10)	Evans-Polanyi-type correlations of nitrate radical reactions with the respective compound classes. . . . .	56
(3.11)	Improved Evans-Polanyi-type correlation of the experimental rate constants plotted against the sum of all <i>BDEs</i> of bonds including a hydrogen atom. .	59
(3.12)	Improved Evans-Polanyi-type correlations of hydroxyl radical reactions with organic compounds for the respective compound classes. . . . .	61
(3.13)	Box plots of the absolute errors of the improved Evans-Polanyi-type correlation of hydroxyl radical reactions with organic compounds of the respective compound class. . . . .	62
(3.14)	Plot of predicted versus experimental data for hydroxyl radical reactions separated by compound class together with the linear regression lines for the improved Evans-Polanyi-type correlations. . . . .	63
(3.15)	Improved Evans-Polanyi-type correlations of nitrate radical reactions for the respective compound classes. . . . .	64
(3.16)	Box plots of the absolute errors of the improved Evans-Polanyi-type correlation of nitrate radical reactions with organic compounds of the respective compound class. . . . .	65
(3.17)	Plot of predicted versus experimental data for nitrate radical reactions with organic compounds of the different compound classes together with the linear regression lines for the improved Evans-Polanyi-type correlations. . . . .	66
(3.18)	Box plots of the absolute errors of the logarithmised experimental minus predicted rate constants for the prediction with the SAR by <i>Monod and Doussin</i> and <i>Minakata et al.</i> . . . . .	68
(3.19)	Scatter plot of the rate constants predicted with the SARs by <i>Monod and Doussin</i> (2008)/ <i>Doussin and Monod</i> (2013) and by <i>Minakata et al.</i> (2009) over experimental rate constants for aqueous phase reactions of hydroxyl radicals with organic compounds of the various compound classes. . . . .	69
(4.1)	Workflow of the generator GECKO-A with a detailed depiction of the final implemented aqueous phase protocol. . . . .	74
(5.1)	Speciation of the different hydration forms of 2-hydroxy-3-oxo butanedial in the sensitivity run woBB (a) and concentrations of the unhydrated (b) and fully hydrated (c) forms of 2-hydroxy-3-oxo butanedial in the different sensitivity runs. . . . .	92
(5.2)	Concentration-time profiles for various products of the 2-hydroxy-3-oxo butanedial oxidation for the different sensitivity runs. . . . .	94
(5.3)	Time profile of the organic and dry mass and the pH-value for varying mass accommodation coefficients. . . . .	96
(5.4)	Concentration-time profiles of selected compounds for varying mass accommodation coefficients. . . . .	97

(5.5)	Overview of the potential of mechanism reduction by omitting minor reaction pathways. . . . .	99
(5.6)	Concentration-time profiles for selected organic compounds in the sensitivity runs investigating the influence of the omission of minor reaction pathways under urban conditions. . . . .	100
(5.7)	Concentration-time profiles for selected organic compounds, as well as pH value and dry and organic mass in the sensitivity runs investigating the influence of the chosen SAR. . . . .	102
(5.8)	Time-resolved evolution of the organic mass fraction distinguished by compound classes in the sensitivity run $\text{WSOC}_{\text{OH}}$ under urban conditions. . . .	105
(5.9)	Logarithmised concentration-time profiles of OH radicals in the aqueous phase over the whole modelling period. . . . .	106
(5.10)	Logarithmised concentration-time profiles of $\text{NO}_3$ radicals in the aqueous phase over the whole modelling period. . . . .	107
(5.11)	Time-resolved evolution of particulate OM, residual OM and organic nitrate concentrations in the sensitivity runs $\text{WSOC}_{\text{OH}}$ , $\text{WSOC}_{\text{NO}_3}$ , and the base case under urban conditions. . . . .	108
(5.12)	Time-resolved evolution of particulate OM, residual OM and organic nitrate concentrations in the sensitivity runs $\text{WSOC}_{\text{NO}_3}$ , Phot, and $\text{NO}_3\text{add}$ under urban conditions. . . . .	110
(5.13)	Time-resolved evolution of particulate OM, residual OM and organic nitrate concentrations in the sensitivity runs $\text{NO}_3\text{add}$ , $\text{O:C}=0.75$ , and $\text{O:C}=1$ under urban conditions. . . . .	112
(5.14)	Time-resolved evolution of particulate organic matter in the sensitivity runs $\text{O:C}=1$ and OxyE4 – OxyE0 under urban conditions. . . . .	115
(5.15)	Aqueous phase concentration-time profiles of organic nitrates in the sensitivity runs $\text{O:C}=1$ and OxyE4 – OxyE0 under urban conditions. . . . .	115
(5.16)	Time-resolved evolution of particulate organic matter in the sensitivity runs OxyE2 and DCA under urban conditions. . . . .	116
(5.17)	Aqueous phase concentration-time profiles of oxalic acid in the sensitivity runs $\text{O:C}=1$ and OxyE4 – OxyE0 under urban conditions. . . . .	117
(5.18)	Concentration-time profiles of selected organic compounds in the sensitivity runs investigating the nitrate radical chemistry under urban conditions. . . .	119
(5.19)	Time-resolved evolution of the total organic mass and the organic nitrate fraction in the sensitivity runs investigating the nitrate radical chemistry under urban winter conditions. . . . .	121
(6.1)	Modelled and measured concentrations of ozone and TME. . . . .	135
(6.2)	Modelled concentration-time profiles of hexane and selected gas phase oxidation products as well as experimentally detected concentrations in the model run simulating the hexane oxidation experiment. . . . .	137
(6.3)	Modelled and measured concentrations of gas phase TMB and the gas phase oxidation products methylglyoxal and acetic acid. . . . .	138

(6.4)	Modelled particle mass concentrations for the various sensitivity runs and measured particle concentrations as monitored by the SMPS and AMS. . . .	142
(6.5)	Modelled liquid water content and mean particle radius in the TMB oxidation experiment. . . . .	144
(6.6)	Multiphase flux analysis of major aqueous phase turnovers in the TMB oxidation experiment for the scenario RXN <sub>0.25</sub> . . . . .	146
(6.7)	Concentrations of organic constituents detected in the C-GIS samples corrected for the blind values at sampling point A1 and modelled concentrations of acetic and oxalic acid for the various sensitivity runs. . . . .	147
(6.8)	Modelled particle pH for the 3 sensitivity runs TMB, UPT, and RXN. . . .	148
(6.9)	Overview of important meteorological and microphysical parameters in the ‘real atmosphere’ scenarios. . . . .	152
(6.10)	Time profile of the particle/cloud droplet pH for CAPRAM 4.0 $\alpha$ in the urban and remote scenario. . . . .	153
(6.11)	Time profile of the organic and dry particulate mass for CAPRAM 4.0 $\alpha$ in the urban and remote scenario. . . . .	155
(6.12)	Time profile of the organic particulate mass for the different CAPRAM mechanisms in the urban scenario. . . . .	157
(6.13)	Evolution of the organic particulate mass differentiated by compound classes for the urban and remote scenario with CAPRAM 4.0 $\alpha$ . . . . .	160
(6.14)	Evolution of the organic particulate mass excluding the residual OM differentiated by chain length for the 3 different mechanisms CAPRAM 3.0p, 3.5 $\alpha$ , and 4.0 $\alpha$ under urban conditions. . . . .	162
(6.15)	Re-evaluation of the evolution of the organic particulate mass differentiated by chain length in CAPRAM 4.0 $\alpha$ under urban conditions. . . . .	164
(6.16)	Concentration-time profiles of hydroxyl radicals in the gas and the aqueous phase for the different CAPRAM versions under urban conditions. . . . .	166
(6.17)	Time-resolved production and degradation fluxes of aqueous phase hydroxyl radicals for the second and third model day in the simulation with CAPRAM 4.0 $\alpha$ under urban conditions. . . . .	168
(6.18)	Concentration-time profiles of nitrate radicals in the gas and the aqueous phase for the different CAPRAM versions under urban conditions. . . . .	170
(6.19)	Time-resolved production and degradation fluxes of aqueous phase nitrate radicals for the second and third model day in the simulations with CAPRAM 4.0 $\alpha$ under urban conditions. . . . .	171
(6.20)	Comparison of the turnovers of reactions of organic compounds with hydroxyl versus nitrate radicals distinguished by compound classes. . . . .	174
(6.21)	Comparison of the logarithmised hydroxyl radical versus nitrate radical turnovers of reactions with organic compounds against the O:C ratio distinguished by compound classes. . . . .	176
(6.22)	Concentration-time profiles of the sum of hydroperoxyl and superoxide radicals in the gas and the aqueous phase for the different CAPRAM versions under urban conditions. . . . .	178

(6.23)	Time-resolved total production and degradation fluxes of hydroperoxyl and superoxide radicals in the CAPRAM 4.0 $\alpha$ and 3.0o simulations for the second and third model day under urban conditions. . . . .	179
(6.24)	Refined time-resolved total production and degradation fluxes of hydroperoxyl and superoxide radicals in CAPRAM 4.0 $\alpha$ for the second and third model day under urban conditions. . . . .	180
(6.25)	Concentration-time profiles of hydrogen peroxide in the gas and the aqueous phase for the various CAPRAM versions under urban conditions. . . . .	182
(6.26)	Time-resolved total production and degradation fluxes of hydrogen peroxide for the second and third model day in CAPRAM 4.0 $\alpha$ under urban conditions.	183
(6.27)	Concentration-time profiles of ozone in the gas phase for the various CAPRAM versions under urban and remote conditions. . . . .	184
(6.28)	Concentration-time profiles of aqueous phase sulfate for the various CAPRAM mechanisms under urban conditions. . . . .	185
(6.29)	Concentration-time profile of aqueous nitrate for the various CAPRAM mechanisms under urban conditions. . . . .	186
(6.30)	Concentration-time profiles of aqueous phase iron(II) for the various CAPRAM mechanisms under urban conditions. . . . .	187
(6.31)	Time-resolved production and degradation fluxes of aqueous phase iron(II) for the second and third model day under urban conditions in the scenarios with CAPRAM 3.0o and 4.0 $\alpha$ . . . . .	188
(6.32)	Concentration-time profiles of methanol and formic acid in the aqueous phase (including all dissociation states for formic acid) and overall gas and aqueous phase concentrations for the various CAPRAM versions under urban conditions.	191
(6.33)	Profiles of the overall aqueous phase concentrations (including all hydrated forms) and the sum of the gas and overall aqueous phase concentration of selected carbonyl compounds for the various CAPRAM mechanisms under urban conditions . . . . .	193
(6.34)	Profiles of the overall aqueous phase concentration (including all hydrated or dissociated forms) and, for glyoxalic acid, the sum of the gas and overall aqueous phase concentrations of selected monocarboxylic acids for the various CAPRAM mechanisms under urban conditions. . . . .	198
(6.35)	Overall aqueous phase concentration-time profiles (including all dissociation states) of selected dicarboxylic acids for the various CAPRAM mechanisms under urban conditions. . . . .	201
(B.1)	Sample molecule 1-carboxyl-2-methyl-4-hydroxyl cyclopentane for the demonstration of the basic principles of the two SARs by <i>Monod and Doussin</i> (2008) and <i>Minakata et al.</i> (2009). . . . .	271
(D.1)	Explanation of box plots as used in this dissertation. . . . .	305
(D.2)	Correlation of hydroxyl radical reactions with terminal diols and the carbon number. . . . .	306
(D.3)	Correlation of nitrate radical reactions with the respective compound classes versus the carbon number. . . . .	307

(D.4)	Box plots of the absolute errors of the correlation of nitrate radical reactions with organic compounds versus the carbon number. . . . .	308
(D.5)	Box plots of the absolute errors of the Evans-Polanyi-type correlation of nitrate radical reactions with the respective compound classes. . . . .	309
(D.6)	Scatter plot of predicted versus experimental data for the evaluation of Evans-Polanyi-type correlations for nitrate radical reactions separated by compound class together with the linear regression lines. . . . .	310
(E.1)	Concentration-time profiles of acylperoxy radicals and the products of the recombination and HO <sub>2</sub> elimination channel to assess the importance of each reaction pathway. . . . .	314
(E.2)	Speciation of the different hydration forms of oxo-butanedial in the sensitivity run woBB (a) and concentrations of the fully hydrated form in the different sensitivity runs (b). . . . .	315
(E.3)	Concentration-time profiles for selected organic compounds in the sensitivity runs investigating the influence of the omission of minor reaction pathways under remote continental conditions. . . . .	316
(E.4)	Complete overview of the time-resolved evolution of particulate OM, residual OM and organic nitrate concentrations in the sensitivity runs WSOC <sub>OH</sub> , WSOC <sub>NO<sub>3</sub></sub> , and the base case under urban conditions as already partly presented in Figure 5.11. . . . .	317
(E.5)	Complete overview of the time-resolved evolution of particulate OM, residual OM and organic nitrate concentrations in the sensitivity runs WSOC <sub>NO<sub>3</sub></sub> , Phot, and NO <sub>3</sub> add under urban conditions as already partly presented in Figure 5.12. . . . .	317
(E.6)	Complete overview of the time-resolved evolution of particulate OM, residual OM and organic nitrate concentrations in the sensitivity runs NO <sub>3</sub> add, O:C=0.75, and O:C=1 under urban conditions as already partly presented in Figure 5.13. . . . .	318
(E.7)	Complete overview of the time-resolved evolution of total organic mass in the sensitivity runs investigating the nitrate radical chemistry under urban winter conditions as already partly presented in Figure 5.19. . . . .	318
(E.8)	Concentration-time profiles for selected organic compounds in the sensitivity runs investigating the nitrate radical chemistry under urban winter conditions.	319
(E.9)	Concentration-time profiles for selected organic compounds in the sensitivity runs investigating the nitrate radical chemistry under remote continental summer conditions. . . . .	320
(E.10)	Concentration-time profiles for selected organic compounds in the sensitivity runs investigating the nitrate radical chemistry under remote continental winter conditions. . . . .	321
(E.11)	Time-resolved evolution of the total organic mass and the organic nitrate fraction in the sensitivity runs investigating the nitrate radical chemistry under remote conditions. . . . .	322



---

(E.12)	Time-resolved evolution of the total organic mass and the organic nitrate fraction in the sensitivity runs investigating the nitrate radical chemistry under remote winter conditions. . . . .	323
(H.1)	Modelled concentration-time profiles of selected aqueous phase compounds and overall particulate mass in the model run simulating the hexane oxidation experiment. . . . .	889
(H.2)	Analysis of the gas phase turnovers from TMB to MGLY averaged over the whole experiment. . . . .	898
(H.3)	Concentrations of gas phase malic acid as monitored by the PTR-MS in the chamber and modelled malic and succinic acid gas phase concentrations. . .	899
(H.4)	Gas phase concentrations of the most important TMB oxidation products methylglyoxal and acetic acid in the sensitivity runs TMB, UPT, and RXN. .	899
(I.1)	Time profiles of the particile/cloud droplet pH and the organic particulate mass for the different CAPRAM mechanisms in the urban scenario. . . . .	901
(I.2)	Evolution of the organic particulate mass differentiated by chain length for the 3 different mechanisms CAPRAM 3.0n, 3.5 $\alpha$ , and 4.0 $\alpha$ under remote conditions. . . . .	902
(I.3)	Concentration-time profiles of hydroxyl radicals in the gas and the aqueous phase for the various CAPRAM mechanisms under remote conditions. . . .	903
(I.4)	Time-resolved production and degradation fluxes of aqueous hydroxyl radicals for the second model day calculated with CAPRAM 3.5 $\alpha$ under remote conditions. . . . .	904
(I.5)	Comparison of the logarithmised hydroxyl radical versus nitrate radical turnovers of reactions with organic compounds against the O:C ratio distinguished by compound classes with a rescaled range for clarification. . . . .	905
(I.6)	Profiles of the overall aqueous phase concentration (including all hydrated or dissociated forms) and the sum of the gas and overall aqueous phase concentration of selected emitted monofunctional organic compounds for the various CAPRAM mechanisms under urban conditions. . . . .	906



# List of Tables

(3.1)	Parameters for the regression equations $k_{(aq)}/\text{M}^{-1}\text{s}^{-1} = A \cdot (k_{(g)}/\text{cm}^3\text{s}^{-1}) + B$ and statistical data derived from the correlation of gas and aqueous phase kinetic data of hydroxyl radical reactions with organic compounds for the various compound classes. . . . .	42
(3.2)	Parameters for the regression equations $k_{2nd}/\text{M}^{-1}\text{s}^{-1} = A \cdot CN + B$ ( $CN$ = carbon number) and statistical data derived from the correlation of hydroxyl radical reaction rate constants of organic compounds plotted against the carbon number of the various organic compounds. . . . .	45
(3.3)	Parameters for the regression equations $\log(k_{NO_3}/\text{M}^{-1}\text{s}^{-1}) = A \cdot \log(k_{OH}/\text{M}^{-1}\text{s}^{-1}) + B$ and statistical data derived from the correlation of hydroxyl radical and nitrate radical kinetic data of the reactions with organic compounds for the various compound classes. . . . .	48
(3.4)	Parameters for the regression equations $\log(k_H/\text{M}^{-1}\text{s}^{-1}) = A \cdot (BDE/\text{kJ mol}^{-1}) + B$ and statistical data derived from the Evans-Polanyi-type correlations of aqueous phase hydroxyl radical reactions with organic compounds for the various compound classes. . . . .	52
(3.5)	Parameters for the regression equations $\log(k_H) = A \cdot (BDE/\text{kJ mol}^{-1}) + B$ and statistical data derived from the Evans-Polanyi-type correlations of aqueous phase nitrate radical reactions with organic compounds for the various compound classes. . . . .	57
(3.6)	Parameters for the regression equations $\log(k_{exp}/\text{M}^{-1}\text{s}^{-1}) = A \cdot (\Sigma BDE/\text{kJ mol}^{-1})^2 + B \cdot (\Sigma BDE/\text{kJ mol}^{-1}) + C$ and statistical data derived from the advanced Evans-Polanyi-type correlations of aqueous phase hydroxyl radical reactions with organic compounds for the various compound classes. . . . .	60
(3.7)	Parameters for the regression equations $\log(k_{exp}/\text{M}^{-1}\text{s}^{-1}) = A \cdot (\Sigma BDE/\text{kJ mol}^{-1}) + B$ and statistical data derived from the improved Evans-Polanyi-type correlations of aqueous phase nitrate radical reactions with organic compounds for the various compound classes. . . . .	65
(3.8)	Choice of the prediction methods in the final revised GECKO-A protocol to generate rate constants for the indicated reactions. . . . .	70
(4.1)	Estimated rate constants for reactions of nitrate radicals with unsaturated organic compounds. . . . .	79
(4.2)	Estimated rate constants for reactions of nitrate radicals with deprotonated carboxylic acids. . . . .	80

(5.1)	Overview of the conditions of the sensitivity runs performed to derive a suitable parameterisation for the monomolecular decay of polycarbonyl compounds. . . . .	91
(5.2)	Overview of the different conditions used for the mechanism generation of the sensitivity runs concerning the cut-off of minor branches and the resulting number of reactions. . . . .	98
(5.3)	Overview of the number of species and processes implemented in the various new CAPRAM versions. . . . .	128
(6.1)	Gas phase oxidation products from the degradation of hexane identified by GC-MS and PTR-MS as well as the corresponding molecular weight ( $M_w$ ) and the mass-to-charge ratio ( $m/z$ ). . . . .	136
(6.2)	Hydration states of various carbonyl compounds. . . . .	195
(6.3)	Hydration states of various di- and polycarbonyl compounds as average over the whole model run. . . . .	196
(6.4)	Influence of the state of hydration on the dissociation state of oxo-substituted carboxylic acids. . . . .	197
(A.1)	Overview of selected compound classes of tropospheric relevance. . . . .	269
(C.1)	Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds. . . . .	275
(C.2)	Recommendations of evaluated aqueous phase rate constants of nitrate radicals with organic compounds. . . . .	295
(D.1)	Compilation of gas and aqueous phase rate constants used for the derivation and evaluation of gas-aqueous phase correlations. . . . .	303
(D.2)	Parameters for the regression equations $k_{2nd}/M^{-1} s^{-1} = A \cdot CN + B$ ( $CN$ = carbon number) and statistical data derived from the correlation of nitrate radical reactions with organic compounds plotted against the carbon number of the various organic compounds. . . . .	307
(D.3)	Parameters for the regression equations $k_{calc}/M^{-1} s^{-1} = A \cdot (k_{exp}/M^{-1} s^{-1}) + B$ and statistical data derived from the evaluation process of the Evans-Polanyi-type correlations of aqueous phase hydroxyl radical reactions with organic compounds for the various compound classes. . . . .	309
(D.4)	Parameters for the regression equations $\log(k_H/M^{-1} s^{-1}) = A \cdot (BDE/kJ mol^{-1}) + B$ and statistical data derived from the Evans-Polanyi-type correlations of aqueous phase nitrate radical reactions with organic compounds for the various compound classes. . . . .	309
(D.5)	Parameters for the regression equations $k_{calc}/M^{-1} s^{-1} = A \cdot (k_{exp}/M^{-1} s^{-1}) + B$ and statistical data derived from the evaluation process of the improved Evans-Polanyi-type correlations of aqueous phase hydroxyl radical reactions with organic compounds for the various compound classes. . . . .	310

(D.6)	Parameters for the regression equations $\log(k_{exp}/M^{-1} s^{-1}) = A \cdot (\Sigma BDE/kJ mol^{-1})^2 + B \cdot (\Sigma BDE/kJ mol^{-1}) + C$ and statistical data derived from the improved Evans-Polanyi-type correlations of aqueous phase nitrate radical reactions with organic compounds for the various compound classes. . . . .	311
(D.7)	Parameters for the regression equations $k_{calc}/M^{-1} s^{-1} = A \cdot (k_{exp}/M^{-1} s^{-1}) + B$ and statistical data derived from the evaluation process of the improved Evans-Polanyi-type correlations of aqueous phase nitrate radical reactions with organic compounds for the various compound classes. . . . .	311
(D.8)	Parameters for the regression equations $(k_{calc}/M^{-1} s^{-1}) = A \cdot (k_{exp}/M^{-1} s^{-1}) + B$ and statistical data derived from the evaluation process of the structure-activity relationship by <i>Monod and Doussin</i> (2008). . . . .	312
(D.9)	Parameters for the regression equations $(k_{calc}/M^{-1} s^{-1}) = A \cdot (k_{exp}/M^{-1} s^{-1}) + B$ and statistical data derived from the evaluation process of the structure-activity relationship by <i>Minakata et al.</i> (2009). . . . .	312
(E.1)	Experimental values of mass accommodation coefficients taken from the CAPRAM database. . . . .	314
(F.1)	Initial fraction of particle constituents in the urban and remote continental model scenario. . . . .	327
(F.2)	Initial concentrations of important trace gases in the urban and remote continental model scenario. . . . .	328
(F.3)	Emission rates used in SPACCIM in the urban and remote continental scenario, respectively. . . . .	329
(F.4)	Deposition velocities $v_d$ used in SPACCIM in the urban and remote continental scenario, respectively. . . . .	330
(G.1)	Parameters for the photolysis reactions in CAPRAM 3.0o. . . . .	332
(G.2)	Henry's Law coefficients of inorganic compounds in CAPRAM 3.0o . . . . .	333
(G.3)	Mass accommodation and gas phase diffusion coefficients of inorganic compounds in CAPRAM 3.0o . . . . .	334
(G.4)	Irreversible inorganic reactions in CAPRAM 3.0o . . . . .	335
(G.5)	Inorganic equilibria in CAPRAM 3.0o. . . . .	343
(G.6)	Henry's Law coefficients of organic compounds in CAPRAM 3.0o . . . . .	346
(G.7)	Mass accommodation and gas phase diffusion coefficients of organic compounds in CAPRAM 3.0o . . . . .	348
(G.8)	Phase transfer processes in CAPRAM 3.5 . . . . .	350
(G.9)	Phase transfer processes in CAPRAM 4.0 . . . . .	357
(G.10)	Irreversible organic reactions in CAPRAM 3.0o . . . . .	365
(G.11)	Organic equilibria in CAPRAM 3.0o. . . . .	391
(G.12)	Additional processes in CAPRAM 3.0p . . . . .	395
(G.13)	Aqueous phase processes in CAPRAM 3.5 . . . . .	396
(G.14)	Aqueous phase processes in CAPRAM 4.0 . . . . .	643
(H.1)	Additional mechanism used for the sensitivity runs UPT and RXN. . . . .	891

(H.2) Measured uncorrected concentrations from the analysis of the different C-GIS  
samples and the PTFE filter. . . . . 897

# Acknowledgements

I would like to thank all people whose great personal commitment, support or motivating encouragement made this thesis possible. In particular, I would like to thank

- Prof. Dr. Hartmut Herrmann for the provision of this interesting topic, his excellent and committed supervision, whose constant remarks and helpful advice improved the quality of this dissertation significantly,
- Prof. Dr. Bernard Aumont for inspiring discussions, the provision of the expert system GECKO-A, a wonderful experience as a guest scientist at the LISA, and his willingness to review this dissertation,
- Dr. Andreas Tilgner, whose personal commitment in the supervision of this thesis always pushed me forward and whose occasional counselling never let me give up and made the thesis what it is today,
- (now) Dr. Camille Mouchel-Vallon for his induction to GECKO-A, his help with programming-related issues, and for fruitful scientific discussions,
- the German Research Foundation (DFG) for the provision of funding and the Leibniz Institute for Tropospheric Research for the provision of a workplace in a very professional working atmosphere,
- the LEAK team, in particular Dr. Anke Mutzel, Maria Rodigast, Dr. Olaf Böge, Dr. Yoshi Iinuma, Dr. Dominik van Pinxteren, and Dr. Laurent Poulain for planning and conducting the experiments and their help and rich support in the analysis process,
- Dr. Ralf Wolke for endless sessions of coding and bug finding in SPACCIM, which he performed patiently and tirelessly with me,
- Jana Preißler for continuing and needed distractions on Skype, her cheerleading on the finish line, her empathy to judge whether a kick up the backside or some cheerful motivation was necessary, which always let me recharge my batteries,
- my colleagues and fellow Ph.D. students, especially the ones in my office, Sebastian Scheinhardt, Janine Schindelka, Ahmad Jhony Rusumdar, Erik Hoffmann, for helpful discussions and a good balance between a professional working atmosphere and fun,
- my family and my partner, Anja, for their direct and indirect support, who covered my back so I could always focus on my thesis, cheered me up and motivated me throughout my entire Ph.D., and
- Prof. Dr. Roland von Glasow for his understanding and support to let me finish this dissertation during my post doctoral time at the University of East Anglia in Norwich, UK.





# Curriculum Vitae

## Personal Details

Contact: Peter Bräuer  
2B Church Close  
Norwich, NR2 4EF  
United Kingdom

Email: peter.braeuer@googlemail.com

Date/place of birth: 16. June 1982 in Dresden, Germany

## Education and Work

since 12/2013	Senior postdoctoral research associate at the University of East Anglia (UEA), Norwich, United Kingdom
since 04/2009	Ph.D. student at the Leibniz Institute for Tropospheric Research (TROPOS), Leipzig, Germany
06/2010	Guest scientist at the Laboratoire Inter-universitaire des Systèmes Atmosphériques (LISA), Créteil, France 3 weeks of working experience on the improvement and development of structure-activity relationships for aqueous phase rate constant prediction
02/2008 – 02/2009	Student job as teaching assistant
10/2006 – 02/2008	Student job at the TROPOS, Chemistry Department, Modelling Group
10/2003 – 03/2009	Study of meteorology at the University of Leipzig, Leipzig, Germany Diploma thesis at the TROPOS Topic: 'Mechanism development of tropospheric halogen chemistry'
10/2002 – 06/2003	Military Service
09/1993 – 07/2002	Gymnasium Dresden-Klotzsche, Dresden, Germany Qualification: Abitur (equivalent to A-Levels)
08/1999 – 06/2000	Rockville Junior and Senior High School 12th grade exchange student year in Rockville, IN, USA



# List of relevant publications

## Peer-reviewed publications

Mouchel-Vallon, C., Bräuer, P., Camredon, M., Valorso, R., Madronich, S., Herrmann, H., and Aumont, B.: Explicit modeling of volatile organic compounds partitioning in the atmospheric aqueous phase, *Atmospheric Chemistry and Physics*, **13**(2), 1023 – 1037, 2013.

Herrmann, H., Hoffmann, D., Schaefer, T., Bräuer, P., and Tilgner, A.: Tropospheric aqueous phase free-radical chemistry: Radical sources, spectra, reaction kinetics and prediction tools, *ChemPhysChem*, **11**(18), 3796 – 3822, 2010.

## Oral conference contributions

Bräuer, P., Mouchel-Vallon, C., Tilgner, A., Wolke, R., Aumont, B., and Herrmann, H.: A new aqueous phase protocol for the mechanism generator GECKO-A used for the CAPRAM mechanism extension, *Goldschmidt Conference 2013*, Florence, Italy, 25-30 August, 2013.

Tilgner, A., Bräuer, P., Wolke, R., and Herrmann, H.: SPACCIM model studies on the multiphase fog chemistry during the HCCT-2010 field campaign, *6th International Conference on Fog, Fog Collection and Dew*, Yokohama, Japan, 19-24 May, 2013.

Bräuer, P., Mouchel-Vallon, C., Tilgner, A., Wolke, R., Aumont, B., and Herrmann, H.: Extension of the CAPRAM mechanism with the improved mechanism generator GECKO-A, *EGU General Assembly 2013*, Vienna, Austria, 7-12 April, 2013.

Bräuer, P., Mouchel-Vallon, C., Tilgner, A., Wolke, R., Aumont, B., and Herrmann, H.: Development of a mechanism generator and its application for the CAPRAM mechanism extension, *12th Science Conference of the International Global Atmosphere Chemistry (IGAC) “Atmospheric Chemistry in the Anthropocene”*, Beijing, China, 17-21 September, 2012.

Herrmann, H., van Pinxteren, D., Müller, K., Poulain, L., Iinuma, Y., Fomba, W., Tilgner, A., Bräuer, P., Lee, T., Collett, J., Whalley, L., Heard, D., Schneider, J., Borrmann, S., D’Anna, B., and George, C.: Recent multiphase atmospheric chemistry investigations: HCCT-2010 and CAPRAM developments, *12th Science Conference of the International*

*Global Atmosphere Chemistry (IGAC) “Atmospheric Chemistry in the Anthropocene”*, Beijing, China, 17-21 September, 2012.

Tilgner, A., Bräuer, P., Wolke, R., and Herrmann, H.: SPACCIM model studies on the multiphase chemistry occurring in orographic hill cap clouds during the HCCT-2010 field campaign, *European Aerosol Conference (EAC)*, Granada, Spain, 2-7 September, 2012.

van Pinxteren, D., Birmili, W., Fahlbusch, B., Fomba, K. W., Gnauk, T., Iinuma, Y., Mertes, S., Mildenberger, K., Merkel, M., Müller, C., Müller, K., Poulain, L., Spindler, G., Schäfer, M., Stratmann, F., Tilgner, A., Schöne, L., Bräuer, P., Weinhold, K., Wex, H., Wiedensohler, A., Wu, Z. J., Borrmann, S., Harris, E., Roth, A., Schneider, J., Sinha, B., George, I., Heard, D., Whalley, L., D’Anna, B., George, C., Müller, M., Haunold, W., Engel, A., Weber, A., Amedro, D., Fittschen, C., Schoemaeker, C., Collett, J., Lee, T., and Herrmann, H.: Hill Cap Cloud Thuringia 2010 (HCCT-2010): Overview and highlight results, *European Aerosol Conference (EAC)*, Granada, Spain, 2-7 September, 2012.

van Pinxteren, D., Birmili, W., Fahlbusch, B., Fomba, K. W., Gnauk, T., Iinuma, Y., Mertes, S., Dieckmann, K., Merkel, M., Müller, C., Müller, K., Poulain, L., Spindler, G., Schäfer, M., Stratmann, F., Tilgner, A., Schöne, L., Bräuer, P., Weinhold, K., Wex, H., Wiedensohler, A., Zhijun, W., Borrmann, S., Harris, E., Roth, A., Schneider, J., Sinha, B., George, I., Heard, D., Whalley, L., D’Anna, B., George, C., Müller, M., Haunold, W., Engel, A., Weber, A., Amedro, D., Fittschen, C., Schoemaeker, C., Collett, J., Lee, T., and Herrmann, H.: Hill Cap Cloud Thuringia 2010: A ground-based field study on aerosol cloud interaction, *16th International Conference on Clouds and Precipitation (ICCP)*, Leipzig, Germany, 30 July - 3 August, 2012.

Bräuer, P., Mouchel-Vallon, C., Tilgner, A., Aumont, B., and Herrmann, H.: CAPRAM mechanism development: Evaluation of prediction methods for aqueous phase rate constants and model results, *Goldschmidt Conference 2011*, Prague, Czech Republic, 14-19 August, 2011.

Mouchel-Vallon, C., Bräuer, P., Raventos-Duran, T., Valorso, R., Camredon, M., Herrmann, H., and Aumont, B.: Organics chemistry in atmospheric aqueous phase: Development of an explicit modelling tool, *EGU General Assembly 2011*, Vienna, Austria, 3-8 April, 2011.

Tilgner, A., Schrödner, R., Bräuer, P., Wolke, R., and Herrmann, H.: SPACCIM simulations of chemical aerosol-cloud interactions with the multiphase chemistry mechanism MCM-CAPRAM 3.0, *2010 AGU Fall Meeting*, San Francisco, CA, USA, 13-17 December, 2010.

## Poster conference contributions

- Tilgner, A., Bräuer, P., Mouchel-Vallon, C., Wolke, R., Aumont, B., and Herrmann, H.: Towards a more detailed description of the organic chemistry in the CAPRAM mechanism using the improved mechanism generator GECKO-A, *6th International Conference on Fog, Fog Collection and Dew*, Yokohama, Japan, 19-24 May, 2013.
- Tilgner, A., Schrödner, R., Bräuer, P., Wolke, R., and Herrmann, H.: Modelling the multiphase chemical processing of monoethanolamine from industrial CCS processes in tropospheric aqueous particles, cloud and fog droplets, *6th International Conference on Fog, Fog Collection and Dew*, Yokohama, Japan, 19-24 May, 2013.
- Tilgner, A., Bräuer, P., Wolke, R., and Herrmann, H.: Modelling the multiphase chemical processing of monoethanolamine from industrial CCS processes in tropospheric aqueous particles and clouds, *EGU General Assembly 2013*, Vienna, Austria, 7-12 April, 2013.
- Bräuer, P., Tilgner, A., Wolke, R., and Herrmann, H.: CAPRAM mechanism development: Model results from an extended C3 and C4 organic aqueous phase chemistry, *16th International Conference on Clouds and Precipitation (ICCP)*, Leipzig, Germany, 30 July - 3 August, 2012.
- Mouchel-Vallon, C., Bräuer, P., Valorso, R., Camredon, M., Herrmann, H., and Aumont, B.: The aqueous chemistry in the atmosphere: Explicit modelling of organics oxidation, *16th International Conference on Clouds and Precipitation (ICCP)*, Leipzig, Germany, 30 July - 3 August, 2012.
- Tilgner, A., Bräuer, P., Wolke, R., and Herrmann, H.: SPACCIM simulations of the multiphase chemistry occurring in orographic hill cap clouds during the HCCT2010 field campaign, *16th International Conference on Clouds and Precipitation (ICCP)*, Leipzig, Germany, 30 July - 3 August, 2012.
- Tilgner, A., Weller, C., Bräuer, P., and Herrmann, H.: Laboratory and model investigations on the multiphase chemical processing of emitted amines from industrial CCS processes in tropospheric aqueous particles and clouds, *16th International Conference on Clouds and Precipitation (ICCP)*, Leipzig, Germany, 30 July - 3 August, 2012.
- Tilgner, A., Bräuer, P., Wolke, R., and Herrmann, H.: SPACCIM model studies of tropospheric aerosol-cloud interactions with the extended multiphase chemistry mechanism MCM-CAPRAM, *European Aerosol Conference (EAC)*, Manchester, UK, 4-9 September, 2011.
- Bräuer, P., Mouchel-Vallon, C., Tilgner, A., Aumont, B., and Herrmann, H.: Evaluation of prediction methods for aqueous phase rate constants of organics and CAPRAM mechanism development, *EGU General Assembly 2011*, Vienna, Austria, 3-8 April, 2011.
- Tilgner, A., Schrödner, R., Bräuer, P., Wolke, R., and Herrmann, H.: SPACCIM simulations of chemical aerosol-cloud interactions with the multiphase chemical mechanism MCM-

CAPRAM 3.0i, *5th International Conference on Fog, Fog Collection and Dew*, Münster, Germany, 25-30 July, 2010.

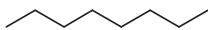
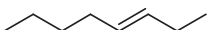

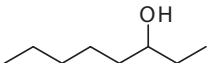
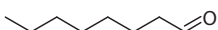
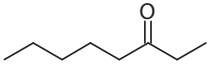
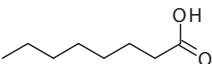
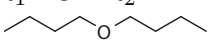
# Appendix



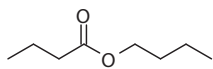
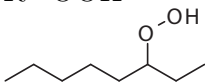
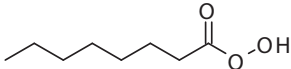
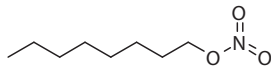
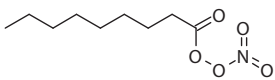
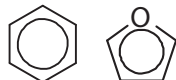


# A Overview of selected compound classes of tropospheric relevance

**Table A.1** Overview of selected compound classes of tropospheric relevance.

Compound class	Chemical formula <sup>a</sup> (example compound)	Description
Alkanes	$C_nH_{2n+2}$ 	Saturated hydrocarbons that bear only C- and H-atoms.
Alkenes	$C_nH_{2n}$ 	Unsaturated hydrocarbons with at least one double bond.
Alkynes	$C_nH_{2n-2}$ 	Unsaturated hydrocarbons with at least one triple bond.
Alcohols	$R-OH$ 	Hydrocarbons with a hydroxyl (OH) function. Organic compounds with 2 hydroxyl functions are named diols and with more functions polyols. In the aqueous phase, gem-diols with 2 OH groups at the same carbon atom are formed from the hydration of carbonyl compounds as a special case of alcohol compounds.
<u>Carbonyls</u>		Carbonyl compounds include an oxygen atom connected to a carbon atom by a double bond.
Aldehydes	$R-CH=O$ 	Terminal carbonyls are called aldehydes, internal carbonyls are called ketones. Carbonyls in aqueous solution are in equilibrium with their gem-diol form (see Alcohols).
Ketons	$R_1-C(=O)-R_2$ 	
Carboxylic acids	$R-C(=O)OH$ 	Organic compounds with a carboxyl ( $C(=O)OH$ ) group. In aqueous solution, carboxylic acids form an equilibrium with the corresponding deprotonated state ( $R-C(=O)O^-$ ).
Ethers	$R_1-O-R_2$ 	Organic compounds containing an ether group – an oxygen atom connected to 2 organic rests by single bonds.

**Table A.1 (continued)** Overview of selected compound classes of tropospheric relevance.

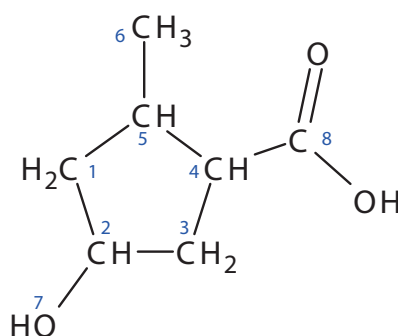
Compound class	Chemical formula <sup>a</sup> (example compound)	Description
Esters	$R_1-C(=O)-O-R_2$ 	Organic compounds containing an ester group, which can be formally seen as a carbonyl group bound to an ether group.
Hydroperoxides	$R-OOH$ 	Organic compounds containing an hydroperoxide (OOH) group.
Carboxylic peracids	$R-C(=O)OOH$ 	Organic compounds containing a carboxylic peracid ( $C(=O)OOH$ ) group – an hydroperoxide group bound to a carbonyl group.
Organic nitrates	$R-ONO_2$ 	Organic compounds containing a nitrate ( $ONO_2$ ) group.
Peroxyacyl nitrates (PANs)	$R_1-C(=O)-OONO_2$ 	Organic compounds containing a PAN group – a carbonyl group bound to a nitrite ( $NO_2$ ) group via a peroxy group (2 single bonded oxygen atoms).
Aromatics	$R_{1,2,...n}-C_6H_{6-n};$ $R_{1,2,...n}-C_4H_{4-n}O; \dots$ 	Organic compounds containing a ring structure with conjugated unsaturated bonds such as a benzene ring shown in the example. Aromatic rings can contain hetero-atoms.

<sup>a</sup>R in a chemical formula denotes an organic rest. If several different organic rests are possible, indices ( $R_1, R_2, \dots$ ) are used. The chemical formulas of alkenes and alkynes are given for a compound with only one double/triple bond.

## B Detailed description of the function of SARs

As structure-activity relationships form the basis of the mechanism generator developed throughout this work, a more detailed description with an example for two recent SARs by *Monod and Doussin* (2008) and *Minakata et al.* (2009) are given in the following. As described in subsection 2.4.3, a structure-activity relationship provides the partial rate constants of certain pre-defined molecular groups, which are multiplied by group contribution factors of these groups and other non-reactive molecular groups. These descriptors are determined by setting the experimental rate constants of organic compounds with the hydroxyl radical in relation to the structure of these organic compounds and minimising the errors of all factors simultaneously in a multi-linear regression.

Figure B.1 shows 1-carboxyl-2-methyl-4-hydroxyl cyclopentane, which gives a good example for the demonstration of the basic principles of a SAR. For clarification, the molecular groups are labelled with numbers. Both methods use the same increments for the sample compound, that is 2 methylene groups ( $\text{CH}_2$ , functional groups 1 and 3 in Figure B.1), 3 methine groups ( $\text{CH}$ , functional groups 2, 4, and 5), 1 methyl group ( $\text{CH}_3$ , functional group 6), 1 hydroxyl group ( $\text{OH}$ , functional group 7), and 1 carboxyl group ( $\text{C}(=\text{O})\text{OH}$ , functional group 8). In the SAR of *Minakata et al.* (2009), all functional groups are reactive groups and a rate constant is assigned to them. In the SAR of *Monod and Doussin* (2008), the carboxyl group (8) is set as non-reactive as its partial rate constant is at least two orders of magnitude smaller than the other partial rate constants. Therefore, in the SAR of *Monod and Doussin* (2008) there are only group contribution factors for the carboxyl function.



**Figure B.1** Sample molecule 1-carboxyl-2-methyl-4-hydroxyl cyclopentane for the demonstration of the basic principles of the two SARs by *Monod and Doussin* (2008) and *Minakata et al.* (2009).

At first, the SAR of *Minakata et al.* (2009) is described, which uses less descriptors than the SAR of *Monod and Doussin* (2008). Starting at the secondary carbon atoms labelled with 1 and 3, the SAR provides a partial rate constant of  $5.11 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , which has to be scaled by the group contribution factors of their direct neighbours (groups 2 and 5 for carbon atom 1 and groups 2 and 4 for carbon atom 3). In both cases the direct neighbours are two CH groups with a group contribution factor  $F$  of 1.174. Moreover, as both carbon atoms are part of a ring structure, they have to be scaled by a correction factor of a 5-membered ring strain (0.8601). Thus, the overall partial rate constants is:

$$k_{1/3} = k_{CH_2} \cdot F(CH)^2 \cdot RS5 = 1.21 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1} \quad (\text{B.1})$$

Functional groups 2, 4, and 5 have in common the initial partial rate constant of  $1.99 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for methine groups and the ring correction factor  $RS5$  of 0.8601, but differ in the groups attached to the ring ( $\text{CH}_3$  with  $F = 1.120$ ,  $\text{OH}$  with  $F = 0.578$ , and  $\text{C(=O)OH}$  with  $F = 0.234$ ). Their individual rate constants can be described as:

$$k_2 = k_{CH} \cdot F(CH_2)^2 \cdot F(OH) \cdot RS5 = 1.36 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1} \quad (\text{B.2})$$

$$k_4 = k_{CH} \cdot F(CH_2) \cdot F(CH) \cdot F(COOH) \cdot RS5 = 1.01 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1} \quad (\text{B.3})$$

$$k_5 = k_{CH} \cdot F(CH_2) \cdot F(CH) \cdot F(CH_3) \cdot RS5 = 2.64 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1} \quad (\text{B.4})$$

Group 6 with an initial partial rate constant of  $1.18 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$  is a terminal group and, hence, has only one direct neighbour (CH with a group contribution factor of 1.174):

$$k_6 = k_{CH_3} \cdot F(CH) = 4.14 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1} \quad (\text{B.5})$$

Alcohol and carboxylic acid functional groups form a special case in the SAR of *Minakata et al.* (2009). No group contribution factors exist for these compounds and only a partial rate constant is assigned to them with values of  $1.0 \cdot 10^8$  and  $7.0 \cdot 10^5 \text{ M}^{-1} \text{ s}^{-1}$  for OH and  $\text{C(=O)OH}$ , respectively:

$$k_7 = k_{OH} = 1.00 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1} \quad (\text{B.6})$$

$$k_8 = k_{COOH} = 7.00 \cdot 10^5 \text{ M}^{-1} \text{ s}^{-1} \quad (\text{B.7})$$

Now it is possible to determine the overall rate constant:

$$\begin{aligned} k_{abs} &= \sum_{i=1}^8 k_i = 2(k_{CH_2} \cdot F(CH)^2 \cdot RS5) + k_{CH} \cdot F(CH_2) \cdot RS5 \\ &\quad \cdot (F(OH) \cdot F(CH_2) + F(COOH) \cdot F(CH) + F(CH_3) \cdot F(CH)) \\ &\quad + k_{CH_3} \cdot F(CH) + k_{OH} + k_{COOH} \\ &= 7.05 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1} \end{aligned} \quad (\text{B.8})$$

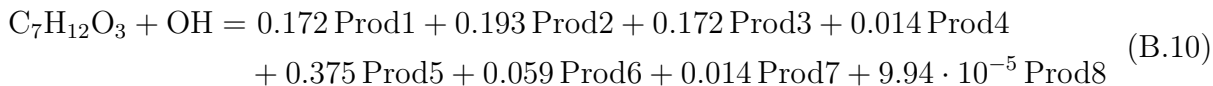
Moreover, the reaction products can be determined from the partial rate constants as an H-atom abstraction occurs at every functional group. Dividing the partial rate constant by

---

the overall rate constant  $k_{abs}$  gives the branching ratios for the corresponding products:

$$r_i = \frac{k_i}{k_{abs}} = \frac{k_i}{\sum_{i=1}^8 k_i} \quad (\text{B.9})$$

Therefore, the final reaction can be determined as:



with Prod  $i$  being the  $i$ -th H-abstraction product at the corresponding functional group.

As mentioned before and can be seen from Prod8 in Equation B.10, H-abstraction at the carboxyl group is of minor importance. Therefore it is omitted in the SAR of *Monod and Doussin* (2008) and no partial rate constant is assigned to this group. However, the group contribution factors are still needed to modulate the partial rate constants of the neighbouring groups. In addition to the SAR of *Minakata et al.* (2009), the structure-activity relationship of *Monod and Doussin* (2008) provides group contribution factors  $G(i)$  also for the second neighbours. Therefore, the partial rate constants are changed to:

$$k_1 = k_{\text{CH}_2} \cdot F(\text{CH})^2 \cdot G(\text{CH}) \cdot G(\text{CH}_2) \cdot G(\text{CH}_3) \cdot G(\text{OH}) \cdot \text{RS5} \quad (\text{B.11})$$

$$k_2 = k_{\text{CH}} \cdot F(\text{CH}_2)^2 \cdot F(\text{OH}) \cdot G(\text{CH})^2 \cdot \text{RS5} \quad (\text{B.12})$$

$$k_3 = k_{\text{CH}_2} \cdot F(\text{CH})^2 \cdot G(\text{CH}) \cdot G(\text{CH}_2) \cdot G(\text{OH}) \cdot G(\text{COOH}) \cdot \text{RS5} \quad (\text{B.13})$$

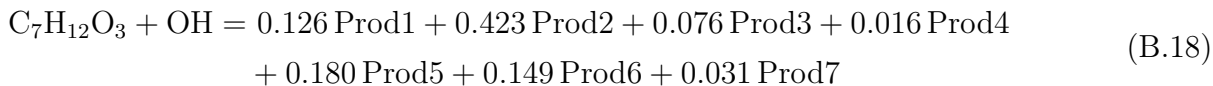
$$k_4 = k_{\text{CH}} \cdot F(\text{CH}) \cdot F(\text{CH}_2) \cdot F(\text{COOH}) \cdot G(\text{CH}) \cdot G(\text{CH}_2) \cdot G(\text{CH}_3) \cdot \text{RS5} \quad (\text{B.14})$$

$$k_5 = k_{\text{CH}} \cdot F(\text{CH}) \cdot F(\text{CH}_2) \cdot F(\text{CH}_3) \cdot G(\text{CH}) \cdot G(\text{CH}_2) \cdot G(\text{COOH}) \cdot \text{RS5} \quad (\text{B.15})$$

$$k_6 = k_{\text{CH}_3} \cdot F(\text{CH}) \cdot G(\text{CH}) \cdot G(\text{CH}_2) \quad (\text{B.16})$$

$$k_7 = k_{\text{OH}} \cdot F(\text{CH}) \cdot G(\text{CH}_2)^2 \quad (\text{B.17})$$

Using the parameters presented in *Monod and Doussin* (2008) gives an overall rate constant of  $3.01 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$  and a reaction with the following branching ratios:



The results show that different SARs do not only lead to different reaction rate constants, which differ by a factor of 2.3 in this example, they also lead to different reaction products and branching ratios. While in the SAR of *Minakata et al.* (2009) the main channel leads to an alkyl radical with the radical function at the carbon atom adjacent to the methyl group, the main attack in the SAR of *Monod and Doussin* (2008) is at the methine group adjacent to the hydroxyl function. Moreover, the acyloxy radical resulting from an H-abstraction at the carboxyl group is missing in the SAR of *Monod and Doussin* (2008).



## C The kinetic database

### C.1 Reactions of hydroxyl radicals with organic compounds

**Table C.1** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}^{(b)}$	$A^{(b)}$	$E_A/R^{(c)}$	Reference/Comment ( <b>n<sub>t</sub> = 465</b> )
<b>Alkanes</b>					n = 12
Methane	C	$1.1 \cdot 10^8$			<i>Buxton et al.</i> (1988a)
Ethane	CC	$1.4 \cdot 10^9$			<i>Getoff</i> (1989) <sup>1</sup>
Propane	CCC	$2.3 \cdot 10^9$			<i>Getoff</i> (1989) <sup>1</sup>
Butane	CCCC	$2.9 \cdot 10^9$			<i>Getoff</i> (1989) <sup>1</sup>
Pentane	CCCCC	$5.4 \cdot 10^9$			<i>Rudakov et al.</i> (1981) <sup>2</sup>
Hexane	CCCCCC	$6.6 \cdot 10^9$			<i>Rudakov et al.</i> (1981) <sup>2</sup>
Heptane	CCCCCCC	$7.7 \cdot 10^9$			<i>Rudakov et al.</i> (1981) <sup>2</sup>
Octane	CCCCCCCC	$9.1 \cdot 10^9$			<i>Rudakov et al.</i> (1981) <sup>2</sup>
Iso-butane	CC(C)C	$4.6 \cdot 10^9$			<i>Rudakov et al.</i> (1981) <sup>2</sup>
2-Methyl butane	CCC(C)C	$5.2 \cdot 10^9$			<i>Rudakov et al.</i> (1981) <sup>2</sup>
3-Ethyl pentane	CCC(CC)CC	$5.9 \cdot 10^9$			<i>Rudakov et al.</i> (1981) <sup>2</sup>
2,2,4-Trimethyl pentane	CC(C)CC(C)(C)C	$6.1 \cdot 10^9$			<i>Rudakov et al.</i> (1981) <sup>2</sup>
<b>Alkenes and alkynes</b>					n = 7
Ethylene	C=C	$3.1 \cdot 10^9$			<i>Thomas</i> (1967) with updated kref from NIST database

**Table C.1 (continued)** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}^{(b)}$	$A^{(b)}$	$E_A/R^{(c)}$	Reference/Comment
Propylene	CC=C	$7.0 \cdot 10^9$			Thomas (1967) with updated kref from NIST database
1-Butene	CCC=C	$7.0 \cdot 10^9$			Thomas (1967) with updated kref from NIST database
Butadien	C=CC=C	$7.0 \cdot 10^9$			Thomas (1967) with updated kref from NIST database
2,3-Dimethyl butadiene	C=C(C)C(C)=C	$3.1 \cdot 10^{10}$			Moise <i>et al.</i> (2005)
Isobutylene	CC(=C)C	$5.4 \cdot 10^9$			Thomas (1967) with updated kref from NIST database
Acetylene	C#C	$4.7 \cdot 10^9$			Average of values within Anderson and Schulte-Frohlinde (1978) <sup>1</sup>
<b>Substituted alkanes and alkenes</b>					n = 19
Methyl nitrite	CN(=O)=O	$1.85 \cdot 10^8$			Anbar <i>et al.</i> (1966a)
Methylene nitrtite	C=N(=O)=O	$8.5 \cdot 10^9$			Asmus and Taub (1968) <sup>2</sup>
Nitroso tert-butane	CC(C)(C)N=O	$4.0 \cdot 10^8$			Bakalik and Thomas (1977) <sup>2</sup>
Methyl hydrogen peroxide	COO	$3.2 \cdot 10^8$			Average of Graedel and Weschler (1981) and Monod <i>et al.</i> (2007)
Ethyl hydrogen peroxide	CCOO	$5.8 \cdot 10^8$			Monod <i>et al.</i> (2007)
Tert-butyl hydrogen peroxide	CC(C)(C)OO	$8.0 \cdot 10^7$			Phulkar <i>et al.</i> (1990) <sup>1</sup>
Methanesulfinate	CS(=O)[O-]	$5.3 \cdot 10^9$			Flyunt <i>et al.</i> (2001)
Methanesulfonate	CS(=O)(=O)[O-]	$1.3 \cdot 10^9$			Lind and Eriksen (1977) <sup>2</sup>
Methylsulfate	COS(=O)(=O)[O-]	$5.0 \cdot 10^7$			Almgren <i>et al.</i> (1979) <sup>2</sup>
Hydroxymethylsulfate (HMS <sup>-</sup> )	OCS(=O)(=O)[O-]	$3.0 \cdot 10^8$			Barlow <i>et al.</i> (1997) <sup>3</sup>
Methyldisulfonate monoanion	OS(=O)(=O)CS(=O)(=O)[O-]	$2.5 \cdot 10^7$			Lind and Eriksen (1977) <sup>2</sup>
Methyldisulfonate dianion	[O-]S(=O)(=O)CS(=O)(=O)[O-]	$4.3 \cdot 10^7$			Lind and Eriksen (1977) <sup>2</sup>
Ethyl sulfonate	CCS(=O)(=O)[O-]	$1.0 \cdot 10^8$			Balazs <i>et al.</i> (1968) <sup>2</sup>
Ethyl sulphate	CCOS(=O)(=O)[O-]	$3.5 \cdot 10^8$			Almgren <i>et al.</i> (1979) <sup>2</sup>
Butyl sulphate	CCCCOS(=O)(=O)[O-]	$1.0 \cdot 10^9$			Almgren <i>et al.</i> (1979) <sup>2</sup>



**Table C.1 (continued)** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}$ <sup>(b)</sup>	$A$ <sup>(b)</sup>	$E_A/R$ <sup>(c)</sup>	Reference/Comment
Hexyl sulphate	CCCCCCCOS(=O)(=O)[O-]	$2.5 \cdot 10^9$			<i>Almgren et al. (1979)</i> <sup>2</sup>
Octyl sulphate	CCCCCCCCCOS(=O)(=O)[O-]	$6.5 \cdot 10^9$			<i>Almgren et al. (1979)</i> <sup>2</sup>
Decyl sulphate	CCCCCCCCCCCOS(=O)(=O)[O-]	$8.2 \cdot 10^9$			<i>Buxton et al. (1988a)</i>
Methylene sulfonate	C=CS(=O)(=O)[O-]	$3.5 \cdot 10^9$			<i>Behar et al. (1982)</i> <sup>2</sup>
<b>Monoalcohols</b>					n = 19
Methanol	CO	$1.0 \cdot 10^9$	$7.0 \cdot 10^9$	580	Average of <i>George et al. (2003)</i> ; <i>Alam et al. (2003)</i> ; and <i>Janata (2002)</i> with $E_A/R$ value of <i>Elliot and McCracken (1989)</i>
Ethanol	CCO	$2.1 \cdot 10^9$	$1.02 \cdot 10^{11}$	1200	<i>Ervens et al. (2003b)</i>
Propanol	CCCO	$3.2 \cdot 10^9$	$5.6 \cdot 10^{10}$	1000	<i>Ervens et al. (2003b)</i>
Butanol	CCCCO	$3.96 \cdot 10^9$	$1.0 \cdot 10^{11}$	1000	<i>Hesper (2003)</i> <sup>4</sup>
Pentanol	CCCCCO	$5.0 \cdot 10^9$			<i>Stemmler and von Gunten (2000)</i>
Hexanol	CCCCCCO	$7.0 \cdot 10^9$			<i>Scholes and Willson (1967)</i> <sup>2</sup>
Heptanol	CCCCCCCO	$7.4 \cdot 10^9$			<i>Scholes and Willson (1967)</i> <sup>2</sup>
octanol	CCCCCCCCO	$7.7 \cdot 10^9$			<i>Scholes and Willson (1967)</i> <sup>2</sup>
Iso-propanol	CC(O)C	$2.1 \cdot 10^9$	$6.1 \cdot 10^{10}$	962	<i>Hesper (2003)</i> <sup>4</sup>
2-Butanol	CCC(O)C	$3.5 \cdot 10^9$	$7.4 \cdot 10^{10}$	910	<i>Hesper (2003)</i> <sup>4</sup>
3-Pentanol	CCC(O)CC	$2.1 \cdot 10^9$			<i>Snook and Hamilton (1974)</i>
Iso-butanol	CC(C)CO	$3.3 \cdot 10^9$			<i>Buxton et al. (1988a)</i>
Tert-butanol	CC(C)(C)O	$5.0 \cdot 10^8$	$3.3 \cdot 10^{10}$	1200	<i>Ervens et al. (2003b)</i>
2,2-Dimethyl propanol	CC(C)(C)CO	$5.2 \cdot 10^9$			<i>Walling (1975)</i> with updated kref from NIST database
1,1-Dimethyl propanol	CCC(C)(C)O	$1.9 \cdot 10^9$			<i>Anbar et al. (1966a)</i>
Isoamyl alcohol	CC(C)CCO	$3.8 \cdot 10^9$			<i>Buxton et al. (1988a)</i>
Allyl alcohol	C=CCO	$5.9 \cdot 10^9$			<i>Maruthamuthu (1980)</i> <sup>1,2</sup>
3-Hydroxy-1,4-pentadien	C=CC(O)C=C	$1.0 \cdot 10^{10}$			<i>Simic et al. (1973b)</i> <sup>2</sup>
2,4-Hexadienol	CC=CC=CCO	$9.8 \cdot 10^9$			<i>Simic et al. (1973b)</i> <sup>2</sup>

**Table C.1 (continued)** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}^{(b)}$	$A^{(b)}$	$E_A/R^{(c)}$	Reference/Comment
<b>Diols and polyols</b>					n = 15
Ethylene glycol	OCCO	$1.7 \cdot 10^9$	$9.0 \cdot 10^{10}$	1191	<i>Hoffmann et al.</i> (2009)
1,3-Propanediol	OCCCO	$2.7 \cdot 10^9$	$2.5 \cdot 10^{11}$	1371	<i>Hoffmann et al.</i> (2009)
1,4-Butanediol	OCCCCO	$3.5 \cdot 10^9$	$2.0 \cdot 10^{11}$	1203	<i>Hoffmann et al.</i> (2009)
1,5-Pentanediol	OCCCCCO	$4.4 \cdot 10^9$	$3.1 \cdot 10^{11}$	1275	<i>Hoffmann et al.</i> (2009)
1,6-Hexanediol	OCCCCCOO	$4.7 \cdot 10^9$			<i>Anbar et al.</i> (1966a)
1,2-Propanediol	CC(O)CO	$1.7 \cdot 10^9$	$1.9 \cdot 10^{11}$	1383	<i>Hoffmann et al.</i> (2009)
1,2-Butanediol	CCC(O)CO	$2.3 \cdot 10^9$	$5.2 \cdot 10^{11}$	1600	<i>Hoffmann et al.</i> (2009)
1,3-Butanediol	CC(O)CCO	$1.8 \cdot 10^9$			Average of <i>Anbar et al.</i> (1966a) and <i>Adams et al.</i> (1965a) <sup>2</sup>
2,3-Butanediol	CC(O)C(O)C	$1.3 \cdot 10^9$			<i>Adams et al.</i> (1965a) <sup>2</sup>
2,4-Pentanediol	CC(O)CC(O)C	$2.3 \cdot 10^9$			<i>Ulanski et al.</i> (1994) <sup>1</sup>
2,3-Dimethyl-2,3-butanediol	OC(C)(C)C(C)(C)O	$5.5 \cdot 10^8$			<i>Anbar et al.</i> (1966a)
Glycerol	OCC(O)CO	$1.9 \cdot 10^9$	$2.8 \cdot 10^{11}$	1479	<i>Hoffmann et al.</i> (2009)
Pentaerythritol	OCC(CO)(CO)CO	$3.3 \cdot 10^9$			<i>Anbar et al.</i> (1966a)
2-Butyne-1,4-diol	OCC#CCO	$7.2 \cdot 10^9$			<i>Gilbert and Whitwood</i> (1989) <sup>8</sup> ; 78% H-Abs, 22% OH addition
2,5-Dimethyl-3-hexyne-2,5-diol	OC(C)(C)C#CC(C)(C)O	$3.3 \cdot 10^9$			<i>Walling and El-Taliawi</i> (1973b) <sup>2</sup>
<b>Aldehydes and gem-diols</b>					n = 16
Formaldehyde	C=O	$1.0 \cdot 10^9$			<i>Witter and Neta</i> (1973) <sup>5</sup>
Hydrated formaldehyde	OCO	$1.0 \cdot 10^9$	$3.1 \cdot 10^{10}$	1022	<i>Hart et al.</i> (1964) <sup>5</sup> ; <i>Chin and Wine</i> (1994)
Acetaldehyde	CC=O	$3.1 \cdot 10^9$			Average of overall rates of <i>Schuchmann and von Sonntag</i> (1988) and <i>Monod et al.</i> (2005); 2.7% H-Abs on methyl group
Hydrated acetaldehyde	CC(O)O	$1.3 \cdot 10^9$			<i>Schuchmann and von Sonntag</i> (1988); 7.7% H-Abs on methyl group

**Table C.1 (continued)** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}^{(b)}$	$A^{(b)}$	$E_A/R^{(c)}$	Reference/Comment
Propionaldehyde	CCC=O	$2.8 \cdot 10^9$	$2.6 \cdot 10^{11}$	1300	Overall rate constant of <i>Hesper</i> (2003)
Butyraldehyde	CCCC=O	$3.9 \cdot 10^9$	$8.1 \cdot 10^{10}$	900	Overall rate constant of <i>Hesper</i> (2003)
Valeraldehyde	CCCCC=O	$3.9 \cdot 10^9$			Overall rate constant of <i>Monod et al.</i> (2005)
Isobutyraldehyde	CC(C)C=O	$2.9 \cdot 10^9$	$3.0 \cdot 10^{10}$	700	<i>Gligorovski and Herrmann</i> (2004)
2-Hydroxy-2-methyl propanal	CC(C)(O)C=O	$3.0 \cdot 10^9$			<i>Acero et al.</i> (2001) <sup>5</sup>
2,3-Dihydroxy-2-propenal	OC=C(O)C=O	$9.9 \cdot 10^9$			<i>Horii et al.</i> (1986) <sup>2</sup>
2,3-Dihydroxy-2-propenal, conjugate base	[O-]C=C(O)C=O	$1.6 \cdot 10^{10}$			<i>Horii et al.</i> (1986) <sup>2</sup>
Acrolein	C=CC=O	$7.0 \cdot 10^9$			<i>Lilie and Henglein</i> (1970) <sup>1,2</sup>
Methacrolein	C=C(C)C=O	$9.4 \cdot 10^9$	$5.6 \cdot 10^{11}$	1200	<i>Schöne et al.</i> (2014)
Crotonaldehyde	CC=CC=O	$5.8 \cdot 10^9$			<i>Lilie and Henglein</i> (1970) <sup>2</sup>
Glyoxal	O=CC=O	$6.6 \cdot 10^7$			Draganic and Marcovic, unpublished data <sup>1,2</sup>
Hydrated glyoxal	OC(O)C(O)O	$1.1 \cdot 10^9$	$1.8 \cdot 10^{11}$	1516	<i>Buxton et al.</i> (1997)
<b>Ketones</b>					n = 14
Acetone	CC(=O)C	$1.7 \cdot 10^8$	$6.9 \cdot 10^{10}$	1788	Average of measurements within MOST <sup>6</sup>
Hydroxy acetone	CC(=O)CO	$1.2 \cdot 10^9$	$4.0 \cdot 10^{10}$	1082	<i>Gligorovski</i> (2005) <sup>7</sup>
Methyl ethyl ketone	CC(=O)CC	$1.3 \cdot 10^9$	$1.7 \cdot 10^{11}$	1451	Average of measurement within the MOST project <sup>6</sup> ; 10% CH <sub>2</sub> COCH <sub>2</sub> CH <sub>3</sub> and 90% CH <sub>3</sub> COCHCH <sub>3</sub> <sup>6</sup>
2-Pentanone	CC(=O)CCC	$1.9 \cdot 10^9$			<i>Adams et al.</i> (1965b) <sup>2</sup>
Diethyl ketone	CCC(=O)CC	$1.4 \cdot 10^9$			<i>Adams et al.</i> (1965b) <sup>2</sup>
Methyl vinyl ketone	CC(=O)C=C	$7.3 \cdot 10^9$	$9.0 \cdot 10^{11}$	1443	<i>Schöne et al.</i> (2014)
Acetoin	CC(O)C(=O)C	$2.9 \cdot 10^9$	$2.9 \cdot 10^{11}$	1323	<i>Hesper</i> (2003)

**Table C.1 (continued)** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}^{(b)}$	$A^{(b)}$	$E_A/R^{(c)}$	Reference/Comment
Methyl iso-butyl ketone	<chem>CC(C)CC(=O)C</chem>	$3.4 \cdot 10^9$			Average of measurements within the MOST project <sup>6</sup> ; 30% <chem>CH3C(CH3)CH2C(=O)CH3</chem> and 70% <chem>CH3CH(CH3)CHC(=O)CH3</chem> <sup>6</sup>
Methylglyoxal	<chem>CC(=O)C=O</chem>	$8.6 \cdot 10^8$	$8.0 \cdot 10^{10}$	1350	Average of <i>Monod et al.</i> (2005); <i>Park et al.</i> (2003) <sup>7</sup> ; <i>Stefan and Bolton</i> (1999); and TROPOS measurements
Hydrated methylglyoxal	<chem>CC(=O)C(O)O</chem>	$7.9 \cdot 10^8$	$1.6 \cdot 10^{11}$	1589	Average of measurement within the MOST project <sup>6</sup>
Diacetyl	<chem>CC(=O)C(=O)C</chem>	$2.8 \cdot 10^8$	$4.3 \cdot 10^{12}$	2880	<i>Gligorovski and Herrmann</i> (2004)
Acetylacetone	<chem>CC(=O)CC(=O)C</chem>	$9.9 \cdot 10^9$			<i>Broszkiewicz et al.</i> (1982) <sup>2</sup>
Acetylacetone, conjugate base	<chem>CC([O-])=CC(=O)C</chem>	$7.4 \cdot 10^9$			<i>Broszkiewicz et al.</i> (1982) <sup>2</sup>
Acetonyl acetone	<chem>CC(=O)CCC(=O)C</chem>	$7.6 \cdot 10^8$	$1.1 \cdot 10^{11}$	1485	<i>Gligorovski and Herrmann</i> (2004)
<b>Monocarboxylic acids</b>					n = 38
Formic acid	<chem>O=CO</chem>	$1.3 \cdot 10^8$	$3.7 \cdot 10^9$	1000	<i>Buxton et al.</i> (1988a) with rounded E/R values of <i>Chin and Wine</i> (1994)/ <i>Adams et al.</i> (1965a)
Formate	<chem>O=C[O-]</chem>	$3.2 \cdot 10^9$	$9.2 \cdot 10^{10}$	1000	<i>Buxton et al.</i> (1988a); <i>Elliot and Simsons</i> (1984)
Acetic acid	<chem>CC(=O)O</chem>	$1.7 \cdot 10^7$	$1.5 \cdot 10^9$	1330	<i>Chin and Wine</i> (1994) <sup>8</sup>
Acetate	<chem>CC(=O)[O-]</chem>	$7.3 \cdot 10^7$	$2.8 \cdot 10^{10}$	1770	<i>Chin and Wine</i> (1994) <sup>8</sup>
Propionic acid	<chem>CCC(=O)O</chem>	$3.2 \cdot 10^8$	$7.6 \cdot 10^{11}$	2300	<i>Ervens et al.</i> (2003b)
Propionate	<chem>CCC(=O)[O-]</chem>	$7.2 \cdot 10^8$	$3.2 \cdot 10^{11}$	1800	<i>Ervens et al.</i> (2003b)
Butyric acid	<chem>CCCC(=O)O</chem>	$2.2 \cdot 10^9$			<i>Scholes and Willson</i> (1967) <sup>2</sup>
Butyrate	<chem>CCCC(=O)[O-]</chem>	$2.0 \cdot 10^9$			<i>Anbar et al.</i> (1966a)

**Table C.1 (continued)** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}$ <sup>(b)</sup>	$A$ <sup>(b)</sup>	$E_A/R$ <sup>(c)</sup>	Reference/Comment
N-Valerate	<chem>CCCCC(=O)[O-]</chem>	$2.9 \cdot 10^9$			<i>Anbar et al.</i> (1966a)
Hexanate	<chem>CCCCC(=O)[O-]</chem>	$4.0 \cdot 10^9$			<i>Anbar et al.</i> (1966a)
Iso-butyrate	<chem>CC(C)C(=O)[O-]</chem>	$1.3 \cdot 10^9$			<i>Anbar et al.</i> (1966a)
Iso-valeric acid	<chem>CC(C)CC(=O)O</chem>	$1.4 \cdot 10^9$			<i>Merz and Waters</i> (1949) <sup>1</sup>
Iso-valerate	<chem>CC(C)CC(=O)[O-]</chem>	$2.4 \cdot 10^9$			<i>Anbar et al.</i> (1966a)
2-Methyl-butyrate	<chem>CCC(C)C(=O)[O-]</chem>	$2.2 \cdot 10^9$			<i>Anbar et al.</i> (1966a)
Pivalic acid	<chem>CC(C)(C)C(=O)O</chem>	$6.5 \cdot 10^8$			<i>Nauser and Buhler</i> (1994)
Pivalate	<chem>CC(C)(C)C(=O)[O-]</chem>	$1.1 \cdot 10^9$			Average of <i>Nauser and Buhler</i> (1994) and <i>Anbar et al.</i> (1966a)
2,2-Dimethyl butyrate	<chem>CC(C)(C)CC(=O)[O-]</chem>	$1.7 \cdot 10^8$			<i>Anbar et al.</i> (1966a)
Acrylic acid	<chem>C=CC(=O)O</chem>	$5.1 \cdot 10^9$	$9.4 \cdot 10^{10}$	842	<i>Schöne et al.</i> (2014)
Acrylate	<chem>C=CC(=O)[O-]</chem>	$5.9 \cdot 10^9$	$1.8 \cdot 10^{10}$	360	<i>Schöne et al.</i> (2014)
Crotonic acid	<chem>CC=CC(=O)O</chem>	$2.9 \cdot 10^9$			<i>Walling and El-Taliawi</i> (1973a) <sup>2</sup>
Crotonate	<chem>CC=CC(=O)[O-]</chem>	$5.0 \cdot 10^9$			<i>Lilie and Henglein</i> (1970); <i>Maruthamuthu and Dhandavel</i> (1980) <sup>2</sup>
Methacrylic acid	<chem>C=C(C)C(=O)O</chem>	$1.1 \cdot 10^{10}$	$1.0 \cdot 10^{12}$	1320	<i>Schöne et al.</i> (2014)
Methacrylate	<chem>C=C(C)C(=O)[O-]</chem>	$1.1 \cdot 10^{10}$	$8.0 \cdot 10^{12}$	1924	<i>Schöne et al.</i> (2014)
Methylcrotonic acid	<chem>CC(C)=CC(=O)O</chem>	$9.0 \cdot 10^9$			<i>Kumar and Rao</i> (1991) <sup>1</sup>
Methylcrotonate	<chem>CC(C)=CC(=O)[O-]</chem>	$5.9 \cdot 10^9$			Average of different measurements of <i>Kumar and Rao</i> (1991) <sup>1</sup>
Sorbic acid	<chem>CC=CC=CC(=O)O</chem>	$9.8 \cdot 10^9$			<i>Simic et al.</i> (1973b) <sup>1</sup>
Linoleate	<chem>CCCCC=CCC=CCCCCCCC(=O)O</chem>	$1.0 \cdot 10^{10}$			<i>Al-Sheikhly et al.</i> (2004)
Linolenic acid	<chem>CCC=CCC=CCC=CCCCCCCC(=O)[O-]</chem>	$9.9 \cdot 10^9$			<i>Patterson and Hasegawa</i> (1978) <sup>2</sup> ; value scaled by a factor of 1.35 based on the ratio of the values of <i>Patterson and Hasegawa</i> (1978) and <i>Al-Sheikhly et al.</i> (2004) for linoleate
Glycolic acid	<chem>OCC(=O)O</chem>	$6.0 \cdot 10^8$			<i>Burton et al.</i> (1988a)

**Table C.1 (continued)** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}^{(b)}$	$A^{(b)}$	$E_A/R^{(c)}$	Reference/Comment
Glycolate	<chem>OCC(=O)[O-]</chem>	$1.2 \cdot 10^9$			<i>Logan</i> (1989) <sup>1</sup>
Hydrated glyoxylic acid	<chem>OC(O)C(=O)O</chem>	$3.6 \cdot 10^8$	$8.1 \cdot 10^9$	1000	<i>Ervens et al.</i> (2003b)
Hydrated glyoxylate	<chem>OC(O)C(=O)[O-]</chem>	$2.6 \cdot 10^9$	$6.0 \cdot 10^{15}$	4330	<i>Ervens et al.</i> (2003b)
Lactic acid	<chem>CC(O)C(=O)O</chem>	$5.24 \cdot 10^8$	$2.28 \cdot 10^{10}$	1120	<i>Martin et al.</i> (2009)
Lactate	<chem>CC(O)C(=O)[O-]</chem>	$7.77 \cdot 10^8$	$6.07 \cdot 10^{10}$	1295	<i>Martin et al.</i> (2009)
2-Hydroxy-butyrlic acid	<chem>CCC(O)C(=O)O</chem>	$1.3 \cdot 10^9$			<i>Merz and Waters</i> (1949) <sup>1</sup>
Pyruvic acid	<chem>CC(=O)C(=O)O</chem>	$1.2 \cdot 10^8$	$1.0 \cdot 10^{12}$	2800	<i>Ervens et al.</i> (2003b)
Pyruvate	<chem>CC(=O)C(=O)[O-]</chem>	$7.0 \cdot 10^8$	$1.3 \cdot 10^{12}$	2300	<i>Ervens et al.</i> (2003b)
Glucuronic acid	<chem>OCC(O)C(O)C(O)C(O)C(=O)O</chem>	$2.2 \cdot 10^9$			Average of different measurements of <i>Phillips and Worthington</i> (1970) <sup>1</sup>
<b>Di- and polycarboxylic acids</b>					n = 40
Oxalic acid	<chem>OC(=O)C(=O)O</chem>	$1.4 \cdot 10^6$			<i>Getoff et al.</i> (1971)
Oxalate monoanion	<chem>OC(=O)C(=O)[O-]</chem>	$1.9 \cdot 10^8$	$2.5 \cdot 10^{12}$	2800	<i>Ervens et al.</i> (2003b)
Oxalate dianion	<chem>[O-]C(=O)C(=O)[O-]</chem>	$1.6 \cdot 10^8$	$4.6 \cdot 10^{14}$	4300	<i>Ervens et al.</i> (2003b)
Malonic acid	<chem>OC(=O)CC(=O)O</chem>	$2.0 \cdot 10^7$			<i>Buxton et al.</i> (1988a)
Malonate monoanion	<chem>OC(=O)CC(=O)[O-]</chem>	$6.0 \cdot 10^7$	$3.2 \cdot 10^9$	1300	<i>Ervens et al.</i> (2003b)
Malonate dianion	<chem>[O-]C(=O)CC(=O)[O-]</chem>	$2.7 \cdot 10^8$			Average of <i>Logan</i> (1989) and <i>Adams et al.</i> (1965a)
Succinic acid	<chem>OC(=O)CCC(=O)O</chem>	$1.1 \cdot 10^8$	$8.1 \cdot 10^9$	1278	<i>Ervens et al.</i> (2003b)
Succinate monoanion	<chem>OC(=O)CCC(=O)[O-]</chem>	$2.6 \cdot 10^8$	$1.2 \cdot 10^{11}$	1808	TROPOS measurements
Succinate dianion	<chem>[O-]C(=O)CCC(=O)[O-]</chem>	$5.0 \cdot 10^8$	$5.4 \cdot 10^{10}$	1413	<i>Ervens et al.</i> (2003b)
Glutaric acid	<chem>OC(=O)CCCC(=O)O</chem>	$5.1 \cdot 10^8$	$2.5 \cdot 10^{10}$	1164	TROPOS measurements
Glutarate dianion	<chem>[O-]C(=O)CCCC(=O)[O-]</chem>	$8.2 \cdot 10^8$	$2.5 \cdot 10^{12}$	2355	TROPOS measurements
Adipic acid	<chem>OC(=O)CCCCC(=O)O</chem>	$1.6 \cdot 10^9$	$3.2 \cdot 10^{11}$	1479	TROPOS measurements
Adipate monoanion	<chem>OC(=O)CCCCC(=O)[O-]</chem>	$1.4 \cdot 10^9$	$9.7 \cdot 10^{12}$	2641	TROPOS measurements
Adipate dianion	<chem>[O-]C(=O)CCCCC(=O)[O-]</chem>	$1.4 \cdot 10^9$	$1.2 \cdot 10^{12}$	1985	TROPOS measurements
Pimelic acid	<chem>OC(=O)CCCCCC(=O)O</chem>	$3.4 \cdot 10^9$	$3.0 \cdot 10^{11}$	1335	TROPOS measurements
Pimelate monoanion	<chem>OC(=O)CCCCCC(=O)[O-]</chem>	$1.8 \cdot 10^9$	$9.7 \cdot 10^{12}$	2641	TROPOS measurements
Pimelate dianion	<chem>[O-]C(=O)CCCCCC(=O)[O-]</chem>	$2.1 \cdot 10^9$	$1.7 \cdot 10^{13}$	2514	TROPOS measurements

**Table C.1 (continued)** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}$ <sup>(b)</sup>	$A$ <sup>(b)</sup>	$E_A/R$ <sup>(c)</sup>	Reference/Comment
Suberic acid	<chem>OC(=O)CCCCCCC(=O)O</chem>	$5.0 \cdot 10^9$			<i>Hesper</i> (2003)
Suberate dianion	<chem>[O-]C(=O)CCCCCCC(=O)[O-]</chem>	$5.8 \cdot 10^9$			<i>Hesper</i> (2003)
Azelaic acid	<chem>OC(=O)CCCCCCCC(=O)O</chem>	$5.4 \cdot 10^9$			<i>Scholes and Willson</i> (1967) <sup>2</sup>
Sebacic acid	<chem>OC(=O)CCCCCCCCC(=O)O</chem>	$6.4 \cdot 10^9$			<i>Scholes and Willson</i> (1967) <sup>2</sup>
Tartronic acid	<chem>OC(=O)C(O)C(=O)O</chem>	$3.4 \cdot 10^8$	$1.5 \cdot 10^{10}$	1112	TROPOS measurements
Tartronate monoanion	<chem>OC(=O)C(O)C(=O)[O-]</chem>	$3.6 \cdot 10^8$			<i>Schuchmann et al.</i> (1995)
Tartronate dianion	<chem>[O-]C(=O)C(O)C(=O)[O-]</chem>	$4.4 \cdot 10^8$			<i>Schuchmann et al.</i> (1995)
Mesoxalic acid	<chem>OC(=O)C(=O)C(=O)O</chem>	$1.8 \cdot 10^8$	$3.8 \cdot 10^{10}$	1588	<i>Gligorovski et al.</i> (2009)
Mesoxalate monoanion	<chem>OC(=O)C(=O)C(=O)[O-]</chem>	$5.7 \cdot 10^7$			<i>Schuchmann et al.</i> (1991)
Mesoxalate dianion	<chem>[O-]C(=O)C(=O)C(=O)[O-]</chem>	$1.0 \cdot 10^8$			<i>Schuchmann et al.</i> (1991)
Malic acid	<chem>OC(=O)CC(O)C(=O)O</chem>	$3.6 \cdot 10^8$	$7.9 \cdot 10^{10}$	1575	<i>Gligorovski et al.</i> (2009)
Maleate monoanion	<chem>OC(=O)CC(O)C(=O)[O-]</chem>	$9.7 \cdot 10^8$	$9.7 \cdot 10^8$	1701	<i>Gligorovski et al.</i> (2009)
Maleate dianion	<chem>[O-]C(=O)CC(O)C(=O)[O-]</chem>	$8.5 \cdot 10^8$	$1.2 \cdot 10^{11}$	1449	<i>Gligorovski et al.</i> (2009)
Tartaric acid	<chem>OC(=O)C(O)C(O)C(=O)O</chem>	$1.1 \cdot 10^9$			Average of <i>Scholes and Willson</i> (1967) <sup>2</sup> and <i>Moore et al.</i> (1979) <sup>1</sup>
Tartrate dianion	<chem>[O-]C(=O)C(O)C(O)C(=O)[O-]</chem>	$1.0 \cdot 10^8$			Average of <i>Kraljic</i> (1967) <sup>1,2</sup> and <i>Logan</i> (1989)
Fumaric acid	<chem>OC(=O)/C=C/C(=O)O</chem>	$6.0 \cdot 10^9$			<i>Cabelli and Bielski</i> (1985) <sup>2</sup>
Maleic acid	<chem>OC(=O)/C=C\C(=O)O</chem>	$6.0 \cdot 10^9$			<i>Cabelli and Bielski</i> (1985) <sup>2</sup>
3-Hexene-1,6-dioate dianion	<chem>[O-]C(=O)CC=CCC(=O)[O-]</chem>	$5.9 \cdot 10^9$	$6.3 \cdot 10^{11}$	1395	<i>Elliot and McCracken</i> (1989) <sup>1</sup>
Crocetin	27876-94-4	$2.3 \cdot 10^{10}$			<i>Bors et al.</i> (1982) <sup>2</sup>
Acetylenedicarboxylate dianion	<chem>[O-]C(=O)C#CC(=O)[O-]</chem>	$2.6 \cdot 10^9$			<i>Simhon et al.</i> (1988) <sup>1</sup>
Disuccinyl peroxide	<chem>[O-]C(=O)CCC(=O)OOC(=O)CCC(=O)[O-]</chem>	$8.0 \cdot 10^7$			<i>Graedel and Weschler</i> (1981) <sup>1,2</sup>
Citric acid	<chem>OC(=O)CC(O)(C(=O)O)CC(=O)O</chem>	$5.0 \cdot 10^7$			<i>Adams et al.</i> (1965a) <sup>2</sup>
Citrate	<chem>[O-]C(=O)CC(O)(C(=O)[O-])CC(=O)[O-]</chem>	$1.5 \cdot 10^8$			<i>Zepp et al.</i> (1992) <sup>1</sup>
<b>Ethers</b>					n = 25
Dimethyl ether	<chem>COC</chem>	$1.0 \cdot 10^9$			<i>Eibenberger</i> (1980) <sup>2</sup>
Diethyl ether	<chem>CCOCC</chem>	$3.6 \cdot 10^9$			<i>Buxton et al.</i> (1988a)
Methylal	<chem>COCOC</chem>	$1.2 \cdot 10^9$			<i>Eibenberger</i> (1980) <sup>2</sup>

**Table C.1 (continued)** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}^{(b)}$	$A^{(b)}$	$E_A/R^{(c)}$	Reference/Comment
Diethoxy methane	CCOCOCC	$1.6 \cdot 10^9$			Anbar et al. (1966a)
Ethylene glycol methyl ether	COCCO	$1.3 \cdot 10^9$			Anbar et al. (1966a)
Ethylene glycol dimethyl ether	COCCOC	$1.6 \cdot 10^9$			Anbar et al. (1966a)
Ethylene glycol ethyl ether	CCOCCO	$1.7 \cdot 10^9$			Anbar et al. (1966a)
Ethylene glycol diethyl ether	CCOCCOCC	$2.3 \cdot 10^9$			Anbar et al. (1966a)
Ethylene glycol butyl ether	CCCCOCCO	$5.1 \cdot 10^9$			Stemmler and von Gunten (2000)
Diethylene glycol	OCCOCCO	$2.1 \cdot 10^9$			Anbar et al. (1966a)
Diethylene glycol diethyl ether	CCOCCOCCOCC	$3.2 \cdot 10^9$			Anbar et al. (1966a)
Hydroxybutyl vinyl ether	OCCCCOC=C	$1.9 \cdot 10^9$			Moise et al. (2005)
Di(ethylene glycol) vinyl ether	C=COCCOCCO	$4.2 \cdot 10^{10}$			Moise et al. (2005)
Di(ethylene glycol) divinyl ether	C=COCCOCCOC=C	$2.3 \cdot 10^{10}$			Moise et al. (2005)
Tri(ethylene glycol) divinyl ether	C=COCCOCCOCCOC=C	$1.54 \cdot 10^{10}$	$2.3 \cdot 10^{13}$	2179	Gligorovski et al. (2009)
Dimethyl acetal	COC(C)OC	$2.2 \cdot 10^9$			Eibenberger (1980) <sup>2</sup>
Methyl tert-butyl ether	CC(C)(C)OC	$2.1 \cdot 10^9$			Average of Eibenberger (1980) <sup>2,5</sup> , Chang and Young (2000) <sup>5</sup> , Adams et al. (1965a) <sup>5</sup> , Mitani et al. (2002) <sup>5</sup> , and Garoma and Gurol (2005)
Ethyl tert-butyl ether	CC(C)(C)OCC	$1.5 \cdot 10^9$	$1.2 \cdot 10^{10}$	580	Monod et al. (2005)
Di(iso-propyl) ether	CC(C)OC(C)C	$2.49 \cdot 10^9$			Mezyk et al. (2001) <sup>3</sup>
Di(tert-butyl) ether	CC(C)(C)OC(C)(C)C	$1.81 \cdot 10^9$			Mezyk et al. (2001) <sup>3</sup>
2-Methyl-2-methoxy-butane	CCC(C)(C)OC	$2.37 \cdot 10^9$			Mezyk et al. (2001) <sup>3</sup>
Methoxyacetate	COCC(=O)[O-]	$6.1 \cdot 10^8$			Anbar et al. (1966a)
2-Methyl-2-methoxy propanol	OCC(C)(C)OC	$8.02 \cdot 10^8$			Mezyk et al. (2009)
2-Methyl-2-methoxy propanal	O=CC(C)(C)OC	$3.5 \cdot 10^9$			Mezyk et al. (2009)



**Table C.1 (continued)** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}^{(b)}$	$A^{(b)}$	$E_A/R^{(c)}$	Reference/Comment
2-Methyl-2-methoxy propanoic acid	<chem>O=C(O)C(C)(C)OC</chem>	$7.73 \cdot 10^8$			<i>Mezyk et al.</i> (2009)
<b>Esters</b>					n = 34
Ethyl formate	<chem>CCOC=O</chem>	$7.9 \cdot 10^8$	$9.3 \cdot 10^{11}$	2106	Average of measurements within the MOST project <sup>6</sup> ; 42.3% <chem>C2H5COCO</chem> and 57.7% <chem>CH3C(H)OCHO</chem> <sup>6</sup>
Butyl formate	<chem>CCCCOC=O</chem>	$2.8 \cdot 10^9$			<i>Stemmler and von Gunten</i> (2000)
Tert-butyl formate	<chem>CC(C)(C)OC=O</chem>	$7.0 \cdot 10^8$			<i>Acero et al.</i> (2001) <sup>5</sup>
Methyl acetate	<chem>CC(=O)OC</chem>	$1.5 \cdot 10^8$			Average of <i>Anbar et al.</i> (1966a) and <i>Adams et al.</i> (1965a) <sup>2</sup>
Methyl propionate	<chem>CCC(=O)OC</chem>	$4.5 \cdot 10^8$			<i>Adams et al.</i> (1965a) <sup>2</sup>
Ethyl acetate	<chem>CC(=O)OCC</chem>	$4.0 \cdot 10^8$			<i>Adams et al.</i> (1965a) <sup>2</sup>
Ethyl propionate	<chem>CCC(=O)OCC</chem>	$5.2 \cdot 10^8$			Average of <i>Adams et al.</i> (1965a) <sup>8</sup> and <i>Biro and Wojnarovits</i> (1992) <sup>1</sup>
2-Hydroxyethyl acetate	<chem>OCCOC(=O)C</chem>	$9.1 \cdot 10^8$			<i>Matsushige et al.</i> (1975) <sup>2</sup>
Methyl methoxy acetate	<chem>COCC(=O)OC</chem>	$1.8 \cdot 10^9$			<i>Massaut et al.</i> (1988) <sup>2</sup>
Propyl acetate	<chem>CCCOC(=O)C</chem>	$1.4 \cdot 10^9$			<i>Adams et al.</i> (1965a) <sup>2</sup>
Methyl butyrate	<chem>CCCC(=O)OC</chem>	$1.7 \cdot 10^9$			<i>Adams et al.</i> (1965a) <sup>1</sup>
Butyl acetate	<chem>CCCCOC(=O)C</chem>	$1.8 \cdot 10^9$	$5.33 \cdot 10^{10}$	1000	<i>Monod et al.</i> (2005)
Ethyl butyrate	<chem>CCCC(=O)OCC</chem>	$1.6 \cdot 10^9$			<i>Adams et al.</i> (1965a) <sup>2</sup>
Butyl propionate	<chem>CCCCOC(=O)CC</chem>	$1.6 \cdot 10^9$			<i>Adams et al.</i> (1965a) <sup>2</sup>
Butyl hydroxyacetate	<chem>CCCCOC(=O)CO</chem>	$3.2 \cdot 10^9$			<i>Stemmler and von Gunten</i> (2000)
1-Hydroxy ethyl butyrate	<chem>CCCC(=O)CCO</chem>	$2.1 \cdot 10^9$			<i>Stemmler and von Gunten</i> (2000)

**Table C.1 (continued)** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}^{(b)}$	$A^{(b)}$	$E_A/R^{(c)}$	Reference/Comment
Iso-propyl acetate	<chem>CC(C)OC(=O)C</chem>	$5.3 \cdot 10^8$			Average of <i>Hardison et al.</i> (2002) <sup>5,7</sup> and <i>Adams et al.</i> (1965a) <sup>1</sup>
Monoethyl adipate	<chem>CCOC(=O)CCCCC(=O)O</chem>	$3.0 \cdot 10^9$			<i>Haag and Yao</i> (1992) <sup>1</sup>
2,4-Dimethoxy pentane	<chem>COC(C)CC(C)OC</chem>	$3.7 \cdot 10^9$			<i>Janik et al.</i> (2000) <sup>3</sup>
Methyl acrylate	<chem>C=CC(=O)OC</chem>	$5.3 \cdot 10^9$			<i>Kumar et al.</i> (1988) <sup>1</sup>
Ethyl acrylate	<chem>C=CC(=O)OCC</chem>	$5.8 \cdot 10^9$			<i>Kumar et al.</i> (1988) <sup>1</sup>
Butyl acrylate	<chem>C=CC(=O)OCCCC</chem>	$5.5 \cdot 10^9$			<i>Kumar et al.</i> (1988) <sup>1</sup>
1-Hydroxy ethyl acrylate	<chem>C=CC(=O)OCCO</chem>	$5.8 \cdot 10^9$			<i>Safrany and Wojnarovits</i> (1993) <sup>1</sup>
Methyl methacrylate	<chem>C=C(C)C(=O)OC</chem>	$1.2 \cdot 10^{10}$			Average of <i>Maruthamuthu</i> (1980) <sup>2</sup> and <i>Kumar et al.</i> (1988) <sup>1</sup>
Butyl methacrylate	<chem>C=C(C)C(=O)OCCCC</chem>	$1.2 \cdot 10^{10}$			<i>Kumar et al.</i> (1988) <sup>1</sup>
Dimethyl malonate	<chem>COC(=O)CC(=O)OC</chem>	$2.7 \cdot 10^8$			<i>George et al.</i> (2003)
Diethyl malonate	<chem>CCOC(=O)CC(=O)OCC</chem>	$6.5 \cdot 10^8$			<i>Adams et al.</i> (1965a) <sup>1</sup>
Dimethyl succinate	<chem>COC(=O)CCC(=O)OC</chem>	$5.3 \cdot 10^8$			<i>George et al.</i> (2003)
Diethyl succinate	<chem>CCOC(=O)CCC(=O)OCC</chem>	$7.8 \cdot 10^8$			<i>Adams et al.</i> (1965a) <sup>2</sup>
Diethyl meleate	<chem>CCOC(=O)/C=C\C(=O)OCC</chem>	$5.9 \cdot 10^9$			<i>Biro and Wojnarovits</i> (1996)
Diethyl fumarate	<chem>CCOC(=O)/C=C/C(=O)OCC</chem>	$5.9 \cdot 10^9$			<i>Biro and Wojnarovits</i> (1996)
Dimethyl carbonate	<chem>COC(=O)OC</chem>	$5.1 \cdot 10^7$			<i>George et al.</i> (2003)
Diethyl carbonate	<chem>CCOC(=O)OCC</chem>	$7.9 \cdot 10^8$			<i>George et al.</i> (2003)
Diacetyl peroxide	<chem>CC(=O)OOC(=O)C</chem>	$6.0 \cdot 10^7$			<i>Graedel and Weschler</i> (1981) <sup>1</sup>
<b>Cyclic alkanes and alkenes</b>					n = 14
Cyclobutane carboxylate	<chem>C1CCC1C(=O)[O-]</chem>	$3.0 \cdot 10^9$			<i>Anbar et al.</i> (1966a)
Cyclopentane	<chem>C1CCCC1</chem>	$3.7 \cdot 10^9$			<i>Buxton et al.</i> (1988a)
Methyl cyclopentane	<chem>C1CCCC1C</chem>	$7.0 \cdot 10^9$			<i>Rudakov et al.</i> (1981) <sup>2</sup>
Cyclopentane carboxylate	<chem>C1CCCC1C(=O)[O-]</chem>	$4.2 \cdot 10^9$			<i>Anbar et al.</i> (1966a)
Cyclohexane	<chem>C1CCCCC1</chem>	$6.1 \cdot 10^9$			<i>Rudakov et al.</i> (1981) <sup>2</sup>
Methyl cyclohexane	<chem>C1CCCCC1C</chem>	$7.1 \cdot 10^9$			<i>Rudakov et al.</i> (1981) <sup>2</sup>
Cyclohexane carboxylate	<chem>C1CCCCC1C(=O)[O-]</chem>	$5.5 \cdot 10^9$			<i>Anbar et al.</i> (1966a)

**Table C.1 (continued)** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}$ <sup>(b)</sup>	$A$ <sup>(b)</sup>	$E_A/R$ <sup>(c)</sup>	Reference/Comment
Cycloheptane	C1CCCCC1	$7.7 \cdot 10^9$			<i>Rudakov et al.</i> (1981) <sup>2</sup>
Cyclopentene	C1CCC=C1	$7.0 \cdot 10^9$			<i>Soylemez and Schuler</i> (1974) <sup>2</sup>
Cyclohexene	C1CCCC=C1	$8.8 \cdot 10^9$			<i>Michael and Hart</i> (1970) <sup>2</sup>
1,3-Cyclohexadiene	C1CC=CC=C1	$9.9 \cdot 10^9$			<i>Michael and Hart</i> (1970) <sup>2</sup>
1,4-Cyclohexadiene	C1C=CCC=C1	$7.7 \cdot 10^9$			<i>Michael and Hart</i> (1970) <sup>2</sup>
Cycloheptatriene	C1C=CC=CC=C1	$1.0 \cdot 10^{10}$			<i>Schöneshöfer</i> (1971) <sup>2</sup>
Quinine	O=C1C=CC(=O)C=C1	$1.2 \cdot 10^9$			<i>Adams and Michael</i> (1967) <sup>2</sup>
<b>Cyclic ethers</b>					n = 13
Oxirane	C1OC1	$6.8 \cdot 10^7$			<i>Anbar et al.</i> (1966a)
Methyl oxirane	C1OC1C	$2.5 \cdot 10^8$			<i>Anbar et al.</i> (1966a)
Ethyl oxirane	C1OC1CC	$7.8 \cdot 10^8$			<i>Anbar et al.</i> (1966a)
Glycidol	C1OC1CO	$4.7 \cdot 10^8$			<i>Anbar et al.</i> (1966a)
Tetrahydrofuran	C1COCC1	$3.8 \cdot 10^9$			<i>George et al.</i> (2003)
Dioxolane	C1OCOC1	$4.0 \cdot 10^9$			<i>Eibenberger</i> (1980) <sup>2</sup>
2-Methyl dioxolane	C1OC(C)OC1	$3.5 \cdot 10^9$			<i>Eibenberger</i> (1980) <sup>2</sup>
2,2-Dimethyl dioxolane	C1OC(C)(C)OC1	$2.1 \cdot 10^9$			<i>Eibenberger</i> (1980) <sup>2</sup>
Tetrahydropyran	C1CCCCO1	$1.5 \cdot 10^9$			<i>Walling et al.</i> (1974)
1,3-Dioxane	C1COCOC1	$4.0 \cdot 10^9$			<i>Eibenberger</i> (1980) <sup>2</sup>
1,4-Dioxane	C1OCCOC1	$2.8 \cdot 10^9$			<i>Buxton et al.</i> (1988a)
Trioxane	C1OCOCO1	$1.0 \cdot 10^9$			Average of <i>Anbar et al.</i> (1966a) and <i>Eibenberger</i> (1980) <sup>2</sup>
Paraldehyde	CC1OC(C)OC(C)O1	$1.6 \cdot 10^9$			Average of <i>Anbar et al.</i> (1966a) and <i>Eibenberger</i> (1980) <sup>2</sup>
<b>Terpenes and terpene oxidation products</b>					n = 4
R(+)-Limonene	CC1=CCC(CC1)C(C)=C	$2.9 \cdot 10^9$			TROPOS measurements
$\alpha$ -Pinene	CC2(C)C1CC=C(C)C2C1	$1.4 \cdot 10^9$			<i>Raabe</i> (1996)
Cis-verbenol	CC2(C)C1CC2C(O)C=C1C	$6.8 \cdot 10^9$			<i>Buxton et al.</i> (2000) <sup>3</sup>
(-)-Myrtenal	CC2(C)C1CC=C(C=O)C2C1	$1.7 \cdot 10^9$	$1.0 \cdot 10^{13}$	2600	TROPOS measurements

**Table C.1 (continued)** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}$ <sup>(b)</sup>	$A$ <sup>(b)</sup>	$E_A/R$ <sup>(c)</sup>	Reference/Comment
<b>Furans (including ascorbic acid)</b>					n = 21
Furan	<chem>c1cocc1</chem>	$3.9 \cdot 10^9$			<i>Lilie</i> (1971) <sup>2</sup>
2-Methylfuran	<chem>c1coc(C)c1</chem>	$1.9 \cdot 10^{10}$			<i>Vysotskaya et al.</i> (1983) <sup>2</sup>
Furfuryl alcohol	<chem>c1coc(CO)c1</chem>	$1.5 \cdot 10^{10}$			<i>Saveleva et al.</i> (1973); <i>Vysotskaya et al.</i> (1983) <sup>2</sup>
Furfural	<chem>c1coc(C=O)c1</chem>	$6.3 \cdot 10^9$			Average of <i>Vysotskaya et al.</i> (1983) <sup>2</sup> and <i>D'Angelantonio et al.</i> (1999)
5-Methyl furfural	<chem>c1c(C)oc(C=O)c1</chem>	$7.2 \cdot 10^9$			<i>Vysotskaya et al.</i> (1983) <sup>2</sup>
5-Hydroxymethylfurfural	<chem>c1c(CO)oc(C=O)c1</chem>	$5.8 \cdot 10^9$			<i>Vysotskaya et al.</i> (1983) <sup>2</sup>
5-Nitro furfural	<chem>c1c(N(=O)=O)oc(C=O)c1</chem>	$5.5 \cdot 10^9$			<i>Greenstock and Dunlop</i> (1973); <i>Chapman et al.</i> (1973) <sup>2</sup>
Acetylfuran	<chem>c1coc(C(=O)C)c1</chem>	$4.5 \cdot 10^9$			<i>Vysotskaya et al.</i> (1983) <sup>1</sup>
Furan-2-carboxylate	<chem>c1coc(C(=O)[O-])c1</chem>	$1.2 \cdot 10^{10}$			<i>Saveleva et al.</i> (1973) <sup>2</sup>
5-Carboxylate furfural	<chem>c1c(C=O)oc(C(=O)[O-])c1</chem>	$3.8 \cdot 10^9$			<i>Vysotskaya et al.</i> (1983) <sup>2</sup>
2-Carboxylate-5-nitro-furan	<chem>c1c(N(=O)=O)oc(C(=O)[O-])c1</chem>	$5.3 \cdot 10^9$			<i>Greenstock and Dunlop</i> (1973); <i>Chapman et al.</i> (1973) <sup>2</sup>
Tetronate	<chem>O=C1C=C([O-])CO1</chem>	$9.2 \cdot 10^9$			<i>Schuler et al.</i> (1974) <sup>1</sup>
$\alpha$ -Hydroxytetronate	<chem>O=C1C([O-])=C(O)CO1</chem>	$4.7 \cdot 10^9$			<i>Schuler et al.</i> (1974) <sup>1</sup>
Ascorbic acid	<chem>O1C(=O)C(O)=C(O)C1C(O)CO</chem>	$1.0 \cdot 10^{10}$			<i>Buxton et al.</i> (1988a)
Ascorbate	<chem>O1C(=O)C([O-])=C(O)C1C(O)CO</chem>	$3.4 \cdot 10^9$			Average of <i>Schuler</i> (1977) <sup>2</sup> , <i>Redpath and Willson</i> (1973) <sup>2</sup> , <i>Schöneshöfer</i> (1972) <sup>2</sup> , <i>Bonifacic et al.</i> (1994) <sup>1</sup> , <i>Bolkenius et al.</i> (1991) <sup>1</sup> , and <i>Ye and Schuler</i> (1990) <sup>1</sup>
L-Ascorbate-2-sulfate	52174-99-9	$4.2 \cdot 10^9$			<i>Cabelli et al.</i> (1983) <sup>2</sup>
1-O-Methyl ascorbic acid	<chem>O1C(=O)C(OC)=C(O)C1C(O)CO</chem>	$2.5 \cdot 10^9$			<i>Cabelli et al.</i> (1983) <sup>2</sup>
2-O-Methyl ascorbic acid	<chem>O1C(=O)C(O)=C(OC)C1C(O)CO</chem>	$2.7 \cdot 10^9$			<i>Cabelli et al.</i> (1983) <sup>2</sup>
3-O-Methyl ascorbic acid	<chem>O1C(=O)C(O)=C(O)C1C(OC)CO</chem>	$3.0 \cdot 10^9$			<i>Cabelli et al.</i> (1983) <sup>2</sup>
3-O-Methyl ascorbate	<chem>O1C(=O)C([O-])=C(O)C1C(OC)CO</chem>	$4.8 \cdot 10^9$			<i>Cabelli et al.</i> (1983) <sup>2</sup>

**Table C.1 (continued)** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}$ <sup>(b)</sup>	$A$ <sup>(b)</sup>	$E_A/R$ <sup>(c)</sup>	Reference/Comment
O-Dimethyl ascorbic acid	<chem>O1C(=O)C(OC)=C(OC)C1C(O)CO</chem>	$4.2 \cdot 10^9$			<i>Cabelli et al. (1983)</i> <sup>2</sup>
<b>Benzols</b>					n = 17
Benzol	<chem>c1ccccc1</chem>	$7.8 \cdot 10^9$			<i>Burton et al. (1988a)</i>
Toluol	<chem>c1ccccc1C</chem>	$8.1 \cdot 10^9$			<i>Albarrañ et al. (2003)</i> ; branching ratios o:m:p = 0.84:0.41:1 (i<0.2)
Ethyl benzol	<chem>c1ccccc1CC</chem>	$7.5 \cdot 10^9$			<i>Sehested and Holcman (1979)</i> <sup>2</sup>
o-Xylene	<chem>Cc1ccccc1C</chem>	$6.7 \cdot 10^9$			<i>Sehested et al. (1975)</i> <sup>2</sup>
m-Xylene	<chem>c1c(C)cccc1C</chem>	$7.5 \cdot 10^9$			<i>Sehested et al. (1975)</i> <sup>2</sup>
p-Xylene	<chem>c1cc(C)ccc1C</chem>	$7.0 \cdot 10^9$			<i>Sehested et al. (1975)</i> <sup>2</sup>
1,2,3-Trimethyl benzol	<chem>Cc1ccc(C)c1C</chem>	$7.0 \cdot 10^9$			<i>Sehested et al. (1975)</i> <sup>2</sup>
1,2,4-Trimethyl benzol	<chem>Cc1ccc(C)cc1C</chem>	$6.2 \cdot 10^9$			<i>Sehested et al. (1975)</i> <sup>2</sup>
Mesitylene	<chem>c1c(C)cc(C)cc1C</chem>	$6.4 \cdot 10^9$			<i>Sehested et al. (1975)</i> <sup>2</sup>
1,2,3,4-Tetramethyl benzol	<chem>Cc1ccc(C)c(C)c1C</chem>	$7.2 \cdot 10^9$			<i>Sehested et al. (1975)</i> <sup>1</sup>
1,2,3,5-Tetramethyl benzol	<chem>Cc1cc(C)cc(C)c1C</chem>	$7.1 \cdot 10^9$			<i>Sehested et al. (1975)</i> <sup>1</sup>
1,2,4,5-Tetramethyl benzol	<chem>Cc1cc(C)c(C)cc1C</chem>	$7.0 \cdot 10^9$			<i>Sehested et al. (1975)</i> <sup>1</sup>
Pentamethyl benzol	<chem>Cc1cc(C)c(C)c(C)c1C</chem>	$7.5 \cdot 10^9$			<i>Sehested et al. (1975)</i> <sup>2</sup>
Hexamethyl benzol	<chem>Cc1c(C)c(C)c(C)c(C)c1C</chem>	$7.2 \cdot 10^9$			<i>Sehested et al. (1975)</i> <sup>2</sup>
Cumene	<chem>c1ccccc1C(C)C</chem>	$7.5 \cdot 10^9$			<i>Sehested and Holcman (1979)</i> <sup>2</sup>
Styrene	<chem>c1ccccc1C=C</chem>	$6.0 \cdot 10^9$			<i>Brede et al. (1977)</i> <sup>2</sup>
$\alpha$ -Methylstyrene	<chem>c1ccccc1C(C)=C</chem>	$9.7 \cdot 10^9$			<i>Brede et al. (1977)</i> <sup>2</sup>
<b>N/S-substituted benzols</b>					n = 7
Nitrosobenzol	<chem>c1ccccc1N=O</chem>	$1.8 \cdot 10^{10}$			<i>Asmus et al. (1966)</i> <sup>2</sup>
Nitrobenzol	<chem>c1ccccc1N(=O)=O</chem>	$3.9 \cdot 10^9$			<i>Burton et al. (1988a)</i>
Benzolsulfonic acid	<chem>c1ccccc1S(=O)(=O)O</chem>	$1.6 \cdot 10^9$			<i>Merz and Waters (1949)</i> <sup>2</sup>
Phenyl sulfonate	<chem>c1ccccc1S(=O)(=O)[O-]</chem>	$3.9 \cdot 10^9$			Average of <i>Anbar et al. (1966b)</i> and <i>Neta and Dorfman (1968)</i> <sup>2</sup>
2,4-Dinitro-toluol	<chem>c1c(N(=O)=O)cc(N(=O)=O)cc1C</chem>	$9.0 \cdot 10^8$			<i>Makarov et al. (2008)</i>
2,4,6-Trinitro-toluol	<chem>c1c(N(=O)=O)cc(N(=O)=O)cc1(N(=O)=O)</chem>	$7.4 \cdot 10^8$			<i>Makarov et al. (2008)</i>

**Table C.1 (continued)** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}^{(b)}$	$A^{(b)}$	$E_A/R^{(c)}$	Reference/Comment
1-Methyl-3-nitro phenyl sulfonate	<chem>c1(C)cc(N(=O)=O)ccc1S(=O)(=O)[O-]</chem>	$1.6 \cdot 10^9$			<i>Basinski and Lerke</i> (1972) <sup>2</sup>
<b>Phenols and other aromatic alcohols</b>					n = 30
Phenol	<chem>c1ccccc1O</chem>	$1.01 \cdot 10^{10}$			<i>Chen and Schuler</i> (1993); partial k @ o/m/p position: $2.37 \cdot 10^9/1.3 \cdot 10^8/3.56 \cdot 10^9$
Phenolate	<chem>c1ccccc1[O-]</chem>	$9.6 \cdot 10^9$			<i>Bonin et al.</i> (2007)
Catechol	<chem>c1ccc(O)c1O</chem>	$1.1 \cdot 10^{10}$			<i>Saveleva et al.</i> (1972) <sup>2</sup>
Resorcinol	<chem>c1ccc(O)cc1O</chem>	$1.2 \cdot 10^{10}$			<i>Saveleva et al.</i> (1972) <sup>2</sup>
Hydroquinone	<chem>c1cc(O)ccc1O</chem>	$1.2 \cdot 10^{10}$			Average of <i>Adams et al.</i> (1965a) <sup>2</sup> ; <i>Al-Suhybani and Hughes</i> (1986) <sup>2</sup> ; and <i>Heckel et al.</i> (1966) <sup>2</sup>
Phloroglucinol	<chem>c1c(O)cc(O)cc1O</chem>	$1.0 \cdot 10^{10}$			<i>Wang et al.</i> (1994) <sup>1</sup>
p-Tert-butyl phenol	<chem>c1cc(O)ccc1C(C)(C)C</chem>	$1.9 \cdot 10^{10}$			<i>Saveleva et al.</i> (1972)
4-Tert-butyl catechol	<chem>c1c(O)c(O)ccc1C(C)(C)C</chem>	$7.6 \cdot 10^9$			<i>Richter</i> (1979) <sup>2</sup>
4-(1,2-Dihydroxyethyl)-catechol	<chem>c1c(O)c(O)ccc1C(O)CO</chem>	$1.6 \cdot 10^{10}$			Average of different measurements of <i>Ek et al.</i> (1989) <sup>8</sup>
Benzyl alcohol	<chem>c1ccccc1CO</chem>	$8.4 \cdot 10^9$			<i>Neta and Dorfman</i> (1968) <sup>2</sup>
Phenetyl alcohol	<chem>c1ccccc1CCO</chem>	$6.4 \cdot 10^9$			<i>Buxton et al.</i> (1988a)
o-Cresol	<chem>c1(O)cccc1C</chem>	$1.1 \cdot 10^{10}$			<i>Saveleva et al.</i> (1972) <sup>1</sup>
p-Cresol	<chem>c1cc(O)ccc1C</chem>	$1.2 \cdot 10^{10}$			<i>Fisher and Hamill</i> (1973) <sup>9</sup>
2,3-Dihydroxy toluol	<chem>c1(O)c(O)cccc1C</chem>	$1.6 \cdot 10^{10}$			<i>Gohn and Getoff</i> (1977) <sup>1</sup>
3,4-Dihydroxy toluol	<chem>c1c(O)c(O)ccc1C</chem>	$1.6 \cdot 10^{10}$			<i>Gohn and Getoff</i> (1977) <sup>2</sup>
1-Phenylethanol	<chem>c1ccccc1C(O)C</chem>	$1.1 \cdot 10^{10}$			<i>Snook and Hamilton</i> (1974)
1-(p-Ethylphenyl)ethanol	<chem>c1cc(CC)ccc1C(O)C</chem>	$1.3 \cdot 10^{10}$			<i>Snook and Hamilton</i> (1974)
1-Phenyl propanol	<chem>c1ccccc1C(O)CC</chem>	$1.0 \cdot 10^{10}$			<i>Snook and Hamilton</i> (1974)
1-Phenyl-2-methyl propanol	<chem>c1ccccc1C(O)C(C)C</chem>	$9.5 \cdot 10^9$			<i>Snook and Hamilton</i> (1974)
1-Phenyl-2,2-dimethyl propanol	<chem>c1ccccc1C(O)C(C)(C)C</chem>	$9.9 \cdot 10^9$			<i>Snook and Hamilton</i> (1974)

**Table C.1 (continued)** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}$ <sup>(b)</sup>	$A$ <sup>(b)</sup>	$E_A/R$ <sup>(c)</sup>	Reference/Comment
1-Phenyl-2-propanol	c1ccccc1CC(O)C	$2.1 \cdot 10^{10}$			<i>Snook and Hamilton</i> (1974)
2-Phenyl-2-propanol	c1ccccc1C(C)(O)C	$4.6 \cdot 10^9$			<i>Snook and Hamilton</i> (1974)
Phenyl tert-butyl alcohol	c1ccccc1CC(C)(O)C	$1.7 \cdot 10^{10}$			<i>Snook and Hamilton</i> (1974)
4-Phenyl-2-butanol	c1ccccc1CCC(O)C	$2.0 \cdot 10^{10}$			<i>Snook and Hamilton</i> (1974)
1,1-Dimethyl-3-phenyl butanol	c1ccccc1CCC(C)(O)C	$5.9 \cdot 10^9$			<i>Snook and Hamilton</i> (1974)
o-Nitro phenol	Oc1ccccc1N(=O)=O	$9.2 \cdot 10^9$			<i>Saveleva et al.</i> (1972) <sup>9</sup>
o-Nitro phenolate	[O-]c1ccccc1N(=O)=O	$9.2 \cdot 10^9$			<i>Saveleva et al.</i> (1972) <sup>2</sup>
m-Nitro phenolate	c1c([O-])cccc1N(=O)=O	$7.1 \cdot 10^9$			<i>Saveleva et al.</i> (1972) <sup>2</sup>
p-Nitro phenol	c1cc(O)ccc1N(=O)=O	$3.8 \cdot 10^9$			<i>Cercek and Ebert</i> (1968) <sup>2</sup>
p-Nitro phenolate	c1cc([O-])ccc1N(=O)=O	$7.6 \cdot 10^9$			<i>Saveleva et al.</i> (1972) <sup>2</sup>
<b>Aromatic aldehydes and ketones</b>					n = 15
Benzaldehyde	c1ccccc1C=O	$3.5 \cdot 10^9$			Average of <i>Geeta et al.</i> (2001) and <i>Shevchuk et al.</i> (1969) <sup>2</sup>
2-Hydroxy benzaldehyde	c1(O)cccc1C=O	$5.2 \cdot 10^9$			<i>Geeta et al.</i> (2001)
2-Hydroxy benzaldehyde, conjugate base	c1([O-])cccc1C=O	$5.2 \cdot 10^9$			<i>Saveleva et al.</i> (1972) <sup>2</sup>
3-Hydroxy benzaldehyde	c1c(O)cccc1C=O	$7.7 \cdot 10^9$			<i>Geeta et al.</i> (2001)
4-Hydroxy benzaldehyde	c1cc(O)ccc1C=O	$1.21 \cdot 10^{10}$			<i>Geeta et al.</i> (2001)
4-Hydroxy benzaldehyde, conjugate base	c1cc([O-])ccc1C=O	$1.0 \cdot 10^{10}$			<i>Saveleva et al.</i> (1972) <sup>2</sup>
3,4-Dihydroxy benzaldehyde	c1c(O)c(O)ccc1C=O	$8.3 \cdot 10^9$			<i>Bors et al.</i> (1979)
Phenyl acetone	c1ccccc1C(=O)C	$5.3 \cdot 10^9$			Average of <i>Geeta et al.</i> (2001); <i>Anbar et al.</i> (1966b); <i>Willson et al.</i> (1971) <sup>1</sup> ; and <i>Neta and Dorfman</i> (1968) <sup>1</sup>
2-Hydroxyphenyl acetone	c1(O)cccc1C(=O)C	$2.7 \cdot 10^9$			<i>Geeta et al.</i> (2001)
3-Hydroxyphenyl acetone	c1c(O)cccc1C(=O)C	$2.6 \cdot 10^9$			<i>Geeta et al.</i> (2001)
4-Hydroxyphenyl acetone	c1cc(O)ccc1C(=O)C	$5.1 \cdot 10^9$			<i>Geeta et al.</i> (2001)
3,4-Dihydroxyphenyl acetone	c1c(O)c(O)ccc1C(=O)C	$1.0 \cdot 10^{10}$			<i>Bors et al.</i> (1979) <sup>1</sup>

**Table C.1 (continued)** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}$ <sup>(b)</sup>	$A$ <sup>(b)</sup>	$E_A/R$ <sup>(c)</sup>	Reference/Comment
2,4-Dihydroxyphenyl acetone	<chem>c1(O)cc(O)ccc1C(=O)C</chem>	$3.0 \cdot 10^{10}$			<i>Bors et al.</i> (1979) <sup>1</sup>
2,5-Dihydroxyphenyl acetone	<chem>c1(O)ccc(O)cc1C(=O)C</chem>	$8.0 \cdot 10^9$			<i>Bors et al.</i> (1979) <sup>1</sup>
2,6-Dihydroxyphenyl acetone	<chem>c1(O)cccc(O)c1C(=O)C</chem>	$8.0 \cdot 10^9$			<i>Bors et al.</i> (1984) <sup>2</sup>
<b>Aromatic acids and diacids</b>					n = 23
Benzoic acid	<chem>c1ccccc1C(=O)O</chem>	$3.1 \cdot 10^9$			Average of <i>Wander et al.</i> (1968) <sup>2</sup> and <i>Ashton et al.</i> (1995) <sup>1</sup>
Benzoate	<chem>c1ccccc1C(=O)[O-]</chem>	$5.9 \cdot 10^9$			<i>Buxton et al.</i> (1988a)
2-Hydroxy benzoic acid	<chem>c1(O)cccc1C(=O)O</chem>	$2.2 \cdot 10^{10}$			<i>Buxton et al.</i> (1988a)
2-Hydroxy benzoate	<chem>c1(O)cccc1C(=O)[O-]</chem>	$1.6 \cdot 10^{10}$			<i>Buxton et al.</i> (1988a)
4-Hydroxy benzoic acid	<chem>c1cc(O)ccc1C(=O)O</chem>	$7.7 \cdot 10^9$			Average of <i>Neta and Dorfman</i> (1968) <sup>1</sup> ; <i>Anderson et al.</i> (1987) <sup>1</sup> ; and <i>Shetiya et al.</i> (1976) <sup>1</sup>
4-Hydroxy benzoate	<chem>c1cc(O)ccc1C(=O)[O-]</chem>	$8.5 \cdot 10^9$			<i>Buxton et al.</i> (1988a)
2,3-Hydroxy benzoate	<chem>c1(O)c(O)cccc1C(=O)[O-]</chem>	$1.0 \cdot 10^{10}$			<i>Oturan et al.</i> (1992) <sup>1</sup>
2,4-Hydroxy benzoate	<chem>c1(O)cc(O)ccc1C(=O)[O-]</chem>	$1.6 \cdot 10^{10}$			<i>Oturan et al.</i> (1992) <sup>1</sup>
2,5-Hydroxy benzoate	<chem>c1(O)ccc(O)cc1C(=O)[O-]</chem>	$1.7 \cdot 10^{10}$			<i>Oturan et al.</i> (1992) <sup>1</sup>
2,6-Hydroxy benzoate	<chem>c1(O)cccc(O)c1C(=O)[O-]</chem>	$1.0 \cdot 10^{10}$			<i>Oturan et al.</i> (1992) <sup>1</sup>
3,4,5-Hydroxy benzoate	<chem>c1c(O)c(O)c(O)cc1C(=O)[O-]</chem>	$4.0 \cdot 10^{10}$			<i>Oturan et al.</i> (1992) <sup>1</sup>
2,3,4-Hydroxy benzoate	<chem>c1(O)c(O)c(O)ccc1C(=O)[O-]</chem>	$1.9 \cdot 10^{10}$			<i>Oturan et al.</i> (1992) <sup>1</sup>
2,4,6-Hydroxy benzoate	<chem>c1(O)cc(O)cc(O)c1C(=O)[O-]</chem>	$4.8 \cdot 10^{10}$			<i>Oturan et al.</i> (1992) <sup>1</sup>
4-Methyl benzoate	<chem>c1cc(C)ccc1C(=O)[O-]</chem>	$8.0 \cdot 10^9$			<i>Neta et al.</i> (1972) <sup>1</sup>
4-Nitrobenzoate	<chem>c1cc(N(=O)=O)ccc1C(=O)[O-]</chem>	$2.6 \cdot 10^9$			<i>Neta and Dorfman</i> (1968) <sup>2</sup> ; <i>Buxton et al.</i> (1988a)
o-Phthalate	<chem>c1(C(=O)[O-])cccc1C(=O)[O-]</chem>	$5.9 \cdot 10^9$			<i>Simic et al.</i> (1973a) <sup>2</sup>
p-Phthalate	<chem>c1cc(C(=O)[O-])ccc1C(=O)[O-]</chem>	$3.3 \cdot 10^9$			<i>Anbar et al.</i> (1966b)
Phenyl acetate	<chem>c1ccccc1CC(=O)[O-]</chem>	$7.9 \cdot 10^9$			<i>Neta and Dorfman</i> (1968) <sup>2</sup>
(3-(4-Hydroxyphenyl) propionate monoanion)	<chem>c1cc(O)ccc1CCC(=O)[O-]</chem>	$1.2 \cdot 10^{10}$			<i>Buxton et al.</i> (1988a)
(3-(4-Hydroxyphenyl) propionate dianion)	<chem>c1cc([O-])ccc1CCC(=O)[O-]</chem>	$1.9 \cdot 10^{10}$			<i>Buxton et al.</i> (1988a)



**Table C.1 (continued)** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}$ <sup>(b)</sup>	$A$ <sup>(b)</sup>	$E_A/R$ <sup>(c)</sup>	Reference/Comment
Cinnamate	<chem>c1ccccc1C=CC(=O)[O-]</chem>	$8.1 \cdot 10^9$			<i>Bobrowski and Raghavan</i> (1982) <sup>2</sup>
p-Hydroxy cinnamate	<chem>c1cc(O)ccc1C=CC(=O)[O-]</chem>	$8.2 \cdot 10^9$			<i>Bobrowski</i> (1984) <sup>2</sup>
3,4-Dihydroxy cinnamate	<chem>c1c(O)c(O)ccc1C=CC(=O)[O-]</chem>	$2.8 \cdot 10^{10}$			<i>Bors et al.</i> (1984) <sup>2</sup>
<b>Anisoles, aromatic ethers and esters</b>					n = 38
Anisole	<chem>c1ccccc1OC</chem>	$5.8 \cdot 10^9$			Average of <i>Anbar et al.</i> (1966b) and <i>O'Neill et al.</i> (1975) <sup>2</sup>
o-Dimethoxy benzol	<chem>COc1ccccc1OC</chem>	$5.2 \cdot 10^9$			<i>O'Neill et al.</i> (1975) <sup>2</sup>
m-Dimethoxy benzol	<chem>c1c(OC)cccc1OC</chem>	$7.2 \cdot 10^9$			<i>O'Neill et al.</i> (1975) <sup>2</sup>
p-Dimethoxy benzol	<chem>c1cc(OC)ccc1OC</chem>	$7.0 \cdot 10^9$			<i>O'Neill et al.</i> (1975) <sup>2</sup>
1,2,3-Trimethoxy benzol	<chem>COc1cccc(OC)c1OC</chem>	$8.0 \cdot 10^9$			<i>O'Neill et al.</i> (1975) <sup>2</sup>
1,2,4-Trimethoxy benzol	<chem>COc1cc(OC)ccc1OC</chem>	$8.1 \cdot 10^9$			<i>O'Neill et al.</i> (1975) <sup>2</sup>
Benzyl methyl ether	<chem>c1ccccc1COC</chem>	$1.0 \cdot 10^{10}$			<i>Snook and Hamilton</i> (1974)
o-Methoxy phenol	<chem>Oc1ccccc1OC</chem>	$2.0 \cdot 10^{10}$			<i>O'Neill and Steenken</i> (1977) <sup>2</sup>
m-Methoxy phenol	<chem>c1c(O)cccc1OC</chem>	$3.2 \cdot 10^{10}$			<i>O'Neill and Steenken</i> (1977) <sup>2</sup>
p-Methoxy phenol	<chem>c1cc(O)ccc1OC</chem>	$2.6 \cdot 10^{10}$			<i>O'Neill and Steenken</i> (1977) <sup>9</sup>
2,3-Dimethoxy phenol	<chem>COc1c(OC)cccc1O</chem>	$2.0 \cdot 10^{10}$			<i>O'Neill and Steenken</i> (1977) <sup>2</sup>
2,6-Dimethoxy phenol	<chem>c1(OC)cccc(OC)c1O</chem>	$2.6 \cdot 10^{10}$			<i>O'Neill and Steenken</i> (1977) <sup>2</sup>
3,5-Dimethoxy phenol	<chem>c1c(OC)cc(OC)cc1O</chem>	$2.0 \cdot 10^{10}$			<i>O'Neill and Steenken</i> (1977) <sup>2</sup>
2-Methoxy benzoate	<chem>c1(OC)cccc1C(=O)[O-]</chem>	$5.4 \cdot 10^9$			<i>O'Neill et al.</i> (1977) <sup>2</sup>
3-Methoxy benzoate	<chem>c1c(OC)cccc1C(=O)[O-]</chem>	$6.6 \cdot 10^9$			<i>O'Neill et al.</i> (1977) <sup>2</sup>
4-Methoxy benzoate	<chem>c1cc(OC)ccc1C(=O)[O-]</chem>	$7.2 \cdot 10^9$			<i>O'Neill et al.</i> (1977) <sup>2</sup>
2-Hydroxy-5-methoxy benzoate	<chem>c1(O)ccc(OC)cc1C(=O)[O-]</chem>	$1.8 \cdot 10^{10}$	$9.0 \cdot 10^{10}$	1323	<i>O'Neill et al.</i> (1977) <sup>2</sup>
3-Methoxy-4-hydroxy benzoate	<chem>c1c(OC)c(O)ccc1C(=O)[O-]</chem>	$1.4 \cdot 10^{10}$			<i>O'Neill et al.</i> (1977) <sup>2</sup>
2,3-Dimethoxy benzoate	<chem>c1(OC)c(OC)cccc1C(=O)[O-]</chem>	$1.0 \cdot 10^{10}$			<i>O'Neill et al.</i> (1977) <sup>2</sup>
2,4-Dimethoxy benzoate	<chem>c1(OC)cc(OC)ccc1C(=O)[O-]</chem>	$1.0 \cdot 10^{10}$			<i>O'Neill et al.</i> (1977) <sup>2</sup>
3,4-Dimethoxy benzoate	<chem>c1c(OC)c(OC)ccc1C(=O)[O-]</chem>	$1.2 \cdot 10^{10}$			<i>O'Neill et al.</i> (1977) <sup>2</sup>
2,6-Dimethoxy benzoate	<chem>c1(OC)cccc(OC)c1C(=O)[O-]</chem>	$6.6 \cdot 10^9$			<i>O'Neill et al.</i> (1977) <sup>2</sup>
3,5-Dimethoxy benzoate	<chem>c1c(OC)cc(OC)cc1C(=O)[O-]</chem>	$7.0 \cdot 10^9$			<i>O'Neill et al.</i> (1977) <sup>2</sup>

**Table C.1 (continued)** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}^{(b)}$	$A^{(b)}$	$E_A/R^{(c)}$	Reference/Comment
3,5-Dimethoxy-4-hydroxy benzoate	<chem>c1c(OC)c(O)c(OC)cc1C(=O)[O-]</chem>	$1.6 \cdot 10^{10}$			<i>O'Neill et al. (1977)</i> <sup>2</sup>
2,3,4-Trimethoxy benzoate	<chem>c1(OC)c(OC)c(OC)ccc1C(=O)[O-]</chem>	$1.0 \cdot 10^{10}$			<i>O'Neill et al. (1977)</i> <sup>2</sup>
2,3,5-Trimethoxy benzoate	<chem>c1(OC)c(OC)cc(OC)cc1C(=O)[O-]</chem>	$7.0 \cdot 10^9$			<i>O'Neill et al. (1977)</i> <sup>2</sup>
2,4,6-Trimethoxy benzoate	<chem>c1(OC)cc(OC)cc(OC)c1C(=O)[O-]</chem>	$1.2 \cdot 10^{10}$			<i>O'Neill et al. (1977)</i> <sup>2</sup>
3,4,5-Trimethoxy benzoate	<chem>c1c(OC)c(OC)c(OC)cc1C(=O)[O-]</chem>	$1.3 \cdot 10^{10}$			<i>O'Neill et al. (1977)</i> <sup>2</sup>
3-Methoxy-4-hydroxy cinnamate	<chem>c1c(OC)c(O)ccc1C=CC(=O)[O-]</chem>	$1.0 \cdot 10^{10}$			<i>Bors et al. (1984)</i> <sup>2</sup>
3,5-Dimethoxy-4-hydroxy cinnamate	<chem>c1c(OC)c(O)c(OC)cc1C=CC(=O)[O-]</chem>	$2.2 \cdot 10^{10}$			<i>Buxton et al. (1988a)</i>
Phenoxy acetic acid	<chem>c1ccccc1OCC(=O)O</chem>	$1.0 \cdot 10^{10}$			<i>Zona et al. (2002)</i> <sup>3</sup>
1-(p-Ethoxyphenyl)ethanol	<chem>c1cc(OCC)ccc1C(O)C</chem>	$2.7 \cdot 10^9$			<i>Snook and Hamilton (1974)</i>
1-Methoxy-2-methyl-1-phenylpropane	<chem>c1ccccc1C(OC)C(C)C</chem>	$7.4 \cdot 10^9$			<i>Snook and Hamilton (1974)</i>
1-(p-Methoxyphenyl)-2,2-dimethyl propanol	<chem>c1cc(OC)ccc1C(O)C(C)(C)C</chem>	$7.6 \cdot 10^9$			<i>Snook and Hamilton (1974)</i>
3,5-Dinitro anisole	<chem>c1c(N(=O)=O)cc(N(=O)=O)cc1OC</chem>	$4.0 \cdot 10^9$			<i>Tamminga et al. (1979)</i> <sup>2</sup>
Isoeugenol	<chem>c1c(OC)c(O)ccc1C=CC</chem>	$3.9 \cdot 10^{10}$			<i>Buxton et al. (1988a)</i>
Phenyl acetate	<chem>c1ccccc1OC(=O)C</chem>	$5.2 \cdot 10^9$			<i>Anbar et al. (1966b)</i>
Propyl 3,4,5-trihydroxybenzoate	<chem>c1c(O)c(O)c(O)cc1C(=O)OCCC</chem>	$1.1 \cdot 10^{10}$			<i>Buxton et al. (1988a)</i>
<b>Sugars</b>					n = 12
Erythritol	<chem>OCC(O)C(O)CO</chem>	$1.9 \cdot 10^9$	$1.3 \cdot 10^{12}$	1948	<i>Hoffmann et al. (2009)</i>
Arabitol	<chem>OCC(O)C(O)C(O)CO</chem>	$1.6 \cdot 10^9$	$2.5 \cdot 10^{10}$	794	<i>Hoffmann et al. (2009)</i>
Mannitol	<chem>OCC(O)C(O)C(O)C(O)CO</chem>	$1.6 \cdot 10^9$	$1.8 \cdot 10^{10}$	734	<i>Hoffmann et al. (2009)</i>
Arabinose	<chem>OCC(O)C(O)C(O)C=O</chem>	$1.8 \cdot 10^9$			<i>Moore et al. (1979)</i> <sup>2</sup>
D-Fructose	<chem>OCC1C(O)C(O)C(CO)(O)O1/ OCC(O)C(O)C(O)C(=O)CO</chem>	$1.6 \cdot 10^9$			<i>Moore et al. (1979)</i> <sup>2</sup>
Ribose	<chem>O1C(O)C(O)C(O)C1CO/OCC(O)C(O)C(O)C=O</chem>	$1.5 \cdot 10^9$			<i>Buxton et al. (1988a)</i>

**Table C.1 (continued)** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}$ <sup>(b)</sup>	$A$ <sup>(b)</sup>	$E_A/R$ <sup>(c)</sup>	Reference/Comment
2-Deoxy-D-ribose	<chem>O1C(O)CC(O)C1CO/OCC(O)C(O)CC=O</chem>	$2.5 \cdot 10^9$			<i>Baker et al.</i> (1982) <sup>2</sup>
Inositol	<chem>C1(O)C(O)C(O)C(O)C(O)C1(O)</chem>	$1.7 \cdot 10^9$			<i>Buxton et al.</i> (1988a)
Levoglucosan	<chem>OC1C(O)C(O)C2OC1OC2</chem>	$2.2 \cdot 10^9$	$1.0 \cdot 10^{11}$	1100	TROPOS measurements
Glucose	<chem>O1C(O)C(O)C(O)C(O)C1CO/OCC(O)C(O)C(O)C(O)C=O</chem>	$1.5 \cdot 10^9$			<i>Buxton et al.</i> (1988a)
Galactose	<chem>O1C(O)C(O)C(O)C(O)C1CO/OCC(O)C(O)C(O)C(O)C=O</chem>	$2.0 \cdot 10^9$			<i>Bucknall et al.</i> (1978) <sup>2</sup>
2-Deoxy-D-glucose	<chem>O1C(O)CC(O)C(O)C1CO/OCC(O)C(O)C(O)CC=O</chem>	$2.8 \cdot 10^9$			<i>Baker et al.</i> (1982) <sup>2</sup>
<b>Polycyclic aromatic compounds</b>					n = 32
Endothall	<chem>OC(=O)C2C(C1CCC2O1)C(=O)O</chem>	$1.5 \cdot 10^9$			<i>Haag and Yao</i> (1992) <sup>8</sup>
Camphor	<chem>CC2(C)C1CC(=O)C2(C)CC1</chem>	$4.1 \cdot 10^9$			<i>Land and Swallow</i> (1979)
2-Phenyl furan	<chem>c1ccccc1c2ccco2</chem>	$1.6 \cdot 10^{10}$			<i>Vysotskaya et al.</i> (1983) <sup>2</sup>
5-Phenyl furfural	<chem>c1ccccc1c2ccc(C=O)o2</chem>	$5.9 \cdot 10^9$			<i>Vysotskaya et al.</i> (1983) <sup>2</sup>
Biphenyl	<chem>c1ccccc1c2ccccc2</chem>	$1.04 \cdot 10^{10}$			<i>Chen and Schuler</i> (1993); partial k @ o/m/p position:1.07e9/5.5e8/1.52e9
Biphenyl-4-carboxylate	<chem>c1ccccc1c2ccc(C(=O)[O-])cc2</chem>	$6.8 \cdot 10^9$			<i>Simic et al.</i> (1973a) <sup>2</sup>
Benzophenone	<chem>c1ccccc1C(=O)c2ccccc2</chem>	$8.8 \cdot 10^9$			<i>Buxton et al.</i> (1988a)
Diphenyl acetate	<chem>c1ccccc1C(C(=O)[O-])c2ccccc2</chem>	$4.0 \cdot 10^9$			<i>Neta et al.</i> (1972) <sup>2</sup>
4-Phenoxybenzoate	<chem>c1ccccc1Oc2ccc(C(=O)[O-])cc2</chem>	$7.0 \cdot 10^9$			<i>Neta and Schuler</i> (1975) <sup>2</sup>
1,4-(3,4-Dihydroxyphenyl)-2,3-dimethyl butane	<chem>c1cc(O)c(O)cc1CC(C)C(C)Cc2cc(O)c(O)cc2</chem>	$1.5 \cdot 10^{10}$			<i>Bors et al.</i> (1984) <sup>2</sup>
1,2,3,4-Tetrahydro-1-naphthol/ $\alpha$ -tetralol	<chem>OC2CCCCc1ccccc12</chem>	$7.0 \cdot 10^9$			<i>Snook and Hamilton</i> (1974) <sup>2</sup>
Coumarin	<chem>O=C1C=Cc2ccccc2O1</chem>	$2.0 \cdot 10^9$			<i>Gopakumar et al.</i> (1977)
$\beta$ -Benzylglucoside	<chem>c1ccccc1COC2C(O)C(O)C(O)C(CO)O2</chem>	$4.2 \cdot 10^{10}$			<i>Mittal and Mittal</i> (1986) <sup>2</sup>

**Table C.1 (continued)** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}^{(b)}$	$A^{(b)}$	$E_A/R^{(c)}$	Reference/Comment
2,4-Dimethylphenyl- $\beta$ -D-glucopyranoside	<chem>Cc1cc(C)ccc1COC2C(O)C(O)C(O)C(CO)O2</chem>	$3.9 \cdot 10^9$			<i>Phillips et al. (1971)</i> <sup>2</sup>
3,4-Dimethylphenyl- $\beta$ -D-glucopyranoside	<chem>c1c(C)c(C)ccc1COC2C(O)C(O)C(O)C(CO)O2</chem>	$4.2 \cdot 10^9$			<i>Phillips et al. (1971)</i> <sup>2</sup>
Naphthalene	<chem>c1cccc2ccccc12</chem>	$9.6 \cdot 10^9$			Average of <i>Evers et al. (1980)</i> <sup>2</sup> ; <i>Zevos and Sehested (1978)</i> <sup>2</sup> ; <i>Roder et al. (1990)</i> <sup>1</sup> ; and <i>Kanodia et al. (1988)</i> <sup>1</sup>
1-Naphthol	<chem>Oc2cccc1ccccc12</chem>	$1.2 \cdot 10^{10}$			Average of <i>Doherty et al. (1986)</i> <sup>8</sup> and <i>Kanodia et al. (1988)</i> <sup>8</sup>
2-Naphthol	<chem>Oc1ccc2ccccc2c1</chem>	$1.2 \cdot 10^{10}$			<i>Kanodia et al. (1988)</i> <sup>1</sup>
1-Naphthoate	<chem>[O-]C(=O)c2cccc1ccccc12</chem>	$7.9 \cdot 10^9$			<i>Simic et al. (1973a)</i> <sup>2</sup>
2-Naphthoate	<chem>[O-]C(=O)c1ccc2ccccc2c1</chem>	$7.6 \cdot 10^9$			<i>Simic et al. (1973a)</i> <sup>2</sup>
1-Naphthylacetate	<chem>[O-]C(=O)Cc2cccc1ccccc12</chem>	$8.7 \cdot 10^9$			<i>Shetiya et al. (1972)</i> <sup>2</sup>
Di-tert-butyl-naphthalenesulfonate	14992-59-7	$1.1 \cdot 10^{10}$			<i>Barber and Thomas (1978)</i> <sup>2</sup>
Chromotropic acid	<chem>O=S(=O)(O)c2cc1cc(cc(O)c1c(O)c2)S(=O)(=O)O</chem>	$1.2 \cdot 10^8$			<i>Ahrens (1967)</i> <sup>2</sup>
9,10-Anthraquinone-1-sulfonate	<chem>[O-]S(=O)(=O)c3cccc2C(=O)c1ccccc1C(=O)c23</chem>	$7.2 \cdot 10^9$			<i>Hulme et al. (1972)</i> <sup>2</sup>
9,10-Anthraquinone-2-sulfonate	<chem>[O-]S(=O)(=O)c2ccc3C(=O)c1ccccc1C(=O)c3c2</chem>	$5.6 \cdot 10^9$			<i>Hulme et al. (1972)</i> <sup>2</sup>
8-Methoxypsoralen	<chem>COc1c3occc3cc2C=CC(=O)Oc12</chem>	$1.1 \cdot 10^{10}$			<i>Redpath et al. (1978)</i> <sup>2</sup>
Flourescein	<chem>[O-]C(=O)c4ccccc4C=1c3ccc([O-])cc3OC2=CC(=O)C=CC=12</chem>	$1.2 \cdot 10^{10}$			<i>Prütz (1973)</i> <sup>2</sup>
Pyrene butyrate	<chem>[O-]C(=O)CCCC1cc2ccc3cccc4ccc(c1)c2c34</chem>	$1.3 \cdot 10^{10}$			<i>Barber and Thomas (1978)</i> <sup>2</sup>
D-Cellobiose	528-50-7	$3.6 \cdot 10^9$			<i>Zakatova et al. (1969)</i> <sup>2</sup>
Crocin	42553-65-1	$3.1 \cdot 10^9$			<i>Buxton et al. (1988a)</i>
Carmine	1390-65-4	$1.3 \cdot 10^{10}$			<i>Sychev et al. (1979)</i> <sup>2</sup>

**Table C.1 (continued)** Recommendations of evaluated aqueous phase rate constants of hydroxyl radicals with organic compounds.

Compound	SMILES string (or CAS number) <sup>(a)</sup>	$k_{298}^{(b)}$	$A^{(b)}$	$E_A/R^{(c)}$	Reference/Comment
9-Anthroate ion		$8.0 \cdot 10^9$			<i>Simic et al. (1973b)</i> <sup>2</sup>

<sup>(a)</sup>for complicated structures with long SMILES strings only the CAS number is given; <sup>(b)</sup>in  $\text{M}^{-1} \text{s}^{-1}$ ; <sup>(c)</sup>in K

<sup>1</sup>as also given in NIST database (*Ross et al.*, 1998); <sup>2</sup>as also given in *Buxton et al. (1988a)*; <sup>3</sup>as also given in *Herrmann (2003)*; <sup>4</sup>as given in *Gligorovski et al. (2009)*; <sup>5</sup>as given in *Cooper et al. (2009)*; <sup>6</sup>given in CAPRAM database available at <http://projects.tropos.de/capram/>; <sup>7</sup>as given in *de Semainville et al. (2007a)*; <sup>8</sup>as given in *Warneck (2005)*; <sup>9</sup>as given in *Barzaghi and Herrmann (2004)*

## C.2 Reactions of nitrate radicals with organic compounds

**Table C.2** Recommendations of evaluated aqueous phase rate constants of nitrate radicals with organic compounds.

Compound	SMILES string	$k_{298}^{(a)}$	$A^{(a)}$	$E_A/R^{(b)}$	Reference/Comment	( $n_t = 129$ )
<b>Alkanes</b>						$n = 1$
Isoprene	<chem>C=C(C)C=C</chem>	$1.0 \cdot 10^9$			TROPOS measurements	
<b>Monoalcohols</b>						$n = 14$
Methanol	<chem>CO</chem>	$5.1 \cdot 10^5$	$9.4 \cdot 10^{11}$	4300	Average of <i>Exner et al. (1993)</i> and <i>Rousse and George (2004)</i>	
Ethanol	<chem>CCO</chem>	$2.2 \cdot 10^6$	$1.4 \cdot 10^{11}$	3300	<i>Herrmann and Zellner (1998)</i>	
Propanol	<chem>CCCO</chem>	$3.2 \cdot 10^6$			<i>Herrmann et al. (1994)</i>	
Butanol	<chem>CCCCO</chem>	$1.9 \cdot 10^6$			<i>Shastri and Huie (1990)</i>	
Pentanol	<chem>CCCCCO</chem>	$2.4 \cdot 10^6$			<i>Shastri and Huie (1990)</i>	
Hexanol	<chem>CCCCCCO</chem>	$3.3 \cdot 10^6$			<i>Shastri and Huie (1990)</i>	
Heptanol	<chem>CCCCCCCO</chem>	$3.6 \cdot 10^6$			<i>Shastri and Huie (1990)</i>	
Octanol	<chem>CCCCCCCCO</chem>	$5.8 \cdot 10^6$			<i>Shastri and Huie (1990)</i>	
Iso-propanol	<chem>CC(O)C</chem>	$3.7 \cdot 10^6$	$3.1 \cdot 10^8$	1323	<i>Herrmann et al. (1994)</i> with $E_a/R$ of <i>Ito et al. (1989b)</i>	
Iso-butanol	<chem>CC(C)CO</chem>	$1.6 \cdot 10^6$			<i>Shastri and Huie (1990)</i>	
Tert-butanol	<chem>CC(C)(C)O</chem>	$6.6 \cdot 10^4$			<i>Herrmann et al. (1994)</i>	

**Table C.2 (continued)** Recommendations of evaluated aqueous phase rate constants of nitrate radicals with organic compounds.

Compound	SMILES string	$k_{298}^{(a)}$	$A^{(a)}$	$E_A/R^{(b)}$	Reference/Comment
Allyl alcohol	C=CCO	$2.2 \cdot 10^8$			Average of ( <i>Alfassi et al.</i> , 1993) and ( <i>Ito et al.</i> , 1989b)
2-Butenol	CC=CCO	$2.1 \cdot 10^9$			<i>Alfassi et al.</i> (1993)
3-Methyl 3-Buten-1-ol	C=C(C)CCO	$2.4 \cdot 10^9$			<i>Alfassi et al.</i> (1993)
<b>Diols and polyols</b>					n = 3
Ethylene glycol	OCCO	$6.6 \cdot 10^6$	$7.1 \cdot 10^9$	2117	<i>Hoffmann et al.</i> (2009)
1,2-Propanediol	CC(O)CO	$9.9 \cdot 10^6$	$6.8 \cdot 10^{10}$	2622	<i>Hoffmann et al.</i> (2009)
Glycerol	OCC(O)CO	$1.3 \cdot 10^7$	$1.4 \cdot 10^{12}$	3452	<i>Hoffmann et al.</i> (2009)
<b>Aldehydes and gem-diols</b>					n = 11
Formaldehyde	C=O	$3.5 \cdot 10^6$	$3.36 \cdot 10^6$	674	Average of <i>Ito et al.</i> (1989a) <sup>1</sup> and <i>Wayne et al.</i> (1991) with $E_a/R$ of <i>Wayne et al.</i> (1991)
Hydrated formaldehyde	OCO	$1.0 \cdot 10^6$	$3.6 \cdot 10^{12}$	4500	<i>Erner et al.</i> (1993) <sup>2</sup>
Acetaldehyde	CC=O	$1.9 \cdot 10^6$			<i>Zellner et al.</i> (1996)
Hydrated acetaldehyde	CC(O)O	$2.0 \cdot 10^6$			Average of <i>Zellner et al.</i> (1996) <sup>3</sup> and <i>Rousse and George</i> (2004)
Propionaldehyde	CCC=O	$5.8 \cdot 10^7$	$3.2 \cdot 10^{11}$	2646	<i>de Semainville et al.</i> (2007b)
Butyraldehyde	CCCC=O	$5.6 \cdot 10^7$	$4.9 \cdot 10^{10}$	2045	<i>de Semainville et al.</i> (2007b)
Iso-butyraldehyde	CC(C)C=O	$6.3 \cdot 10^7$	$3.7 \cdot 10^8$	529	<i>Wayne et al.</i> (1991)
2,2-Dimethyl propanal	CC(C)(C)C=O	$7.0 \cdot 10^7$	$3.8 \cdot 10^8$	505	<i>Wayne et al.</i> (1991)
Methacrolein	C=C(C)C=O	$4.0 \cdot 10^7$	$5.8 \cdot 10^8$	842	<i>Schöne et al.</i> (2014)
Glyoxal	O=CC=O	$1.1 \cdot 10^6$	$9.9 \cdot 10^{10}$	3400	TROPOS measurements
Hydrated glyoxal	OC(O)C(O)O	$1.1 \cdot 10^6$	$8.9 \cdot 10^{10}$	3368	<i>Herrmann et al.</i> (1995c) <sup>3</sup>
<b>Ketones</b>					n = 3
Acetone	CC(=O)C	$3.7 \cdot 10^3$	$7.6 \cdot 10^9$	4330	<i>Herrmann and Zellner</i> (1998)
Hydroxy acetone	CC(=O)CO	$1.8 \cdot 10^7$	$4.0 \cdot 10^9$	1564	<i>de Semainville et al.</i> (2007b)
Methyl ethyl ketone	CC(=O)CC	$9.7 \cdot 10^6$	$6.2 \cdot 10^8$	1200	<i>de Semainville et al.</i> (2007b)

**Table C.2 (continued)** Recommendations of evaluated aqueous phase rate constants of nitrate radicals with organic compounds.

Compound	SMILES string	$k_{298}^{(a)}$	$A^{(a)}$	$E_A/R^{(b)}$	Reference/Comment
<b>Monocarboxylic acids</b>					n = 16
Formic acid	C(=O)O	$3.8 \cdot 10^5$	$3.4 \cdot 10^{10}$	3400	<i>Exner et al. (1994)</i>
Formate	C(=O)[O-]	$5.1 \cdot 10^7$	$8.2 \cdot 10^{10}$	2200	<i>Exner et al. (1994)</i> <sup>4</sup>
Acetic acid	CC(=O)O	$1.3 \cdot 10^4$	$4.9 \cdot 10^9$	3800	<i>Exner et al. (1994)</i> <sup>5</sup>
Acetate	CC(=O)[O-]	$2.9 \cdot 10^6$	$1.0 \cdot 10^{12}$	3800	<i>Exner et al. (1994)</i> <sup>5</sup>
Propionic acid	CCC(=O)O	$7.7 \cdot 10^4$			<i>Rousse and George (2004)</i>
Crotonic acid	CC=CC(=O)O	$5.1 \cdot 10^7$			<i>Neta and Huie (1986)</i>
Glycolic acid	OCC(=O)O	$9.1 \cdot 10^5$	$4.5 \cdot 10^{11}$	3969	<i>de Semainville et al. (2007b)</i>
Glycolate	OCC(=O)[O-]	$1.0 \cdot 10^7$	$1.8 \cdot 10^{11}$	3007	<i>de Semainville et al. (2007b)</i>
Lactic acid	CC(O)C(=O)O	$2.1 \cdot 10^6$	$1.0 \cdot 10^{11}$	3248	<i>de Semainville et al. (2007b)</i>
Lactate	CC(O)C(=O)[O-]	$1.0 \cdot 10^7$	$8.3 \cdot 10^{10}$	2646	<i>de Semainville et al. (2007b)</i>
Pyruvic acid	CC(=O)C(=O)O	$2.4 \cdot 10^6$	$8.8 \cdot 10^8$	1804	<i>de Semainville et al. (2007b)</i>
Pyruvate	CC(=O)C(=O)[O-]	$1.9 \cdot 10^7$	$3.7 \cdot 10^{11}$	2887	<i>de Semainville et al. (2007b)</i>
Acrylic acid	C=CC(=O)O	$6.9 \cdot 10^6$	$2.2 \cdot 10^{13}$	4450	<i>Schöne et al. (2014)</i>
Acrylate	C=CC(=O)[O-]	$4.4 \cdot 10^7$	$2.2 \cdot 10^9$	1200	<i>Schöne et al. (2014)</i>
Methacrylic acid	C=C(C)C(=O)O	$9.2 \cdot 10^7$			<i>Schöne et al. (2014)</i>
Methacrylate	C=C(C)C(=O)[O-]	$1.7 \cdot 10^8$			<i>Schöne et al. (2014)</i>
<b>Dicarboxylic acids</b>					n = 13
Oxalic acid	OC(=O)C(=O)O	$2.4 \cdot 10^4$			<i>Yang et al. (2004)</i>
Oxalate monoanion	OC(=O)C(=O)[O-]	$6.1 \cdot 10^7$	$8.4 \cdot 10^9$	-2180	Average of <i>Yang et al. (2004)</i> and <i>de Semainville et al. (2010a)</i> with $E_a/R$ of <i>Raabe (1996)</i>
Oxalate dianion	[O-]C(=O)C(=O)[O-]	$2.2 \cdot 10^8$	$2.2 \cdot 10^{12}$	2766	Average of <i>Yang et al. (2004)</i> and <i>de Semainville et al. (2010a)</i> with $E_a/R$ of <i>de Semainville et al. (2010a)</i>
Malonic acid	OC(=O)CC(=O)O	$5.1 \cdot 10^4$			<i>de Semainville et al. (2010a)</i>
Malonate monoanion	OC(=O)CC(=O)[O-]	$5.6 \cdot 10^6$	$5.0 \cdot 10^{11}$	3368	<i>de Semainville et al. (2010a)</i>
Malonate dianion	[O-]C(=O)CC(=O)[O-]	$2.3 \cdot 10^7$	$6.3 \cdot 10^{11}$	3007	<i>de Semainville et al. (2010a)</i>
Succinic acid	OC(=O)CCC(=O)O	$5.0 \cdot 10^3$			<i>de Semainville et al. (2010a)</i>
Succinate monoanion	OC(=O)CCC(=O)[O-]	$1.1 \cdot 10^7$			<i>de Semainville et al. (2010a)</i>

**Table C.2 (continued)** Recommendations of evaluated aqueous phase rate constants of nitrate radicals with organic compounds.

Compound	SMILES string	$k_{298}^{(a)}$	$A^{(a)}$	$E_A/R^{(b)}$	Reference/Comment
Succinate dianion	[O-]C(=O)CCC(=O)[O-]	$1.8 \cdot 10^7$	$6.2 \cdot 10^{11}$	3127	<i>de Semainville et al. (2010a)</i>
Mesoxalic acid	OC(=O)C(=O)C(=O)O	$1.7 \cdot 10^6$	$5.1 \cdot 10^8$	1564	<i>de Semainville et al. (2010a)</i>
Mesoxalate monoanion	OC(=O)C(=O)C(=O)[O-]	$2.3 \cdot 10^7$			<i>de Semainville et al. (2010a)</i>
Mesoxalate dianion	[O-]C(=O)C(=O)C(=O)[O-]	$4.9 \cdot 10^7$	$1.4 \cdot 10^{12}$	3127	<i>de Semainville et al. (2010a)</i>
Fumaric acid	OC(=O)/C=C/C(=O)O	$<1.0 \cdot 10^6$			<i>Neta and Huie (1986)</i> <sup>4</sup>
<b>Ethers and esters</b>					n = 9
Methyl tert-butyl ether	CC(C)(C)OC	$3.9 \cdot 10^5$			<i>Rousse and George (2004)</i>
Methyl formate	COC=O	$3.5 \cdot 10^6$			<i>Buxton et al. (2001)</i> <sup>6</sup>
Ethyl formate	CCOC=O	$4.7 \cdot 10^6$			<i>Buxton et al. (2001)</i>
Methyl acetate	CC(O)OC	$<104$			<i>Buxton et al. (2001)</i>
Ethyl acetate	CC(=O)OCC	$<104$			<i>Buxton et al. (2001)</i>
Dimethyl malonate	COC(=O)CC(=O)OC	$2.6 \cdot 10^4$			<i>Rousse and George (2004)</i>
Dimethyl succinate	COC(=O)CCC(=O)OC	$3.4 \cdot 10^4$			<i>Rousse and George (2004)</i>
Dimethyl carbonate	COC(=O)OC	$8.4 \cdot 10^4$			<i>Rousse and George (2004)</i>
Diethyl carbonate	CCOC(=O)OCC	$1.5 \cdot 10^4$			<i>Rousse and George (2004)</i>
<b>Cyclic alcohols and ethers</b>					n = 6
Cyclopentanol	C1CCCC1O	$3.2 \cdot 10^6$			<i>Shastri and Huie (1990)</i> <sup>1</sup>
Oxetane	C1COC1	$1.5 \cdot 10^6$			<i>Shastri and Huie (1990)</i> <sup>1</sup>
Tetrahydrofuran	C1COCC1	$1.5 \cdot 10^7$			<i>Herrmann and Zellner (1998)</i> <sup>5</sup>
Tetrahydropyran	C1CCCCO1	$4.9 \cdot 10^6$			<i>Shastri and Huie (1990)</i> <sup>4</sup>
1,3-Dioxane	C1COCOC1	$7.7 \cdot 10^5$			<i>Shastri and Huie (1990)</i>
1,4-Dioxane	C1OCCOC1	$1.3 \cdot 10^6$			<i>Shastri and Huie (1990)</i>
<b>Benzols</b>					n = 6
Benzol	c1ccccc1	$4.0 \cdot 10^8$			<i>Herrmann et al. (1996)</i>
Toluol	c1ccccc1C	$1.2 \cdot 10^9$	$5.7 \cdot 10^{11}$	1800	<i>Herrmann and Zellner (1998)</i>
Ethyl benzol	c1ccccc1CC	$1.3 \cdot 10^9$			<i>Herrmann et al. (1996)</i>
p-Xylene	c1cc(C)ccc1C	$1.6 \cdot 10^9$			<i>Herrmann et al. (1996)</i>
Tert-butyl benzol	c1ccccc1C(C)(C)C	$1.1 \cdot 10^9$			TROPOS measurements



**Table C.2 (continued)** Recommendations of evaluated aqueous phase rate constants of nitrate radicals with organic compounds.

Compound	SMILES string	$k_{298}^{(a)}$	$A^{(a)}$	$E_A/R^{(b)}$	Reference/Comment
Mesitylene	<chem>c1c(C)cc(C)cc1C</chem>	$1.3 \cdot 10^9$			<i>Herrmann et al.</i> (1996)
<b>Phenols and other aromatic alcohols</b>					n = 16
Phenol	<chem>c1ccccc1O</chem>	$1.9 \cdot 10^9$	$1.4 \cdot 10^{12}$	2100	<i>Umschlag et al.</i> (2002)
Catechol	<chem>c1ccc(O)c1O</chem>	$5.6 \cdot 10^8$	$3.7 \cdot 10^{15}$	4691	<i>Barzaghi and Herrmann</i> (2004)
Hydroquinone	<chem>c1cc(O)ccc1O</chem>	$1.1 \cdot 10^9$			TROPOS measurements
Pyrogallol	<chem>Oc1c(O)ccc1O</chem>	$1.7 \cdot 10^9$	$6.9 \cdot 10^{10}$	1100	TROPOS measurements
o-Ethyl phenol	<chem>CCc1ccccc1O</chem>	$6.7 \cdot 10^8$	2165		<i>Barzaghi and Herrmann</i> (2004)
p-Ethyl phenol	<chem>c1cc(CC)ccc1O</chem>	$1.6 \cdot 10^9$	$4.6 \cdot 10^{11}$	1672	TROPOS measurements
p-Tert-butyl phenol	<chem>c1cc(O)ccc1C(C)(C)C</chem>	$1.1 \cdot 10^9$			TROPOS measurements
Benzyl alcohol	<chem>c1ccccc1CO</chem>	$4.5 \cdot 10^8$			<i>Ito et al.</i> (1989b) <sup>4</sup>
o-Cresol	<chem>c1(O)cccc1C</chem>	$8.5 \cdot 10^8$	$6.1 \cdot 10^{12}$	2646	<i>Barzaghi and Herrmann</i> (2004)
p-Cresol	<chem>c1cc(O)ccc1C</chem>	$1.7 \cdot 10^9$	$9.0 \cdot 10^{11}$	1756	TROPOS measurements
o-Nitro phenol	<chem>Oc1ccccc1N(=O)=O</chem>	$2.3 \cdot 10^7$			<i>Barzaghi and Herrmann</i> (2004)
p-Nitro phenol	<chem>c1cc(O)ccc1N(=O)=O</chem>	$1.4 \cdot 10^9$	$4.0 \cdot 10^{11}$	1684	TROPOS measurements
2,4-Dinitro phenol	<chem>Oc1ccc(N(=O)=O)cc1N(=O)=O</chem>	$5.3 \cdot 10^7$			<i>Umschlag et al.</i> (2002) <sup>6</sup>
2,6-Dinitro phenol	<chem>Oc1c(N(=O)=O)cccc1N(=O)=O</chem>	$2.8 \cdot 10^8$	$3.2 \cdot 10^{11}$	2165	TROPOS measurements
2-Nitro-4-methyl phenol	<chem>Oc1ccc(C)cc1N(=O)=O</chem>	$1.0 \cdot 10^8$			<i>Umschlag et al.</i> (2002)
2,6-Dinitro p-cresol	<chem>Oc1c(N(=O)=O)cc(C)cc1N(=O)=O</chem>	$1.4 \cdot 10^8$			<i>Umschlag et al.</i> (2002)
<b>Aromatic ketones</b>					n = 1
Phenyl acetone	<chem>c1ccccc1C(=O)C</chem>	$1.4 \cdot 10^7$			<i>Neta and Huie</i> (1986) <sup>4</sup>
<b>Aromatic acids</b>					n = 9
Benzoic acid	<chem>c1ccccc1C(=O)O</chem>	$6.5 \cdot 10^7$	$4.9 \cdot 10^9$	1300	<i>Umschlag et al.</i> (2002)
4-Hydroxy benzoic acid	<chem>c1cc(O)ccc1C(=O)O</chem>	$1.6 \cdot 10^9$	$3.2 \cdot 10^{11}$	1588	TROPOS measurements
4-Hydroxy benzoate	<chem>c1cc(O)ccc1C(=O)[O-]</chem>	$6.0 \cdot 10^9$			Anderson et al.,(1987) <sup>7</sup>
4-Methyl benzoic acid	<chem>c1cc(C)ccc1C(=O)O</chem>	$6.0 \cdot 10^8$	$1.6 \cdot 10^{12}$	2400	<i>Umschlag et al.</i> (2002)
3-Nitro benzoic acid	<chem>c1c(N(=O)=O)ccc1C(=O)O</chem>	$2.0 \cdot 10^7$			<i>Umschlag et al.</i> (2002)
4-Nitro benzoic acid	<chem>c1cc(N(=O)=O)ccc1C(=O)O</chem>	$2.0 \cdot 10^7$			<i>Umschlag et al.</i> (2002)
3-Nitro-4-methyl benzoate	<chem>c1cc(C)c(N(=O)=O)cc1C(=O)[O-]</chem>	$3.3 \cdot 10^7$			<i>Umschlag et al.</i> (2002)

**Table C.2 (continued)** Recommendations of evaluated aqueous phase rate constants of nitrate radicals with organic compounds.

Compound	SMILES string	$k_{298}^{(a)}$	$A^{(a)}$	$E_A/R^{(b)}$	Reference/Comment
Phenyl acetic acid	<chem>c1ccccc1CC(=O)O</chem>	$1.8 \cdot 10^9$			<i>Neta and Huie</i> (1986)
Phenyl acetate	<chem>c1ccccc1CC(=O)[O-]</chem>	$1.4 \cdot 10^8$			TROPOS measurements
<b>Anisoles, aromatic ethers and esters</b>					n = 15
Anisole	<chem>c1ccccc1OC</chem>	$1.0 \cdot 10^9$			<i>Herrmann et al.</i> (1995a)
m-Methyl anisole	<chem>c1c(C)cccc1OC</chem>	$2.0 \cdot 10^9$			TROPOS measurements
p-Methyl anisole	<chem>c1cc(C)ccc1OC</chem>	$3.2 \cdot 10^9$			TROPOS measurements
p-Dimethoxy benzol	<chem>c1cc(OC)ccc1OC</chem>	$1.2 \cdot 10^9$	$7.8 \cdot 10^9$	500	TROPOS measurements
o-Methoxy phenol	<chem>Oc1ccccc1OC</chem>	$1.1 \cdot 10^8$	$2.7 \cdot 10^{12}$	3007	<i>Barzaghi and Herrmann</i> (2004)
p-Methoxy phenol	<chem>c1cc(O)ccc1OC</chem>	$2.8 \cdot 10^9$	$1.8 \cdot 10^{10}$	698	TROPOS measurements
2,6-Dimethoxy phenol	<chem>c1(OC)cccc(OC)c1O</chem>	$1.6 \cdot 10^9$	$1.0 \cdot 10^{12}$	1924	TROPOS measurements
3-Methoxy-4-hydroxy benzaldehyde	<chem>c1c(OC)c(O)ccc1C=O</chem>	$1.1 \cdot 10^9$	$7.8 \cdot 10^{11}$	1924	TROPOS measurements
2,4-Dimethoxy-3-hydroxy benzaldehyde	<chem>c1c(OC)c(O)c(OC)cc1C=O</chem>	$1.7 \cdot 10^9$	$2.8 \cdot 10^{12}$	2165	TROPOS measurements
4-Methoxy benzoic acid	<chem>c1cc(OC)ccc1C(=O)O</chem>	$6.9 \cdot 10^8$			<i>Umschlag et al.</i> (2002)
4-Methoxy benzoate	<chem>c1cc(OC)ccc1C(=O)[O-]</chem>	$8.0 \cdot 10^9$			<i>O'Neill et al.</i> (1977) <sup>7</sup>
3-Hydroxy-4-methoxy benzoic acid	<chem>c1c(O)c(OC)ccc1C(=O)O</chem>	$1.0 \cdot 10^9$			TROPOS measurements
3-Methoxy-4-hydroxy benzoic acid	<chem>c1c(OC)c(O)ccc1C(=O)O</chem>	$1.0 \cdot 10^9$	$3.8 \cdot 10^{11}$	1804	TROPOS measurements
3,5-Dimethoxy-4-hydroxy benzoic acid	<chem>c1c(OC)c(O)c(OC)cc1C(=O)O</chem>	$1.4 \cdot 10^9$	$2.8 \cdot 10^{12}$	2285	TROPOS measurements
4-Hydroxyphenyl ethyl ether	<chem>c1cc(O)ccc1OCC</chem>	$8.0 \cdot 10^8$			<i>Barzaghi and Herrmann</i> (2004)
<b>Sugars</b>					n = 4
Erythritol	<chem>OCC(O)C(O)CO</chem>	$1.4 \cdot 10^7$	$3.4 \cdot 10^{10}$	2321	<i>Hoffmann et al.</i> (2009)
Arabitol	<chem>OCC(O)C(O)C(O)CO</chem>	$1.5 \cdot 10^7$	$1.1 \cdot 10^{10}$	1997	<i>Hoffmann et al.</i> (2009)
Mannitol	<chem>OCC(O)C(O)C(O)C(O)CO</chem>	$1.4 \cdot 10^7$	$5.1 \cdot 10^{10}$	2466	<i>Hoffmann et al.</i> (2009)
Levogluconan	<chem>OC1C(O)C(O)C2OC1OC2</chem>	$1.6 \cdot 10^7$	$2.5 \cdot 10^{10}$	2150	TROPOS measurements

**Table C.2 (continued)** Recommendations of evaluated aqueous phase rate constants of nitrate radicals with organic compounds.

Compound	SMILES string	$k_{298}^{(a)}$	$A^{(a)}$	$E_A/R^{(b)}$	Reference/Comment
<b>Polycyclic aromatic compounds</b>					n = 2
2-Phenylphenol	<chem>c1ccccc1c2ccccc2O</chem>	$2.4 \cdot 10^8$			<i>Barzaghi and Herrmann</i> (2004)
Naphthalene	<chem>c1cccc2ccccc12</chem>	$1.7 \cdot 10^9$			TROPOS measurements

<sup>(a)</sup>in  $\text{M}^{-1} \text{s}^{-1}$ ; <sup>(b)</sup>in K

<sup>1</sup>as given in *Wayne et al.* (1991); <sup>2</sup>as given in *Toyota et al.* (2004); <sup>3</sup>as given in CAPRAM database available at <http://projects.tropos.de/capram/>; <sup>4</sup>as given in NIST database (*Ross et al.*, 1998); <sup>5</sup>as given in *de Semainville et al.* (2007b); <sup>6</sup>as given in *Herrmann* (2003); <sup>7</sup>as given in *Barzaghi and Herrmann* (2004)



# D Detailed information about the evaluation of prediction methods

## D.1 Rate data used for the derivation and evaluation of gas-aqueous phase correlations

**Table D.1** Compilation of gas and aqueous phase rate constants used for the derivation and evaluation of gas-aqueous phase correlations.

Compound	Chemical formula	$k_{298(g)}$ [cm <sup>3</sup> s <sup>-1</sup> ]	$k_{298(aq)}^a$ [M <sup>-1</sup> s <sup>-1</sup> ]
Methane	CH <sub>4</sub>	$6.4 \cdot 10^{-15}^b$	$3.9 \cdot 10^6$
Ethane	CH <sub>3</sub> CH <sub>3</sub>	$2.4 \cdot 10^{-13}^b$	$1.4 \cdot 10^8$
Propane	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	$1.1 \cdot 10^{-12}^b$	$2.3 \cdot 10^9$
Butane	CH <sub>3</sub> [CH <sub>2</sub> ] <sub>2</sub> CH <sub>3</sub>	$2.3 \cdot 10^{-12}^b$	$2.9 \cdot 10^9$
Pentane	CH <sub>3</sub> [CH <sub>2</sub> ] <sub>3</sub> CH <sub>3</sub>	$3.8 \cdot 10^{-12}^c$	$5.4 \cdot 10^9$
Hexane	CH <sub>3</sub> [CH <sub>2</sub> ] <sub>4</sub> CH <sub>3</sub>	$5.2 \cdot 10^{-12}^c$	$6.6 \cdot 10^9$
Heptane	CH <sub>3</sub> [CH <sub>2</sub> ] <sub>5</sub> CH <sub>3</sub>	$6.8 \cdot 10^{-12}^c$	$7.7 \cdot 10^9$
Octane	CH <sub>3</sub> [CH <sub>2</sub> ] <sub>6</sub> CH <sub>3</sub>	$8.1 \cdot 10^{-12}^c$	$9.1 \cdot 10^9$
iso-butane	CH(CH <sub>3</sub> ) <sub>3</sub>	$2.1 \cdot 10^{-12}^c$	$4.6 \cdot 10^9$
2-methyl butane	CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>3</sub>	$3.6 \cdot 10^{-12}^c$	$5.2 \cdot 10^9$
2,2,4-trimethyl pentane	CH <sub>3</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>3</sub>	$3.3 \cdot 10^{-12}^c$	$6.1 \cdot 10^9$
Ethylene	C <sub>d</sub> H <sub>2</sub> =C <sub>d</sub> H <sub>2</sub>	$7.9 \cdot 10^{-12}^b$	$3.1 \cdot 10^9$
Propylene	CH <sub>3</sub> C <sub>d</sub> H=C <sub>d</sub> H <sub>2</sub>	$2.9 \cdot 10^{-11}^b$	$7.0 \cdot 10^9$
1-butylene	CH <sub>3</sub> CH <sub>2</sub> C <sub>d</sub> H=C <sub>d</sub> H <sub>2</sub>	$3.1 \cdot 10^{-11}^c$	$7.0 \cdot 10^9$
Butadien	C <sub>d</sub> H <sub>2</sub> =C <sub>d</sub> HC <sub>d</sub> H=C <sub>d</sub> H <sub>2</sub>	$6.7 \cdot 10^{-11}^c$	$7.0 \cdot 10^9$
Isobutylene	C <sub>d</sub> H <sub>2</sub> =C <sub>d</sub> (CH <sub>3</sub> ) <sub>2</sub>	$5.1 \cdot 10^{-11}^c$	$5.4 \cdot 10^9$
Acetylene	C <sub>t</sub> H≡C <sub>t</sub> H	$7.8 \cdot 10^{-13}^b$	$4.7 \cdot 10^9$
Methanol	CH <sub>3</sub> OH	$9.0 \cdot 10^{-13}^b$	$1.0 \cdot 10^9$
Ethanol	CH <sub>3</sub> CH <sub>2</sub> OH	$3.2 \cdot 10^{-12}^b$	$2.1 \cdot 10^9$
Propanol	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	$5.8 \cdot 10^{-12}^b$	$3.2 \cdot 10^9$
Butanol	CH <sub>3</sub> [CH <sub>2</sub> ] <sub>2</sub> CH <sub>2</sub> OH	$8.5 \cdot 10^{-12}^b$	$4.1 \cdot 10^9$
Pentanol	CH <sub>3</sub> [CH <sub>2</sub> ] <sub>3</sub> CH <sub>2</sub> OH	$1.1 \cdot 10^{-11}^c$	$5.0 \cdot 10^9$
Hexanol	CH <sub>3</sub> [CH <sub>2</sub> ] <sub>4</sub> CH <sub>2</sub> OH	$1.5 \cdot 10^{-11}^c$	$7.0 \cdot 10^9$
Heptanol	CH <sub>3</sub> [CH <sub>2</sub> ] <sub>5</sub> CH <sub>2</sub> OH	$1.4 \cdot 10^{-11}^c$	$7.4 \cdot 10^9$
Octanol	CH <sub>3</sub> [CH <sub>2</sub> ] <sub>6</sub> CH <sub>2</sub> OH	$1.4 \cdot 10^{-11}^c$	$7.7 \cdot 10^9$
iso-propanol	(CH <sub>3</sub> ) <sub>2</sub> CHOH	$5.1 \cdot 10^{-12}^b$	$2.1 \cdot 10^9$
2-butanol	CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH <sub>3</sub>	$8.7 \cdot 10^{-12}^b$	$3.5 \cdot 10^9$
tert-butanol	(CH <sub>3</sub> ) <sub>3</sub> COH	$1.1 \cdot 10^{-12}^c$	$5.7 \cdot 10^9$
3-pentanol	CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH <sub>2</sub> CH <sub>3</sub>	$1.3 \cdot 10^{-11}^c$	$2.1 \cdot 10^9$
Ethylene glycol	CH <sub>2</sub> (OH)CH <sub>2</sub> OH	$7.7 \cdot 10^{-12}^d$	$1.7 \cdot 10^9$

**Table D.1 (continued)** Compilation of gas and aqueous phase rate constants used for the derivation and evaluation of gas-aqueous phase correlations.

Compound	Chemical formula	$k_{298(g)}$ [cm <sup>3</sup> s <sup>-1</sup> ]	$k_{298(aq)}^a$ [M <sup>-1</sup> s <sup>-1</sup> ]
1,2-propanediol	CH <sub>3</sub> CH <sub>2</sub> (OH)CH <sub>2</sub> OH	$1.2 \cdot 10^{-11} \text{ }^d$	$1.7 \cdot 10^9$
Formaldehyde	HCH=O	$8.5 \cdot 10^{-12} \text{ }^b$	$1.0 \cdot 10^9$
Acetaldehyde	CH <sub>3</sub> CH=O	$1.5 \cdot 10^{-11} \text{ }^b$	$3.6 \cdot 10^9$
Propionaldehyde	CH <sub>3</sub> CH <sub>2</sub> CH=O	$2.0 \cdot 10^{-11} \text{ }^b$	$2.8 \cdot 10^9$
Butyraldehyde	CH <sub>3</sub> [CH <sub>2</sub> ] <sub>2</sub> CH=O	$2.4 \cdot 10^{-11} \text{ }^b$	$3.9 \cdot 10^9$
Valeraldehyde	CH <sub>3</sub> [CH <sub>2</sub> ] <sub>3</sub> CH=O	$2.8 \cdot 10^{-11} \text{ }^c$	$3.9 \cdot 10^9$
Isobutyraldehyde	(CH <sub>3</sub> ) <sub>2</sub> CHCH=O	$2.6 \cdot 10^{-11} \text{ }^c$	$2.9 \cdot 10^9$
Acrolein	C <sub>d</sub> H <sub>2</sub> =C <sub>d</sub> HCH=O	$2.0 \cdot 10^{-11} \text{ }^e$	$7.0 \cdot 10^9$
Methacrolein	C <sub>d</sub> H <sub>2</sub> =C <sub>d</sub> (CH <sub>3</sub> )CH=O	$2.9 \cdot 10^{-11} \text{ }^b$	$1.4 \cdot 10^{10}$
Crotonaldehyde	CH <sub>3</sub> C <sub>d</sub> H=C <sub>d</sub> HCH=O	$3.5 \cdot 10^{-11} \text{ }^e$	$5.8 \cdot 10^9$
Acetone	CH <sub>3</sub> C(=O)CH <sub>3</sub>	$1.8 \cdot 10^{-13} \text{ }^b$	$1.7 \cdot 10^8$
Hydroxy acetone	CH <sub>3</sub> C(=O)CH <sub>2</sub> OH	$3.0 \cdot 10^{-12} \text{ }^b$	$1.2 \cdot 10^9$
Methyl ethyl ketone	CH <sub>3</sub> CH <sub>2</sub> C(=O)CH <sub>3</sub>	$1.2 \cdot 10^{-12} \text{ }^b$	$1.3 \cdot 10^9$
2-pentanone	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> C(=O)CH <sub>3</sub>	$4.4 \cdot 10^{-12} \text{ }^c$	$1.9 \cdot 10^9$
Diethyl ketone	CH <sub>3</sub> CH <sub>2</sub> C(=O)CH <sub>2</sub> CH <sub>3</sub>	$2.0 \cdot 10^{-12} \text{ }^c$	$1.4 \cdot 10^9$
Methyl vinyl ketone	CH <sub>3</sub> C(=O)C <sub>d</sub> H=C <sub>d</sub> H <sub>2</sub>	$2.0 \cdot 10^{-11} \text{ }^b$	$7.4 \cdot 10^9$
Methyl iso-butyl ketone	CH <sub>3</sub> C(=O)CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	$1.3 \cdot 10^{-11} \text{ }^c$	$3.4 \cdot 10^9$
Glyoxal	O=CHCH=O	$1.1 \cdot 10^{-11} \text{ }^b$	$6.6 \cdot 10^7$
Methylglyoxal	CH <sub>3</sub> C(=O)CH=O	$1.5 \cdot 10^{-11} \text{ }^b$	$8.6 \cdot 10^8$
Diacetyl	CH <sub>3</sub> C(=O)C(=O)CH <sub>3</sub>	$2.4 \cdot 10^{-13} \text{ }^d$	$2.8 \cdot 10^8$
Acetylacetone	CH <sub>3</sub> C(=O)CH <sub>2</sub> C(=O)CH <sub>3</sub>	$1.2 \cdot 10^{-11} \text{ }^d$	$9.9 \cdot 10^9$
Acetonyl acetone	CH <sub>3</sub> C(=O)CH <sub>2</sub> CH <sub>2</sub> C(=O)CH <sub>3</sub>	$6.8 \cdot 10^{-13} \text{ }^d$	$7.6 \cdot 10^{89}$
Formic acid	HC(=O)OH	$4.5 \cdot 10^{-13} \text{ }^b$	$1.3 \cdot 10^8$
Acetic acid	CH <sub>3</sub> C(=O)OH	$7.4 \cdot 10^{-13} \text{ }^b$	$1.7 \cdot 10^7$
Propionic acid	CH <sub>3</sub> CH <sub>2</sub> C(=O)OH	$1.2 \cdot 10^{-12} \text{ }^b$	$3.2 \cdot 10^8$
Dimethyl ether	CH <sub>3</sub> -O-CH <sub>3</sub>	$2.8 \cdot 10^{-12} \text{ }^b$	$1.0 \cdot 10^9$
Diethyl ether	CH <sub>3</sub> CH <sub>2</sub> -O-CH <sub>2</sub> CH <sub>3</sub>	$1.3 \cdot 10^{-11} \text{ }^c$	$3.6 \cdot 10^9$
Methylal	CH <sub>3</sub> -O-CH <sub>2</sub> -O-CH <sub>3</sub>	$4.9 \cdot 10^{-12} \text{ }^f$	$1.2 \cdot 10^9$
Diethoxy methane	CH <sub>3</sub> CH <sub>2</sub> -O-CH <sub>2</sub> -O-CH <sub>2</sub> CH <sub>3</sub>	$1.8 \cdot 10^{-11} \text{ }^g$	$1.6 \cdot 10^9$
Ethylene glycol methyl ether	CH <sub>3</sub> -O-CH <sub>2</sub> CH <sub>2</sub> OH	$1.3 \cdot 10^{-11} \text{ }^f$	$1.3 \cdot 10^9$
Ethylene glycol ethyl ether	CH <sub>3</sub> CH <sub>2</sub> -O-CH <sub>2</sub> CH <sub>2</sub> OH	$1.9 \cdot 10^{-11} \text{ }^f$	$1.7 \cdot 10^9$
Ethylene glycol butyl ether	CH <sub>3</sub> [CH <sub>2</sub> ] <sub>3</sub> -O-CH <sub>2</sub> CH <sub>2</sub> OH	$2.6 \cdot 10^{-11} \text{ }^f$	$5.1 \cdot 10^9$
Methyl tert-butyl ether	CH <sub>3</sub> -O-C(CH <sub>3</sub> ) <sub>3</sub>	$3.2 \cdot 10^{-12} \text{ }^h$	$2.1 \cdot 10^9$
Ethyl tert-butyl ether	CH <sub>3</sub> CH <sub>2</sub> -O-C(CH <sub>3</sub> ) <sub>3</sub>	$8.9 \cdot 10^{-12} \text{ }^h$	$1.5 \cdot 10^9$
Di-iso-propyl ether	(CH <sub>3</sub> ) <sub>2</sub> CH-O-CH(CH <sub>3</sub> ) <sub>2</sub>	$1.0 \cdot 10^{-11} \text{ }^i$	$2.5 \cdot 10^9$
Di-tert-butyl ether	(CH <sub>3</sub> ) <sub>3</sub> C-O-C(CH <sub>3</sub> ) <sub>3</sub>	$3.9 \cdot 10^{-12} \text{ }^j$	$1.8 \cdot 10^9$
Ethyl formate	CH <sub>3</sub> CH <sub>2</sub> -O-CH=O	$1.0 \cdot 10^{-12} \text{ }^f$	$7.9 \cdot 10^8$
Butyl formate	CH <sub>3</sub> [CH <sub>2</sub> ] <sub>3</sub> -O-CH=O	$3.1 \cdot 10^{-12} \text{ }^f$	$2.8 \cdot 10^9$
tert-butyl formate	(CH <sub>3</sub> ) <sub>3</sub> C-O-CH=O	$7.5 \cdot 10^{-13} \text{ }^k$	$7.0 \cdot 10^8$
Methyl acetate	CH <sub>3</sub> C(=O)-O-CH <sub>3</sub>	$3.4 \cdot 10^{-13} \text{ }^l$	$1.5 \cdot 10^8$
Methyl propionate	CH <sub>3</sub> CH <sub>2</sub> C(=O)-O-CH <sub>3</sub>	$1.0 \cdot 10^{-12} \text{ }^f$	$4.5 \cdot 10^8$
Ethyl acetate	CH <sub>3</sub> CH <sub>2</sub> -O-C(=O)CH <sub>3</sub>	$1.6 \cdot 10^{-12} \text{ }^f$	$4.0 \cdot 10^8$
Ethyl propionate	CH <sub>3</sub> CH <sub>2</sub> C(=O)-O-CH <sub>2</sub> CH <sub>3</sub>	$2.14 \cdot 10^{-12} \text{ }^m$	$5.2 \cdot 10^8$
Propyl acetate	CH <sub>3</sub> [CH <sub>2</sub> ] <sub>2</sub> -O-C(=O)CH <sub>3</sub>	$3.6 \cdot 10^{-12} \text{ }^l$	$1.4 \cdot 10^9$
Methyl butyrate	CH <sub>3</sub> [CH <sub>2</sub> ] <sub>2</sub> C(=O)-O-CH <sub>3</sub>	$3.4 \cdot 10^{-12} \text{ }^n$	$1.7 \cdot 10^9$
Butyl acetate	CH <sub>3</sub> [CH <sub>2</sub> ] <sub>3</sub> -O-C(=O)CH <sub>3</sub>	$5.7 \cdot 10^{-12} \text{ }^l$	$1.8 \cdot 10^9$
Ethyl butyrate	CH <sub>3</sub> [CH <sub>2</sub> ] <sub>2</sub> C(=O)-O-CH <sub>2</sub> CH <sub>3</sub>	$4.4 \cdot 10^{-12} \text{ }^o$	$1.6 \cdot 10^9$
iso-propyl acetate	(CH <sub>3</sub> ) <sub>2</sub> CH-O-C(=O)CH <sub>3</sub>	$4.0 \cdot 10^{-12} \text{ }^p$	$5.3 \cdot 10^8$

**Table D.1 (continued)** Compilation of gas and aqueous phase rate constants used for the derivation and evaluation of gas-aqueous phase correlations.

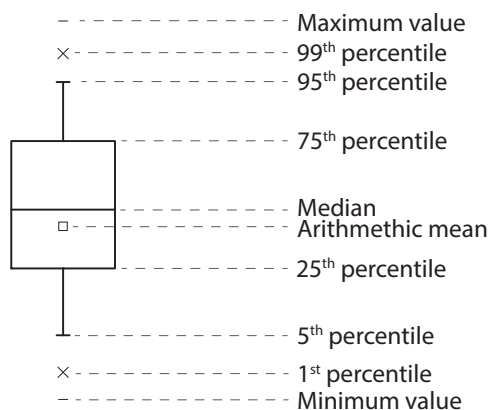
Compound	Chemical formula	$k_{298(g)}$ [cm <sup>3</sup> s <sup>-1</sup> ]	$k_{298(aq)}^a$ [M <sup>-1</sup> s <sup>-1</sup> ]
Dimethyl succinate	CH <sub>3</sub> –O–C(=O)[CH <sub>2</sub> ] <sub>2</sub> C(=O)–O–CH <sub>3</sub>	$1.5 \cdot 10^{-12}$ <sup>f</sup>	$5.3 \cdot 10^8$

<sup>a</sup>taken from the kinetic database (see Table C.1); <sup>b</sup>Atkinson *et al.* (2006); <sup>c</sup>Atkinson and Arey (2003); <sup>d</sup>Atkinson (1989); <sup>e</sup>Magneron *et al.* (2002); <sup>f</sup>Carter (2010a); <sup>g</sup>Thüner *et al.* (1999); <sup>h</sup>Teton *et al.* (1996); <sup>i</sup>Mellouki *et al.* (1995); <sup>j</sup>mean of Nielsen *et al.* (1995) and Langer *et al.* (1996); <sup>k</sup>Le Calvé *et al.* (1997c); <sup>l</sup>El Boudali *et al.* (1996); <sup>m</sup>Wallington *et al.* (1988); <sup>n</sup>Le Calvé *et al.* (1997a); <sup>o</sup>Ferrari *et al.* (1996); <sup>p</sup>Le Calvé *et al.* (1997b)

## D.2 Explanation of the use of box plots

Box plots are used for the statistical analysis of datasets. They directly provide an overview over the scatter of the data by showing the percentages of a dataset related to specific values within this data. In box plots, the median, quartiles and further percentiles as well as the arithmetic mean are illustrated as shown in Figure D.1. The box plots as used in this dissertation do not illustrate outliers as a clear definition is missing, when a value should be counted as outlier. As shown in Figure D.1, information about the 1<sup>st</sup>, 5<sup>th</sup>, 95<sup>th</sup>, and 99<sup>th</sup> percentile, the upper and lower quartile, the median, and the arithmetic mean is provided.

Box plots are used to assess the quality of a given prediction method. Therefore, the absolute error  $\Delta x$  is derived by subtraction of the predicted values from the experimental values. For convenience, the logarithmised rate constants are used. Analysing the logarithmised absolute errors with box plots allows conclusions about the quality of the prediction methods as in these graphics the percentages predicted within a certain error are directly shown. The analysis can be performed for certain subsets such as the evaluation of the predicted data for every compound class separately or for the overall dataset.

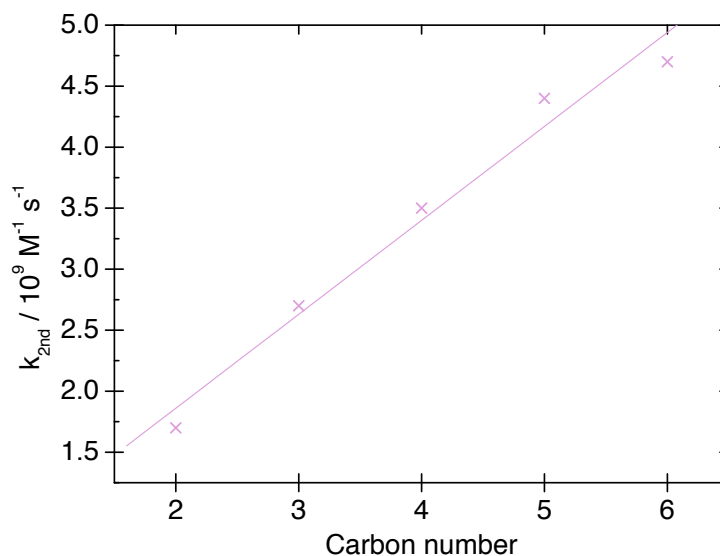
**Figure D.1** Explanation of box plots as used in this dissertation.

### D.3 Additional correlations of homologous series of various compound classes

For completeness, the correlation of terminal diols versus the carbon number is given in Figure D.2. A discussion of the correlation method, their strengths and weaknesses can be found in subsection 2.4.1 and section 3.3 of the main part. No correlation is given for carbonyl compounds. A reliable correlation could not be derived, which is partly due to the very limited number of available experimental values.

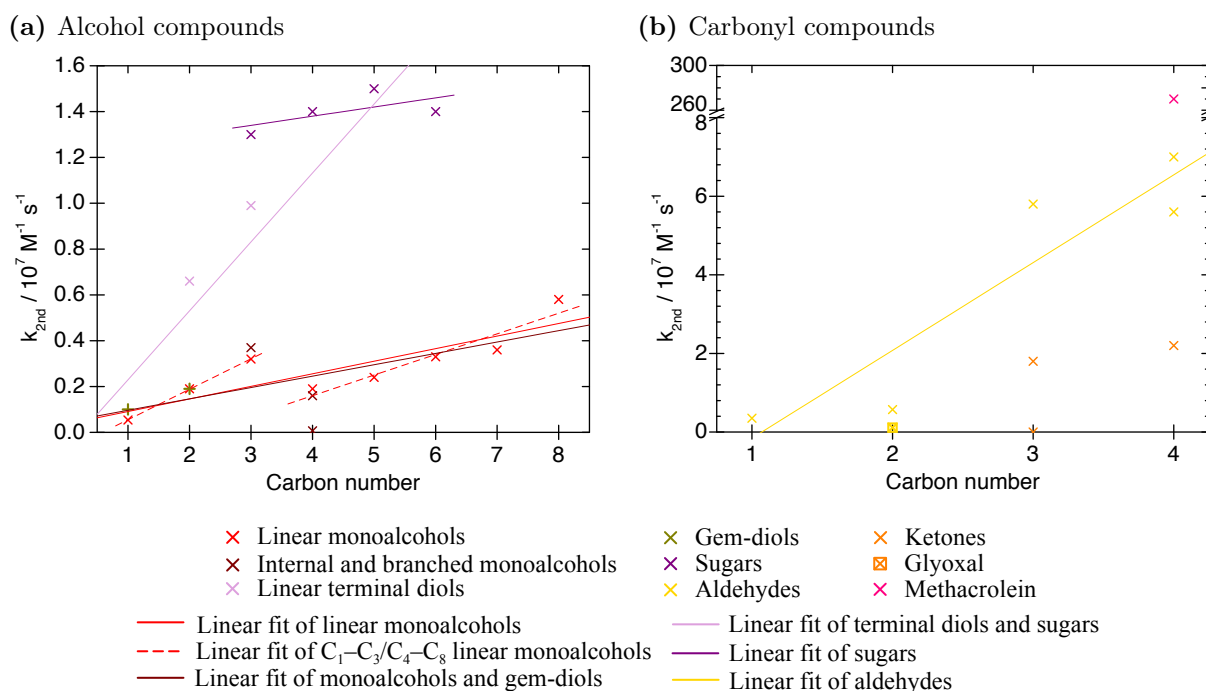
In the following, a detailed discussion of the correlation of nitrate radical reactions with homologous series of various compound classes is given. As it is not recommended to use these correlations for reliable rate constant predictions, the description was moved to the Appendix.

From Figure D.3, the restrictions of the method become obvious, especially, when the experimental dataset used to derive the correlations is small. A different behaviour can be seen for monoalcohols and gem-diols compared to linear terminal diols and sugars. Figure D.3a shows that di- and polyols (except gem-diols) react faster than the other alcohols. Moreover, different correlations are obtained whether only sugars are correlated to the carbon number or terminal diols are included in the correlation. Sugars have typical reaction rate constants around  $1.4 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1}$  while the other diols react slower. There is only a slight increase in the reaction rate constants of sugars with the carbon number, which is in the range of the errors of the measurements from the kinetic experiments. From the small dataset it cannot be verified whether all reaction rate constants of sugars are similar or the larger increase in the rate constants with increasing carbon numbers from the overall correlation of all di- and polyols is true.



**Figure D.2** Correlation of hydroxyl radical reactions with terminal diols and the carbon number. The respective equations for the regression lines can be found in Table 3.2 in section 3.3.





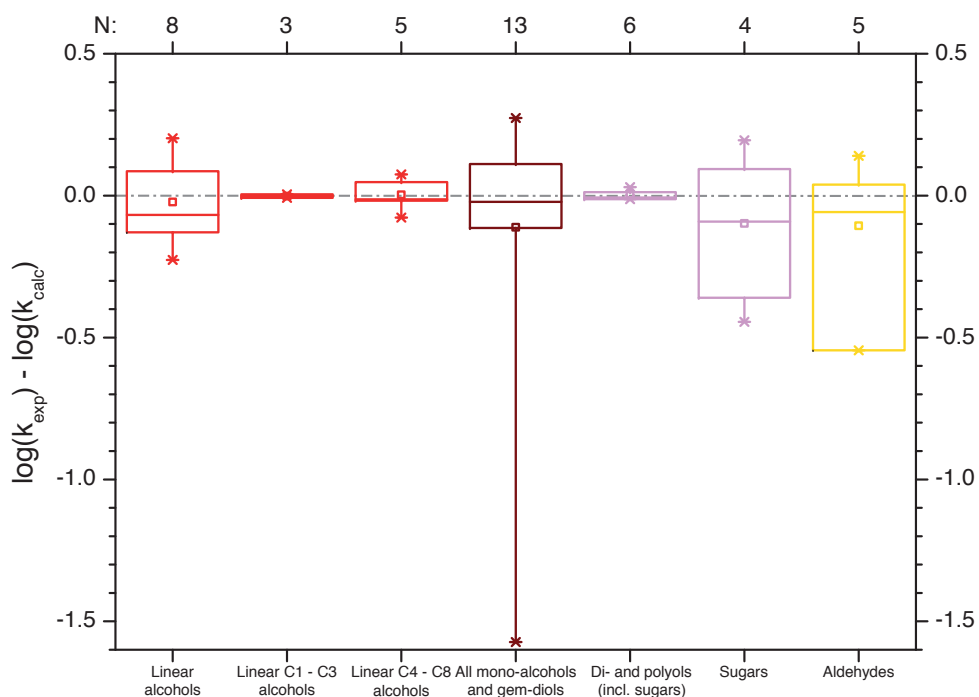
**Figure D.3** Correlation of nitrate radical reactions with the respective compound classes versus the carbon number. Parameters of the respective regression equations and further statistical information can be found in Table D.2.

Branching in monoalcohols seems to have only a small influence on the rate constants of the reactions with the nitrate radical (see Figure D.3a) in contrast to the reactions of alkanes with OH radicals. Moreover, gem-diols seem to follow the same regression line as monoalcohols rather than the regression of the other diols or sugars. A larger dataset is desirable to evaluate this behaviour. From the few data points it cannot be assessed whether this is a coincidence or a general trend. Therefore, it is not recommended to use either of the correlations for automated mechanism construction. The correlations should rather be viewed as a ‘first guess’ to estimate the appropriate order of magnitude for a certain rate constant. Figure D.3b shows the data for the correlation of nitrate radical reactions with carbonyl compounds. The data is too scattered to derive a general regression

**Table D.2** Parameters for the regression equations  $k_{2nd}/\text{M}^{-1}\text{s}^{-1} = A \cdot CN + B$  ( $CN$  = carbon number) and statistical data derived from the correlation of nitrate radical reactions with organic compounds plotted against the carbon number of the various organic compounds.

Compound class	$10^{-6}A^{(a)}$	$10^{-6}B^{(a)}$	$R^2$	$10^{-6}\sigma^{(a)}$	$N$
Linear monoalcohols	$0.55 \pm 0.13$	$0.36 \pm 0.66$	0.748	0.8	8
– C1 – C3	$1.33 \pm 0.02$	$0.78 \pm 0.04$	1.000	0.02	3
– C4 – C8	$0.90 \pm 0.18$	$2.0 \pm 1.1$	0.894	0.6	5
Linear monoalcohols (substituted and unsubstituted) and gem-diols	$0.50 \pm 0.15$	$0.47 \pm 0.66$	0.501	1.1	13
Terminal diols and sugars	$3.0 \pm 0.9$	$0.71 \pm 3.42$	0.746	3.7	6
– Sugars	$0.40 \pm 0.35$	$12 \pm 2$	0.400	0.8	4
Aldehydes	$22 \pm 5$	$24 \pm 16$	0.853	14.	5

<sup>(a)</sup>in  $\text{M}^{-1}\text{s}^{-1}$



**Figure D.4** Box plots (as described in Appendix D.2) of the absolute errors of the correlation of nitrate radical reactions with organic compounds versus the carbon number.

line, however, for linear aldehydes a correlation with an appreciable correlation coefficient  $R^2$  of 0.853 could be obtained (see Table D.2).

The box plot (Figure D.4) confirms the assertion that the method is able to predict at least the correct order of magnitude of the reaction rate constant. However, it should be noted again that the dataset to derive the correlations was very small. Moreover, the same data has been used to derive the correlation and assess its accuracy. No different test set was used. Therefore, constraints of the method remain.

## D.4 Additional information of Evans-Polanyi-type correlations

For a better interpretation of the results from the evaluation process the predicted data has been plotted against the experimental data. It is shown in the main part in Figure 3.9 on page 54. For a thorough interpretation, additional statistical information is needed as described in section 3.5. Therefore, in Table D.3 the parameters of the regression equations, the correlation coefficients, standard deviations and number of data points are given.

**Table D.3** Parameters for the regression equations  $k_{calc}/\text{M}^{-1}\text{s}^{-1} = A \cdot (k_{exp}/\text{M}^{-1}\text{s}^{-1}) + B$  and statistical data derived from the evaluation process of the Evans-Polanyi-type correlations of aqueous phase hydroxyl radical reactions with organic compounds for the various compound classes.

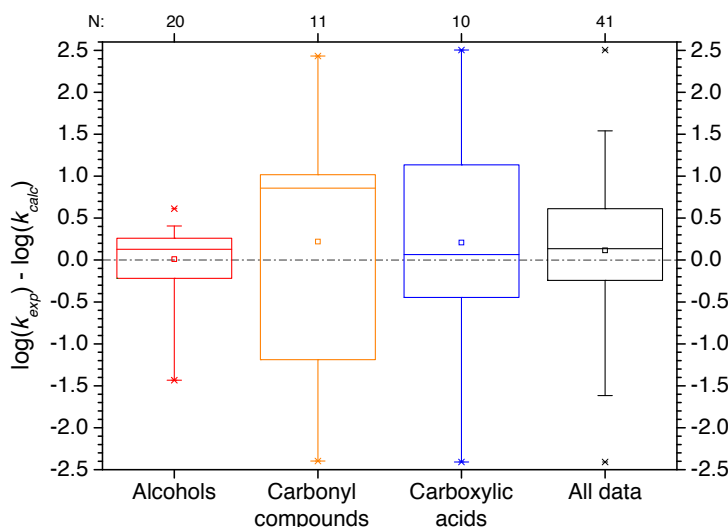
Compound class	$A$	$10^{-9}B^{(a)}$	$R^2$	$10^{-9}\sigma^{(a)}$	$N$
Alkanes	$1.03 \pm 0.41$	$0.15 \pm 2.3$	0.418	3.0	11
Linear terminal monoalcohols	$0.33 \pm 0.16$	$2.60 \pm 0.8$	0.411	1.1	8
All monoalcohols	$-(0.11 \pm 0.12)$	$4.08 \pm 0.5$	0.054	1.1	16
Diols and sugars	$0.13 \pm 0.29$	$2.17 \pm 0.7$	0.011	1.4	19
Carbonyls (without glyoxal and formaldehyde)	$0.01 \pm 0.13$	$2.02 \pm 0.4$	0.001	1.2	18
Monocarboxylic acids	$0.24 \pm 0.26$	$0.40 \pm 0.2$	0.091	0.5	11
Unsubstituted dicarboxylic acids	$0.08 \pm 0.14$	$1.12 \pm 0.5$	0.041	1.1	9
All dicarboxylic acids	$0.11 \pm 0.16$	$1.16 \pm 0.4$	0.026	1.3	19

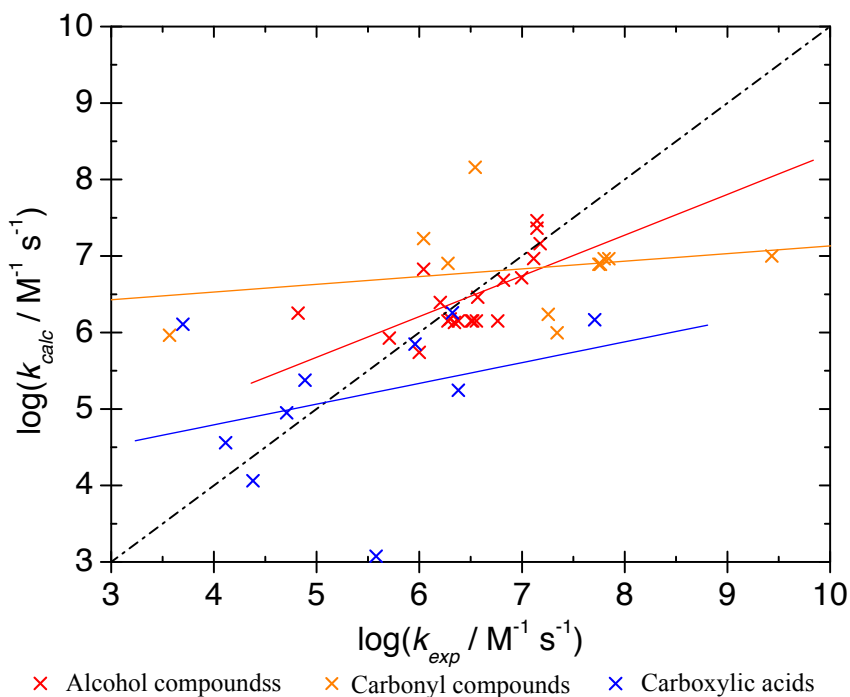
<sup>(a)</sup>in  $\text{M}^{-1}\text{s}^{-1}$ 

Due to the similarity of the Evans-Polanyi-type correlations of the nitrate radical with the hydroxyl radical correlations and to increase the clarity of the main part as well as reduce size of the main part, the plots of the evaluation of  $\text{NO}_3$  radical reactions and tables with supporting information have been moved to the Appendix and are given in the following (Table D.4, Figure D.5 and D.6).

**Table D.4** Parameters for the regression equations  $\log(k_H/\text{M}^{-1}\text{s}^{-1}) = A \cdot (BDE/\text{kJ mol}^{-1}) + B$  and statistical data derived from the Evans-Polanyi-type correlations of aqueous phase nitrate radical reactions with organic compounds for the various compound classes.

Compound class	$A / \text{mol kJ}^{-1}$	$B$	$R^2$	$\sigma$	$N$
Alcohols	$0.53 \pm 0.15$	$3.01 \pm 1.0$	0.397	0.4	20
Carbonyl compounds	$0.10 \pm 0.13$	$6.13 \pm 1.0$	0.059	0.6	11
Carboxylic acids	$0.27 \pm 0.28$	$3.71 \pm 1.5$	0.106	1.0	10

**Figure D.5** Box plots (as described in the text) of the absolute errors of the Evans-Polanyi-type correlation of nitrate radical reactions with the respective compound classes.



**Figure D.6** Scatter plot of predicted versus experimental data for the evaluation of Evans-Polanyi-type correlations for nitrate radical reactions separated by compound class together with the linear regression lines. For the calculation of the predicted values the regression lines of Table 3.4 together with the data from the kinetic database have been used. The regression lines have the same colour code as the data points. The black dashed-dotted line is the line of same reactivity. Parameters of the respective regression equations and further statistical information can be found in Table D.3.

The following tables list parameters and statistical information concerning the improved Evans-Polanyi-type correlations. In Table D.5 the predicted data is compared to the experimental data for hydroxyl radical reactions with organic compounds of the respective compound class. Table D.6 lists the parameters for the quadratic regression equations and further statistical data for nitrate radical reactions with organic compounds of the respective compound classes predicted with the improved Evans-Polanyi-type correlations. Differences in the errors are small compared to linear regressions, except for di- and polyols, where  $R^2$  is significantly higher with 0.80 compared to 0.61 for the linear regression (see also

**Table D.5** Parameters for the regression equations  $k_{calc}/M^{-1}s^{-1} = A \cdot (k_{exp}/M^{-1}s^{-1}) + B$  and statistical data derived from the evaluation process of the improved Evans-Polanyi-type correlations of aqueous phase hydroxyl radical reactions with organic compounds for the various compound classes.

Compound class	$A$	$10^{-8}B^{(a)}$	$R^2$	$10^{-8}\sigma^{(a)}$	$N$
Alkanes	$0.83 \pm 0.12$	$7.66 \pm 6.73$	0.844	8.7	11
Linear terminal monoalcohols	$0.99 \pm 0.05$	$0.52 \pm 2.48$	0.987	3.2	8
All other alcohols	$0.16 \pm 0.08$	$18.97 \pm 2.02$	0.150	4.8	27
Monoaldehydes	$0.76 \pm 0.25$	$6.73 \pm 7.54$	0.655	5.8	7
Ketones (excl. acetylacetone)	$0.54 \pm 0.16$	$5.94 \pm 2.57$	0.532	5.6	12
(Ketones incl. acetylacetone)	$0.08 \pm 0.08$	$11.16 \pm 2.59$	0.085	7.4	13)
Carboxylic acids	$0.89 \pm 0.06$	$-(0.27 \pm 1.26)$	0.892	5.3	31

<sup>(a)</sup>in  $M^{-1}s^{-1}$

**Table D.6** Parameters for the regression equations  $\log(k_{exp}/M^{-1}s^{-1}) = A \cdot (\Sigma BDE/kJ mol^{-1})^2 + B \cdot (\Sigma BDE/kJ mol^{-1}) + C$  and statistical data derived from the improved Evans-Polanyi-type correlations of aqueous phase nitrate radical reactions with organic compounds for the various compound classes.

Compound class	$10^8 A/mol^2 kJ^{-2}$	$10^4 B/mol kJ^{-1}$	$C$	$R^2$	$\sigma$	$N$
Monoalcohols <sup>(a)</sup> and gem-diols	$-(1.85 \pm 1.6)$	$2.77 \pm 1.4$	$5.59 \pm 0.27$	0.639	0.18	15
Di- and polyols	$-(6.71 \pm 2.2)$	$6.37 \pm 1.8$	$5.68 \pm 0.35$	0.905	0.05	6
Carbonyl compounds <sup>(b)</sup>	$-(3.84 \pm 10.0)$	$7.16 \pm 4.6$	$5.67 \pm 0.44$	0.803	0.36	11
Carboxylic acids <sup>(c)</sup>	$8.15 \pm 106.3$	$-(6.71 \pm 36.7)$	$5.44 \pm 2.83$	0.175	0.77	6

<sup>(a)</sup>except tert-butanol; <sup>(b)</sup>except acetone; <sup>(c)</sup>substituted carboxylic acids count to the respective compound class of the substitution

Table 3.7). Therefore, linear regressions have been chosen as explained in subsection 3.5.3.

Finally, the predicted data is compared to the experimental data and the parameters and statistical information is given in Table D.7.

**Table D.7** Parameters for the regression equations  $k_{calc}/M^{-1}s^{-1} = A \cdot (k_{exp}/M^{-1}s^{-1}) + B$  and statistical data derived from the evaluation process of the improved Evans-Polanyi-type correlations of aqueous phase nitrate radical reactions with organic compounds for the various compound classes.

Compound class	$A$	$10^{-6} B^{(a)}$	$R^2$	$10^{-6} \sigma^{(a)}$	$N$
Monoalcohols <sup>(b)</sup> and gem-diols	$0.87 \pm 0.15$	$0.15 \pm 0.41$	0.719	0.8	15
(All Monoalcohols and gem-diols)	$0.66 \pm 0.15$	$0.80 \pm 0.40$	0.575	0.9	16)
Di- and polyols	$0.70 \pm 0.31$	$3.43 \pm 3.86$	0.561	2.2	6
Carbonyl compounds <sup>(c)</sup>	$0.88 \pm 0.30$	$1.71 \pm 11.95$	0.523	25.6	10
(All Carbonyls)	$0.83 \pm 0.27$	$4.16 \pm 10.36$	0.515	24.5	11)
Carboxylic acids <sup>(d)</sup>	$0.08 \pm 0.08$	$0.04 \pm 0.01$	0.191	0.03	6

<sup>(a)</sup>in  $M^{-1}s^{-1}$ ; <sup>(b)</sup>except tert-butanol; <sup>(c)</sup>except acetone; <sup>(d)</sup>substituted carboxylic acids count to the respective compound class of the substitution

## D.5 Additional information of structure-activity relationships

To maintain the clarity of the main part, several data have been moved to the Appendix. Parameters for the regression lines of the comparison of predicted versus experimental data with the aid of scatter plots are given in Table D.8 for the SAR by *Monod and Doussin (2008)*/*Doussin and Monod (2013)* and in Table D.9 for the SAR by *Minakata et al. (2009)*.

**Table D.8** Parameters for the regression equations  $(k_{calc}/\text{M}^{-1}\text{s}^{-1}) = A \cdot (k_{exp}/\text{M}^{-1}\text{s}^{-1}) + B$  and statistical data derived from the evaluation process of the structure-activity relationship by *Monod and Doussin (2008)*.

Compound class	$A$	$10^{-8}B$	$R^2$	$10^{-8}\sigma$	$N$
Alkanes	$0.80 \pm 0.08$	$4.28 \pm 4.8$	0.908	6.81	11
Monoalcohols	$0.97 \pm 0.09$	$1.52 \pm 4.0$	0.886	7.93	16
Di- and polyols	$1.40 \pm 0.21$	$0.10 \pm 5.3$	0.701	10.75	21
Carbonyl compounds <sup>(a)</sup>	$1.14 \pm 0.15$	$-(0.65 \pm 3.6)$	0.828	7.78	14
Monocarboxylic acids	$0.96 \pm 0.10$	$1.48 \pm 1.8$	0.869	4.38	16
Dicarboxylic acids	$0.90 \pm 0.07$	$3.20 \pm 2.1$	0.902	6.49	19
Polyfunctional compounds	$0.44 \pm 0.29$	$-(0.004 \pm 1.7)$	0.333	5.22	24

<sup>(a)</sup>including dicarbonyl compounds except acetylacetone

**Table D.9** Parameters for the regression equations  $(k_{calc}/\text{M}^{-1}\text{s}^{-1}) = A \cdot (k_{exp}/\text{M}^{-1}\text{s}^{-1}) + B$  and statistical data derived from the evaluation process of the structure-activity relationship by *Minakata et al. (2009)*.

Compound class	$A$	$10^{-8}B$	$R^2$	$10^{-8}\sigma$	$N$
Alkanes	$0.98 \pm 0.11$	$4.04 \pm 6.4$	0.891	9.11	11
Monoalcohols	$0.99 \pm 0.17$	$4.04 \pm 7.54$	0.697	1.49	16
Di- and polyols	$0.78 \pm 0.36$	$21.4 \pm 9.0$	0.201	18.39	21
Carbonyl compounds <sup>(a)</sup>	$0.89 \pm 0.17$	$-(0.43 \pm 4.1)$	0.695	8.87	14
Monocarboxylic acids	$1.09 \pm 0.18$	$-(1.89 \pm 3.2)$	0.726	7.86	16
Dicarboxylic acids	$1.22 \pm 0.07$	$2.65 \pm 2.1$	0.934	6.75	20
Polyfunctional compounds	$0.58 \pm 0.29$	$-(0.11 \pm 3.7)$	0.160	11.48	23

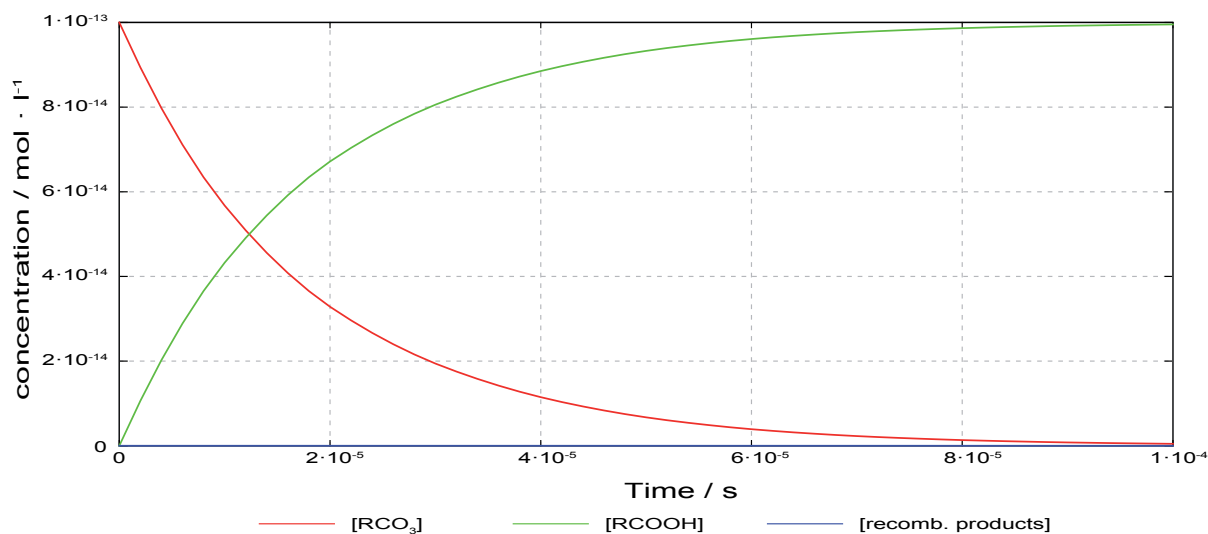
<sup>(a)</sup>including dicarbonyl compounds except acetylacetone

# E Additional information for the development of the protocol of GECKO-A

## E.1 Investigations on the decay of acylperoxy radicals

Simple test simulations with the Gepasi 3.3 model (*Mendes*, 1997) have been performed to confirm the assumption that immediate hydrolysis and subsequent HO<sub>2</sub> elimination is the dominant degradation pathway for acylperoxy radicals (RCO<sub>3</sub>) and recombinations can be neglected. A very simple chemical system has been chosen for this sensitivity study. Only the two degradation pathways of acylperoxy radicals have been implemented according to the Reactions R14 and R4b. The monomolecular decay by hydrolysis and HO<sub>2</sub> elimination has been estimated with a rate constant of 1000 s<sup>-1</sup>. In this reaction, a carboxylic acid and HO<sub>2</sub> radicals are formed. The recombination of acylperoxy radicals leads to oxygen and acyloxy radicals, which immediately decay to CO<sub>2</sub> and an alkylradical with a chain length shortened by one carbon atom. The second order rate constant has been estimated with the rate constant for the acetylperoxy radical recombination. The most recently determined value of  $7.3 \cdot 10^8 \text{ M}^{-1} \text{ s}^{-1}$  by *Schaefer et al.* (2012) has been used for the Gepasi runs. The model was initialised with an RCO<sub>3</sub> concentration of  $1 \cdot 10^{-13} \text{ M}$ , which is typical for the acetylperoxy radical under tropospheric conditions as determined by previous model runs. For water, 55.5 M was used. The initial concentrations of all products were zero.

Figure E.1 shows the concentration-time profiles of acylperoxy radicals and the products from the recombination and the HO<sub>2</sub> elimination channel. After the model start, the RCO<sub>3</sub> concentrations decrease immediately as no sources for this compound have been implemented. Within 0.1 ms all acylperoxy radicals are depleted. At the same time, carboxylic acid concentrations increase while the acyloxy radical concentrations stay close to zero. Therefore, only hydrolysis and subsequent HO<sub>2</sub> elimination is important for the RCO<sub>3</sub> degradation process and recombination reactions can be neglected as assumed in subsection 4.8.3.



**Figure E.1** Concentration-time profiles of acylperoxy radicals and the products of the recombination and HO<sub>2</sub> elimination channel to assess the importance of each reaction pathway.

## E.2 Additional information about the sensitivity of mass accommodation coefficients

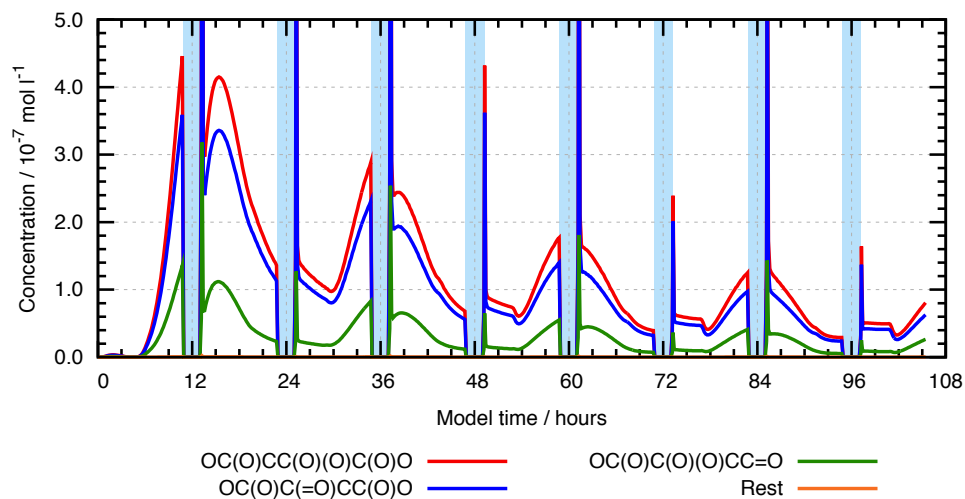
**Table E.1** Experimental values of mass accommodation coefficients taken from the CAPRAM database.

Compound	$\alpha$	Reference
CH <sub>3</sub> OOH	$6.758 \cdot 10^{-3}$	Davidovits <i>et al.</i> (1995)
CH <sub>3</sub> OH	0.0271	Davidovits <i>et al.</i> (1995)
C <sub>2</sub> H <sub>5</sub> OH	0.0176	Davidovits <i>et al.</i> (1995)
HC(=O)OH	0.0229	Davidovits <i>et al.</i> (1995)
CH <sub>3</sub> C(=O)OH	0.0322	Davidovits <i>et al.</i> (1995)
O <sub>3</sub>	0.1	Mirabel (1996)
H <sub>2</sub> O <sub>2</sub>	0.1532	Davidovits <i>et al.</i> (1995)
HO <sub>2</sub>	0.01	Hanson <i>et al.</i> (1992)
NH <sub>3</sub>	0.091	Bongartz <i>et al.</i> (1995)
N <sub>2</sub> O <sub>5</sub>	0.018	George <i>et al.</i> (1994)
HNO <sub>2</sub>	0.5	Bongartz <i>et al.</i> (1995)
HNO <sub>3</sub>	0.0868	Davidovits <i>et al.</i> (1995)
HNO <sub>4</sub>	0.1	Jacob (1986)
NO <sub>3</sub>	0.004	Kirchner <i>et al.</i> (1990), Rudich <i>et al.</i> (1996)
H <sub>2</sub> SO <sub>4</sub>	0.12	Davidovits <i>et al.</i> (1995)
SO <sub>2</sub>	0.11	Tang and Lee (1987), Gardner <i>et al.</i> (1987)
ClNO <sub>2</sub>	0.01	Schweitzer <i>et al.</i> (1998)
BrNO <sub>2</sub>	0.01	Schweitzer <i>et al.</i> (1998)
HCl	0.1158	Davidovits <i>et al.</i> (1995)
BrCl	0.33	Katrib <i>et al.</i> (2001)

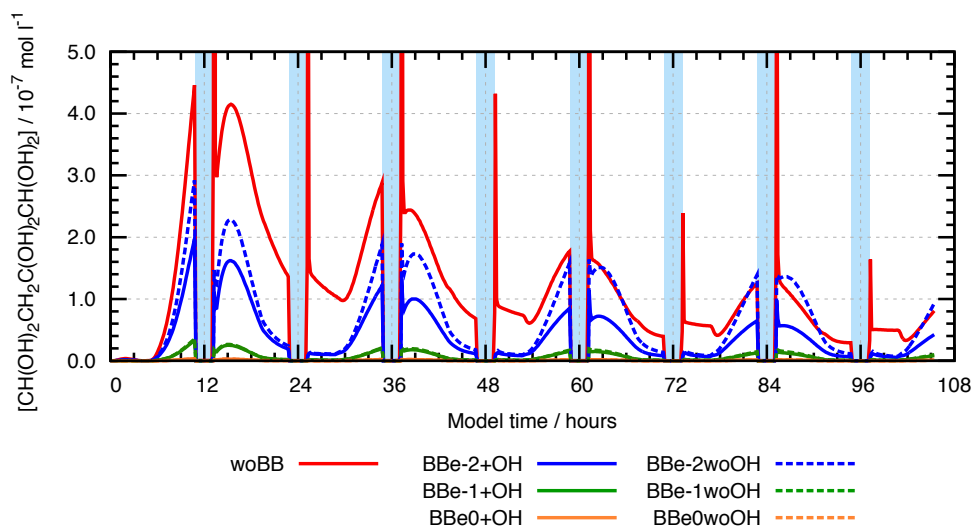


## E.3 Additional information about the sensitivity studies concerning the decay of polycarbonyls

(a) Speciation of oxo-butanedial in the run woBB



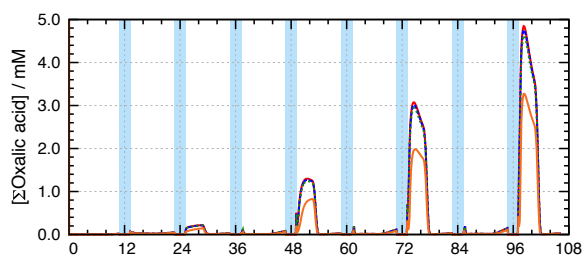
(b) Concentration of the fully hydrated form in all sensitivity runs



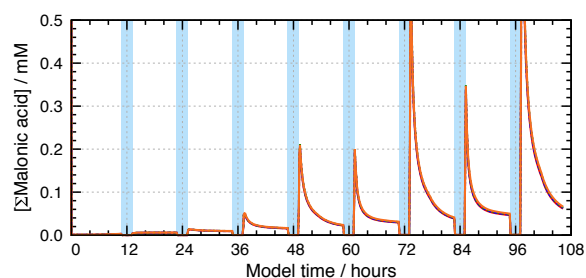
**Figure E.2** Speciation of the different hydration forms of oxo-butanedial in the sensitivity run woBB (a) and concentrations of the fully hydrated form in the different sensitivity runs (b).

## E.4 Additional information about the sensitivity studies concerning the omission of minor reaction pathways

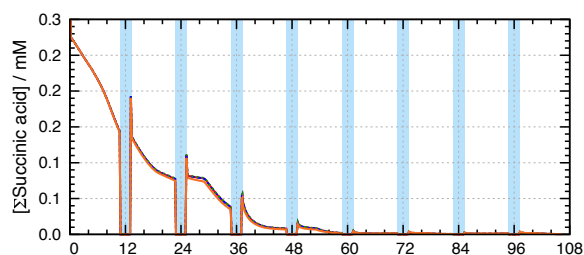
(a) Oxalic acid



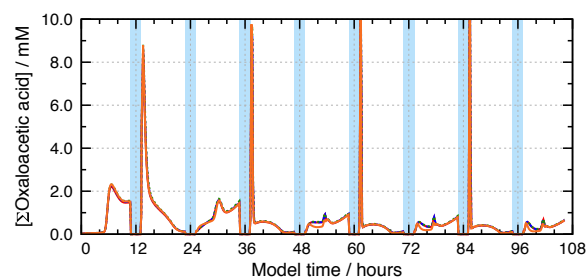
(b) Malonic acid



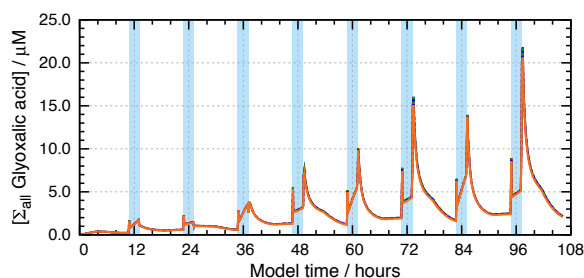
(c) Succinic acid



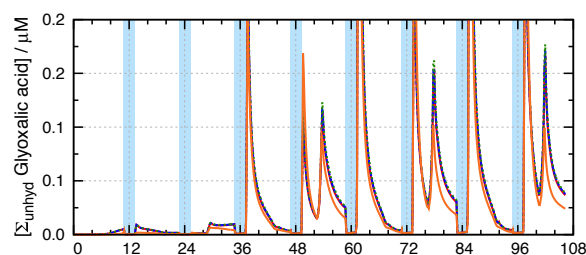
(d) Oxaloacetic acid



(e) Glyoxalic acid (all forms)

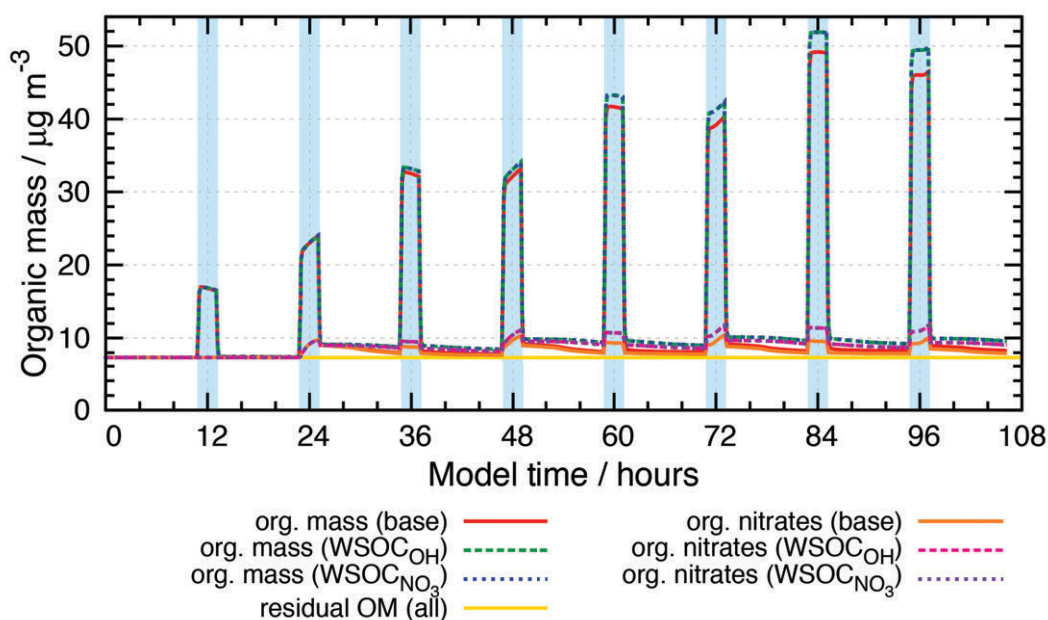


(f) Glyoxalic acid (unhydrated forms)

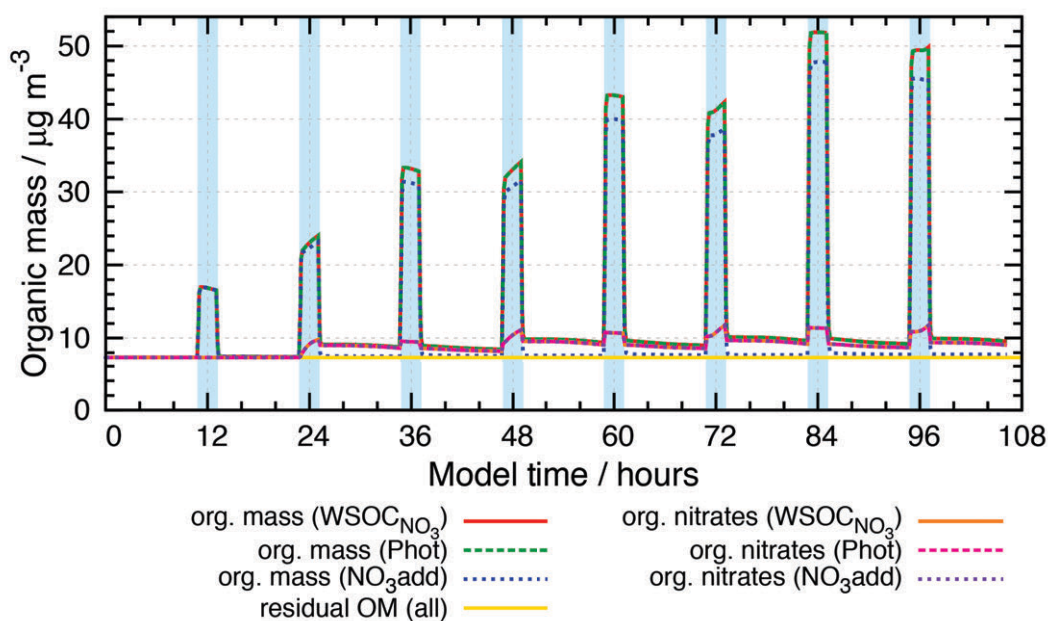


**Figure E.3** Concentration-time profiles for selected organic compounds in the sensitivity runs investigating the influence of the omission of minor reaction pathways under remote continental conditions. Red solid lines belong to mechanisms using a 0.5% threshold, for blue dashed lines a 3% threshold is used, for green dotted lines a 5% threshold is used and for orange solid lines a 10% is used. Moreover, for the 10% run the mass preservation factor was reduced from 0.8 to 0.6 (see section 4.3 for details).

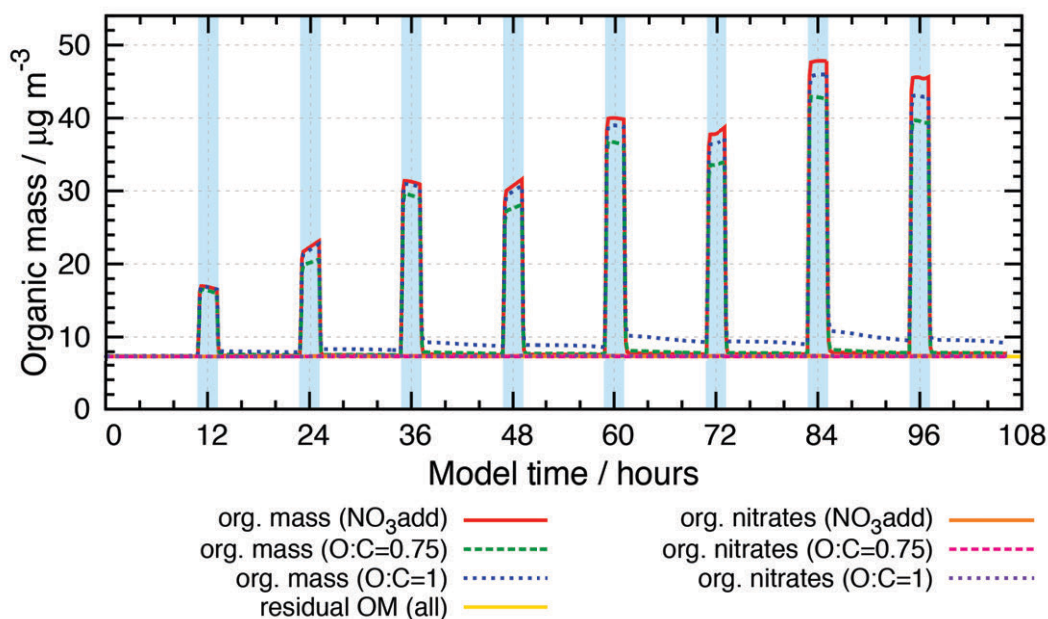
## E.5 Additional information about the sensitivity studies concerning the processing of the organic mass fraction



**Figure E.4** Complete overview of the time-resolved evolution of particulate OM, residual OM and organic nitrate concentrations in the sensitivity runs  $\text{WSOC}_{\text{OH}}$ ,  $\text{WSOC}_{\text{NO}_3}$ , and the base case under urban conditions as already partly presented in Figure 5.11.

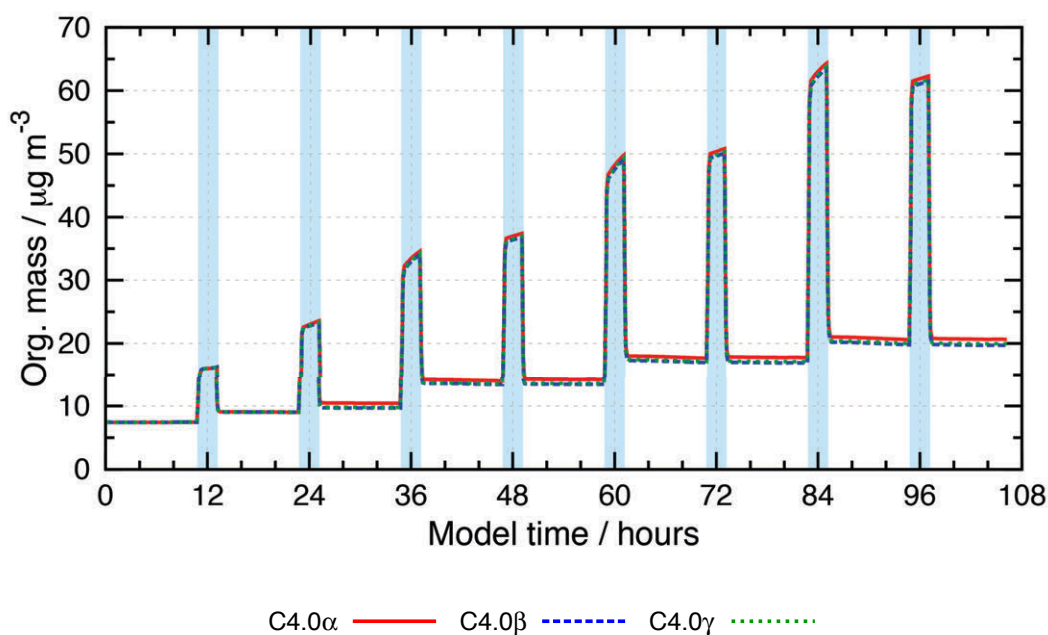


**Figure E.5** Complete overview of the time-resolved evolution of particulate OM, residual OM and organic nitrate concentrations in the sensitivity runs  $\text{WSOC}_{\text{NO}_3}$ , Phot, and  $\text{NO}_3\text{add}$  under urban conditions as already partly presented in Figure 5.12.

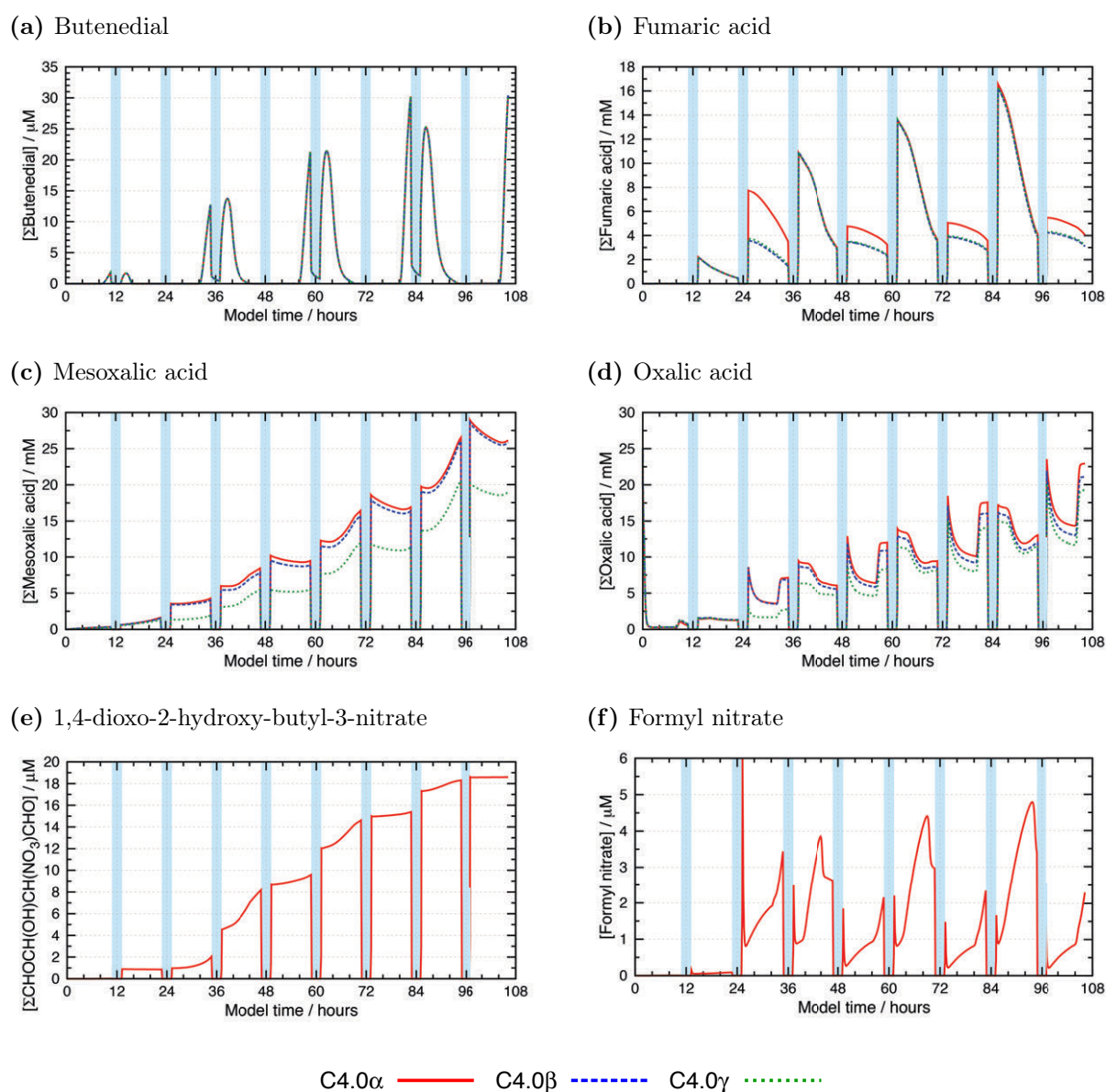


**Figure E.6** Complete overview of the time-resolved evolution of particulate OM, residual OM and organic nitrate concentrations in the sensitivity runs  $\text{NO}_3\text{add}$ ,  $\text{O:C}=0.75$ , and  $\text{O:C}=1$  under urban conditions as already partly presented in Figure 5.13.

## E.6 Additional information about the influence of the nitrate radical chemistry

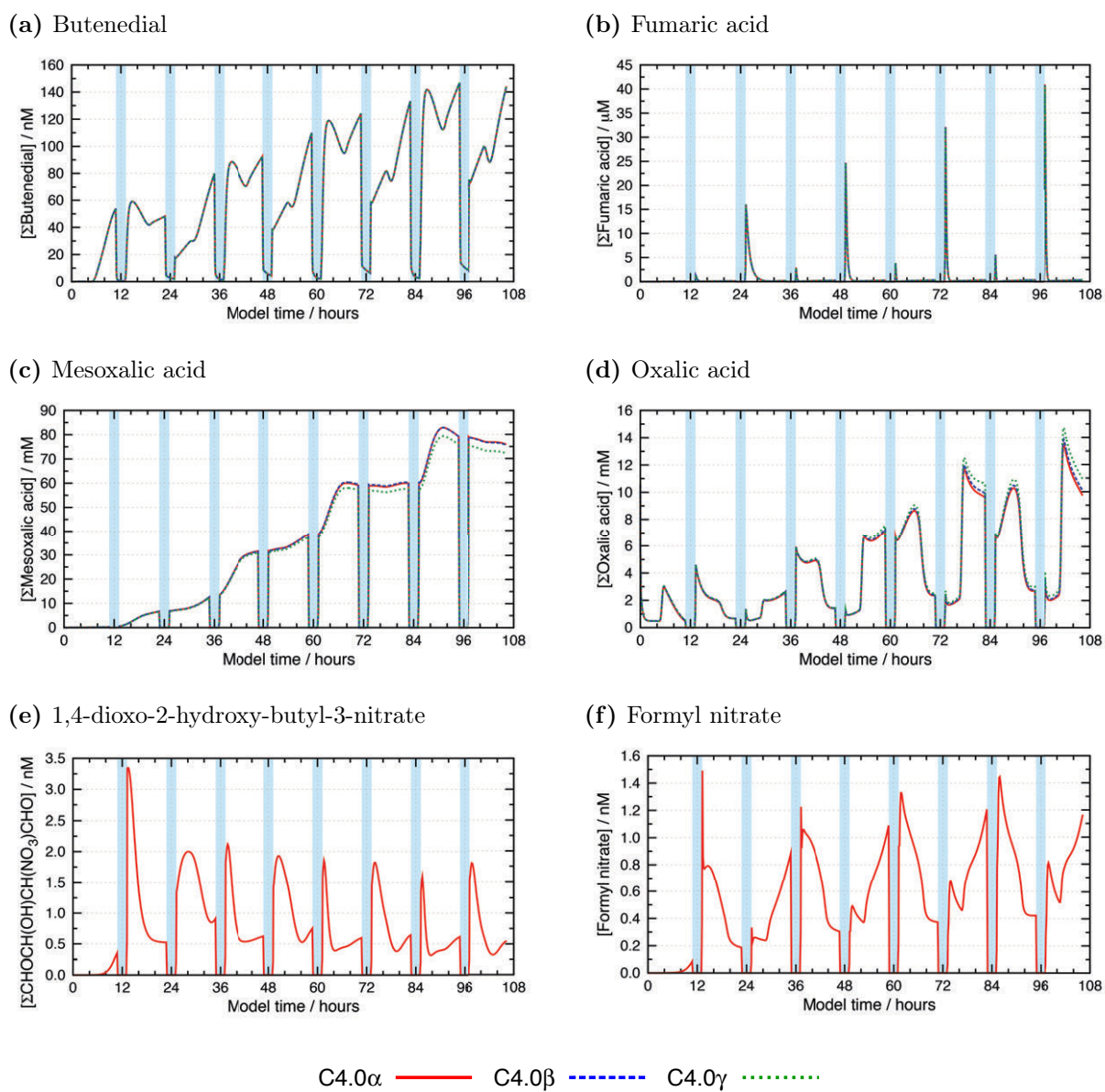


**Figure E.7** Complete overview of the time-resolved evolution of total organic mass in the sensitivity runs investigating the nitrate radical chemistry under urban winter conditions as already partly presented in Figure 5.19.

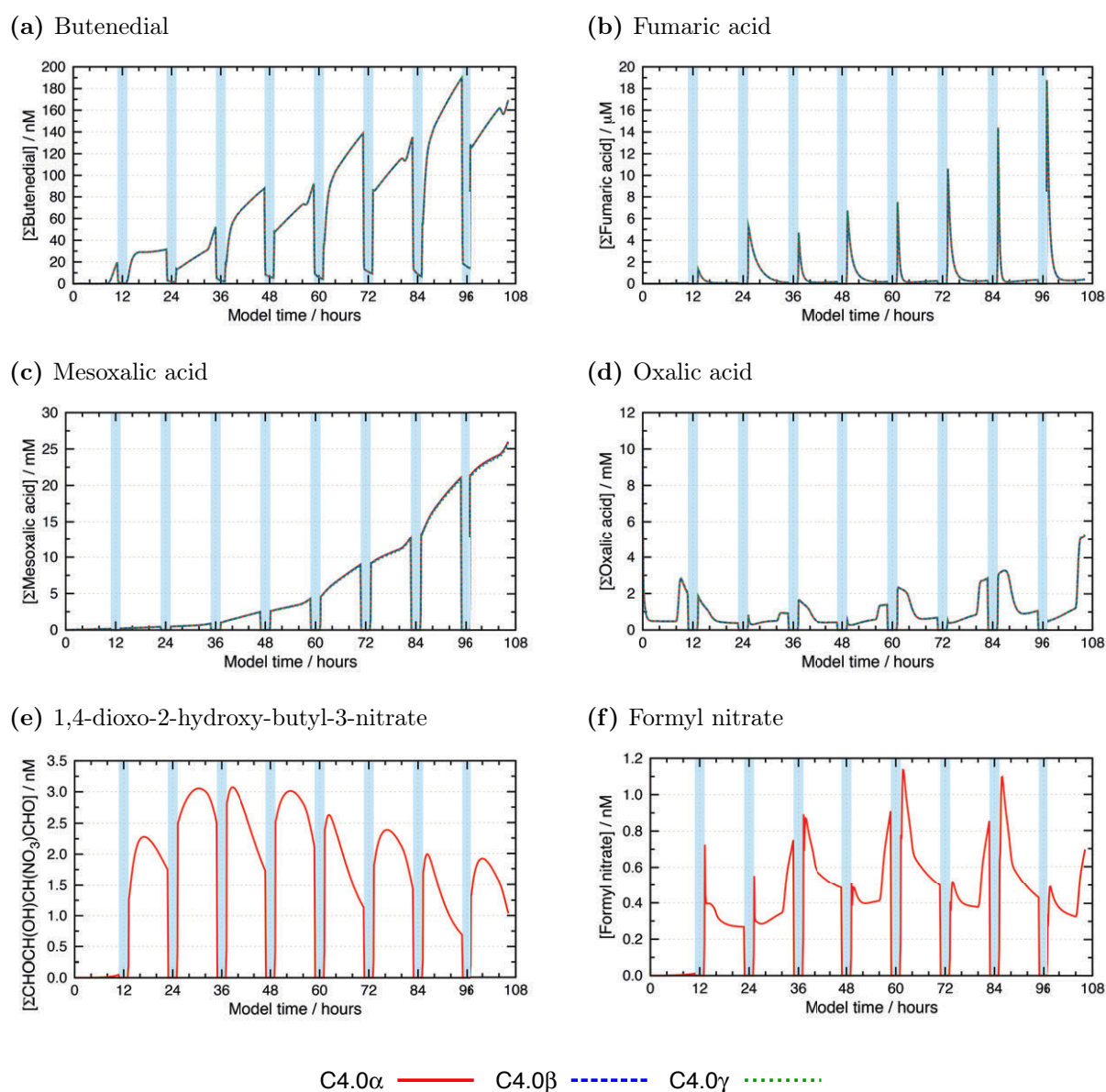


**Figure E.8** Concentration-time profiles for selected organic compounds in the sensitivity runs investigating the nitrate radical chemistry under urban winter conditions.



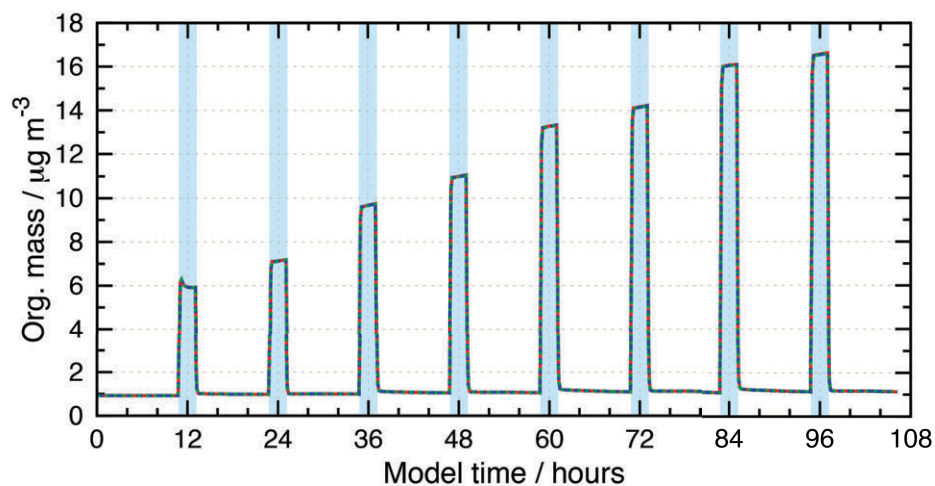


**Figure E.9** Concentration-time profiles for selected organic compounds in the sensitivity runs investigating the nitrate radical chemistry under remote continental conditions.

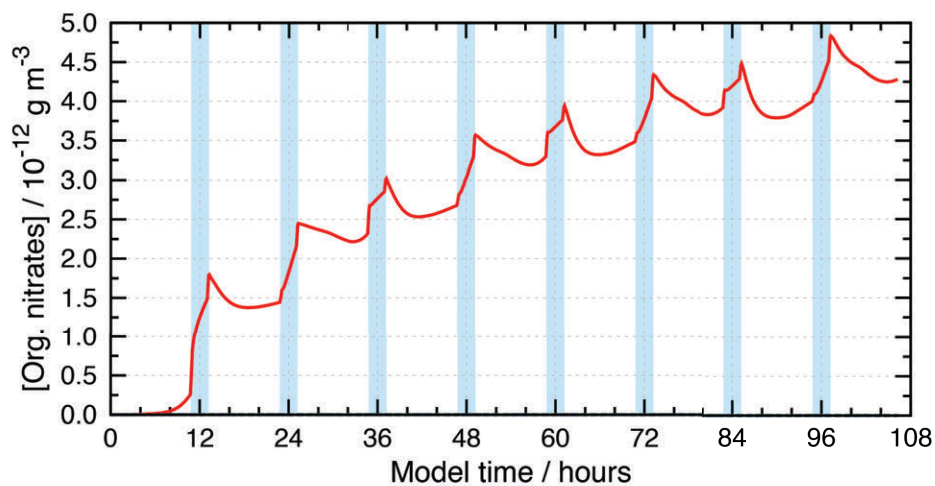


**Figure E.10** Concentration-time profiles for selected organic compounds in the sensitivity runs investigating the nitrate radical chemistry under remote continental conditions.

(a) Total organic mass



(b) Organic nitrate fraction

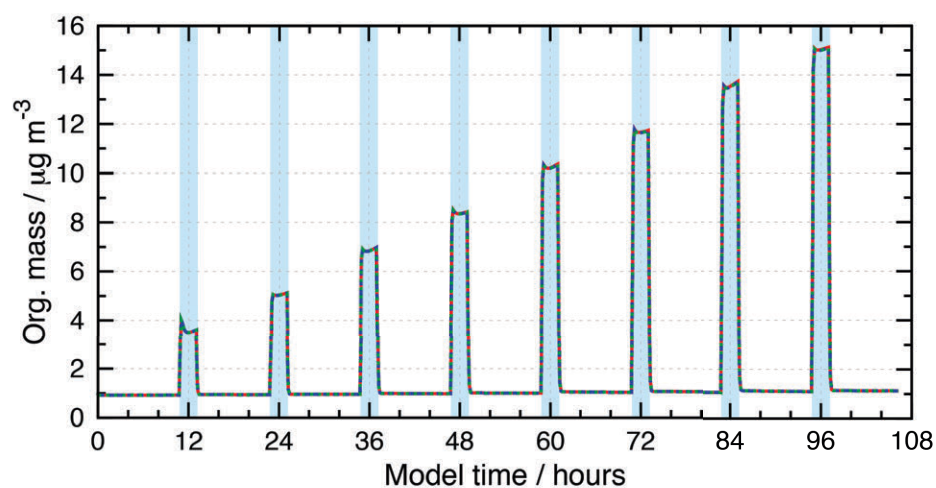


C4.0α — C4.0β - - - C4.0γ . . .

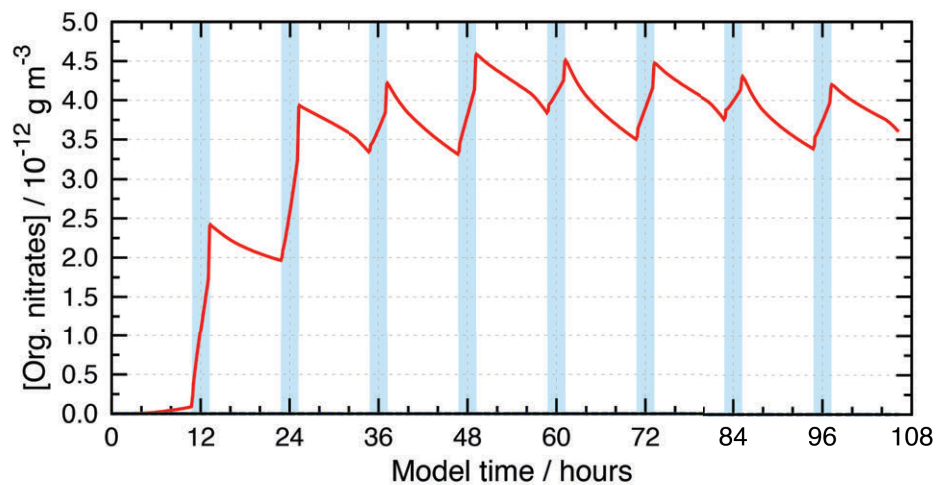
**Figure E.11** Time-resolved evolution of the total organic mass (a) and the organic nitrate fraction (b) in the sensitivity runs investigating the nitrate radical chemistry under remote conditions.



(a) Total organic mass



(b) Organic nitrate fraction



C4.0α — C4.0β - - - C4.0γ . . .

**Figure E.12** Time-resolved evolution of the total organic mass (a) and the organic nitrate fraction (b) in the sensitivity runs investigating the nitrate radical chemistry under remote winter conditions.



## F Additional information about the mechanism generation and model initialisation

### F.1 List of primary compounds used for the generation of CAPRAM 3.5

CH<sub>3</sub>CH<sub>2</sub>OH, CH<sub>3</sub>CH=O, CH<sub>3</sub>C(=O)OH, C(=O)(OH)C(=O)OH, O=CHCH=O, O=CHC(=O)OH, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH, CH<sub>3</sub>CH<sub>2</sub>CH=O, CH<sub>3</sub>CH<sub>2</sub>C(=O)OH, CH<sub>3</sub>CH(OH)CH<sub>3</sub>, CH<sub>3</sub>C(=O)CH<sub>3</sub>, CH<sub>3</sub>C(=O)CH<sub>2</sub>OH, CH<sub>3</sub>C(=O)CH=O, C(=O)(OH)CH<sub>2</sub>C(=O)OH, CH<sub>3</sub>C(=O)C(=O)OH, C(=O)(OH)CH<sub>2</sub>CH<sub>2</sub>C(=O)OH, CH<sub>3</sub>CH(OH)C(=O)OH, CH<sub>2</sub>(OH)C(=O)OH, C(=O)(OH)CH=O, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH=O, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>C(=O)OH, CH<sub>3</sub>CH<sub>2</sub>CH(OH)CH<sub>3</sub>, CH<sub>3</sub>CH<sub>2</sub>C(=O)CH<sub>3</sub>, O=CHC<sub>d</sub>H=C<sub>d</sub>HCH=O, O=CHCH(OH)C(=O)CH=O, C(=O)(OH)CH(OH)C(=O)CH=O, O=CHCH(OH)CH(OH)CH=O, C(=O)(OH)CH(OH)CH(OH)CH=O, CH<sub>2</sub>(OH)CH<sub>2</sub>OH, CH<sub>2</sub>(OH)CH=O, CH<sub>2</sub>(OH)C(=O)C(=O)OH, C(=O)(OH)C(=O)CH=O, C(=O)(OH)CH<sub>2</sub>CH(OH)C(=O)OH, C(=O)(OH)CH<sub>2</sub>C(=O)C(=O)OH, C(=O)(OH)CH(OH)CH=O, C(=O)(OH)CH(OH)C(=O)(OH)

### F.2 List of primary compounds used for the generation of CAPRAM 4.0

The list given below is the full input list for the generator GECKO-A. An evaluation of the solubility of the given compounds is performed by the generator itself. No pre-evaluation is performed. Therefore, several of the below compounds might have an HLC lower than 10<sup>2</sup> M atm<sup>-1</sup> and are, hence, not considered in CAPRAM 4.0. In total, 92 compounds were added to the primary stack of the generator.



## F.3 Model initialization of the ‘real atmosphere’ scenarios

The section provides details about the data used for the model initialization. In Table F.1, the fraction of the respective particle constituents in g/g is given for the urban and the remote case, respectively.

SPACCIM is initialized with the concentration of important trace gases. The data is based on previous CAPRAM model studies (see, e.g., *Tilgner et al.*, 2013). Slight modifications have become necessary due to the adoption of the scenario to the new gas phase mechanism MCMv3.1. In the previously used mechanism RACM-MIM2ext (*Tilgner and Herrmann*, 2010), several gas phase compounds have been lumped. In the current model versions, their initialization data has been delumped according to *Middleton et al.* (1990) and is now being treated explicitly for the explicit mechanism MCMv3.1. Table F.2, page 328, lists the data applied in this dissertation for the urban and remote continental case, respectively.

**Table F.1** Initial fraction of particle constituents in the urban and remote continental model scenario. Data are taken from the CAPRAM database (<http://projects.tropos.de/capram>).

Compound	Fraction / $\text{g g}^{-1}$ (urban case)	Fraction / $\text{g g}^{-1}$ (remote case)
Sulfate	0.260 787 388 0	0.191 128 836 0
Nitrate	0.024 858 800 0	0.092 680 000 0
Chloride	0.019 242 016 0	0.000 096 992 0
Bromide	0.000 653 093 0	0.000 176 586 6
Iodide	0.000 122 643 3	0.000 000 151 6
Ammonium	0.100 292 400 0	0.097 976 000 0
Manganese(III)	0.000 152 639 2	0.000 115 178 0
Iron(III)	0.001 455 510 0	0.001 424 570 0
Copper(II)	0.000 152 639 2	0.000 108 351 4
Further metals	0.032 501 740 8	0.040 486 974 8
Further monovalent cations	0.032 646 240 0	0.015 276 240 0
Further divalent cations	0.014 850 186 0	0.018 458 790 0
Further monovalent anions	0.000 079 562 5	0.000 189 437 5
Oxalate	0.004 384 578 0	0.001 619 516 8
Malonate	0.002 790 186 0	0.001 030 601 6
Succinate	0.001 594 392 0	0.000 588 915 2
Water-soluble organic carbon	0.150 670 044 0	0.055 652 486 4
Water-insoluble organic carbon	0.239 158 800 0	0.088 337 280 0
Elemental organic carbon	0.015 600 000 0	0.167 300 000 0
Silica	0.095 329 878 0	0.226 979 466 0
Phosphor	0.002 866 182 0	0.000 272 790 0

**Table F.2** Initial concentrations of important trace gases in the urban and remote continental model scenario. Data are taken from the CAPRAM database (<http://projects.tropos.de/capram>).

Compound	Concentration / molec cm <sup>-3</sup> (urban case)	Concentration / molec cm <sup>-3</sup> (remote case)
Ozone	$2.290 \cdot 10^{12}$	$1.020 \cdot 10^{12}$
Hydrogen peroxide	$2.550 \cdot 10^{10}$	$2.550 \cdot 10^{10}$
Nitrogen dioxide	$1.150 \cdot 10^{11}$	$3.830 \cdot 10^{10}$
Nitric acid	$2.550 \cdot 10^{10}$	$7.650 \cdot 10^{09}$
Sulfur dioxide	$1.275 \cdot 10^{11}$	$2.550 \cdot 10^{10}$
Ammonia	$1.275 \cdot 10^{11}$	$3.830 \cdot 10^{10}$
Hydrogen chloride	$5.100 \cdot 10^{09}$	$2.550 \cdot 10^{09}$
Molecular hydrogen	$1.275 \cdot 10^{13}$	$1.275 \cdot 10^{13}$
Carbon monoxide	$7.650 \cdot 10^{12}$	$3.830 \cdot 10^{12}$
Carbon dioxide	$9.100 \cdot 10^{15}$	$9.100 \cdot 10^{15}$
Methane	$4.330 \cdot 10^{13}$	$4.330 \cdot 10^{13}$
Ethane	$6.120 \cdot 10^{10}$	$3.830 \cdot 10^{10}$
Ethylene	$2.550 \cdot 10^{10}$	$1.280 \cdot 10^{10}$
Methanol	$1.280 \cdot 10^{11}$	$5.100 \cdot 10^{10}$
Ethanol	$2.550 \cdot 10^{10}$	$6.120 \cdot 10^{09}$
Propanol	$1.785 \cdot 10^{08}$	$8.960 \cdot 10^{06}$
Iso-propanol	$4.845 \cdot 10^{09}$	$2.430 \cdot 10^{09}$
Butanol	$1.020 \cdot 10^{08}$	$5.120 \cdot 10^{07}$
Sec-Butanol	$7.650 \cdot 10^{07}$	$3.840 \cdot 10^{07}$
Ethylene glycol	$1.607 \cdot 10^{08}$	—
Formaldehyde	$2.550 \cdot 10^{10}$	$1.275 \cdot 10^{10}$
Acetaldehyde	$1.250 \cdot 10^{09}$	$1.250 \cdot 10^{09}$
Propionaldehyde	$5.100 \cdot 10^{07}$	—
Butyraldehyde	$5.100 \cdot 10^{07}$	—
Acetone	$1.301 \cdot 10^{10}$	$3.902 \cdot 10^{09}$
Methyl ethyl ketone	$6.885 \cdot 10^{09}$	$2.066 \cdot 10^{09}$
Methyl isobutyl ketone	$1.785 \cdot 10^{09}$	—
Glyoxal	$2.550 \cdot 10^{09}$	$2.550 \cdot 10^{09}$
Methylglyoxal	$2.550 \cdot 10^{09}$	$2.550 \cdot 10^{09}$
Isoprene	—	$2.550 \cdot 10^{10}$
$\alpha$ -pinene	—	$7.200 \cdot 10^{08}$
$\beta$ -pinene	—	$4.800 \cdot 10^{08}$
Tolene	$2.550 \cdot 10^{09}$	—
o-xylene	$1.020 \cdot 10^{09}$	—
m-xylene	$6.700 \cdot 10^{08}$	$1.148 \cdot 10^{08}$
p-xylene	$8.500 \cdot 10^{08}$	$1.403 \cdot 10^{08}$
Phenol	—	$2.550 \cdot 10^{07}$
o-cresol	$2.550 \cdot 10^{07}$	—
Peroxyacetylnitrate	$1.275 \cdot 10^{10}$	$2.550 \cdot 10^{08}$
Methyl hydroperoxide	$2.550 \cdot 10^{10}$	$2.550 \cdot 10^{07}$
Ethyl hydroperoxide	$2.550 \cdot 10^{09}$	$2.550 \cdot 10^{09}$
Peroxyacetic acid	$2.550 \cdot 10^{07}$	$2.550 \cdot 10^{07}$
Water vapour*	$5.100 \cdot 10^{17}$	$5.100 \cdot 10^{17}$
Oxygen*	$5.100 \cdot 10^{18}$	$5.100 \cdot 10^{18}$
Nitrogen*	$1.960 \cdot 10^{19}$	$1.960 \cdot 10^{19}$

\*constant throughout the whole model run

For several compounds, emissions have been described in SPACCIM. Emission rates are held constant throughout the whole model run. In SPACCIM instant dilution in the whole air parcel is assumed for the emitted compounds. Therefore, the emission rates given in Table F.3 are multiplied with the height of the air parcel of 1000 m or  $10^5$  cm. Furthermore, the deposition velocities ( $v_d$ ) in Table F.4 are scaled by the air parcel height of  $10^5$  cm to derive the deposition flux of molecules per second being removed from the system.

**Table F.3** Emission rates used in SPACCIM in the urban and remote continental scenario, respectively. Data are taken from the CAPRAM database (<http://projects.tropos.de/capram>).

Compound	Emission rate / molec cm <sup>-2</sup> s <sup>-1</sup> (urban case)	Emission rate / molec cm <sup>-2</sup> s <sup>-1</sup> (remote case)
Nitrogen oxide	$1.010 \cdot 10^{12}$	$2.860 \cdot 10^{10}$
Sulfur dioxide	$3.270 \cdot 10^{11}$	$2.910 \cdot 10^{10}$
Ammonia	$3.030 \cdot 10^{11}$	$9.060 \cdot 10^{10}$
Carbon monoxide	$8.990 \cdot 10^{12}$	$3.700 \cdot 10^{11}$
Ethane	$1.540 \cdot 10^{11}$	$1.500 \cdot 10^9$
Ethylene	$2.610 \cdot 10^{11}$	$4.540 \cdot 10^9$
Butadien	$1.240 \cdot 10^{11}$	$1.550 \cdot 10^9$
Methanol	$1.160 \cdot 10^{11}$	$1.070 \cdot 10^9$
Ethanol	$4.030 \cdot 10^{11}$	$3.736 \cdot 10^8$
Propanol	$3.430 \cdot 10^9$	$4.417 \cdot 10^6$
Iso-propanol	$9.310 \cdot 10^{10}$	$1.199 \cdot 10^9$
Butanol	$1.960 \cdot 10^9$	$2.524 \cdot 10^7$
Sec-Butanol	$1.470 \cdot 10^9$	$1.893 \cdot 10^7$
Ethylene glycol	$2.010 \cdot 10^{10}$	$2.540 \cdot 10^8$
Acetic acid	$8.018 \cdot 10^9$	$3.183 \cdot 10^8$
Propionic acid	$2.532 \cdot 10^8$	$1.001 \cdot 10^7$
Butyric acid	$8.440 \cdot 10^7$	$3.350 \cdot 10^6$
Formaldehyde	$2.580 \cdot 10^{10}$	$3.028 \cdot 10^8$
Acetaldehyde	$2.906 \cdot 10^{10}$	$2.917 \cdot 10^8$
Propionaldehyde	$1.186 \cdot 10^9$	$1.127 \cdot 10^7$
Butyraldehyde	$1.186 \cdot 10^9$	$1.127 \cdot 10^7$
Acetone	$5.049 \cdot 10^{10}$	$4.549 \cdot 10^8$
Methyl ethyl ketone	$2.673 \cdot 10^{10}$	$2.401 \cdot 10^8$
Methyl isobutyl ketone	$6.930 \cdot 10^9$	$6.244 \cdot 10^7$
Isoprene	$1.540 \cdot 10^{10}$	$1.500 \cdot 10^{11}$
$\alpha$ -pinene	$1.158 \cdot 10^9$	$1.135 \cdot 10^{10}$
$\beta$ -pinene	$7.720 \cdot 10^8$	$7.455 \cdot 10^9$
Tolene	$1.700 \cdot 10^{11}$	$2.108 \cdot 10^9$
o-xylene	$3.950 \cdot 10^{10}$	$4.520 \cdot 10^8$
m-xylene	$2.620 \cdot 10^{10}$	$3.786 \cdot 10^8$
p-xylene	$3.310 \cdot 10^{10}$	$2.995 \cdot 10^8$
Phenol	$1.820 \cdot 10^{11}$	$2.880 \cdot 10^9$

**Table F.4** Deposition velocities deposition velocity ( $v_d$ ) used in SPACCIM in the urban and remote continental scenario, respectively. Data are taken from the CAPRAM database (<http://projects.tropos.de/capram>).

Compound	$v_d$ / $\text{cm s}^{-1}$ (urban case)	$v_d$ / $\text{cm s}^{-1}$ (remote case)
Ozone	0.4	0.4
Hydrogen peroxide	1.0	1.0
Nitrogen dioxide	0.4	0.4
Nitric acid	2.0	2.0
Dinitrogen pentoxide	2.0	2.0
Sulfur dioxide	1.0	1.0
Sulfuric acid	2.0	2.0
Ammonia	1.0	1.0
Hydrogen chloride	1.0	1.0
Carbon monoxide	0.1	0.1
Methanol	1.0	1.0
Ethanol	0.5	0.5
Formic acid	1.0	1.0
Formaldehyde	1.0	1.0
Methyl hydroperoxide	0.5	0.5



## G The CAPRAM oxidation scheme

In the present appendix, tables with the oxidation scheme of all current CAPRAM versions as used in this dissertation are provided. The appendix is structured according to the following topics:

- (i) Photolysis processes
- (ii) Inorganic oxidation scheme
- (iii) Organic oxidation scheme

For the oxidation schemes, respectively, first all phase transfer processes are listed before the chemical aqueous phase oxidation scheme is presented. In each section, tables of all CAPRAM versions are listed. The tables are presented successively for every CAPRAM version. For higher versions, processes of the tables of lower versions are included as well and are not given explicitly in the tables of the higher versions again. A few exceptions exist and some reactions are marked as obsolete from certain CAPRAM versions onwards. Moreover, for reactions of stable organic compounds with hydroxyl and nitrate radicals, branching ratios have been introduced in CAPRAM 3.5. The modified reactions are reprinted in Table G.13. In Table G.10, the original equations with out branching ratios are shown. As in both version, reactants are identical and only branching ratios have been introduced in CAPRAM 3.5, the same label for these reactions have been used consequently in all versions. Reaction labels have been taken from CAPRAM 3.5 to fit in the logical order of the oxidation scheme in this version.

It should furthermore be noted that CAPRAM 3.0o resembles the CAPRAM version as presented by (*Tilgner and Herrmann*, 2010) with only a few modifications as described in subsection 2.2.3.2. In CAPRAM 3.0p, parameterisations for the processing of WSOC and HULIS species were introduced (see also subsection 5.5.1. From CAPRAM 3.5 onwards, GECKO-A has been used to automatically self-generate new CAPRAM versions. The chemical reaction scheme is provided in subsection G.3.2. In contrast to CAPRAM 3.0o, aqueous phase irreversible reactions and equilibria are listed in the same table. Moreover, if no reference or comment is provided for a reaction in the new self-generated CAPRAM versions, the kinetic data has been estimated by GECKO-A with the estimation methods explained in this dissertation.

## G.1 Photolysis processes

**Table G.1** Parameters for the photolysis reactions in CAPRAM 3.0o. Photolysis reactions are parameterised with  $j = l \cdot \cos^m \chi \cdot \exp \{-n \cdot \sec \chi\}$ .

	Reaction	$l/\text{s}^{-1}$	$m$	$n$	Reference/comment
P <sub>i</sub> 0001	$[\text{Fe}(\text{OH})]^{2+} \xrightarrow{h\nu} \text{Fe}^{2+} + \text{OH}$	$4.764 \cdot 10^{-2}$	0.829	0.291	absorption spectra from <i>Weschler et al.</i> (1986)/quantum yields from <i>Benkelberg and Warneck</i> (1995)
P <sub>i</sub> 0002	$[\text{Fe}(\text{OH})_2]^+ \xrightarrow{h\nu} \text{Fe}^{2+} + \text{OH} + \text{OH}^-$	$1.343 \cdot 10^{-2}$	0.855	0.300	absorption spectra from <i>Weschler et al.</i> (1986)/quantum yields from <i>Benkelberg and Warneck</i> (1995)
P <sub>i</sub> 0003	$\text{NO}_3^- \xrightarrow{h\nu} \text{NO}_2 + \text{OH} + \text{OH}^-$	$6.109 \cdot 10^{-7}$	1.076	0.409	absorption spectra from <i>Graedel and Weschler</i> (1981)/quantum yields from <i>Zellner et al.</i> (1990)
P <sub>i</sub> 0004	$\text{NO}_2^- \xrightarrow{h\nu} \text{NO} + \text{OH} + \text{OH}^-$	$7.245 \cdot 10^{-5}$	0.480	0.303	absorption spectra from <i>Graedel and Weschler</i> (1981)/quantum yields from <i>Zellner et al.</i> (1990)
P <sub>i</sub> 0005	$\text{HONO} \xrightarrow{h\nu} \text{OH} + \text{NO}$	$2.999 \cdot 10^{-4}$	0.439	0.308	<i>Graedel and Weschler</i> (1981)
P <sub>i</sub> 0006	$\text{Fe}^{3+} \xrightarrow{h\nu} \text{Fe}^{2+} + \text{OH} + \text{H}^+$	$1.224 \cdot 10^{-5}$	1.467	0.248	absorption spectra from <i>Weschler et al.</i> (1986)/quantum yields from <i>Benkelberg and Warneck</i> (1995)
P <sub>i</sub> 0007	$[\text{Fe}(\text{SO}_4)]^+ \xrightarrow{h\nu} \text{Fe}^{2+} + \text{SO}_4^-$	$8.215 \cdot 10^{-5}$	0.885	0.313	<i>Benkelberg and Warneck</i> (1995)
P <sub>i</sub> 0008	$\text{H}_2\text{O}_2 \xrightarrow{h\nu} 2 \text{OH}$	$8.625 \cdot 10^{-6}$	1.043	0.271	absorption spectra from <i>Graedel and Weschler</i> (1981)/quantum yields from <i>Zellner et al.</i> (1990)
P <sub>i</sub> 0009	$[\text{Fe}(\text{C}_2\text{O}_4)_2]^- \xrightarrow{h\nu} \text{Fe}^{2+} + \text{C}_2\text{O}_4^{2-} + \text{CO}_2 + \text{CO}_2^-$	$7.993 \cdot 10^{-2}$	0.625	0.279	<i>Weller et al.</i> (2013)

**Table G.1 (continued)** Parameters for the photolysis reactions in CAPRAM 3.0o. Photolysis reactions are parameterised with  $j = l \cdot \cos^m \chi \cdot \exp \{-n \cdot \sec \chi\}$ .

	Reaction	$l/\text{s}^{-1}$	$m$	$n$	Reference/comment
P <sub>i</sub> 0010	$[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-} \xrightarrow{h\nu} \text{Fe}^{2+} + 2 \text{C}_2\text{O}_4^{2-} + \text{CO}_2 + \text{CO}_2^-$	$4.659 \cdot 10^{-2}$	0.561	0.276	Weller <i>et al.</i> (2013)
P <sub>i</sub> 0011	$\text{NO}_3 \xrightarrow{h\nu} \text{NO} + \text{O}_2$	$2.584 \cdot 10^{-3}$	0.072	0.196	Graedel and Weschler (1981)
P <sub>i</sub> 0012	$\text{NO}_3 \xrightarrow{h\nu} \text{NO}_2 + \text{O}(^3\text{P})$	$2.325 \cdot 10^{-2}$	0.072	0.196	Graedel and Weschler (1981)
P <sub>i</sub> 0013	$\text{O}_3 \xrightarrow{h\nu} 2 \text{OH} + \text{O}_2$	$3.652 \cdot 10^{-4}$	0.515	0.044	Graedel and Weschler (1981)
P <sub>o</sub> 0001	$\text{CH}_3\text{OOH} \xrightarrow{h\nu} \text{CH}_3\text{O} + \text{OH}$	$8.625 \cdot 10^{-5}$	1.043	0.271	estimated same as $\text{H}_2\text{O}_2$
P <sub>o</sub> 0002	$\text{CH}_2(\text{OOH})\text{COOH} \xrightarrow{h\nu} \text{OCH}_2\text{COOH} + \text{OH}$	$7.640 \cdot 10^{-6}$	0.264	0.764	Photochemical rate constant estimated equal to $j(\text{H}_2\text{O}_2)$

## G.2 Inorganic chemistry

### G.2.1 Phase transfer processes

**Table G.2** Henry's Law coefficients of inorganic compounds in CAPRAM 3.0o

	Species	$K_{H,298} / \text{M atm}^{-1}$	$\Delta H/R / \text{K}$	Reference/comment
U <sub>i</sub> 00001	$\text{CO}_2$	$3.10 \cdot 10^{-2}$	-2423	Chameides (1984)
U <sub>i</sub> 00002	$\text{O}_3$	$1.14 \cdot 10^{-2}$	-2300	Kosak-Channing and Helz (1983)
U <sub>i</sub> 00003	$\text{HO}_2$	$9.00 \cdot 10^3$		Weinstein-Lloyd and Schwartz (1991)
U <sub>i</sub> 00004	$\text{OH}$	$2.50 \cdot 10^1$	-5280	Kläning <i>et al.</i> (1985)
U <sub>i</sub> 00005	$\text{H}_2\text{O}_2$	$1.02 \cdot 10^5$	-6340	Lind and Kok (1994)
U <sub>i</sub> 00006	$\text{NO}_2$	$1.20 \cdot 10^{-2}$	-1263	Ervens <i>et al.</i> (2003)
U <sub>i</sub> 00007	$\text{HONO}$	$4.90 \cdot 10^1$	-4880	Park and Lee (1988)
U <sub>i</sub> 00008	$\text{HNO}_3$	$2.10 \cdot 10^5$	-8700	Lelieveld and Crutzen (1991)
U <sub>i</sub> 00009	$\text{NO}_3$	$6.00 \cdot 10^{-1}$		Rudich <i>et al.</i> (1996)

**Table G.2** (continued) Henry's Law coefficients of inorganic compounds in CAPRAM 3.0o

	Species	$K_{H,298}$ / Matm <sup>1</sup>	$\Delta H/R$ / K	Reference/comment
U <sub>i</sub> 00010	N <sub>2</sub> O <sub>5</sub>	$1.40 \cdot 10^0$		estimated equal as N <sub>2</sub> O <sub>4</sub> ( <i>Schwartz and White</i> , 1983)
U <sub>i</sub> 00011	NH <sub>3</sub>	$6.07 \cdot 10^1$	-3920	<i>Clegg and Brimblecombe</i> (1990)
U <sub>i</sub> 00012	HCl	$1.10 \cdot 10^0$	-2020	<i>Marsh and McElroy</i> (1985)
U <sub>i</sub> 00013	SO <sub>2</sub>	$1.24 \cdot 10^0$	-3247	<i>Beilke and Gravenhorst</i> (1978)
U <sub>i</sub> 00014	Br <sub>2</sub>	$7.60 \cdot 10^{-1}$	-4100	<i>Law et al.</i> (2007)
U <sub>i</sub> 00015	Cl <sub>2</sub>	$9.15 \cdot 10^{-2}$	-2490	<i>Wilhelm et al.</i> (1977)
U <sub>i</sub> 00016	H <sub>2</sub> SO <sub>4</sub>	$8.70 \cdot 10^{11}$		<i>Brimblecombe and Clegg</i> (1988)
U <sub>i</sub> 00017	HNO <sub>4</sub>	$3.00 \cdot 10^4$		<i>Amels et al.</i> (1996); <i>Jacob et al.</i> (1989) and <i>Regimbal and Mozurkewich</i> (1997)
U <sub>i</sub> 00018	O <sub>2</sub>	$1.30 \cdot 10^{-3}$	-1700	<i>Loomis</i> (1928)
U <sub>i</sub> 00019	ClNO <sub>2</sub>	$2.40 \cdot 10^{-2}$		<i>Behnke et al.</i> (1997)
U <sub>i</sub> 00020	BrNO <sub>2</sub>	$3.00 \cdot 10^{-1}$		<i>Frenzel et al.</i> (1998)
U <sub>i</sub> 00021	BrCl	$9.40 \cdot 10^{-1}$	5600	<i>Bartlett and Margerum</i> (1999)
U <sub>i</sub> 00022	NO	$1.90 \cdot 10^{-3}$	-1400	<i>Lide and Frederikse</i> (1995)

**Table G.3** Mass accommodation and gas phase diffusion coefficients of inorganic compounds in CAPRAM 3.0o

	Species	$\alpha$ (298 K)	Reference/comment	$D_g$ / $10^{-5}$ m <sup>2</sup> s <sup>-1</sup>	Reference/comment
U <sub>i</sub> 00001	CO <sub>2</sub>	$1.50 \cdot 10^{-4}$	estimated	1.55	<i>McElroy</i> (1997)
U <sub>i</sub> 00002	O <sub>3</sub>	$1.00 \cdot 10^{-1}$	<i>Mirabel</i> (1996)	1.48	<i>Schwartz</i> (1986)
U <sub>i</sub> 00003	HO <sub>2</sub>	$1.00 \cdot 10^{-2}$	<i>Hanson et al.</i> (1992)	1.04	<i>Hanson et al.</i> (1992)
U <sub>i</sub> 00004	OH	$5.00 \cdot 10^{-2}$	estimated	1.53	<i>Hanson et al.</i> (1992)
U <sub>i</sub> 00005	H <sub>2</sub> O <sub>2</sub>	$1.53 \cdot 10^{-1}$	<i>Davidovits et al.</i> (1995)	1.46	<i>McElroy</i> (1997)
U <sub>i</sub> 00006	NO <sub>2</sub>	$1.50 \cdot 10^{-3}$	estimated	1.92	<i>Ponche et al.</i> (1993)
U <sub>i</sub> 00007	HONO	$5.00 \cdot 10^{-2}$	<i>Bongartz et al.</i> (1995)	1.30	<i>Kirchner et al.</i> (1990)
U <sub>i</sub> 00008	HNO <sub>3</sub>	$8.68 \cdot 10^{-2}$	<i>Davidovits et al.</i> (1995)	1.32	<i>Kirchner et al.</i> (1990)

**Table G.3 (continued)** Mass accommodation and gas phase diffusion coefficients of inorganic compounds in CAPRAM 3.0o

Species	$\alpha$ (298 K)	Reference/comment	$D_g$ / $10^{-5} \text{ m}^2 \text{ s}^{-1}$	Reference/comment
U <sub>i</sub> 00009 NO <sub>3</sub>	$4.20 \cdot 10^{-3}$	<i>Kirchner et al.</i> (1990), <i>Rudich et al.</i> (1996)	1.00	<i>Ervens et al.</i> (2003)
U <sub>i</sub> 00010 N <sub>2</sub> O <sub>5</sub>	$1.80 \cdot 10^{-2}$	<i>George et al.</i> (1994)	1.10	<i>Kirchner et al.</i> (1990)
U <sub>i</sub> 00011 NH <sub>3</sub>	$9.10 \cdot 10^{-2}$	<i>Bongartz et al.</i> (1995)	2.30	<i>Ponche et al.</i> (1993)
U <sub>i</sub> 00012 HCl	$1.03 \cdot 10^{-1}$	<i>Davidovits et al.</i> (1995)	1.89	<i>Marsh and McElroy</i> (1985)
U <sub>i</sub> 00013 SO <sub>2</sub>	$1.10 \cdot 10^{-1}$	<i>Tang and Lee</i> (1987), <i>Gardner et al.</i> (1987)	1.28	<i>McElroy</i> (1997)
U <sub>i</sub> 00014 Br <sub>2</sub>	$8.00 \cdot 10^{-2}$	estimated	1.00	<i>Schwartz</i> (1986)
U <sub>i</sub> 00015 Cl <sub>2</sub>	$8.00 \cdot 10^{-2}$	estimated	1.28	<i>Schwartz</i> (1986)
U <sub>i</sub> 00016 H <sub>2</sub> SO <sub>4</sub>	$1.20 \cdot 10^{-1}$	<i>Davidovits et al.</i> (1995)	1.30	<i>Schwartz</i> (1986)
U <sub>i</sub> 00017 HNO <sub>4</sub>	$1.00 \cdot 10^{-1}$	<i>Jacob</i> (1986)	1.30	<i>Schweitzer et al.</i> (1998)
U <sub>i</sub> 00018 O <sub>2</sub>	$1.00 \cdot 10^{-2}$	estimated	1.12	<i>Fuller</i> (1986)
U <sub>i</sub> 00019 ClNO <sub>2</sub>	$1.00 \cdot 10^{-2}$	<i>Schweitzer et al.</i> (1998)	1.27	<i>Fuller</i> (1986)
U <sub>i</sub> 00020 BrNO <sub>2</sub>	$1.00 \cdot 10^{-2}$	<i>Schweitzer et al.</i> (1998)	1.06	<i>Fuller</i> (1986)
U <sub>i</sub> 00021 BrCl	$3.30 \cdot 10^{-1}$	<i>Katrib et al.</i> (2001)	1.05	<i>Fuller</i> (1986)
U <sub>i</sub> 00022 NO	$1.00 \cdot 10^{-3}$		2.24	

## G.2.2 Chemical conversions

**Table G.4** Irreversible inorganic reactions in CAPRAM 3.0o

Reaction	$k_{298}$ / K <sup>a</sup>	$E_A/R$ <sup>b</sup>	Reference/comment
R <sub>i</sub> 00001 O( <sup>3</sup> P) + O <sub>2</sub> → O <sub>3</sub>	$4.00 \cdot 10^9$		<i>Kläning et al.</i> (1984)
R <sub>i</sub> 00002 H <sub>2</sub> O <sub>2</sub> + Fe <sup>2+</sup> → Fe <sup>3+</sup> + OH + OH <sup>-</sup>	$5.00 \cdot 10^1$		<i>Barb et al.</i> (1951)
R <sub>i</sub> 00003 [Mn(OH)] <sup>2+</sup> + H <sub>2</sub> O <sub>2</sub> → MnO <sub>2</sub> <sup>+</sup> + H <sup>+</sup> + H <sub>2</sub> O	$2.80 \cdot 10^3$		<i>Jacobsen et al.</i> (1997b)
R <sub>i</sub> 00004 Mn <sup>4+</sup> + H <sub>2</sub> O <sub>2</sub> → Mn <sup>2+</sup> + 2 H <sup>+</sup> + O <sub>2</sub>	$1.00 \cdot 10^6$		<i>Jacobsen et al.</i> (1997b)
R <sub>i</sub> 00005 H <sub>2</sub> O <sub>2</sub> + Cu <sup>+</sup> → Cu <sup>2+</sup> + OH + OH <sup>-</sup>	$7.00 \cdot 10^3$		<i>Berdnikov</i> (1973)

**Table G.4 (continued)** Irreversible inorganic reactions in CAPRAM 3.0o

Reaction	$k_{298} / \text{K}^a$	$E_A/R^b$	Reference/comment
R <sub>i</sub> 00006 $\text{Mn}^{3+} + \text{H}_2\text{O}_2 \longrightarrow \text{HO}_2 + \text{H}^+ + \text{Mn}^{2+}$	$7.30 \cdot 10^4$		<i>Davies et al.</i> (1968)
R <sub>i</sub> 00007 $\text{O}_2^- + \text{Fe}^{3+} \longrightarrow \text{Fe}^{2+} + \text{O}_2$	$1.50 \cdot 10^8$		<i>Rush and Bielski</i> (1985)
R <sub>i</sub> 00008 $\text{HO}_2 + [\text{Fe}(\text{OH})]^{2+} \longrightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}_2\text{O}$	$1.30 \cdot 10^5$		<i>Ziajka et al.</i> (1994)
R <sub>i</sub> 00009 $\text{O}_2^- + [\text{Fe}(\text{OH})]^{2+} \longrightarrow \text{Fe}^{2+} + \text{O}_2 + \text{OH}^-$	$1.50 \cdot 10^8$		<i>Rush and Bielski</i> (1985)
R <sub>i</sub> 00010 $\text{O}_2^- + [\text{Fe}(\text{OH})_2]^+ \longrightarrow \text{Fe}^{2+} + \text{O}_2 + 2 \text{OH}^-$	$1.50 \cdot 10^8$		<i>Rush and Bielski</i> (1985)
R <sub>i</sub> 00011 $\text{O}_2^- + \text{Fe}^{2+} \xrightarrow{\text{H}_2\text{O}, 2\text{H}^+} \text{Fe}^{3+} + \text{H}_2\text{O}_2 + 2 \text{OH}^-$	$1.00 \cdot 10^7$		<i>Rush and Bielski</i> (1985)
R <sub>i</sub> 00012 $\text{HO}_2 + \text{Fe}^{2+} \xrightarrow{\text{H}_2\text{O}, \text{H}^+} \text{Fe}^{3+} + \text{H}_2\text{O}_2 + \text{OH}^-$	$1.20 \cdot 10^6$	5050	<i>Jayson et al.</i> (1973a)
R <sub>i</sub> 00013 $\text{OH} + \text{Fe}^{2+} \longrightarrow [\text{Fe}(\text{OH})]^{2+}$	$4.30 \cdot 10^8$	1100	<i>Christensen and Sehested</i> (1981)
R <sub>i</sub> 00014 $\text{MnO}_2^+ + \text{HO}_2 \xrightarrow{\text{H}_2\text{O}, \text{H}^+} \text{Mn}^{2+} + \text{H}_2\text{O}_2 + \text{O}_2 + \text{OH}^-$	$1.00 \cdot 10^7$		<i>Jacobsen et al.</i> (1997b)
R <sub>i</sub> 00015 $\text{OH} + \text{Mn}^{2+} \longrightarrow \text{Mn}^{3+} + \text{OH}^-$	$2.00 \cdot 10^7$		<i>Jacobsen et al.</i> (1997b)
R <sub>i</sub> 00016 $\text{O}_2^- + \text{Cu}^+ \xrightarrow{\text{H}_2\text{O}, 2\text{H}^+} \text{Cu}^{2+} + \text{H}_2\text{O}_2 + 2 \text{OH}^-$	$1.00 \cdot 10^{10}$		<i>Rabani et al.</i> (1973)
R <sub>i</sub> 00017 $\text{HO}_2 + \text{Cu}^+ \xrightarrow{\text{H}_2\text{O}, \text{H}^+} \text{Cu}^{2+} + \text{H}_2\text{O}_2 + \text{OH}^-$	$2.30 \cdot 10^9$		<i>Kozlov and Berdnikov</i> (1973)
R <sub>i</sub> 00018 $\text{OH} + \text{Cu}^+ \longrightarrow \text{OH}^- + \text{Cu}^{2+}$	$3.00 \cdot 10^9$		<i>Goldstein et al.</i> (1992)
R <sub>i</sub> 00019 $\text{HO}_2 + \text{Cu}^{2+} \longrightarrow \text{Cu}^+ + \text{O}_2 + \text{H}^+$	$1.00 \cdot 10^8$		<i>Rabani et al.</i> (1973)
R <sub>i</sub> 00020 $\text{O}_2^- + \text{Cu}^{2+} \longrightarrow \text{Cu}^+ + \text{O}_2$	$8.00 \cdot 10^9$		<i>Rabani et al.</i> (1973)
R <sub>i</sub> 00021 $\text{Fe}^{3+} + \text{Cu}^+ \longrightarrow \text{Fe}^{2+} + \text{Cu}^{2+}$	$1.30 \cdot 10^7$		<i>Buxton et al.</i> (1995)
R <sub>i</sub> 00022 $[\text{Fe}(\text{OH})]^{2+} + \text{Cu}^+ \longrightarrow \text{Fe}^{2+} + \text{Cu}^{2+} + \text{OH}^-$	$1.30 \cdot 10^7$		<i>Buxton et al.</i> (1995)
R <sub>i</sub> 00023 $[\text{Fe}(\text{OH})_2]^+ + \text{Cu}^+ \longrightarrow \text{Fe}^{2+} + \text{Cu}^{2+} + 2 \text{OH}^-$	$1.30 \cdot 10^7$		<i>Buxton et al.</i> (1995)
R <sub>i</sub> 00024 $\text{Fe}^{2+} + \text{Mn}^{3+} \longrightarrow \text{Fe}^{3+} + \text{Mn}^{2+}$	$1.60 \cdot 10^4$		<i>Diebler and Sutin</i> (1964)
R <sub>i</sub> 00025 $\text{O}_3 + \text{O}_2^- \longrightarrow \text{O}_3^- + \text{O}_2$	$1.50 \cdot 10^9$	2200	<i>Sehested et al.</i> (1983)
R <sub>i</sub> 00026 $\text{HO}_3 \longrightarrow \text{OH} + \text{O}_2$	$3.30 \cdot 10^2$	4500	<i>Bühler et al.</i> (1984)
R <sub>i</sub> 00027 $\text{HO}_2 + \text{HO}_2 \longrightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$4.15 \cdot 10^5$	2720	<i>Bielski et al.</i> (1985)
R <sub>i</sub> 00028 $\text{HO}_2 + \text{O}_2^- \xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{O}_2 + \text{O}_2 + \text{OH}^-$	$4.85 \cdot 10^7$	1060	<i>Bielski et al.</i> (1985)
R <sub>i</sub> 00029 $\text{HO}_2 + \text{OH} \longrightarrow \text{O}_2 + \text{H}_2\text{O}$	$1.00 \cdot 10^{10}$		<i>Elliot and Buxton</i> (1992)

**Table G.4 (continued)** Irreversible inorganic reactions in CAPRAM 3.0o

Reaction	$k_{298} / \text{K}^a$	$E_A / \text{R}^b$	Reference/comment
R <sub>i</sub> 00030 $\text{O}_2^- + \text{OH} \longrightarrow \text{OH}^- + \text{O}_2$	$1.10 \cdot 10^{10}$	2120	<i>Christensen et al.</i> (1989)
R <sub>i</sub> 00031 $\text{H}_2\text{O}_2 + \text{OH} \longrightarrow \text{HO}_2 + \text{H}_2\text{O}$	$3.00 \cdot 10^7$	1680	<i>Christensen et al.</i> (1982)
R <sub>i</sub> 00032 $\text{HSO}_3^- + \text{OH} \longrightarrow \text{SO}_3^- + \text{H}_2\text{O}$	$2.70 \cdot 10^9$		<i>Buxton et al.</i> (1996b)
R <sub>i</sub> 00033 $\text{SO}_3^{2-} + \text{OH} \longrightarrow \text{SO}_3^- + \text{OH}^-$	$4.60 \cdot 10^9$		<i>Buxton et al.</i> (1996b)
R <sub>i</sub> 00034 $\text{MnO}_2^+ + \text{MnO}_2^+ \xrightarrow{2\text{H}_2\text{O}} 2\text{Mn}^{2+} + \text{H}_2\text{O}_2 + 2\text{OH}^-$	$6.00 \cdot 10^6$		<i>Jacobsen et al.</i> (1997b)
R <sub>i</sub> 00035 $\text{Cu}^+ + \text{O}_2 \longrightarrow \text{Cu}^{2+} + \text{O}_2^-$	$4.60 \cdot 10^5$		<i>Bjergbakke et al.</i> (1976)
R <sub>i</sub> 00036 $\text{Fe}^{2+} + \text{O}_3 \longrightarrow \text{FeO}^{2+} + \text{O}_2$	$8.20 \cdot 10^5$	4690	<i>Løgager et al.</i> (1992)
R <sub>i</sub> 00037 $\text{FeO}^{2+} + \text{H}_2\text{O}_2 \longrightarrow \text{Fe}^{3+} + \text{HO}_2 + \text{OH}^-$	$9.50 \cdot 10^3$	2766	<i>Jacobsen et al.</i> (1998)
R <sub>i</sub> 00038 $\text{FeO}^{2+} + \text{H}_2\text{O} \longrightarrow \text{Fe}^{3+} + \text{OH} + \text{OH}^-$	$2.34 \cdot 10^{-4}$	4089	<i>Jacobsen et al.</i> (1998)
R <sub>i</sub> 00039 $\text{FeO}^{2+} + \text{HO}_2 \longrightarrow \text{Fe}^{3+} + \text{O}_2 + \text{OH}^-$	$2.00 \cdot 10^6$		<i>Jacobsen et al.</i> (1997a)
R <sub>i</sub> 00040 $\text{FeO}^{2+} + \text{OH} \xrightarrow{\text{H}_2\text{O}} \text{Fe}^{3+} + \text{H}_2\text{O}_2 + \text{OH}^-$	$1.00 \cdot 10^7$		<i>Løgager et al.</i> (1992)
R <sub>i</sub> 00041 $\text{FeO}^{2+} + \text{HONO} \longrightarrow \text{Fe}^{3+} + \text{NO}_2 + \text{OH}^-$	$1.10 \cdot 10^4$	4150	<i>Jacobsen et al.</i> (1998)
R <sub>i</sub> 00042 $\text{FeO}^{2+} + \text{HSO}_3^- \longrightarrow \text{Fe}^{3+} + \text{SO}_3^- + \text{OH}^-$	$2.50 \cdot 10^5$		<i>Jacobsen et al.</i> (1998)
R <sub>i</sub> 00043 $\text{FeO}^{2+} + \text{Cl}^- \xrightarrow{\text{H}_2\text{O}} \text{Fe}^{3+} + \text{ClOH}^- + \text{OH}^-$	$1.00 \cdot 10^2$		<i>Jacobsen et al.</i> (1998)
R <sub>i</sub> 00044 $\text{FeO}^{2+} + \text{Mn}^{2+} \xrightarrow{\text{H}_2\text{O}} \text{Mn}^{3+} + \text{Fe}^{3+} + 2\text{OH}^-$	$1.00 \cdot 10^4$	2562	<i>Jacobsen et al.</i> (1998)
R <sub>i</sub> 00045 $\text{FeO}^{2+} + \text{HCOOH} \xrightarrow{\text{H}_2\text{O}} \text{Fe}^{3+} + \cdot\text{COOH} + \text{OH}^-$	$1.60 \cdot 10^2$	2680	<i>Jacobsen et al.</i> (1998)
R <sub>i</sub> 00046 $\text{FeO}^{2+} + \text{HCOO}^- \xrightarrow{\text{H}_2\text{O}} \text{Fe}^{3+} + \cdot\text{COOH} + 2\text{OH}^-$	$3.00 \cdot 10^5$		<i>Jacobsen et al.</i> (1998)
R <sub>i</sub> 00047 $\text{FeO}^{2+} + \text{CH}_3\text{CH}_2\text{OH} \longrightarrow$ $\text{Fe}^{3+} + \text{CH}_3\text{C}\cdot\text{HOH} + \text{OH}^-$	$2.50 \cdot 10^3$		<i>Jacobsen et al.</i> (1998)
R <sub>i</sub> 00048 $\text{FeO}^{2+} + \text{CH}_2(\text{OH})_2 \longrightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot\text{CH}(\text{OH})_2$	$4.00 \cdot 10^2$	5352	<i>Jacobsen et al.</i> (1998)
R <sub>i</sub> 00049 $\text{FeO}^{2+} + \text{NO}_2^- \xrightarrow{\text{H}_2\text{O}} \text{Fe}^{3+} + \text{NO}_2 + 2\text{OH}^-$	$1.00 \cdot 10^5$		<i>Jacobsen et al.</i> (1998)
R <sub>i</sub> 00050 $\text{FeO}^{2+} + \text{Fe}^{2+} \longrightarrow 2\text{Fe}^{3+} + 2\text{OH}^-$	$7.20 \cdot 10^4$	842	<i>Jacobsen et al.</i> (1997a)
R <sub>i</sub> 00051 $\text{FeO}^{2+} + \text{Fe}^{2+} \xrightarrow{\text{H}_2\text{O}} [\text{FeOH}_2\text{Fe}]^{4+}$	$1.80 \cdot 10^4$	5052	<i>Jacobsen et al.</i> (1997a)
R <sub>i</sub> 00052 $[\text{FeOH}_2\text{Fe}]^{4+} \longrightarrow 2\text{Fe}^{3+} + 2\text{OH}^-$	$4.90 \cdot 10^{-1}$	8780	<i>Jacobsen et al.</i> (1997a)
R <sub>i</sub> 00053 $[\text{FeOH}_2\text{Fe}]^{4+} + \text{H}^+ \longrightarrow 2\text{Fe}^{3+} + \text{OH}^- + \text{H}_2\text{O}$	$1.95 \cdot 10^0$	5653	<i>Jacobsen et al.</i> (1997a)

**Table G.4 (continued)** Irreversible inorganic reactions in CAPRAM 3.0o

	Reaction	$k_{298} / \text{K}^a$	$E_A / \text{R}^b$	Reference/comment
R <sub>i</sub> 00054	$\text{Fe}^{2+} + \text{CH}_3\text{OO}\cdot \longrightarrow [\text{Fe}(\text{CH}_3(\text{OO}\cdot))]^{2+}$	$8.60 \cdot 10^5$		<i>Khaikin et al.</i> (1996)
R <sub>i</sub> 00055	$[\text{Fe}(\text{CH}_3\text{OO}\cdot)]^{2+} + \text{H}^+ \longrightarrow \text{Fe}^{3+} + \text{CH}_3\text{OOH}$	$3.00 \cdot 10^4$		<i>Khaikin et al.</i> (1996)
R <sub>i</sub> 00056	$[\text{Fe}(\text{CH}_3\text{OO}\cdot)]^{2+} \longrightarrow \text{Fe}^{3+} + \text{CH}_3\text{OOH} + \text{OH}^-$	$1.00 \cdot 10^2$		<i>Khaikin et al.</i> (1996)
R <sub>i</sub> 00057	$\text{MnO}^{2+} + \text{Mn}^{2+} \xrightarrow{\text{H}_2\text{O}} \text{Mn}^{3+} + \text{Mn}^{3+} + 2\text{OH}^-$	$1.00 \cdot 10^5$		<i>Jacobsen et al.</i> (1998)
R <sub>i</sub> 00058	$\text{Mn}^{2+} + \text{O}_3 \longrightarrow \text{MnO}^{2+} + \text{O}_2$	$1.65 \cdot 10^3$		<i>Jacobsen et al.</i> (1998)
R <sub>i</sub> 00059	$\text{Cu}^+ + \text{O}_3 \xrightarrow{\text{H}_2\text{O}} \text{Cu}^{2+} + \text{OH} + \text{O}_2 + \text{OH}^- + \text{H}_2\text{O}$	$3.00 \cdot 10^7$		<i>Hoigné and Böhler</i> (1996)
R <sub>i</sub> 00060	$\text{N}_2\text{O}_5 \longrightarrow \text{NO}_2^+ + \text{NO}_3^-$	$1.00 \cdot 10^9$		estimated
R <sub>i</sub> 00061	$\text{NO}_2^+ + \text{H}_2\text{O} \longrightarrow \text{NO}_3^- + 2\text{H}^+$	$8.90 \cdot 10^7$		<i>Behnke et al.</i> (1997)
R <sub>i</sub> 00062	$\text{NO}_3 + \text{OH}^- \longrightarrow \text{NO}_3^- + \text{OH}$	$9.40 \cdot 10^7$	2700	<i>Exner et al.</i> (1992)
R <sub>i</sub> 00063	$\text{NO}_3 + \text{Fe}^{2+} \longrightarrow \text{NO}_3^- + \text{Fe}^{3+}$	$8.00 \cdot 10^6$		<i>Pikaev et al.</i> (1974)
R <sub>i</sub> 00064	$\text{NO}_3 + \text{Mn}^{2+} \longrightarrow \text{NO}_3^- + \text{Mn}^{3+}$	$1.10 \cdot 10^6$		<i>Neta and Huie</i> (1986)
R <sub>i</sub> 00065	$\text{NO}_3 + \text{H}_2\text{O}_2 \longrightarrow \text{NO}_3^- + \text{H}^+ + \text{HO}_2$	$4.90 \cdot 10^6$	2000	<i>Herrmann et al.</i> (1994)
R <sub>i</sub> 00066	$\text{NO}_3 + \text{HO}_2 \longrightarrow \text{NO}_3^- + \text{H}^+ + \text{O}_2$	$3.00 \cdot 10^9$		<i>Sehested et al.</i> (1994)
R <sub>i</sub> 00067	$\text{NO}_3 + \text{O}_2^- \longrightarrow \text{NO}_3^- + \text{O}_2$	$3.00 \cdot 10^9$		estimated same as R <sub>i</sub> 00066
R <sub>i</sub> 00068	$\text{NO}_3 + \text{HSO}_3^- \longrightarrow \text{NO}_3^- + \text{H}^+ + \text{SO}_3^-$	$1.30 \cdot 10^9$	2000	<i>Exner et al.</i> (1992)
R <sub>i</sub> 00069	$\text{NO}_3 + \text{SO}_3^{2-} \longrightarrow \text{NO}_3^- + \text{SO}_3^-$	$3.00 \cdot 10^8$		<i>Exner et al.</i> (1992)
R <sub>i</sub> 00070	$\text{NO}_3 + \text{HSO}_4^- \longrightarrow \text{NO}_3^- + \text{H}^+ + \text{SO}_4^-$	$2.60 \cdot 10^5$		<i>Raabe</i> (1996)
R <sub>i</sub> 00071	$\text{NO}_3 + \text{SO}_4^{2-} \longrightarrow \text{NO}_3^- + \text{SO}_4^-$	$1.00 \cdot 10^5$		<i>Løgager et al.</i> (1993)
R <sub>i</sub> 00072	$\text{NO}_2 + \text{OH} \longrightarrow \text{HOONO}$	$1.20 \cdot 10^{10}$		<i>Wagner et al.</i> (1980)
R <sub>i</sub> 00073	$\text{NO}_2 + \text{O}_2^- \longrightarrow \text{NO}_2^- + \text{O}_2$	$1.00 \cdot 10^8$		<i>Warneck and Wurzinger</i> (1988)
R <sub>i</sub> 00074	$\text{NO}_2 + \text{NO}_2 \xrightarrow{\text{H}_2\text{O}} \text{HONO} + \text{NO}_3^- + \text{H}^+$	$8.40 \cdot 10^7$	-2900	<i>Park and Lee</i> (1988)
R <sub>i</sub> 00075	$\text{NO}_4^- \longrightarrow \text{NO}_2^- + \text{O}_2$	$4.50 \cdot 10^{-2}$		<i>Løgager and Sehested</i> (1993)
R <sub>i</sub> 00076	$\text{NO}_2^- + \text{OH} \longrightarrow \text{NO}_2 + \text{OH}^-$	$9.10 \cdot 10^9$		<i>Barker et al.</i> (1970)
R <sub>i</sub> 00077	$\text{NO}_2^- + \text{SO}_4^- \longrightarrow \text{NO}_2 + \text{SO}_4^{2-}$	$7.20 \cdot 10^8$		<i>Reese</i> (1997)
R <sub>i</sub> 00078	$\text{NO}_2^- + \text{NO}_3 \longrightarrow \text{NO}_2 + \text{NO}_3^-$	$1.40 \cdot 10^9$		<i>Herrmann and Zellner</i> (1998)



**Table G.4 (continued)** Irreversible inorganic reactions in CAPRAM 3.0o

Reaction	$k_{298} / \text{K}^a$	$E_A / \text{R}^b$	Reference/comment
R <sub>i</sub> 00079 $\text{NO}_2^- + \text{Cl}_2^- \longrightarrow 2 \text{Cl}^- + \text{NO}_2$	$6.00 \cdot 10^7$		<i>Jacobi et al.</i> (1996)
R <sub>i</sub> 00080 $\text{NO}_2^- + \text{Br}_2^- \longrightarrow 2 \text{Br}^- + \text{NO}_2$	$1.20 \cdot 10^7$	1720	<i>Shoute et al.</i> (1991)
R <sub>i</sub> 00081 $\text{NO}_2^- + \text{CO}_3^- \longrightarrow \text{CO}_3^{2-} + \text{NO}_2$	$6.60 \cdot 10^5$	850	<i>Huie et al.</i> (1991)
R <sub>i</sub> 00082 $\text{NO}_2^- + \text{O}_3 \longrightarrow \text{NO}_3^- + \text{O}_2$	$5.00 \cdot 10^5$	6900	<i>Damschen and Martin</i> (1983)
R <sub>i</sub> 00083 $\text{HONO} + \text{OH} \longrightarrow \text{NO}_2 + \text{H}_2\text{O}$	$1.10 \cdot 10^{10}$		<i>Barker et al.</i> (1970)
R <sub>i</sub> 00084 $\text{HNO}_4 + \text{HSO}_3^- \longrightarrow \text{HSO}_4^- + \text{H}^+ + \text{NO}_3^-$	$3.30 \cdot 10^5$		<i>Amels et al.</i> (1996)
R <sub>i</sub> 00085 $\text{NO}_2^+ + \text{Cl}^- \longrightarrow \text{ClNO}_2$	$1.00 \cdot 10^{10}$		<i>Chr. George</i> , pers. comm., 1999
R <sub>i</sub> 00086 $\text{NO}_2^+ + \text{Br}^- \longrightarrow \text{BrNO}_2$	$1.00 \cdot 10^{10}$		<i>Chr. George</i> , pers. comm., 1999
R <sub>i</sub> 00087 $\text{ClNO}_2 + \text{Br}^- \longrightarrow \text{NO}_2^- + \text{BrCl}$	$5.00 \cdot 10^6$		<i>Chr. George</i> , pers. comm., 1999
R <sub>i</sub> 00088 $\text{BrNO}_2 + \text{Br}^- \longrightarrow \text{Br}_2 + \text{NO}_2^-$	$2.55 \cdot 10^4$		<i>Chr. George</i> , pers. comm., 1999
R <sub>i</sub> 00089 $\text{BrNO}_2 + \text{Cl}^- \longrightarrow \text{NO}_2^- + \text{BrCl}$	$1.00 \cdot 10^1$		<i>Chr. George</i> , pers. comm., 1999
R <sub>i</sub> 00090 $\text{CH}_2\text{OHSO}_3 \longrightarrow \text{SO}_3 + \cdot\text{CH}_2\text{OH}$	$1.00 \cdot 10^5$		estimated
R <sub>i</sub> 00091 $\cdot\text{OOCHOHSO}_3^- \longrightarrow \text{HO}_2 + \text{CHOSO}_3^-$	$1.70 \cdot 10^4$		<i>Barlow et al.</i> (1997)
R <sub>i</sub> 00092 $\text{CHOSO}_3^- + \text{H}_2\text{O} \longrightarrow \text{HSO}_3^- + \text{HCOOH}$	$1.26 \cdot 10^{-2}$		<i>Buxton et al.</i> (1997)
R <sub>i</sub> 00093 $\cdot\text{OOCHOHSO}_3^- \longrightarrow \cdot\text{OOCHO} + \text{HSO}_3^-$	$7.00 \cdot 10^3$		<i>Barlow et al.</i> (1997)
R <sub>i</sub> 00094 $\cdot\text{CHOHSO}_3^{2-} + \text{O}_2 \longrightarrow \text{CHOSO}_3^- + \text{O}_2^-$	$1.60 \cdot 10^9$		<i>Barlow et al.</i> (1997)
R <sub>i</sub> 00095 $\text{CH}_2(\text{OH})\text{SO}_3^- + \text{OH} \longrightarrow \cdot\text{CHOHSO}_3^- + \text{H}_2\text{O}$	$3.00 \cdot 10^8$		<i>Barlow et al.</i> (1997)
R <sub>i</sub> 00096 $\text{CH}_2(\text{OH})\text{SO}_3^- + \text{SO}_4^- \longrightarrow \text{CH}_2\text{OHSO}_3 + \text{SO}_4^{2-}$	$1.30 \cdot 10^6$		<i>Barlow et al.</i> (1997)
R <sub>i</sub> 00097 $\text{CH}_2(\text{OH})\text{SO}_3^- + \text{NO}_3 \longrightarrow \text{CH}_2\text{OHSO}_3 + \text{NO}_3^-$	$4.20 \cdot 10^6$		<i>Barlow et al.</i> (1997)
R <sub>i</sub> 00098 $\text{CH}_2(\text{OH})\text{SO}_3^- + \text{Cl}_2^- \longrightarrow 2 \text{Cl}^- + \text{CH}_2\text{OHSO}_3$	$5.00 \cdot 10^5$		<i>Barlow et al.</i> (1997)
R <sub>i</sub> 00099 $\text{CH}_2(\text{OH})\text{SO}_3^- + \text{Br}_2^- \longrightarrow 2 \text{Br}^- + \text{CH}_2\text{OHSO}_3$	$5.00 \cdot 10^4$		estimated a factor 10 smaller than R <sub>i</sub> 00098
R <sub>i</sub> 00100 $\cdot\text{CHOHSO}_3^- + \text{O}_2 \longrightarrow \cdot\text{CHOHSO}_3^-$	$2.60 \cdot 10^9$		<i>Barlow et al.</i> (1997)
R <sub>i</sub> 00101 $\text{HSO}_3^- + \text{HCHO} \longrightarrow \text{CH}_2(\text{OH})\text{SO}_3^-$	$7.90 \cdot 10^2$	3293	<i>Olson and Hoffmann</i> (1989)
R <sub>i</sub> 00102 $\text{CH}_2(\text{OH})\text{SO}_3^- \longrightarrow \text{HSO}_3^- + \text{HCHO}$	$1.20 \cdot 10^{-7}$	5831	$k_b$ calculated from $k_f$ (R <sub>i</sub> 00101) and $K$
R <sub>i</sub> 00103 $\text{SO}_3^{2-} + \text{HCHO} \xrightarrow{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{SO}_3^- + \text{OH}^-$	$2.50 \cdot 10^7$	2752	<i>Olson and Hoffmann</i> (1989)
R <sub>i</sub> 00104 $\text{CH}_2(\text{OH})\text{SO}_3^- \longrightarrow \text{HCHO} + \text{SO}_3^{2-} + \text{H}^+$	$3.79 \cdot 10^{-3}$	5290	$k_b$ calculated from $k_f$ (R <sub>i</sub> 00103) and $K$

**Table G.4 (continued)** Irreversible inorganic reactions in CAPRAM 3.0o

	Reaction	$k_{298} / \text{K}^a$	$E_A/R^b$	Reference/comment
R <sub>i</sub> 00105	$\text{SO}_3 + \text{H}_2\text{O} \longrightarrow \text{SO}_4^{2-} + 2\text{H}^+$	$1.00 \cdot 10^{10}$		estimated as diffusion controlled
R <sub>i</sub> 00106	$\text{HSO}_3^- + \text{H}_2\text{O}_2 + \text{H}^+ \longrightarrow \text{SO}_4^{2-} + 2\text{H}^+ + \text{H}_2\text{O}$	$7.20 \cdot 10^7$	4000	rate constant from ( <i>Lind et al.</i> , 1987) with temperature dependency as given in ( <i>Ervens et al.</i> , 2003)
R <sub>i</sub> 00107	$\text{HSO}_3^- + \text{CH}_3\text{OOH} + \text{H}^+ \longrightarrow \text{SO}_4^{2-} + \text{CH}_3\text{OH} + 2\text{H}^+$	$1.70 \cdot 10^7$	3800	<i>Lind et al.</i> (1987)
R <sub>i</sub> 00108	$\text{HSO}_3^- + \text{CH}_3\text{C}(\text{O})\text{OOH} + \text{H}^+ \longrightarrow \text{SO}_4^{2-} + 2\text{H}^+ + \text{CH}_3\text{COOH}$	$5.60 \cdot 10^7$	3990	<i>Lind et al.</i> (1987)
R <sub>i</sub> 00109	$\text{SO}_2 + \text{O}_3 \xrightarrow{\text{H}_2\text{O}} \text{HSO}_4^- + \text{O}_2 + \text{H}^+$	$2.40 \cdot 10^4$		<i>Hoffmann</i> (1986)
R <sub>i</sub> 00110	$\text{HSO}_3^- + \text{O}_3 \longrightarrow \text{SO}_4^{2-} + \text{H}^+ + \text{O}_2$	$3.70 \cdot 10^5$	5530	<i>Hoffmann</i> (1986)
R <sub>i</sub> 00111	$\text{SO}_3^{2-} + \text{O}_3 \longrightarrow \text{SO}_4^{2-} + \text{O}_2$	$1.50 \cdot 10^9$	5280	<i>Hoffmann</i> (1986)
R <sub>i</sub> 00112	$\text{HSO}_3^- + [\text{Fe}(\text{OH})]^{2+} \longrightarrow \text{SO}_3^- + \text{Fe}^{2+} + \text{H}_2\text{O}$	$3.00 \cdot 10^1$		<i>Ziajka et al.</i> (1994)
R <sub>i</sub> 00113	$\text{SO}_5^- + \text{Fe}^{2+} \xrightarrow{\text{H}_2\text{O}} \text{HSO}_5^- + [\text{Fe}(\text{OH})]^{2+}$	$2.65 \cdot 10^7$	5809	<i>Herrmann et al.</i> (1996b)
R <sub>i</sub> 00114	$\text{HSO}_5^- + \text{Fe}^{2+} \longrightarrow \text{SO}_4^- + [\text{Fe}(\text{OH})]^{2-}$	$3.00 \cdot 10^4$		<i>Ziajka et al.</i> (1994)
R <sub>i</sub> 00115	$\text{HSO}_5^- + \text{Mn}^{2+} \longrightarrow \text{SO}_4^- + \text{Mn}^{3+} + \text{OH}^-$	$3.00 \cdot 10^4$		estimated equal as R <sub>i</sub> 00114
R <sub>i</sub> 00116	$\text{SO}_5^- + \text{Mn}^{2+} \xrightarrow{\text{H}_2\text{O}} \text{Mn}^{3+} + \text{HSO}_5^- + \text{OH}^-$	$1.00 \cdot 10^{10}$		<i>Berglund et al.</i> (1994)
R <sub>i</sub> 00117	$\text{Fe}^{2+} + \text{SO}_4^- \xrightarrow{\text{H}_2\text{O}} [\text{Fe}(\text{OH})]^{2-} + \text{SO}_4^{2-} + \text{H}^+$	$4.60 \cdot 10^9$	-2165	<i>Buxton et al.</i> (1997)
R <sub>i</sub> 00118	$\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2-} \longrightarrow \text{Fe}^{3+} + \text{SO}_4^{2-} + \text{SO}_4^-$	$1.70 \cdot 10^1$		<i>Buxton et al.</i> (1997)
R <sub>i</sub> 00119	$\text{SO}_5^- + \text{SO}_5^- \longrightarrow \text{S}_2\text{O}_8^{2-} + \text{O}_2$	$4.80 \cdot 10^7$	2600	<i>Buxton et al.</i> (1997)
R <sub>i</sub> 00120	$\text{SO}_5^- + \text{SO}_5^- \longrightarrow \text{SO}_4^- + \text{SO}_4^- + \text{O}_2$	$2.20 \cdot 10^8$	2600	<i>Buxton et al.</i> (1997)
R <sub>i</sub> 00121	$\text{SO}_5^- + \text{HO}_2 \longrightarrow \text{SO}_5\text{O}_2\text{H}^-$	$1.70 \cdot 10^9$		<i>Buxton et al.</i> (1996a)
R <sub>i</sub> 00122	$\text{SO}_5^- + \text{O}_2^- \xrightarrow{\text{H}_2\text{O}} \text{HSO}_5^- + \text{O}_2 + \text{OH}^-$	$2.34 \cdot 10^8$		<i>Buxton et al.</i> (1996b)
R <sub>i</sub> 00123	$\text{SO}_5\text{O}_2\text{H}^- + \text{HSO}_3^- \longrightarrow 2\text{SO}_4^{2-} + 2\text{H}^+$	$3.00 \cdot 10^5$		<i>Buxton et al.</i> (1997)
R <sub>i</sub> 00124	$\text{SO}_5\text{O}_2^{2-} + \text{HSO}_3^- \longrightarrow 2\text{SO}_4^{2-} + \text{H}^+$	$5.20 \cdot 10^6$		<i>Buxton et al.</i> (1997)
R <sub>i</sub> 00125	$\text{SO}_5\text{O}_2^{2-} \xrightarrow{\text{H}_2\text{O}} \text{HSO}_5^- + \text{O}_2 + \text{OH}^-$	$1.20 \cdot 10^3$		<i>Buxton et al.</i> (1997)

**Table G.4 (continued)** Irreversible inorganic reactions in CAPRAM 3.0o

Reaction	$k_{298} / \text{K}^a$	$E_A / \text{R}^b$	Reference/comment
R <sub>i</sub> 00126 $\text{SO}_3^- + \text{O}_2 \longrightarrow \text{SO}_5^-$	$2.50 \cdot 10^9$		<i>Buxton et al.</i> (1996b)
R <sub>i</sub> 00127 $\text{SO}_5^- + \text{HSO}_3^- \longrightarrow \text{HSO}_5^- + \text{SO}_3^-$	$8.60 \cdot 10^3$		<i>Buxton et al.</i> (1996b)
R <sub>i</sub> 00128 $\text{SO}_5^- + \text{HSO}_3^- \longrightarrow \text{SO}_4^{2-} + \text{SO}_4^- + \text{H}^+$	$3.60 \cdot 10^2$		<i>Buxton et al.</i> (1996b)
R <sub>i</sub> 00129 $\text{SO}_5^- + \text{SO}_3^{2-} \xrightarrow{\text{H}_2\text{O}} \text{HSO}_5^- + \text{SO}_3^- + \text{OH}^-$	$2.13 \cdot 10^5$		<i>Buxton et al.</i> (1996b)
R <sub>i</sub> 00130 $\text{SO}_5^- + \text{SO}_3^{2-} \longrightarrow \text{SO}_4^- + \text{SO}_4^{2-}$	$5.50 \cdot 10^5$		<i>Buxton et al.</i> (1996b)
R <sub>i</sub> 00131 $\text{OH} + \text{HSO}_4^- \longrightarrow \text{SO}_4^- + \text{H}_2\text{O}$	$3.50 \cdot 10^5$		<i>Tang et al.</i> (1988)
R <sub>i</sub> 00132 $\text{SO}_4^- + \text{SO}_4^- \longrightarrow \text{S}_2\text{O}_8^{2-}$	$6.10 \cdot 10^8$	840	<i>Ervens</i> (1997)
R <sub>i</sub> 00133 $\text{SO}_4^- + \text{HSO}_3^- \longrightarrow \text{SO}_4^{2-} + \text{SO}_3^- + \text{H}^+$	$5.80 \cdot 10^8$		mean value of ( <i>Reese et al.</i> , 1997); ( <i>Wine et al.</i> , 1989); ( <i>Buxton et al.</i> , 1996b)
R <sub>i</sub> 00134 $\text{SO}_4^- + \text{SO}_3^{2-} \longrightarrow \text{SO}_4^{2-} + \text{SO}_3^-$	$3.40 \cdot 10^8$	1200	<i>Reese et al.</i> (1997)
R <sub>i</sub> 00135 $\text{SO}_4^- + \text{Mn}^{2+} \longrightarrow \text{SO}_4^{2-} + \text{Mn}^{3+}$	$1.40 \cdot 10^7$	4089	<i>Buxton et al.</i> (1996a)
R <sub>i</sub> 00136 $\text{SO}_4^- + \text{Cu}^+ \longrightarrow \text{SO}_4^{2-} + \text{Cu}^{2+}$	$3.00 \cdot 10^8$		estimated equal as R <sub>i</sub> 00114 ( <i>McElroy and Waygood</i> , 1990)
R <sub>i</sub> 00137 $\text{SO}_4^- + \text{H}_2\text{O}_2 \longrightarrow \text{SO}_4^{2-} + \text{H}^+ + \text{HO}_2$	$1.70 \cdot 10^7$		mean value of <i>Reese et al.</i> (1997), <i>Wine et al.</i> (1989), <i>Maruthamuthu and Neta</i> (1978)
R <sub>i</sub> 00138 $\text{SO}_4^- + \text{HO}_2 \longrightarrow \text{SO}_4^{2-} + \text{H}^+ + \text{O}_2$	$3.50 \cdot 10^9$		<i>Jiang et al.</i> (1992)
R <sub>i</sub> 00139 $\text{SO}_4^- + \text{O}_2^- \longrightarrow \text{SO}_4^{2-} + \text{O}_2$	$3.50 \cdot 10^9$		estimated equal as R <sub>i</sub> 00138
R <sub>i</sub> 00140 $\text{SO}_4^- + \text{NO}_3^- \longrightarrow \text{SO}_4^{2-} + \text{NO}_3$	$5.00 \cdot 10^4$		<i>Exner et al.</i> (1992)
R <sub>i</sub> 00141 $\text{SO}_4^- + \text{OH}^- \longrightarrow \text{SO}_4^{2-} + \text{OH}$	$1.40 \cdot 10^7$		<i>Herrmann et al.</i> (1995c)
R <sub>i</sub> 00142 $\text{SO}_4^- + \text{H}_2\text{O} \longrightarrow \text{SO}_4^{2-} + \text{OH} + \text{H}^+$	$1.10 \cdot 10^1$	1110	<i>Herrmann et al.</i> (1995c)
R <sub>i</sub> 00143 $\text{HSO}_5^- + \text{HSO}_3^- + \text{H}^+ \longrightarrow 2\text{SO}_4^{2-} + 3\text{H}^+$	$7.14 \cdot 10^6$		<i>Betterton and Hoffmann</i> (1988)
R <sub>i</sub> 00144 $\text{HSO}_5^- + \text{SO}_3^{2-} + \text{H}^+ \longrightarrow 2\text{SO}_4^{2-} + 2\text{H}^+$	$7.14 \cdot 10^6$		<i>Betterton and Hoffmann</i> (1988)
R <sub>i</sub> 00145 $\text{HSO}_5^- + \text{OH} \longrightarrow \text{SO}_5^- + \text{H}_2\text{O}$	$1.70 \cdot 10^7$		see <i>Ervens et al.</i> (2003)
R <sub>i</sub> 00146 $\text{OH} + \text{SO}_4^- \longrightarrow \text{HSO}_5^-$	$1.00 \cdot 10^{10}$		<i>Wilhelm et al.</i> (1977)
R <sub>i</sub> 00147 $[\text{Mn}(\text{HSO}_3)]^+ + \text{Mn}^{3+} \longrightarrow 2\text{Mn}^{2+} + \text{SO}_3^- + \text{H}^+$	$1.30 \cdot 10^6$		<i>Berglund et al.</i> (1994)
R <sub>i</sub> 00148 $\text{CH}_3\text{OO} \cdot + \text{HSO}_3^- \longrightarrow \text{CH}_3\text{OOH} + \text{SO}_3^-$	$5.00 \cdot 10^5$		<i>Herrmann et al.</i> (1999)

**Table G.4 (continued)** Irreversible inorganic reactions in CAPRAM 3.0o

	Reaction	$k_{298} / \text{K}^a$	$E_A / \text{R}^b$	Reference/comment
R <sub>i</sub> 00149	$\text{Cl}_2^- + \text{Cl}_2^- \longrightarrow \text{Cl}_2 + 2 \text{Cl}^-$	$1.80 \cdot 10^9$		<i>Jacob (1999)</i>
R <sub>i</sub> 00150	$\text{Cl}_2^- + \text{Fe}^{2+} \longrightarrow 2 \text{Cl}^- + \text{Fe}^{3+}$	$1.00 \cdot 10^7$	3030	<i>Thornton and Laurence (1973)</i>
R <sub>i</sub> 00151	$\text{Cl}_2^- + \text{Fe}^{2+} \longrightarrow \text{FeCl}^{2+} + \text{Cl}^-$	$4.00 \cdot 10^6$	3490	<i>Thornton and Laurence (1973)</i>
R <sub>i</sub> 00152	$\text{Cl}_2^- + \text{Mn}^{2+} \longrightarrow \text{MnCl}_2^+$	$2.00 \cdot 10^7$	4090	<i>Laurence and Thornton (1973)</i>
R <sub>i</sub> 00153	$\text{MnCl}_2^+ \longrightarrow \text{Mn}^{2+} + \text{Cl}_2^-$	$3.00 \cdot 10^5$		<i>Laurence and Thornton (1973)</i>
R <sub>i</sub> 00154	$\text{MnCl}_2^+ \longrightarrow \text{Mn}^{3+} + 2 \text{Cl}^-$	$2.10 \cdot 10^5$		<i>Laurence and Thornton (1973)</i>
R <sub>i</sub> 00155	$\text{Cl}_2^- + \text{Cu}^+ \longrightarrow 2 \text{Cl}^- + \text{Cu}^{2+}$	$1.00 \cdot 10^8$		estimated a factor 10 faster than R <sub>i</sub> 00150
R <sub>i</sub> 00156	$\text{Cl}_2^- + \text{H}_2\text{O}_2 \longrightarrow 2 \text{Cl}^- + \text{H}^+ + \text{HO}_2$	$5.00 \cdot 10^4$	3340	rate constant from <i>Elliot and McCracken (1989)</i> with temperature dependency from <i>Jacob (1999)</i>
R <sub>i</sub> 00157	$\text{Cl}_2^- + \text{OH}^- \longrightarrow 2 \text{Cl}^- + \text{OH}$	$4.00 \cdot 10^6$		<i>Jacobi et al. (1996)</i>
R <sub>i</sub> 00158	$\text{Cl}_2^- + \text{HO}_2 \longrightarrow 2 \text{Cl}^- + \text{H}^+ + \text{O}_2$	$1.30 \cdot 10^{10}$		<i>Jacobi et al. (1996)</i>
R <sub>i</sub> 00159	$\text{Cl}_2^- + \text{O}_2^- \longrightarrow 2 \text{Cl}^- + \text{O}_2$	$6.00 \cdot 10^9$		<i>Jacobi et al. (1996)</i>
R <sub>i</sub> 00160	$\text{Cl}_2^- + \text{HSO}_3^- \longrightarrow 2 \text{Cl}^- + \text{H}^+ + \text{SO}_3^-$	$1.70 \cdot 10^8$	400	<i>Jacobi et al. (1996)</i>
R <sub>i</sub> 00161	$\text{Cl}_2^- + \text{SO}_3^{2-} \longrightarrow 2 \text{Cl}^- + \text{SO}_3^-$	$6.20 \cdot 10^7$		<i>Jacobi et al. (1996)</i>
R <sub>i</sub> 00162	$\text{Cl}_2^- + \text{H}_2\text{O} \longrightarrow \text{H}^+ + \text{Cl}^- + \text{ClOH}^-$	$2.34 \cdot 10^1$		<i>Jacobi et al. (1996); Buxton et al. (1998)</i>
R <sub>i</sub> 00163	$\text{Br}^- + \text{SO}_4^- \longrightarrow \text{SO}_4^{2-} + \text{Br}$	$2.10 \cdot 10^9$		<i>Herrmann et al. (1997)</i>
R <sub>i</sub> 00164	$\text{Br}^- + \text{NO}_3 \longrightarrow \text{NO}_3^- + \text{Br}$	$3.80 \cdot 10^9$		<i>Zellner et al. (1996)</i>
R <sub>i</sub> 00165	$\text{Br}_2^- + \text{Br}_2^- \longrightarrow \text{Br}_2 + 2 \text{Br}^-$	$1.70 \cdot 10^9$		<i>Reese et al. (1999)</i>
R <sub>i</sub> 00166	$\text{Br}_2^- + \text{Fe}^{2+} \longrightarrow 2 \text{Br}^- + \text{Fe}^{3+}$	$3.60 \cdot 10^6$	3330	<i>Thornton and Laurence (1973)</i>
R <sub>i</sub> 00167	$\text{Br}_2^- + \text{Mn}^{2+} \longrightarrow \text{MnBr}_2^+$	$6.30 \cdot 10^6$	4330	<i>Laurence and Thornton (1973)</i>
R <sub>i</sub> 00168	$\text{MnBr}_2^+ \longrightarrow \text{Mn}^{2+} + \text{Br}_2^-$	$3.00 \cdot 10^5$		<i>Laurence and Thornton (1973)</i>
R <sub>i</sub> 00169	$\text{MnBr}_2^+ \longrightarrow \text{Mn}^{3+} + \text{Br}^- + \text{Br}^-$	$2.20 \cdot 10^5$		<i>Laurence and Thornton (1973)</i>
R <sub>i</sub> 00170	$\text{Br}_2^- + \text{Cu}^+ \longrightarrow 2 \text{Br}^- + \text{Cu}^{2+}$	$3.60 \cdot 10^6$		estimated equal as R <sub>i</sub> 00166
R <sub>i</sub> 00171	$\text{Br}_2^- + \text{H}_2\text{O}_2 \longrightarrow 2 \text{Br}^- + \text{H}^+ + \text{HO}_2$	$1.00 \cdot 10^5$		<i>Reese et al. (1997)</i>
R <sub>i</sub> 00172	$\text{Br}_2^- + \text{OH}^- \longrightarrow 2 \text{Br}^- + \text{OH}$	$1.10 \cdot 10^4$		<i>Jacobi et al. (1996)</i>

**Table G.4 (continued)** Irreversible inorganic reactions in CAPRAM 3.0o

Reaction	$k_{298} / \text{K}^a$	$E_A/R^b$	Reference/comment
R <sub>i</sub> 00173 $\text{Br}_2^- + \text{HO}_2 \longrightarrow 2 \text{Br}^- + \text{O}_2 + \text{H}^+$	$4.40 \cdot 10^9$		<i>Matthew et al.</i> (2003)
R <sub>i</sub> 00174 $\text{Br}_2^- + \text{O}_2^- \longrightarrow 2 \text{Br}^- + \text{O}_2$	$1.70 \cdot 10^8$		<i>Wagner and Strehlow</i> (1987)
R <sub>i</sub> 00175 $\text{Br}_2^- + \text{HSO}_3^- \longrightarrow 2 \text{Br}^- + \text{H}^+ + \text{SO}_3^-$	$5.00 \cdot 10^7$	780	<i>Shoute et al.</i> (1991); <i>Jacobi et al.</i> (1996)
R <sub>i</sub> 00176 $\text{Br}_2^- + \text{SO}_3^{2-} \longrightarrow 2 \text{Br}^- + \text{SO}_3^-$	$3.30 \cdot 10^7$	650	<i>Shoute et al.</i> (1991); <i>Jacobi et al.</i> (1996)
R <sub>i</sub> 00177 $\text{HCO}_3^- + \text{OH}^- \longrightarrow \text{CO}_3^- + \text{H}_2\text{O}$	$1.70 \cdot 10^7$	1900	<i>Exner</i> (1990)
R <sub>i</sub> 00178 $\text{HCO}_3^- + \text{SO}_4^- \longrightarrow \text{SO}_4^{2-} + \text{CO}_3^- + \text{H}^+$	$2.80 \cdot 10^6$	2090	<i>Huie and Clifton</i> (1990)
R <sub>i</sub> 00179 $\text{HCO}_3^- + \text{NO}_3 \longrightarrow \text{NO}_3^- + \text{CO}_3^- + \text{H}^+$	$4.10 \cdot 10^7$		estimated
R <sub>i</sub> 00180 $\text{HCO}_3^- + \text{Cl}_2^- \longrightarrow 2 \text{Cl}^- + \text{CO}_3^- + \text{H}^+$	$2.70 \cdot 10^6$		estimated
R <sub>i</sub> 00181 $\text{HCO}_3^- + \text{Br}_2^- \longrightarrow 2 \text{Br}^- + \text{CO}_3^- + \text{H}^+$	$1.10 \cdot 10^5$		estimated
R <sub>i</sub> 00182 $\text{CO}_3^{2-} + \text{OH}^- \longrightarrow \text{OH}^- + \text{CO}_3^-$	$3.90 \cdot 10^8$	2840	<i>Buxton et al.</i> (1988a,b)
R <sub>i</sub> 00183 $\text{CO}_3^{2-} + \text{SO}_4^- \longrightarrow \text{SO}_4^{2-} + \text{CO}_3^-$	$4.10 \cdot 10^6$		<i>Padmaja et al.</i> (1993)
R <sub>i</sub> 00184 $\text{CO}_3^{2-} + \text{NO}_3 \longrightarrow \text{NO}_3^- + \text{CO}_3^-$	$4.10 \cdot 10^7$		estimated
R <sub>i</sub> 00185 $\text{CO}_3^{2-} + \text{Cl}_2^- \longrightarrow 2 \text{Cl}^- + \text{CO}_3^-$	$2.70 \cdot 10^6$		estimated
R <sub>i</sub> 00186 $\text{CO}_3^- + \text{CO}_3^- \xrightarrow{\text{O}_2} 2 \text{O}_2^- + 2 \text{CO}_2$	$2.20 \cdot 10^6$		<i>Huie and Clifton</i> (1990)
R <sub>i</sub> 00187 $\text{CO}_3^- + \text{Fe}^{2+} \longrightarrow \text{Fe}^{3+} + \text{CO}_3^{2-}$	$2.00 \cdot 10^7$		estimated
R <sub>i</sub> 00188 $\text{CO}_3^- + \text{Mn}^{2+} \longrightarrow \text{Mn}^{3+} + \text{CO}_3^{2-}$	$1.50 \cdot 10^7$		<i>Cope et al.</i> (1978)
R <sub>i</sub> 00189 $\text{CO}_3^- + \text{Cu}^+ \longrightarrow \text{Cu}^{2+} + \text{CO}_3^{2-}$	$2.00 \cdot 10^7$		estimated
R <sub>i</sub> 00190 $\text{CO}_3^- + \text{H}_2\text{O}_2 \longrightarrow \text{HCO}_3^- + \text{HO}_2$	$4.30 \cdot 10^5$		<i>Draganic et al.</i> (1991)
R <sub>i</sub> 00191 $\text{CO}_3^- + \text{HO}_2 \longrightarrow \text{HCO}_3^- + \text{O}_2$	$6.50 \cdot 10^8$		estimated equal as R <sub>i</sub> 00192
R <sub>i</sub> 00192 $\text{CO}_3^- + \text{O}_2^- \longrightarrow \text{CO}_3^{2-} + \text{O}_2$	$6.50 \cdot 10^8$		<i>Eriksen et al.</i> (1985)
R <sub>i</sub> 00193 $\text{CO}_3^- + \text{HSO}_3^- \longrightarrow \text{HCO}_3^- + \text{SO}_3^-$	$1.00 \cdot 10^7$		estimated
R <sub>i</sub> 00194 $\text{CO}_3^- + \text{SO}_3^{2-} \longrightarrow \text{CO}_3^{2-} + \text{SO}_3^-$	$5.00 \cdot 10^6$	470	<i>Exner</i> (1990); <i>Huie et al.</i> (1991)
R <sub>i</sub> 00195 $\text{CO}_3^- + \text{NO}_2 \longrightarrow \text{CO}_2 + \text{NO}_3^-$	$1.00 \cdot 10^9$		<i>Lilie et al.</i> (1978)
R <sub>i</sub> 00196 $\text{CO}_3^- + \text{O}_3 \longrightarrow \text{CO}_2 + \text{O}_2 + \text{O}_2^-$	$1.00 \cdot 10^5$		<i>Sehested et al.</i> (1983)
R <sub>i</sub> 00197 $\text{OH} + \text{O}_3 \longrightarrow \text{O}_2 + \text{HO}_2$	$1.00 \cdot 10^8$		<i>Sehested et al.</i> (1984)

**Table G.5** Inorganic equilibria in CAPRAM 3.0o.

	Equilibrium	$K^{(\alpha)}$	$k_f^{(\beta)}$	$\frac{E_A^{(\gamma)}}{R}$	Ref.	$k_b^{(\beta)}$	Ref.
E <sub>i</sub> 0001	$\text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{H}^+$	$1.80 \cdot 10^{-16}$	$2.34 \cdot 10^{-5}$	6800	<i>a</i>	$1.30 \cdot 10^{11}$	<i>b</i>
E <sub>i</sub> 0002	$\text{CO}_2 \xrightleftharpoons{\text{H}_2\text{O}} \text{HCO}_3^- + \text{H}^+$	$4.30 \cdot 10^{-7}$	$2.41 \cdot 10^8$	913	<i>c</i>	$5.60 \cdot 10^4$	<i>b</i>
E <sub>i</sub> 0003	$\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$	$4.70 \cdot 10^{-11}$	2.35	1820	<i>a</i>	$5.00 \cdot 10^{10}$	<i>b</i>
E <sub>i</sub> 0004	$\text{HCl} \rightleftharpoons \text{Cl}^- + \text{H}^+$	$1.72 \cdot 10^6$	$4.99 \cdot 10^{11}$	-6890	<i>d</i>	$2.90 \cdot 10^5$	<i>b</i>
E <sub>i</sub> 0005	$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$	$3.17 \cdot 10^{-7}$	10.78	560	<i>a</i>	$3.4 \cdot 10^{10}$	<i>b</i>
E <sub>i</sub> 0006	$\text{HO}_2 \rightleftharpoons \text{O}_2^- + \text{H}^+$	$1.60 \cdot 10^{-5}$	$8.00 \cdot 10^5$		<i>e,f</i>	$5.00 \cdot 10^{10}$	<i>g</i>
E <sub>i</sub> 0007	$\text{HNO}_3 \rightleftharpoons \text{NO}_3^- + \text{H}^+$	$2.20 \cdot 10^1$	$1.10 \cdot 10^{12}$	-1800	<i>h,i</i>	$5.00 \cdot 10^{10}$	<i>b</i>
E <sub>i</sub> 0008	$\text{HONO} \rightleftharpoons \text{NO}_2^- + \text{H}^+$	$5.30 \cdot 10^{-4}$	$2.65 \cdot 10^7$	1760	<i>j</i>	$5.00 \cdot 10^{10}$	<i>b</i>
E <sub>i</sub> 0009	$\text{HNO}_4 \rightleftharpoons \text{NO}_4^- + \text{H}^+$	$1.00 \cdot 10^{-5}$	$5.00 \cdot 10^5$		<i>k</i>	$5.00 \cdot 10^{10}$	<i>g</i>
E <sub>i</sub> 0010	$\text{NO}_2 + \text{HO}_2 \rightleftharpoons \text{HNO}_4$	$2.20 \cdot 10^9$	$1.00 \cdot 10^7$		<i>l</i>	$4.60 \cdot 10^{-3}$	<i>k</i>
E <sub>i</sub> 0011	$\text{SO}_2 \xrightleftharpoons{\text{H}_2\text{O}} \text{HSO}_3^- + \text{H}^+$	$3.13 \cdot 10^{-4}$	$6.26 \cdot 10^4$	-1940	<i>m</i>	$2.00 \cdot 10^8$	<i>b</i>
E <sub>i</sub> 0012	$\text{HSO}_3^- \rightleftharpoons \text{SO}_3^{2-} + \text{H}^+$	$6.22 \cdot 10^{-8}$	$3.11 \cdot 10^3$	-1960	<i>m</i>	$5.0 \cdot 10^{10}$	<i>b</i>
E <sub>i</sub> 0013	$\text{H}_2\text{SO}_4 \rightleftharpoons \text{HSO}_4^- + \text{H}^+$	$1.00 \cdot 10^3$	$5.00 \cdot 10^{13}$		<i>n</i>	$5.00 \cdot 10^{10}$	<i>b</i>
E <sub>i</sub> 0014	$\text{HSO}_4^- \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-}$	$1.02 \cdot 10^{-2}$	$1.02 \cdot 10^9$	-2700	<i>g</i>	$1.00 \cdot 10^{11}$	<i>c</i>
E <sub>i</sub> 0015	$\text{Fe}^{3+} + \text{H}_2\text{O} \rightleftharpoons [\text{FeOH}]^{2+} + \text{H}^+$	$1.10 \cdot 10^{-4}$	$4.70 \cdot 10^4$		<i>o</i>	$4.30 \cdot 10^8$	<i>o</i>
E <sub>i</sub> 0016	$[\text{FeOH}]^{2+} + \text{H}_2\text{O} \rightleftharpoons [\text{FeOH}_2]^+ + \text{H}^+$	$1.40 \cdot 10^{-7}$	$1.10 \cdot 10^3$		<i>p</i>	$8.00 \cdot 10^9$	<i>p</i>
E <sub>i</sub> 0017	$[\text{FeSO}_4]^+ \rightleftharpoons \text{Fe}^{3+} + \text{SO}_4^{2-}$	$1.80 \cdot 10^{-2}$	$3.20 \cdot 10^3$		<i>o</i>	$1.80 \cdot 10^5$	<i>o</i>
E <sub>i</sub> 0018	$\text{Fe}^{3+} + \text{C}_2\text{O}_4^{2-} \rightleftharpoons [\text{FeC}_2\text{O}_4]^+$	$2.90 \cdot 10^9$	$8.70 \cdot 10^6$		<i>n,(\varepsilon)</i>	$3.00 \cdot 10^{-3}$	<i>n,(\varepsilon)</i>
E <sub>i</sub> 0019	$[\text{FeC}_2\text{O}_4]^+ + \text{C}_2\text{O}_4^{2-} \rightleftharpoons [\text{Fe}(\text{C}_2\text{O}_4)_2]^-$	$6.30 \cdot 10^6$	$1.89 \cdot 10^4$		<i>n,(\varepsilon)</i>	$3.00 \cdot 10^{-3}$	<i>n,(\varepsilon)</i>
E <sub>i</sub> 0020	$[\text{Fe}(\text{C}_2\text{O}_4)_2]^- + \text{C}_2\text{O}_4^{2-} \rightleftharpoons [\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$	$3.80 \cdot 10^4$	$1.14 \cdot 10^2$		<i>n,(\varepsilon)</i>	$3.00 \cdot 10^{-3}$	<i>n,(\varepsilon)</i>
E <sub>i</sub> 0021	$\text{Cl} + \text{Cl}^- \rightleftharpoons \text{Cl}_2^-$	$1.40 \cdot 10^5$	$8.50 \cdot 10^9$		<i>q</i>	$6.00 \cdot 10^4$	<i>q</i>
E <sub>i</sub> 0022	$\text{Br} + \text{Br}^- \rightleftharpoons \text{Br}_2^-$	$6.32 \cdot 10^5$	$1.20 \cdot 10^{10}$		<i>r</i>	$1.90 \cdot 10^4$	<i>r</i>
E <sub>i</sub> 0023	$\text{ClOH}^- + \text{H}^+ \rightleftharpoons \text{Cl} + \text{H}_2\text{O}$	$5.10 \cdot 10^6$	$2.09 \cdot 10^{10}$		<i>s</i>	$4.10 \cdot 10^3$	<i>n</i>
E <sub>i</sub> 0024	$\text{ClOH}^- + \text{Cl}^- \rightleftharpoons \text{Cl}_2^- + \text{OH}^-$	$2.20 \cdot 10^{-4}$	$1.00 \cdot 10^4$		<i>t</i>	$4.50 \cdot 10^7$	<i>t</i>

**Table G.5 (continued).** Inorganic equilibria in CAPRAM 3.0o.

	Equilibrium	$K^{(\alpha)}$	$k_f^{(\beta)}$	$\frac{E_A^{(\gamma)}}{R}$	Ref.	$k_b^{(\beta)}$	Ref.
E <sub>i</sub> 0025	$\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{Cl}^- + \text{HOCl}$	$1.90 \cdot 10^{-5} \text{e}^{-4500/T}$	0.4	8000	<i>u</i>	$2.10 \cdot 10^{4(\delta)}$	<i>u</i>
E <sub>i</sub> 0026	$\text{Br}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{Br}^- + \text{HOBr}$	$1.06 \cdot 10^{-10}$	1.7	7500	<i>v</i>	$1.6 \cdot 10^{10}$	<i>v</i>
E <sub>i</sub> 0027	$\text{Br}^- + \text{HO} \rightleftharpoons \text{BrOH}^-$	$3.33 \cdot 10^2$	$1.10 \cdot 10^{10}$		<i>u</i>	$3.30 \cdot 10^7$	<i>u</i>
E <sub>i</sub> 0028	$\text{Br} + \text{OH}^- \rightleftharpoons \text{BrOH}^-$	$3.10 \cdot 10^3$	$1.30 \cdot 10^{10}$		<i>w</i>	$4.20 \cdot 10^6$	<i>u</i>
E <sub>i</sub> 0029	$\text{BrOH}^- + \text{H}^+ \rightleftharpoons \text{Br} + \text{H}_2\text{O}$	$1.80 \cdot 10^{12}$	$4.40 \cdot 10^{10}$		<i>u</i>	$2.45 \cdot 10^{-2}$	<i>w</i>
E <sub>i</sub> 0030	$\text{BrOH}^- + \text{Br}^- \rightleftharpoons \text{Br}_2^- + \text{OH}^-$	$7.00 \cdot 10^1$	$1.90 \cdot 10^8$		<i>u</i>	$2.70 \cdot 10^6$	<i>x</i>
E <sub>i</sub> 0031	$\text{Mn}^{3+} + \text{H}_2\text{O} \rightleftharpoons [\text{MnOH}]^{2+} + \text{H}^+$	$9.30 \cdot 10^{-1}$	$1.86 \cdot 10^{10}$		<i>g</i>	$2.00 \cdot 10^{10}$	<i>g</i>
E <sub>i</sub> 0032	$\text{Mn}^{2+} + \text{O}_2^- \rightleftharpoons \text{MnO}_2^+$	$2.30 \cdot 10^4$	$1.50 \cdot 10^8$		<i>y</i>	$6.50 \cdot 10^3$	<i>y</i>
E <sub>i</sub> 0033	$\text{Mn}^{2+} + \text{HO}_2 \rightleftharpoons \text{MnO}_2^+ + \text{H}^+$	$1.70 \cdot 10^{-1}$	$1.10 \cdot 10^6$		<i>y</i>	$6.50 \cdot 10^6$	<i>y</i>
E <sub>i</sub> 0034	$\text{Mn}^{3+} + \text{Mn}^{3+} \rightleftharpoons \text{Mn}^{2+} + \text{Mn}^{4+}$	$1.00 \cdot 10^{-3}$	$1.00 \cdot 10^7$		<i>z</i>	$1.00 \cdot 10^{10}$	<i>z</i>
E <sub>i</sub> 0035	$[\text{MnOH}]^{2+} \xrightleftharpoons{\text{H}_2\text{O}} [\text{Mn}(\text{OH})_2]^+ + \text{H}^+$	$1.00 \cdot 10^{-5}$	$2.00 \cdot 10^5$		<i>A</i>	$2.00 \cdot 10^{10}$	<i>A</i>
E <sub>i</sub> 0036	$\text{Mn}^{2+} + \text{HSO}_3^- \rightleftharpoons [\text{Mn}(\text{HSO}_3)]^+$	$3.00 \cdot 10^4$	$3.10 \cdot 10^7$		<i>B</i>	$1.03 \cdot 10^3$	<i>B</i>
E <sub>i</sub> 0037	$\text{Cu}^{2+} + \text{HO} \rightleftharpoons [\text{CuOH}]^{2+}$	$1.17 \cdot 10^4$	$3.50 \cdot 10^8$		<i>C</i>	$3.00 \cdot 10^4$	<i>D</i>
E <sub>i</sub> 0038	$\text{HO}_3 \rightleftharpoons \text{H}^+ + \text{O}_3^-$	$6.30 \cdot 10^{-9}$	$3.30 \cdot 10^2$		<i>E</i>	$5.20 \cdot 10^{10}$	<i>E</i>
E <sub>i</sub> 0039	$\text{HOONO} \rightleftharpoons \text{OONO}^- + \text{H}^+$	$1.00 \cdot 10^{-6}$	$5.00 \cdot 10^4$		<i>F</i>	$5.00 \cdot 10^{10}$	( <i>ζ</i> )
E <sub>i</sub> 0040	$\cdot\text{CH}(\text{OH})\text{SO}_3^- \rightleftharpoons \cdot\text{CH}(\text{O}^-)\text{SO}_3^- + \text{H}^+$	$1.34 \cdot 10^{-6}$	$5.90 \cdot 10^4$		<i>G</i>	$4.40 \cdot 10^{10}$	<i>G</i>
E <sub>i</sub> 0041	$\text{SO}_5\text{O}_2\text{H}^- \rightleftharpoons \text{H}^+ + \text{SO}_5\text{O}_2^{2-}$	$1.50 \cdot 10^{-5}$	$7.50 \cdot 10^5$		<i>n, (η)</i>	$5.00 \cdot 10^{10}$	( <i>ζ</i> )
E <sub>i</sub> 0042	$\text{SO}_4^- + \text{Cl}^- \rightleftharpoons \text{SO}_4^{2-} + \text{Cl}$	$1.20 \cdot 10^0$	$2.52 \cdot 10^8$		<i>H</i>	$2.10 \cdot 10^8$	<i>H</i>
E <sub>i</sub> 0043	$\text{Cl}^- + \text{HO} \rightleftharpoons \text{ClOH}^-$	$7.00 \cdot 10^{-1}$	$4.30 \cdot 10^9$		<i>s</i>	$6.10 \cdot 10^9$	<i>s</i>
E <sub>i</sub> 0044	$\text{NO}_3 + \text{Cl}^- \rightleftharpoons \text{NO}_3^- + \text{Cl}$	$3.40 \cdot 10^0$	$3.40 \cdot 10^8$	4300	<i>I</i>	$1.00 \cdot 10^8$	<i>I</i>

**Table G.5** (continued). Inorganic equilibria in CAPRAM 3.0o.

	Equilibrium	$K^{(\alpha)}$	$k_f^{(\beta)}$	$\frac{E_A^{(\gamma)}}{R}$	Ref.	$k_b^{(\beta)}$	Ref.
E <sub>i</sub> 0045	$\text{Cl}^- + \text{Fe}^{3+} \rightleftharpoons \text{FeCl}^{2+}$	$1.39 \cdot 10^0$	$3.00 \cdot 10^3$		<sup>n</sup>	$2.16 \cdot 10^3$	<sup>n</sup>

( $\alpha$ ) in  $M^{\text{order}(k_b - k_f)}$ ; ( $\beta$ ) in  $M^{-(\text{order}-1)} \text{ s}^{-1}$ ; ( $\gamma$ ) in K; ( $\delta$ ) temperature dependent backward reaction with  $E_a/R = 3500 \text{ K}$ ; ( $\varepsilon$ ) corrected values for  $k_f/k_b$ ; ( $\zeta$ ) estimate given in *Ervens et al.* (2003); ( $\eta$ ) corrections for value of  $K$  and charge of  $\text{SO}_5\text{O}_2\text{H}^-/\text{SO}_5\text{O}_2^{2-}$

<sup>a</sup>*Harned and Owen* (1958); <sup>b</sup>*Graedel and Weschler* (1981); <sup>c</sup>*Chameides* (1984); <sup>d</sup>*Marsh and McElroy* (1985); <sup>e</sup>*Bielski et al.* (1985); <sup>f</sup>*Baxendale et al.* (1971); <sup>g</sup>*Wells and Davies* (1967); <sup>h</sup>*Redlich* (1946); <sup>i</sup>*Redlich and Hood* (1957); <sup>j</sup>*Park and Lee* (1988); <sup>k</sup>*Lammel et al.* (1990); <sup>l</sup>*Warneck and Wurzinger* (1988); <sup>m</sup>*Beilke and Gravenhorst* (1978); <sup>n</sup>*Ervens et al.* (2003); <sup>o</sup>*Brandt and van Eldik* (1995); <sup>p</sup>*Hemmes et al.* (1971); <sup>q</sup>*Buxton et al.* (1998); <sup>r</sup>*Merenyi and Lind* (1994); <sup>s</sup>*Jayson et al.* (1973b); <sup>t</sup>*Grigorov et al.* (1987); <sup>u</sup>*Zehavi and Rabani* (1972); <sup>v</sup>*Beckwith et al.* (1996); <sup>w</sup>*Klänning and Wolff* (1985); <sup>x</sup>*Fornier de Violet* (1981); <sup>y</sup>*Jacobsen et al.* (1997b); <sup>z</sup>*Rosseinsky* (1963); <sup>A</sup>*von Piechowski et al.* (1993); <sup>B</sup>*Berglund et al.* (1993); <sup>C</sup>*Buxton et al.* (1988a); <sup>D</sup>*Meyerstein* (1971); <sup>E</sup>*Bühler et al.* (1984); <sup>F</sup>*Wagner et al.* (1980); <sup>G</sup>*Barlow et al.* (1997); <sup>H</sup>*Buxton et al.* (1999a); <sup>I</sup>*Buxton et al.* (1999b)

## G.3 Organic chemistry

### G.3.1 Phase transfer processes

**Table G.6** Henry's Law coefficients of organic compounds in CAPRAM 3.0o

	Species	$K_{H,298} / \text{M atm}^{-1}$	$\Delta H/R / \text{K}$	Reference/comment
U <sub>o</sub> 0001	HCHO	$2.50 \cdot 10^0$	-7216	<i>Betterton and Hoffmann</i> (1988)
U <sub>o</sub> 0002	HCOOH	$5.53 \cdot 10^3$	-5630	<i>Khan and Brimblecombe</i> (1992)
U <sub>o</sub> 0003	CH <sub>3</sub> OOH	$3.10 \cdot 10^2$	-5607	<i>Lind and Kok</i> (1994)
U <sub>o</sub> 0026	CH <sub>3</sub> COOH	$5.50 \cdot 10^3$	-5890	<i>Khan and Brimblecombe</i> (1992)
U <sub>o</sub> 0004	CH <sub>3</sub> CO(OOH)	$6.69 \cdot 10^2$	-5890	<i>Lind and Kok</i> (1994)
U <sub>o</sub> 0005	CH <sub>3</sub> OO·	$3.10 \cdot 10^2$	-5607	$K_{H, \text{CH}_3\text{O}_2} = K_{H, \text{CH}_3\text{OOH}}$
U <sub>o</sub> 0006	CH <sub>3</sub> CH <sub>2</sub> OO·	$3.40 \cdot 10^2$	-61	estimated equal as CH <sub>3</sub> CH <sub>2</sub> OOH
U <sub>o</sub> 0021	CH <sub>3</sub> CH <sub>2</sub> OH	$1.90 \cdot 10^2$	-6290	<i>Ervens et al.</i> (2003)



**Table G.6 (continued)** Henry's Law coefficients of organic compounds in CAPRAM 3.0o

	Species	$K_{H,298}$ / M atm <sup>-1</sup>	$\Delta H/R$ / K	Reference/comment
U <sub>o</sub> 0007	CH <sub>3</sub> OH	$2.20 \cdot 10^2$	-5390	<i>Ervens et al.</i> (2003)
U <sub>o</sub> 0024	CH <sub>3</sub> CHO	$4.80 \cdot 10^1$	-6254	<i>Betterton and Hoffmann</i> (1988)
U <sub>o</sub> 0008	CH <sub>3</sub> CO <sub>3</sub>	$6.69 \cdot 10^2$	-5893	$K_{H,CH_3CO_3} = K_{H,CH_3CO_3H}$
U <sub>o</sub> 0025	CHOCHO	$1.40 \cdot 10^0$		<i>Betterton and Hoffmann</i> (1988)
U <sub>o</sub> 0029	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	$1.35 \cdot 10^2$	-7500	<i>Jayne et al.</i> (1991)
U <sub>o</sub> 0054	CH <sub>3</sub> CH(OH)CH <sub>3</sub>	$1.28 \cdot 10^2$	-7400	<i>Jayne et al.</i> (1991)
U <sub>o</sub> 0061	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	$1.30 \cdot 10^2$	-7200	<i>Snider and Dawson</i> (1985)
U <sub>o</sub> 0120	CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH <sub>3</sub>	$1.10 \cdot 10^2$	-7300	<i>Snider and Dawson</i> (1985)
U <sub>o</sub> 0052	CH <sub>3</sub> CH <sub>2</sub> CHO	$1.30 \cdot 10^1$	-5700	<i>Zhou and Mopper</i> (1990)
U <sub>o</sub> 0118	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CHO	$9.60 \cdot 10^0$	-6200	<i>Zhou and Mopper</i> (1990)
U <sub>o</sub> 0053	CH <sub>3</sub> CH <sub>2</sub> COOH	$5.71 \cdot 10^3$		<i>Khan et al.</i> (1995)
U <sub>o</sub> 0119	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	$4.70 \cdot 10^3$		<i>Khan et al.</i> (1995)
U <sub>o</sub> 0041	CH <sub>3</sub> COCHO	$1.40 \cdot 10^0$	-7541	<i>Betterton and Hoffmann</i> (1988)
U <sub>o</sub> 0055	CH <sub>3</sub> COCH <sub>3</sub>	$3.20 \cdot 10^1$	-5770	<i>Betterton</i> (1991)
U <sub>o</sub> 0123	CH <sub>3</sub> CH <sub>2</sub> COCH <sub>3</sub>	$1.98 \cdot 10^1$	-2184	<i>Zhou and Mopper</i> (1990)
U <sub>o</sub> 0032	CH <sub>3</sub> COCH <sub>2</sub> OH	$1.29 \cdot 10^2$		<i>Meylan and Howard</i> (1991)
U <sub>o</sub> 0124	CHOCH=CHCHO	$3.00 \cdot 10^5$		estimated after the effective Henry constant of Glyoxal
U <sub>o</sub> 0009	CH <sub>3</sub> COCH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	$3.91 \cdot 10^0$		<i>Kim et al.</i> (2000)
U <sub>o</sub> 0010	CH <sub>3</sub> C–O–CHO	$2.59 \cdot 10^0$		<i>Bocek</i> (1976)
U <sub>o</sub> 0011	C1H <sub>2</sub> CH <sub>2</sub> N(CH <sub>3</sub> )COC1H <sub>2</sub>	$3.13 \cdot 10^5$		<i>Kim et al.</i> (2000)
U <sub>o</sub> 0022	CH <sub>2</sub> (OH)CH <sub>2</sub> OH	$4.00 \cdot 10^6$		<i>Bone et al.</i> (1983)
U <sub>o</sub> 0023	CH <sub>2</sub> (OH)CHO	$4.10 \cdot 10^3$	-4631	<i>Betterton and Hoffmann</i> (1988)
U <sub>o</sub> 0012	CO(OH)CHO	$1.09 \cdot 10^4$	-4800	implemented as effective HLC; immediate hydration assumed
U <sub>o</sub> 0027	CH <sub>2</sub> (OH)COOH	$2.83 \cdot 10^4$	-4029	<i>Ip et al.</i> (2009)

**Table G.6** (continued) Henry's Law coefficients of organic compounds in CAPRAM 3.0o

	Species	$K_{H,298}$ / M atm <sup>-1</sup>	$\Delta H/R$ / K	Reference/comment
U <sub>o</sub> 0047	CH <sub>3</sub> COCOOH	$3.10 \cdot 10^5$	-5100	<i>Khan et al.</i> (1995)
U <sub>o</sub> 0046	CH <sub>2</sub> (OH)COCOOH	$2.94 \cdot 10^6$		currently obsolete due to considerations in subsection 5.5.3
U <sub>o</sub> 0013	CO(OH)CH <sub>2</sub> CHO	$7.00 \cdot 10^3$		<i>Saxena and Hildemann</i> (1996)
U <sub>o</sub> 0014	CH <sub>3</sub> COCOCH <sub>3</sub>	$7.94 \cdot 10^1$		see footnote*
U <sub>o</sub> 0102	CHOCH(OH)COCHO	$2.58 \cdot 10^7$		currently obsolete due to considerations in subsection 5.5.3
U <sub>o</sub> 0103	CHOCH(OH)CH(OH)CHO	$2.58 \cdot 10^7$		currently obsolete due to considerations in subsection 5.5.3
U <sub>o</sub> 0015	CH <sub>3</sub> COCOCH(CH <sub>3</sub> ) <sub>2</sub>	$2.87 \cdot 10^3$		see footnote*
U <sub>o</sub> 0016	CH <sub>3</sub> COCH(OH)CH(CH <sub>3</sub> ) <sub>2</sub>	$5.53 \cdot 10^1$		see footnote*
U <sub>o</sub> 0017	CH <sub>3</sub> CH(CH <sub>3</sub> )CHO	$8.33 \cdot 10^1$		see footnote*
U <sub>o</sub> 0018	CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CH <sub>2</sub> COCHO	$4.33 \cdot 10^7$		see footnote*
U <sub>o</sub> 0019	CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CH <sub>2</sub> COCH <sub>2</sub> OH	$1.51 \cdot 10^3$		see footnote*
U <sub>o</sub> 0020	CH <sub>3</sub> CH <sub>2</sub> COCOOH	$3.46 \cdot 10^5$		see footnote*

\*estimated with EPI Suite v4.10. (US Environmental Protection Agency, 2011: <http://www.epa.gov/opptintr/exposure/pubs/episuite.htm>)

**Table G.7** Mass accommodation and gas phase diffusion coefficients of organic compounds in CAPRAM 3.0o

	Species	$\alpha$ (298 K)	Reference/comment	$D_g$ / 10 <sup>-5</sup> m <sup>2</sup> s <sup>-1</sup>	Reference/comment
U <sub>o</sub> 00001	HCHO	$2.00 \cdot 10^{-2}$	estimated	1.64	<i>Fuller</i> (1986)
U <sub>o</sub> 00002	HCOOH	$2.29 \cdot 10^{-2}$	<i>Davidovits et al.</i> (1995)	1.53	<i>Schwartz</i> (1986)
U <sub>o</sub> 00003	CH <sub>3</sub> OOH	$6.76 \cdot 10^{-3}$	<i>Davidovits et al.</i> (1995)	1.31	<i>Fuller</i> (1986)
U <sub>o</sub> 00004	CH <sub>3</sub> COOH	$3.22 \cdot 10^{-2}$	<i>Davidovits et al.</i> (1995)	1.24	<i>Schwartz</i> (1986)
U <sub>o</sub> 00005	CH <sub>3</sub> CO(OOH)	$1.90 \cdot 10^{-2}$	estimated same as U <sub>o</sub> 00004	1.02	<i>Fuller</i> (1986)
U <sub>o</sub> 00006	CH <sub>3</sub> OO·	$6.76 \cdot 10^{-3}$	estimated same as U <sub>o</sub> 00003	1.35	<i>Fuller</i> (1986)

**Table G.7 (continued)** Mass accommodation and gas phase diffusion coefficients of organic compounds in CAPRAM 3.0o

Species	$\alpha$ (298 K)	Reference/comment	$D_g / 10^{-5} \text{ m}^2 \text{ s}^{-1}$	Reference/comment
U <sub>o</sub> 00007 CH <sub>3</sub> CH <sub>2</sub> OO·	$8.20 \cdot 10^{-3}$	estimated	1.08	Fuller (1986)
U <sub>o</sub> 00008 CH <sub>3</sub> CH <sub>2</sub> OH	$1.76 \cdot 10^{-2}$	Davidovits <i>et al.</i> (1995)	0.95	Schwartz (1986)
U <sub>o</sub> 00009 CH <sub>3</sub> OH	$2.71 \cdot 10^{-2}$	Davidovits <i>et al.</i> (1995)	1.16	Schwartz (1986)
U <sub>o</sub> 00010 CH <sub>3</sub> CHO	$3.00 \cdot 10^{-2}$	estimated	1.22	Fuller (1986)
U <sub>o</sub> 00011 CH <sub>3</sub> CO <sub>3</sub>	$1.90 \cdot 10^{-2}$	estimated same as U <sub>o</sub> 00004	1.00	Fuller (1986)
U <sub>o</sub> 00012 CHOCHO	$2.30 \cdot 10^{-2}$		1.15	Fuller (1986)
U <sub>o</sub> 00013 CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> OH	$1.10 \cdot 10^{-2}$	Jayne <i>et al.</i> (1991)	0.97	Fuller (1986)
U <sub>o</sub> 00014 CH <sub>3</sub> CH(OH)CH <sub>3</sub>	$1.30 \cdot 10^{-2}$	Jayne <i>et al.</i> (1991)	0.97	Fuller (1986)
U <sub>o</sub> 00015 CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	$1.00 \cdot 10^{-2}$		0.85	Fuller (1986)
U <sub>o</sub> 00016 CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH <sub>3</sub>	$1.00 \cdot 10^{-2}$		0.85	Fuller (1986)
U <sub>o</sub> 00017 CH <sub>3</sub> CH <sub>2</sub> CHO	$3.00 \cdot 10^{-2}$	estimated same as U <sub>o</sub> 00010	1.00	Fuller (1986)
U <sub>o</sub> 00018 CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CHO	$3.00 \cdot 10^{-2}$	estimated same as U <sub>o</sub> 00010	0.87	Fuller (1986)
U <sub>o</sub> 00019 CH <sub>3</sub> CH <sub>2</sub> COOH	$3.22 \cdot 10^{-2}$		0.93	Fuller (1986)
U <sub>o</sub> 00020 CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> COOH	$3.00 \cdot 10^{-2}$		0.82	Fuller (1986)
U <sub>o</sub> 00021 CH <sub>3</sub> COCHO	$3.00 \cdot 10^{-2}$	estimated same as U <sub>o</sub> 00010	0.95	Fuller (1986)
U <sub>o</sub> 00022 CH <sub>3</sub> COCH <sub>3</sub>	$5.40 \cdot 10^{-3}$	Schütze and Herrmann (2004)	1.00	Fuller (1986)
U <sub>o</sub> 00023 CH <sub>3</sub> CH <sub>2</sub> COCH <sub>3</sub>	$1.00 \cdot 10^{-2}$	Schütze and Herrmann (2004)	1.00	Fuller (1986)
U <sub>o</sub> 00024 CH <sub>3</sub> COCH <sub>2</sub> OH	$8.00 \cdot 10^{-3}$	Tilgner and Herrmann (2010)	0.96	Fuller (1986)
U <sub>o</sub> 00025 CHOCH=CHCHO	$2.30 \cdot 10^{-2}$	estimated same as U <sub>o</sub> 00012	0.86	Fuller (1986)
U <sub>o</sub> 00026 CH <sub>3</sub> COCH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	$1.00 \cdot 10^{-2}$	estimated	0.75	Fuller (1986)
U <sub>o</sub> 00027 CH <sub>3</sub> C–O–CHO	$1.00 \cdot 10^{-2}$	estimated	0.93	Fuller (1986)
U <sub>o</sub> 00028 C1H <sub>2</sub> CH <sub>2</sub> N(CH <sub>3</sub> )COC1H <sub>2</sub>	$1.00 \cdot 10^{-2}$	estimated	0.82	Fuller (1986)
U <sub>o</sub> 00029 CH <sub>2</sub> (OH)CH <sub>2</sub> OH	$4.00 \cdot 10^{-2}$	Jayne <i>et al.</i> (1991)	1.06	Fuller (1986)

**Table G.7** (continued) Mass accommodation and gas phase diffusion coefficients of organic compounds in CAPRAM 3.0o

Species	$\alpha$ (298 K)	Reference/comment	$D_g / 10^{-5} \text{ m}^2 \text{ s}^{-1}$	Reference/comment
U <sub>o</sub> 00030 CH <sub>2</sub> (OH)CHO	$4.00 \cdot 10^{-2}$	estimated same as U <sub>o</sub> 00029	1.10	Fuller (1986)
U <sub>o</sub> 00031 CO(OH)CHO	$1.00 \cdot 10^{-1}$	estimated	1.05	Fuller (1986)
U <sub>o</sub> 00032 CH <sub>2</sub> (OH)COOH	$1.00 \cdot 10^{-1}$	estimated	1.02	Fuller (1986)
U <sub>o</sub> 00033 CH <sub>3</sub> COCOOH	$1.00 \cdot 10^{-1}$	estimated	0.90	Fuller (1986)
U <sub>o</sub> 00034 CH <sub>2</sub> (OH)COCOOH	$1.00 \cdot 10^{-1}$	see footnote*	0.86	Fuller (1986)
U <sub>o</sub> 00035 CO(OH)CH <sub>2</sub> CHO	$1.00 \cdot 10^{-1}$	estimated	0.90	Fuller (1986)
U <sub>o</sub> 00036 CH <sub>3</sub> COCOCH <sub>3</sub>	$1.00 \cdot 10^{-1}$	estimated	0.84	Fuller (1986)
U <sub>o</sub> 00 CHOCH(OH)COCHO	$1.00 \cdot 10^{-1}$	see footnote*	0.79	Fuller (1986)
U <sub>o</sub> 00 CHOCH(OH)CH(OH)CHO	$1.00 \cdot 10^{-1}$	see footnote*	0.77	Fuller (1986)
U <sub>o</sub> 00039 CH <sub>3</sub> COCOCH(CH <sub>3</sub> ) <sub>2</sub>	$1.00 \cdot 10^{-1}$	estimated	0.69	Fuller (1986)
U <sub>o</sub> 00040 CH <sub>3</sub> COCH(OH)CH(CH <sub>3</sub> ) <sub>2</sub>	$1.00 \cdot 10^{-1}$	estimated	0.68	Fuller (1986)
U <sub>o</sub> 00041 CH <sub>3</sub> CH(CH <sub>3</sub> )CHO	$1.00 \cdot 10^{-1}$	estimated	0.87	Fuller (1986)
U <sub>o</sub> 00042 CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CH <sub>2</sub> COCHO	$1.00 \cdot 10^{-1}$	estimated	0.67	Fuller (1986)
U <sub>o</sub> 00043 CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CH <sub>2</sub> COCH <sub>2</sub> OH	$1.00 \cdot 10^{-1}$	estimated	0.66	Fuller (1986)
U <sub>o</sub> 00044 CH <sub>3</sub> CH <sub>2</sub> COCOOH	$1.00 \cdot 10^{-1}$	estimated	0.80	Fuller (1986)

\*currently obsolete due to considerations in subsection 5.5.3

**Table G.8** Phase transfer processes in CAPRAM 3.5

C4.0 $\alpha$	$\beta$	$\gamma$	Compound	$K_{H, 298}^a$	$E_A/R^b$	Reference/comment	$D_g^c$
U <sub>o</sub> 0028	*	*	CO(OH)CO(OH)	$7.0 \cdot 10^{+06}$		Gaffney et al. (1987)	0.99
U <sub>o</sub> 0030	*	*	CH <sub>3</sub> CH(OH)CH <sub>2</sub> (OH)	$7.3 \cdot 10^{+05}$			0.92
U <sub>o</sub> 0031	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH <sub>2</sub> (OH)	$9.2 \cdot 10^{+05}$		Hilal et al. (2008)	0.92
U <sub>o</sub> 0033	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CHO	$1.0 \cdot 10^{+03}$			0.94
U <sub>o</sub> 0034	*	*	CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> (OH)	$1.5 \cdot 10^{+09}$		currently obsolete due to considerations in subsection 5.5.3	0.87

**Table G.8 (continued)** Phase transfer processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Compound	$K_{H,298}^a$	$E_A/R^b$	Reference/comment	$D_g^c$
U <sub>o</sub> 0035	*	*	CH <sub>2</sub> (OH)COCH <sub>2</sub> (OH)	$7.7 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.89
U <sub>o</sub> 0036	*	*	CH <sub>3</sub> CH(OH)CHO	$3.4 \cdot 10^{+02}$			0.94
U <sub>o</sub> 0037	*	*	CH <sub>2</sub> (OH)CH(OH)CHO	$4.5 \cdot 10^{+04}$		currently obsolete due to considerations in subsection 5.5.3	0.89
U <sub>o</sub> 0038	*	*	CH <sub>2</sub> (OH)COCHO	$1.4 \cdot 10^{+04}$		currently obsolete due to considerations in subsection 5.5.3	0.91
U <sub>o</sub> 0039	*	*	CHOCH <sub>2</sub> CHO	$3.9 \cdot 10^{+02}$			0.96
U <sub>o</sub> 0040	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CO(OH)	$3.2 \cdot 10^{+05}$		currently obsolete due to considerations in subsection 5.5.3	0.89
U <sub>o</sub> 0042	*	*	CHOCOCHO	$3.3 \cdot 10^{+03}$		currently obsolete due to considerations in subsection 5.5.3	0.93
U <sub>o</sub> 0043	*	*	CHOCH(OH)CHO	$1.8 \cdot 10^{+02}$		currently obsolete due to considerations in subsection 5.5.3	0.91
U <sub>o</sub> 0044	*	*	CH <sub>2</sub> (OH)CH(OH)CO(OH)	$1.5 \cdot 10^{+07}$		currently obsolete due to considerations in subsection 5.5.3	0.85
U <sub>o</sub> 0045	*	*	CH <sub>3</sub> CH(OH)CO(OH)	$1.2 \cdot 10^{+04}$		see footnote <i>d</i> , currently obsolete due to considerations in subsection 5.5.3	0.89
U <sub>o</sub> 0048	*	*	CO(OH)CH(OH)CHO	$6.0 \cdot 10^{+04}$		currently obsolete due to considerations in subsection 5.5.3	0.87
U <sub>o</sub> 0049	*	*	CO(OH)COCHO	$1.1 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.89
U <sub>o</sub> 0050	*	*	CO(OH)CH(OH)CO(OH)	$2.0 \cdot 10^{+07}$		currently obsolete due to considerations in subsection 5.5.3	0.83
U <sub>o</sub> 0051	*	*	CO(OH)CH <sub>2</sub> CO(OH)	$3.7 \cdot 10^{+06}$		see footnote <i>d</i> , currently obsolete due to considerations in subsection 5.5.3	0.87

**Table G.8 (continued)** Phase transfer processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Compound	$K_{H,298}^a$	$E_A/R^b$	Reference/comment	$D_g^c$
U <sub>o</sub> 0056	*	*	CO(OH)CH <sub>2</sub> CH <sub>2</sub> CO(OH)	$2.8 \cdot 10^{+09}$		see footnote <i>d</i> , currently obsolete due to considerations in subsection 5.5.3	0.78
U <sub>o</sub> 0057	*	*	CO(OH)CH <sub>2</sub> COCO(OH)	$7.7 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.77
U <sub>o</sub> 0058	*	*	CO(OH)CH <sub>2</sub> CH(OH)CO(OH)	$7.4 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.75
U <sub>o</sub> 0059	*	*	CO(OH)CH(OH)CH(OH)CO(OH)	$7.7 \cdot 10^{+09}$		currently obsolete due to considerations in subsection 5.5.3	0.73
U <sub>o</sub> 0060	*	*	CO(OH)CH(OH)COCO(OH)	$5.1 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.74
U <sub>o</sub> 0062	*	*	CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH <sub>2</sub> (OH)	$5.6 \cdot 10^{+05}$			0.81
U <sub>o</sub> 0063	*	*	CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> (OH)	$2.6 \cdot 10^{+05}$			0.81
U <sub>o</sub> 0064	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> (OH)	$1.8 \cdot 10^{+06}$		<i>Hilal et al.</i> (2008)	0.81
U <sub>o</sub> 0065	*	*	CH <sub>3</sub> CH <sub>2</sub> COCH <sub>2</sub> (OH)	$1.1 \cdot 10^{+03}$			0.83
U <sub>o</sub> 0066	*	*	CH <sub>3</sub> COCH <sub>2</sub> CH <sub>2</sub> (OH)	$3.0 \cdot 10^{+03}$			0.83
U <sub>o</sub> 0067	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH <sub>2</sub> CHO	$1.3 \cdot 10^{+05}$			0.83
U <sub>o</sub> 0068	*	*	CH <sub>3</sub> CH(OH)CH(OH)CH <sub>2</sub> (OH)	$1.1 \cdot 10^{+09}$			0.78
U <sub>o</sub> 0069	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CH <sub>2</sub> (OH)	$1.5 \cdot 10^{+09}$			0.78
U <sub>o</sub> 0070	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> COCH <sub>2</sub> (OH)	$2.1 \cdot 10^{+05}$			0.79
U <sub>o</sub> 0071	*	*	CH <sub>3</sub> CH(OH)COCH <sub>2</sub> (OH)	$5.8 \cdot 10^{+06}$			0.79
U <sub>o</sub> 0072	*	*	CH <sub>3</sub> COCH(OH)CH <sub>2</sub> (OH)	$1.5 \cdot 10^{+05}$			0.79
U <sub>o</sub> 0073	*	*	CH <sub>3</sub> COCOCH <sub>2</sub> (OH)	$4.6 \cdot 10^{+04}$			0.81
U <sub>o</sub> 0074	*	*	CH <sub>3</sub> CH(OH)CH <sub>2</sub> CHO	$7.7 \cdot 10^{+02}$			0.83
U <sub>o</sub> 0075	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CHO	$2.6 \cdot 10^{+06}$			0.79
U <sub>o</sub> 0076	*	*	CH <sub>3</sub> CH <sub>2</sub> CH(OH)CHO	$2.6 \cdot 10^{+02}$			0.83

**Table G.8 (continued)** Phase transfer processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Compound	$K_{H,298}^a$	$E_A/R^b$	Reference/comment	$D_g^c$
U <sub>o</sub> 0077	*	*	CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> CHO	$4.2 \cdot 10^{+06}$			0.79
U <sub>o</sub> 0078	*	*	CH <sub>3</sub> COCH <sub>2</sub> CHO	$1.2 \cdot 10^{+03}$			0.85
U <sub>o</sub> 0079	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> COCHO	$2.1 \cdot 10^{+04}$			0.81
U <sub>o</sub> 0080	*	*	CH <sub>3</sub> CH <sub>2</sub> COCHO	$1.2 \cdot 10^{+02}$			0.85
U <sub>o</sub> 0081	*	*	CH <sub>2</sub> (OH)COCH <sub>2</sub> CHO	$7.4 \cdot 10^{+04}$			0.81
U <sub>o</sub> 0082	*	*	CHOCH <sub>2</sub> CH <sub>2</sub> CHO	$5.1 \cdot 10^{+03}$			0.85
U <sub>o</sub> 0083	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH <sub>2</sub> CO(OH)	$4.0 \cdot 10^{+07}$			0.79
U <sub>o</sub> 0084	*	*	CH <sub>2</sub> (OH)CH(OH)COCH <sub>2</sub> (OH)	$7.6 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.76
U <sub>o</sub> 0085	*	*	CH <sub>2</sub> (OH)COCOCH <sub>2</sub> (OH)	$4.1 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.78
U <sub>o</sub> 0086	*	*	CH <sub>3</sub> CH(OH)CH(OH)CHO	$3.4 \cdot 10^{+04}$			0.79
U <sub>o</sub> 0087	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OH)CHO	$2.3 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.76
U <sub>o</sub> 0088	*	*	CH <sub>3</sub> COCOCHO	$1.1 \cdot 10^{+04}$			0.83
U <sub>o</sub> 0089	*	*	CH <sub>3</sub> COCH(OH)CHO	$6.1 \cdot 10^{+02}$			0.81
U <sub>o</sub> 0090	*	*	CH <sub>2</sub> (OH)CH(OH)COCHO	$1.3 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.78
U <sub>o</sub> 0091	*	*	CH <sub>3</sub> CH(OH)COCHO	$1.1 \cdot 10^{+04}$			0.81
U <sub>o</sub> 0092	*	*	CH <sub>2</sub> (OH)COCH(OH)CHO	$2.9 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.78
U <sub>o</sub> 0093	*	*	CHOCH <sub>2</sub> COCHO	$7.4 \cdot 10^{+03}$			0.83
U <sub>o</sub> 0094	*	*	CHOCH <sub>2</sub> CH(OH)CHO	$7.1 \cdot 10^{+03}$			0.81
U <sub>o</sub> 0095	*	*	CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> CO(OH)	$1.3 \cdot 10^{+09}$		currently obsolete due to considerations in subsection 5.5.3	0.76

**Table G.8** (continued) Phase transfer processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Compound	$K_{H,298}^a$	$E_A/R^b$	Reference/comment	$D_g^c$
U <sub>o</sub> 0096	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CO(OH)	$8.6 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.76
U <sub>o</sub> 0097	*	*	CH <sub>3</sub> CH(OH)CH <sub>2</sub> CO(OH)	$2.4 \cdot 10^{+05}$			0.79
U <sub>o</sub> 0098	*	*	CH <sub>2</sub> (OH)COCH <sub>2</sub> CO(OH)	$2.4 \cdot 10^{+07}$		currently obsolete due to considerations in subsection 5.5.3	0.78
U <sub>o</sub> 0099	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> COCO(OH)	$6.7 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.78
U <sub>o</sub> 0100	*	*	CH <sub>3</sub> COCH <sub>2</sub> CO(OH)	$3.7 \cdot 10^{+05}$			0.81
U <sub>o</sub> 0101	*	*	CO(OH)CH <sub>2</sub> CH <sub>2</sub> CHO	$1.6 \cdot 10^{+06}$			0.81
U <sub>o</sub> 0104	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(OH)	$7.7 \cdot 10^{+10}$		currently obsolete due to considerations in subsection 5.5.3	0.74
U <sub>o</sub> 0105	*	*	CH <sub>3</sub> CH(OH)CH(OH)CO(OH)	$1.1 \cdot 10^{+07}$		currently obsolete due to considerations in subsection 5.5.3	0.76
U <sub>o</sub> 0106	*	*	CH <sub>2</sub> (OH)COCH(OH)CO(OH)	$9.4 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.75
U <sub>o</sub> 0107	*	*	CH <sub>3</sub> CH(OH)COCO(OH)	$3.4 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.78
U <sub>o</sub> 0108	*	*	CH <sub>2</sub> (OH)CH(OH)COCO(OH)	$4.1 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.75
U <sub>o</sub> 0109	*	*	CH <sub>3</sub> COCH(OH)CO(OH)	$2.0 \cdot 10^{+05}$		currently obsolete due to considerations in subsection 5.5.3	0.78
U <sub>o</sub> 0110	*	*	CH <sub>3</sub> COCOCO(OH)	$3.6 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.79
U <sub>o</sub> 0111	*	*	CO(OH)CH(OH)CH <sub>2</sub> CHO	$2.3 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.78



**Table G.8 (continued)** Phase transfer processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Compound	$K_{H,298}^a$	$E_A/R^b$	Reference/comment	$D_g^c$
U <sub>o</sub> 0112	*	*	CO(OH)CH <sub>2</sub> CH(OH)CHO	$2.3 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.78
U <sub>o</sub> 0113	*	*	CO(OH)COCH <sub>2</sub> CHO	$2.4 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.79
U <sub>o</sub> 0114	*	*	CO(OH)CH <sub>2</sub> COCHO	$2.4 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.79
U <sub>o</sub> 0115	*	*	CO(OH)CH(OH)COCHO	$1.6 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.77
U <sub>o</sub> 0116	*	*	CO(OH)CH(OH)CH(OH)CHO	$2.2 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.75
U <sub>o</sub> 0117	*	*	CO(OH)COCH(OH)CHO	$1.6 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.77
U <sub>o</sub> 0121	*	*	CH <sub>3</sub> CH(OH)CH(OH)CH <sub>3</sub>	$5.6 \cdot 10^{+05}$			0.81
U <sub>o</sub> 0122	*	*	CH <sub>3</sub> CH(OH)COCH <sub>3</sub>	$1.1 \cdot 10^{+03}$			0.83
U <sub>o</sub> 0125			CHOCH(OH)CH(ONO <sub>2</sub> )CHO	$1.8 \cdot 10^{+05}$		currently obsolete due to considerations in subsection 5.5.3	0.71
U <sub>o</sub> 0126			CHOCH(ONO <sub>2</sub> )CHO	$9.3 \cdot 10^{+03}$		currently obsolete due to considerations in subsection 5.5.3	0.81
U <sub>o</sub> 0127			CH(OH)(ONO <sub>2</sub> )CHO	$6.7 \cdot 10^{+03}$		currently obsolete due to considerations in subsection 5.5.3	0.89
U <sub>o</sub> 0128			CO(ONO <sub>2</sub> )CHO	$3.5 \cdot 10^{+01}$		currently obsolete due to considerations in subsection 5.5.3	0.91
U <sub>o</sub> 0129	*	*	CO(OH)C <sub>d</sub> H = C <sub>d</sub> HCHO	$4.4 \cdot 10^{+05}$			0.83
U <sub>o</sub> 0130			CO(ONO <sub>2</sub> )COCHO	$2.7 \cdot 10^{+03}$		currently obsolete due to considerations in subsection 5.5.3	0.80

**Table G.8 (continued)** Phase transfer processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Compound	$K_{H,298}^a$	$E_A/R^b$	Reference/comment	$D_g^c$
U <sub>o</sub> 0131			CO(ONO <sub>2</sub> )CH(OH)CHO	$1.5 \cdot 10^{+02}$		currently obsolete due to considerations in subsection 5.5.3	0.78
U <sub>o</sub> 0132			CO(OH)CH(ONO <sub>2</sub> )CH(OH)CHO	$5.8 \cdot 10^{+07}$		currently obsolete due to considerations in subsection 5.5.3	0.70
U <sub>o</sub> 0133			CO(OH)CH(OH)CH(ONO <sub>2</sub> )CHO	$5.8 \cdot 10^{+07}$		currently obsolete due to considerations in subsection 5.5.3	0.70
U <sub>o</sub> 0134			CO(OH)CH(ONO <sub>2</sub> )CHO	$3.0 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.78
U <sub>o</sub> 0135			CO(OH)CO(ONO <sub>2</sub> )	$1.1 \cdot 10^{+04}$			0.87
U <sub>o</sub> 0136			CO(OH)CH(OH)(ONO <sub>2</sub> )	$2.2 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.85
U <sub>o</sub> 0137	*	*	CO(OH)C <sub>d</sub> H = C <sub>d</sub> HCO(OH)	$1.4 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.79
U <sub>o</sub> 0138			CH(OH)(ONO <sub>2</sub> )COCHO	$1.5 \cdot 10^{+05}$		currently obsolete due to considerations in subsection 5.5.3	0.78
U <sub>o</sub> 0139			CH(OH)(ONO <sub>2</sub> )CH(OH)CHO	$7.0 \cdot 10^{+05}$		currently obsolete due to considerations in subsection 5.5.3	0.77
U <sub>o</sub> 0140			CO(OH)CH(OH)CO(ONO <sub>2</sub> )	$4.8 \cdot 10^{+04}$		currently obsolete due to considerations in subsection 5.5.3	0.76
U <sub>o</sub> 0141			CO(OH)COCO(ONO <sub>2</sub> )	$8.7 \cdot 10^{+05}$		currently obsolete due to considerations in subsection 5.5.3	0.77
U <sub>o</sub> 0142			CO(OH)CH(OH)CH(ONO <sub>2</sub> )CO(OH)	$1.9 \cdot 10^{+10}$		currently obsolete due to considerations in subsection 5.5.3	0.68
U <sub>o</sub> 0143			CO(OH)CH(ONO <sub>2</sub> )CO(OH)	$9.9 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.76

**Table G.8 (continued)** Phase transfer processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Compound	$K_{H,298}^a$	$E_A/R^b$	Reference/comment	$D_g^c$
U <sub>o</sub> 0144			CO(OH)COCH(OH)(ONO <sub>2</sub> )	$4.9 \cdot 10^{+07}$		currently obsolete due to considerations in subsection 5.5.3	0.76
U <sub>o</sub> 0145			CO(OH)CH(OH)CH(OH)(ONO <sub>2</sub> )	$2.3 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.74

<sup>a</sup>in Matm<sup>-1</sup>; <sup>b</sup>in K; <sup>c</sup>in 10<sup>5</sup> m<sup>2</sup> s<sup>-1</sup>, estimated with FSG method (*Fuller*, 1986) at  $T = 298$  K,  $p = 1$  atm,  $\alpha$  estimated with 0.1; <sup>d</sup>estimated with EPI Suite v4.10. (US Environmental Protection Agency, 2011: <http://www.epa.gov/opptintr/exposure/pubs/episuite.htm>)

**Table G.9** Phase transfer processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Compound	$K_{H,298}^a$	$E_A/R^b$	Reference/comment	$D_g^c$
U <sub>o</sub> 0146	*	*	CH <sub>3</sub> C <sub>d</sub> (CO(OH)) = C <sub>d</sub> H <sub>2</sub>	$2.6 \cdot 10^{+03}$		<i>Khan et al.</i> (1995)	0.85
U <sub>o</sub> 0147			CH <sub>3</sub> COCH <sub>2</sub> (ONO <sub>2</sub> )	$8.3 \cdot 10^{+02}$		<i>Kames and Schurath</i> (1992); currently obsolete due to considerations in subsection 5.5.3	0.82
U <sub>o</sub> 0148	*	*	CH <sub>2</sub> (OH)C <sub>d</sub> (CO(OH)) = C <sub>d</sub> H <sub>2</sub>	$3.1 \cdot 10^{+05}$			0.81
U <sub>o</sub> 0149	*	*	CO(OH)C <sub>d</sub> (CHO) = C <sub>d</sub> H <sub>2</sub>	$3.5 \cdot 10^{+04}$			0.83
U <sub>o</sub> 0150			CO(OH)COCH <sub>2</sub> (ONO <sub>2</sub> )	$2.6 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.78
U <sub>o</sub> 0151			CH <sub>3</sub> COCH(OH)(ONO <sub>2</sub> )	$2.4 \cdot 10^{+04}$		currently obsolete due to considerations in subsection 5.5.3	0.79
U <sub>o</sub> 0152			CH <sub>3</sub> COCO(ONO <sub>2</sub> )	$1.1 \cdot 10^{+02}$		currently obsolete due to considerations in subsection 5.5.3	0.81
U <sub>o</sub> 0153			CH <sub>2</sub> (OH)COCH <sub>2</sub> (ONO <sub>2</sub> )	$3.3 \cdot 10^{+04}$		currently obsolete due to considerations in subsection 5.5.3	0.79
U <sub>o</sub> 0154			CH <sub>2</sub> (ONO <sub>2</sub> )COCHO	$7.9 \cdot 10^{+03}$		currently obsolete due to considerations in subsection 5.5.3	0.81

**Table G.9 (continued)** Phase transfer processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Compound	$K_{H,298}^a$	$E_A/R^b$	Reference/comment	$D_g^c$
U <sub>o</sub> 0155			CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> )	$1.6 \cdot 10^{+05}$		currently obsolete due to considerations in subsection 5.5.3	0.89
U <sub>o</sub> 0156	*	*	CO(OH)C <sub>d</sub> (CO(OH)) = C <sub>d</sub> H <sub>2</sub>	$1.1 \cdot 10^{+07}$		currently obsolete due to considerations in subsection 5.5.3	0.79
U <sub>o</sub> 0157			CH <sub>2</sub> (OH)COCO(ONO <sub>2</sub> )	$1.1 \cdot 10^{+04}$		currently obsolete due to considerations in subsection 5.5.3	0.78
U <sub>o</sub> 0158			CH <sub>2</sub> (OH)COCH(OH)(ONO <sub>2</sub> )	$9.3 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.77
U <sub>o</sub> 0159			CH <sub>2</sub> (OH)CO(ONO <sub>2</sub> )	$3.3 \cdot 10^{+02}$		currently obsolete due to considerations in subsection 5.5.3	0.89
U <sub>o</sub> 0160	*	*	CH <sub>3</sub> C(OH)(CH <sub>2</sub> (OH))CO(OH)	$1.1 \cdot 10^{+07}$		currently obsolete due to considerations in subsection 5.5.3	0.76
U <sub>o</sub> 0161			CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CHO	$2.3 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.71
U <sub>o</sub> 0162			CH <sub>3</sub> C(ONO <sub>2</sub> )(CH <sub>2</sub> (OH))CO(OH)	$9.7 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.70
U <sub>o</sub> 0163	*	*	CH <sub>3</sub> C(OH)(CO(OH))CHO	$4.6 \cdot 10^{+04}$		currently obsolete due to considerations in subsection 5.5.3	0.78
U <sub>o</sub> 0164			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CO(OH)	$7.0 \cdot 10^{+11}$		currently obsolete due to considerations in subsection 5.5.3	0.68
U <sub>o</sub> 0165	*	*	CH <sub>2</sub> (OH)C(OH)(CO(OH))CO(OH)	$1.8 \cdot 10^{+10}$		currently obsolete due to considerations in subsection 5.5.3	0.73
U <sub>o</sub> 0166	*	*	CO(OH)C(OH)(CO(OH))CHO	$7.4 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.74
U <sub>o</sub> 0167	*	*	CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CO(OH)	$1.6 \cdot 10^{+10}$		currently obsolete due to considerations in subsection 5.5.3	0.74

**Table G.9 (continued)** Phase transfer processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Compound	$K_{H,298}^a$	$E_A/R^b$	Reference/comment	$D_g^c$
U <sub>o</sub> 0168			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CH <sub>2</sub> (OH))CO(OH)	$1.1 \cdot 10^{+10}$		currently obsolete due to considerations in subsection 5.5.3	0.69
U <sub>o</sub> 0169	*	*	CH <sub>2</sub> (OH)C(OH)(CO(OH))CHO	$5.3 \cdot 10^{+07}$		currently obsolete due to considerations in subsection 5.5.3	0.75
U <sub>o</sub> 0170	*	*	CO(OH)C(OH)(CO(OH))CO(OH)	$2.4 \cdot 10^{+11}$		currently obsolete due to considerations in subsection 5.5.3	0.72
U <sub>o</sub> 0171			CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CO(OH)	$7.5 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.70
U <sub>o</sub> 0172	*	*	CH <sub>3</sub> C(OH)(CO(OH))CO(OH)	$1.5 \cdot 10^{+07}$		currently obsolete due to considerations in subsection 5.5.3	0.75
U <sub>o</sub> 0173	*	*	CH <sub>3</sub> CH(CO(OH))CHO	$9.5 \cdot 10^{+04}$			0.81
U <sub>o</sub> 0174	*	*	CH <sub>2</sub> (OH)CH(CO(OH))CHO	$1.6 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.78
U <sub>o</sub> 0175	*	*	CH <sub>3</sub> CH(CO(OH))CO(OH)	$3.0 \cdot 10^{+07}$		currently obsolete due to considerations in subsection 5.5.3	0.78
U <sub>o</sub> 0176	*	*	CH <sub>2</sub> (OH)CH(CO(OH))CO(OH)	$5.3 \cdot 10^{+10}$		currently obsolete due to considerations in subsection 5.5.3	0.75
U <sub>o</sub> 0177	*	*	CH <sub>3</sub> CH(CH <sub>3</sub> )CO(OH)	$1.1 \cdot 10^{+03}$		<i>Khan et al.</i> (1995)	0.83
U <sub>o</sub> 0178	*	*	CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CO(OH)	$2.4 \cdot 10^{+05}$			0.79
U <sub>o</sub> 0179	*	*	CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CO(OH)	$5.1 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.76
U <sub>o</sub> 0180	*	*	CH <sub>3</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> (OH)	$1.0 \cdot 10^{+02}$		<i>Snider and Dawson</i> (1985)	0.85
U <sub>o</sub> 0181	*	*	CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH)	$2.6 \cdot 10^{+05}$			0.81
U <sub>o</sub> 0182	*	*	CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CHO	$7.7 \cdot 10^{+02}$			0.83
U <sub>o</sub> 0183	*	*	CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH)	$6.2 \cdot 10^{+07}$			0.78
U <sub>o</sub> 0184	*	*	CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CHO	$1.6 \cdot 10^{+06}$			0.79

**Table G.9** (continued) Phase transfer processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Compound	$K_{H,298}^a$	$E_A/R^b$	Reference/comment	$D_g^c$
U <sub>o</sub> 0185	*	*	CH <sub>3</sub> CH(CHO)CHO	$3.0 \cdot 10^{+02}$			0.85
U <sub>o</sub> 0186	*	*	CH <sub>2</sub> (OH)CH(CHO)CHO	$5.1 \cdot 10^{+05}$			0.81
U <sub>o</sub> 0187	*	*	CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CO(OH)	$8.4 \cdot 10^{+04}$			0.79
U <sub>o</sub> 0188	*	*	CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CHO	$2.6 \cdot 10^{+02}$			0.83
U <sub>o</sub> 0189	*	*	CH <sub>3</sub> C(OH)(CH <sub>2</sub> (OH))CHO	$3.4 \cdot 10^{+04}$			0.79
U <sub>o</sub> 0190	*	*	CH <sub>3</sub> C(OH)(CHO)CHO	$1.4 \cdot 10^{+02}$			0.81
U <sub>o</sub> 0191	*	*	CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CHO	$4.8 \cdot 10^{+07}$		currently obsolete due to considerations in subsection 5.5.3	0.76
U <sub>o</sub> 0192	*	*	CH <sub>2</sub> (OH)C(OH)(CHO)CHO	$1.6 \cdot 10^{+05}$		currently obsolete due to considerations in subsection 5.5.3	0.78
U <sub>o</sub> 0193	*	*	CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CH <sub>2</sub> (OH)	$5.6 \cdot 10^{+05}$			0.81
U <sub>o</sub> 0194	*	*	CH <sub>3</sub> C(OH)(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH)	$1.1 \cdot 10^{+09}$			0.78
U <sub>o</sub> 0195	*	*	CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH)	$1.8 \cdot 10^{+11}$		currently obsolete due to considerations in subsection 5.5.3	0.75
U <sub>o</sub> 0196	*	*	CO(OH)C <sub>d</sub> H = C <sub>d</sub> H <sub>2</sub>	$2.7 \cdot 10^{+03}$		see footnote <i>d</i>	0.96
U <sub>o</sub> 0197			CH <sub>2</sub> (ONO <sub>2</sub> )CHO	$5.0 \cdot 10^{+02}$			0.93
U <sub>o</sub> 0198			CO(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> )	$8.4 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.77
U <sub>o</sub> 0199	*	*	CHOCOC <sub>d</sub> H = C <sub>d</sub> H <sub>2</sub>	$1.5 \cdot 10^{+02}$			0.87
U <sub>o</sub> 0200			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)COCHO	$6.9 \cdot 10^{+05}$		currently obsolete due to considerations in subsection 5.5.3	0.71
U <sub>o</sub> 0201			CH(OH)(ONO <sub>2</sub> )CH(OH)COCHO	$1.7 \cdot 10^{+07}$		currently obsolete due to considerations in subsection 5.5.3	0.70
U <sub>o</sub> 0202			CO(ONO <sub>2</sub> )CH(OH)COCHO	$4.0 \cdot 10^{+03}$		currently obsolete due to considerations in subsection 5.5.3	0.71
U <sub>o</sub> 0203	*	*	CO(OH)COC <sub>d</sub> H = C <sub>d</sub> H <sub>2</sub>	$4.7 \cdot 10^{+04}$			0.83

**Table G.9 (continued)** Phase transfer processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Compound	$K_{H,298}^a$	$E_A/R^b$	Reference/comment	$D_g^c$
U <sub>o</sub> 0204			CO(OH)COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> )	$2.3 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.70
U <sub>o</sub> 0205			CO(OH)COCH(OH)CO(ONO <sub>2</sub> )	$1.3 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.69
U <sub>o</sub> 0206			CO(OH)COCH(OH)CH(OH)(ONO <sub>2</sub> )	$5.6 \cdot 10^{+09}$		currently obsolete due to considerations in subsection 5.5.3	0.68
U <sub>o</sub> 0207	*	*	CHOCH(OH)C <sub>d</sub> H = C <sub>d</sub> H <sub>2</sub>	$1.1 \cdot 10^{+03}$			0.85
U <sub>o</sub> 0208			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)CHO	$9.7 \cdot 10^{+05}$		currently obsolete due to considerations in subsection 5.5.3	0.70
U <sub>o</sub> 0209			CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)CHO	$1.2 \cdot 10^{+04}$		currently obsolete due to considerations in subsection 5.5.3	0.71
U <sub>o</sub> 0210	*	*	CO(OH)CH(OH)C <sub>d</sub> H = C <sub>d</sub> H <sub>2</sub>	$3.5 \cdot 10^{+05}$			0.81
U <sub>o</sub> 0211			CH(OH)(ONO <sub>2</sub> )COCH(OH)CHO	$2.9 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.70
U <sub>o</sub> 0212			CO(ONO <sub>2</sub> )COCH(OH)CHO	$4.0 \cdot 10^{+03}$		currently obsolete due to considerations in subsection 5.5.3	0.71
U <sub>o</sub> 0213			CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)CHO	$3.5 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.69
U <sub>o</sub> 0214			CO(ONO <sub>2</sub> )CH(OH)CH(OH)CHO	$5.6 \cdot 10^{+03}$		currently obsolete due to considerations in subsection 5.5.3	0.70
U <sub>o</sub> 0215			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CHO	$2.6 \cdot 10^{+04}$		currently obsolete due to considerations in subsection 5.5.3	0.79
U <sub>o</sub> 0216			CO(OH)CH(OH)COCH <sub>2</sub> (ONO <sub>2</sub> )	$3.9 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.70
U <sub>o</sub> 0217			CO(OH)CH(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> )	$3.2 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.69

**Table G.9** (continued) Phase transfer processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Compound	$K_{H,298}^a$	$E_A/R^b$	Reference/comment	$D_g^c$
U <sub>o</sub> 0218			CO(OH)CH(OH)CH(OH)CO(ONO <sub>2</sub> )	$1.8 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.68
U <sub>o</sub> 0219			CO(OH)CH(OH)COCO(ONO <sub>2</sub> )	$1.3 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.69
U <sub>o</sub> 0220			CO(OH)CH(OH)COCH(OH)(ONO <sub>2</sub> )	$9.5 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.68
U <sub>o</sub> 0221	*	*	C <sub>d</sub> H(OH) = C <sub>d</sub> H <sub>2</sub>	$1.9 \cdot 10^{+02}$			1.22
U <sub>o</sub> 0222	*	*	CH <sub>2</sub> (OH)COC <sub>d</sub> H = C <sub>d</sub> H <sub>2</sub>	$1.3 \cdot 10^{+03}$			0.85
U <sub>o</sub> 0223			CH <sub>2</sub> (OH)COCOCH <sub>2</sub> (ONO <sub>2</sub> )	$2.2 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.71
U <sub>o</sub> 0224			CH <sub>2</sub> (OH)COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> )	$4.2 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.70
U <sub>o</sub> 0225			CH <sub>2</sub> (OH)COCH(OH)CH(OH)(ONO <sub>2</sub> )	$1.1 \cdot 10^{+10}$		currently obsolete due to considerations in subsection 5.5.3	0.69
U <sub>o</sub> 0226			CH <sub>2</sub> (OH)COCH(OH)CO(ONO <sub>2</sub> )	$2.4 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.70
U <sub>o</sub> 0227			CH <sub>2</sub> (OH)COCOCH(OH)(ONO <sub>2</sub> )	$4.1 \cdot 10^{+07}$		currently obsolete due to considerations in subsection 5.5.3	0.70
U <sub>o</sub> 0228			CH <sub>2</sub> (OH)COCOCO(ONO <sub>2</sub> )	$7.5 \cdot 10^{+05}$		currently obsolete due to considerations in subsection 5.5.3	0.71
U <sub>o</sub> 0229	*	*	CH <sub>2</sub> (OH)CH(OH)C <sub>d</sub> H = C <sub>d</sub> H <sub>2</sub>	$2.3 \cdot 10^{+06}$			0.83
U <sub>o</sub> 0230			CH <sub>2</sub> (OH)CH(OH)COCH <sub>2</sub> (ONO <sub>2</sub> )	$3.1 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.70
U <sub>o</sub> 0231			CH <sub>2</sub> (OH)CH(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> )	$3.4 \cdot 10^{+10}$		currently obsolete due to considerations in subsection 5.5.3	0.69



**Table G.9 (continued)** Phase transfer processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Compound	$K_{H,298}^a$	$E_A/R^b$	Reference/comment	$D_g^c$
U <sub>o</sub> 0232			CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(ONO <sub>2</sub> )	$2.0 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.69
U <sub>o</sub> 0233			CH <sub>2</sub> (OH)CH(OH)COCH(OH)(ONO <sub>2</sub> )	$8.3 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.69
U <sub>o</sub> 0234			CH <sub>2</sub> (OH)CH(OH)COCO(ONO <sub>2</sub> )	$1.1 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.70
U <sub>o</sub> 0235	*	*	CH <sub>2</sub> (OH)C <sub>d</sub> H = C <sub>d</sub> H <sub>2</sub>	$2.0 \cdot 10^{+02}$		<i>Hine and Mookerjee</i> (1975)	1.01
U <sub>o</sub> 0236			CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> )	$6.3 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.78
U <sub>o</sub> 0237			CH <sub>2</sub> (OH)CH(OH)CH(OH)(ONO <sub>2</sub> )	$2.6 \cdot 10^{+09}$		currently obsolete due to considerations in subsection 5.5.3	0.75
U <sub>o</sub> 0238			CH <sub>2</sub> (OH)CH(OH)CO(ONO <sub>2</sub> )	$3.6 \cdot 10^{+04}$		currently obsolete due to considerations in subsection 5.5.3	0.77
U <sub>o</sub> 0239	*	*	CH <sub>2</sub> (OH)C <sub>d</sub> H = C <sub>d</sub> HCO(OH)	$4.0 \cdot 10^{+07}$			0.81
U <sub>o</sub> 0240			CH <sub>2</sub> (OH)CH(OH)(ONO <sub>2</sub> )	$5.9 \cdot 10^{+06}$			0.87
U <sub>o</sub> 0241			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CHO	$3.9 \cdot 10^{+04}$		currently obsolete due to considerations in subsection 5.5.3	0.79
U <sub>o</sub> 0242			CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CO(OH)	$1.5 \cdot 10^{+10}$		currently obsolete due to considerations in subsection 5.5.3	0.69
U <sub>o</sub> 0243			CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CO(OH)	$1.9 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.70
U <sub>o</sub> 0244			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCO(OH)	$1.9 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.70

**Table G.9 (continued)** Phase transfer processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Compound	$K_{H,298}^a$	$E_A/R^b$	Reference/comment	$D_g^c$
U <sub>o</sub> 0245			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CO(OH)	$3.5 \cdot 10^{+10}$		currently obsolete due to considerations in subsection 5.5.3	0.69
U <sub>o</sub> 0246			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CO(OH)	$1.3 \cdot 10^{+07}$		currently obsolete due to considerations in subsection 5.5.3	0.77
U <sub>o</sub> 0247	*	*	CH <sub>2</sub> (OH)C <sub>d</sub> H = C <sub>d</sub> HCHO	$1.3 \cdot 10^{+05}$			0.85
U <sub>o</sub> 0248			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CHO	$1.1 \cdot 10^{+08}$		currently obsolete due to considerations in subsection 5.5.3	0.70
U <sub>o</sub> 0249			CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CHO	$4.7 \cdot 10^{+07}$		currently obsolete due to considerations in subsection 5.5.3	0.70
U <sub>o</sub> 0250			CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CHO	$5.7 \cdot 10^{+05}$		currently obsolete due to considerations in subsection 5.5.3	0.71
U <sub>o</sub> 0251			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCHO	$5.7 \cdot 10^{+05}$		currently obsolete due to considerations in subsection 5.5.3	0.71
U <sub>o</sub> 0252	*	*	CH <sub>2</sub> (OH)C <sub>d</sub> H = C <sub>d</sub> HCH <sub>2</sub> (OH)	$1.2 \cdot 10^{+07}$			0.83
U <sub>o</sub> 0253			CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CH <sub>2</sub> (OH)	$2.8 \cdot 10^{+10}$		currently obsolete due to considerations in subsection 5.5.3	0.69
U <sub>o</sub> 0254			CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CH <sub>2</sub> (OH)	$2.6 \cdot 10^{+06}$		currently obsolete due to considerations in subsection 5.5.3	0.70

<sup>a</sup>in Matm<sup>-1</sup>; <sup>b</sup>in K; <sup>c</sup>in 10<sup>5</sup> m<sup>2</sup> s<sup>-1</sup>, estimated with FSG method (*Fuller*, 1986) at  $T = 298$  K,  $p = 1$  atm,  $\alpha$  estimated with 0.1; <sup>d</sup>estimated with EPI Suite v4.10. (US Environmental Protection Agency, 2011: <http://www.epa.gov/opptintr/exposure/pubs/episuite.htm>)

## G.3.2 Chemical conversions

Table G.10 Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00001	$\text{CH}_3\text{OOH} + \text{OH} \rightarrow \text{CH}_3\text{OO}\cdot + \text{H}_2\text{O}$	$2.40 \cdot 10^7$	1680	<i>Ervens et al.</i> (2003)
R <sub>o</sub> 00002	$\text{CH}_3\text{OOH} + \text{OH} \rightarrow \text{HCOOH} + \text{HO}_2$	$6.00 \cdot 10^6$	1680	branching ratio 0.8 : 0.2 (correlation for H abstractions, see <i>Ervens et al.</i> , 2003)
R <sub>o</sub> 00003	$\text{CH}_3\text{OOH} + \text{NO}_3 \rightarrow \text{CH}_3\text{OO}\cdot + \text{NO}_3^- + \text{H}^+$	$4.90 \cdot 10^6$	2000	estimated same as R <sub>i</sub> 00065
R <sub>o</sub> 00004	$\text{CH}_3\text{OOH} + \text{SO}_4^- \rightarrow \text{CH}_3\text{OO}\cdot + \text{SO}_4^{2-} + \text{H}^+$	$1.70 \cdot 10^7$		estimated same as R <sub>i</sub> 00137
R <sub>o</sub> 00005	$\text{CH}_3\text{OOH} + \text{Cl}_2^- \rightarrow \text{CH}_3\text{OO}\cdot + 2 \text{Cl}^- + \text{H}^+$	$5.00 \cdot 10^4$	3340	estimated same as R <sub>i</sub> 00156
R <sub>o</sub> 00006	$\text{CH}_3\text{OOH} + \text{Br}_2^- \rightarrow \text{CH}_3\text{OO}\cdot + 2 \text{Br}^- + \text{H}^+$	$1.00 \cdot 10^5$		estimated same as R <sub>i</sub> 00171
R <sub>o</sub> 00007	$\text{CH}_3\text{OOH} + \text{CO}_3^- \rightarrow \text{HCO}_3^- + \text{CH}_3\text{OO}\cdot$	$4.30 \cdot 10^5$		estimated same as R <sub>i</sub> 00190
R <sub>o</sub> 00008	$\text{HCO}(\text{OO}\cdot) + \text{H}_2\text{O} \rightarrow \text{HCOOH} + \text{HO}_2$	$4.43 \cdot 10^1$		<i>Barlow et al.</i> (1997)
R <sub>o</sub> 00009	$\text{CH}_3\text{OH} + \text{OH} \rightarrow \cdot\text{CH}_2\text{OH} + \text{H}_2\text{O}$	$1.00 \cdot 10^9$	580	<i>Elliot and McCracken</i> (1989)
R <sub>o</sub> 00010	$\text{CH}_3\text{OH} + \text{SO}_4^- \rightarrow \cdot\text{CH}_2\text{OH} + \text{SO}_4^{2-} + \text{H}^+$	$9.00 \cdot 10^6$	2190	<i>Clifton and Huie</i> (1989)
R <sub>o</sub> 00011	$\text{CH}_3\text{OH} + \text{NO}_3 \rightarrow \cdot\text{CH}_2\text{OH} + \text{NO}_3^- + \text{H}^+$	$5.40 \cdot 10^5$	4300	<i>Herrmann and Zellner</i> (1998)
R <sub>o</sub> 00012	$\text{CH}_3\text{OH} + \text{Cl}_2^- \rightarrow \cdot\text{CH}_2\text{OH} + 2 \text{Cl}^- + \text{H}^+$	$5.10 \cdot 10^4$	5533	<i>Zellner et al.</i> (1996)
R <sub>o</sub> 00013	$\text{CH}_3\text{OH} + \text{Br}_2^- \rightarrow \cdot\text{CH}_2\text{OH} + 2 \text{Br}^- + \text{H}^+$	$1.00 \cdot 10^3$		<i>Reese et al.</i> (1997)
R <sub>o</sub> 00014	$\text{CH}_3\text{OH} + \text{CO}_3^- \rightarrow \cdot\text{CH}_2\text{OH} + \text{CO}_3^{2-} + \text{H}^+$	$2.60 \cdot 10^3$		<i>Zellner et al.</i> (1996)
R <sub>o</sub> 00015	$\cdot\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{CH}_2(\text{OH})\text{OO}\cdot$	$2.00 \cdot 10^9$		<i>von Sonntag</i> (1987)
R <sub>o</sub> 00016	$\text{CH}_2(\text{OH})\text{OO}\cdot + \text{OH}^- \rightarrow \text{HCHO} + \text{O}_2^- + \text{H}_2\text{O}$	$1.65 \cdot 10^{10}$		<i>von Sonntag</i> (1987)
R <sub>o</sub> 00017	$\text{CH}_2(\text{OH})\text{OO}\cdot \xrightarrow{\text{RO}_2} 0.5 \text{CH}_3\text{OH} + 0.5 \text{HCHO} + \text{O}_2$	$1.05 \cdot 10^9$		<i>von Sonntag</i> (1987)
R <sub>o</sub> 00311*	$\text{CH}_3\text{CH}_2\text{OH} + \text{OH} \rightarrow \text{CH}_3\text{C}\cdot\text{H}(\text{OH}) + \text{H}_2\text{O}$	$2.10 \cdot 10^9$	1200	<i>Ervens et al.</i> (2003b)
R <sub>o</sub> 00018	$\text{CH}_3\text{CH}_2\text{OH} + \text{SO}_4^- \rightarrow \text{CH}_3\text{C}\cdot\text{H}(\text{OH}) + \text{SO}_4^{2-} + \text{H}^+$	$4.10 \cdot 10^7$	1760	<i>Clifton and Huie</i> (1989)
R <sub>o</sub> 00312*	$\text{CH}_3\text{CH}_2\text{OH} + \text{NO}_3 \rightarrow \text{CH}_3\text{C}\cdot\text{H}(\text{OH}) + \text{NO}_3^- + \text{H}^+$	$2.20 \cdot 10^6$	3300	<i>Herrmann and Zellner</i> (1998)
R <sub>o</sub> 00019	$\text{CH}_3\text{CH}_2\text{OH} + \text{Cl}_2^- \rightarrow \text{CH}_3\text{C}\cdot\text{H}(\text{OH}) + 2 \text{Cl}^- + \text{H}^+$	$1.20 \cdot 10^5$		<i>Zellner et al.</i> (1996)

**Table G.10** (continued) Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00020	$\text{CH}_3\text{CH}_2\text{OH} + \text{Br}_2^- \rightarrow \text{CH}_3\text{C}\cdot\text{H}(\text{OH}) + 2\text{Br}^- + \text{H}^+$	$3.80 \cdot 10^3$		<i>Reese et al.</i> (1999)
R <sub>o</sub> 00021	$\text{CH}_3\text{CH}_2\text{OH} + \text{CO}_3^- \rightarrow \text{CH}_3\text{C}\cdot\text{H}(\text{OH}) + \text{CO}_3^{2-} + \text{H}^+$	$1.50 \cdot 10^4$		<i>Kuzmin</i> (1972)
R <sub>o</sub> 00022	$\text{CH}_3\text{C}\cdot\text{H}(\text{OH}) + \text{O}_2 \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{OO}\cdot$	$4.60 \cdot 10^9$		<i>Adams and Willson</i> (1969)
R <sub>o</sub> 00023	$\text{CH}_3\text{CH}(\text{OH})\text{OO}\cdot \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2$	$5.20 \cdot 10^1$	7217	<i>von Sonntag</i> (1987)
R <sub>o</sub> 00024	$\text{CH}_3\text{CH}(\text{OH})\text{OO}\cdot + \text{OH}^- \rightarrow \text{CH}_3\text{CHO} + \text{O}_2^- + \text{H}_2\text{O}$	$8.00 \cdot 10^9$		<i>von Sonntag</i> (1987)
R <sub>o</sub> 00025	$\text{CH}_2(\text{OH})_2 + \text{OH} \rightarrow \cdot\text{CH}(\text{OH})_2 + \text{H}_2\text{O}$	$1.00 \cdot 10^9$	1020	<i>Hart et al.</i> (1964)
R <sub>o</sub> 00026	$\text{CH}_2(\text{OH})_2 + \text{SO}_4^- \rightarrow \cdot\text{CH}(\text{OH})_2 + \text{SO}_4^{2-} + \text{H}^+$	$1.40 \cdot 10^7$	1300	<i>Buxton et al.</i> (1990)
R <sub>o</sub> 00027	$\text{CH}_2(\text{OH})_2 + \text{NO}_3 \rightarrow \cdot\text{CH}(\text{OH})_2 + \text{NO}_3^- + \text{H}^+$	$1.00 \cdot 10^6$	4500	<i>Erner et al.</i> (1993)
R <sub>o</sub> 00028	$\text{CH}_2(\text{OH})_2 + \text{Cl}_2^- \rightarrow \cdot\text{CH}(\text{OH})_2 + 2\text{Cl}^- + \text{H}^+$	$3.60 \cdot 10^4$	4330	<i>Jacob</i> (1999)
R <sub>o</sub> 00029	$\text{CH}_2(\text{OH})_2 + \text{Br}_2^- \rightarrow \cdot\text{CH}(\text{OH})_2 + 2\text{Br}^- + \text{H}^+$	$3.00 \cdot 10^3$		estimated
R <sub>o</sub> 00030	$\text{CH}_2(\text{OH})_2 + \text{CO}_3^- \rightarrow \cdot\text{CH}(\text{OH})_2 + \text{CO}_3^{2-} + \text{H}^+$	$1.30 \cdot 10^4$		<i>Zellner et al.</i> (1996)
R <sub>o</sub> 00031	$\cdot\text{CH}(\text{OH})_2 + \text{O}_2 \rightarrow \text{HCOOH} + \text{HO}_2$	$2.00 \cdot 10^9$		estimated
R <sub>o</sub> 00340*	$\text{CH}_3\text{CH}(\text{OH})_2 + \text{OH} \rightarrow \text{CH}_3\text{C}\cdot(\text{OH})_2 + \text{H}_2\text{O}$	$1.30 \cdot 10^9$		<i>Schuchmann and von Sonntag</i> (1988)
R <sub>o</sub> 00333*	$\text{CH}_3\text{CHO} + \text{OH} \rightarrow \text{CH}_3\text{CO}\cdot + \text{H}_2\text{O}$	$3.10 \cdot 10^9$		<i>Schuchmann and von Sonntag</i> (1988)
R <sub>o</sub> 00032	$\text{CH}_3\text{CH}(\text{OH})_2 + \text{SO}_4^- \rightarrow \cdot\text{CH}_3\text{C}\cdot(\text{OH})_2 + \text{SO}_4^{2-} + \text{H}^+$	$2.00 \cdot 10^7$		estimated
R <sub>o</sub> 00033	$\text{CH}_3\text{CHO} + \text{SO}_4^- \rightarrow \text{CH}_3\text{CO}\cdot + \text{SO}_4^{2-} + \text{H}^+$	$2.00 \cdot 10^7$		estimated
R <sub>o</sub> 00341*	$\text{CH}_3\text{CH}(\text{OH})_2 + \text{NO}_3 \rightarrow \cdot\text{CH}_3\text{C}\cdot(\text{OH})_2 + \text{NO}_3^- + \text{H}^+$	$2.00 \cdot 10^6$		<i>Zellner et al.</i> (1996)
R <sub>o</sub> 00334*	$\text{CH}_3\text{CHO} + \text{NO}_3 \rightarrow \text{CH}_3\text{CO}\cdot + \text{NO}_3^- + \text{H}^+$	$1.90 \cdot 10^6$		<i>Zellner et al.</i> (1996)
R <sub>o</sub> 00034	$\text{CH}_3\text{CH}(\text{OH})_2 + \text{Cl}_2^- \rightarrow \cdot\text{CH}_3\text{C}\cdot(\text{OH})_2 + 2\text{Cl}^- + \text{H}^+$	$4.00 \cdot 10^4$		<i>Jacobi et al.</i> (1996)
R <sub>o</sub> 00035	$\text{CH}_3\text{CHO} + \text{Cl}_2^- \rightarrow \text{CH}_3\text{CO}\cdot + 2\text{Cl}^- + \text{H}^+$	$4.00 \cdot 10^4$		<i>Jacobi et al.</i> (1996)
R <sub>o</sub> 00036	$\text{CH}_3\text{CH}(\text{OH})_2 + \text{Br}_2^- \rightarrow \cdot\text{CH}_3\text{C}\cdot(\text{OH})_2 + 2\text{Br}^- + \text{H}^+$	$2.15 \cdot 10^5$	2526	TROPOS measurements
R <sub>o</sub> 00037	$\text{CH}_3\text{CHO} + \text{Br}_2^- \rightarrow \text{CH}_3\text{CO}\cdot + 2\text{Br}^- + \text{H}^+$	$2.15 \cdot 10^5$	2526	TROPOS measurements
R <sub>o</sub> 00038	$\text{CH}_3\text{CH}(\text{OH})_2 + \text{CO}_3^- \rightarrow \cdot\text{CH}_3\text{C}\cdot(\text{OH})_2 + \text{CO}_3^{2-} + \text{H}^+$	$1.00 \cdot 10^4$		estimated
R <sub>o</sub> 00039	$\text{CH}_3\text{CHO} + \text{CO}_3^- \rightarrow \text{CH}_3\text{CO}\cdot + \text{CO}_3^{2-} + \text{H}^+$	$1.00 \cdot 10^4$		estimated

**Table G.10 (continued)** Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00040	$\text{HCOOH} + \text{OH} \rightarrow \cdot\text{COOH} + \text{H}_2\text{O}$	$1.30 \cdot 10^8$	1000	<i>Buxton et al.</i> (1988a)
R <sub>o</sub> 00041	$\text{HCOO}^- + \text{OH} \rightarrow \cdot\text{COOH} + \text{OH}^-$	$3.20 \cdot 10^9$	1000	<i>Elliot and Simsons</i> (1984)
R <sub>o</sub> 00042	$\text{HCOOH} + \text{SO}_4^- \rightarrow \cdot\text{COOH} + \text{SO}_4^{2-} + \text{H}^+$	$2.50 \cdot 10^6$		<i>Reese et al.</i> (1997)
R <sub>o</sub> 00043	$\text{HCOO}^- + \text{SO}_4^- \rightarrow \cdot\text{COOH} + \text{SO}_4^{2-}$	$2.10 \cdot 10^7$		<i>Reese et al.</i> (1997)
R <sub>o</sub> 00044	$\text{HCOOH} + \text{NO}_3 \rightarrow \cdot\text{COOH} + \text{NO}_3^- + \text{H}^+$	$3.80 \cdot 10^5$	3400	<i>Exner et al.</i> (1994)
R <sub>o</sub> 00045	$\text{HCOO}^- + \text{NO}_3 \rightarrow \cdot\text{COOH} + \text{NO}_3^-$	$5.10 \cdot 10^7$	2200	<i>Exner et al.</i> (1994)
R <sub>o</sub> 00046	$\text{HCOOH} + \text{Cl}_2^- \rightarrow \cdot\text{COOH} + 2 \text{Cl}^- + \text{H}^+$	$8.00 \cdot 10^4$	4450	<i>Jacob</i> (1999)
R <sub>o</sub> 00047	$\text{HCOO}^- + \text{Cl}_2^- \rightarrow \cdot\text{COOH} + 2 \text{Cl}^-$	$1.30 \cdot 10^6$		<i>Jacobi et al.</i> (1996)
R <sub>o</sub> 00048	$\text{HCOOH} + \text{Br}_2^- \rightarrow \cdot\text{COOH} + 2 \text{Br}^- + \text{H}^+$	$4.00 \cdot 10^3$		<i>Reese et al.</i> (1999)
R <sub>o</sub> 00049	$\text{HCOO}^- + \text{Br}_2^- \rightarrow \cdot\text{COOH} + 2 \text{Br}^-$	$4.90 \cdot 10^3$		<i>Jacobi et al.</i> (1996)
R <sub>o</sub> 00050	$\text{HCOO}^- + \text{CO}_3^- \rightarrow \cdot\text{COOH} + \text{CO}_3^{2-}$	$1.40 \cdot 10^5$	3300	<i>Zellner et al.</i> (1996)
R <sub>o</sub> 00051	$\cdot\text{COOH} + \text{O}_2 \rightarrow \text{CO}_2 + \text{HO}_2$	$2.00 \cdot 10^9$		estimated
R <sub>o</sub> 00356*	$\text{CH}_3\text{COOH} + \text{OH} \rightarrow \cdot\text{CH}_2\text{COOH} + \text{H}_2\text{O}$	$1.70 \cdot 10^7$	1330	<i>Chin and Wine</i> (1994)
R <sub>o</sub> 00366*	$\text{CH}_3\text{COO}^- + \text{OH} \rightarrow \cdot\text{CH}_2\text{COO}^- + \text{H}_2\text{O}$	$7.30 \cdot 10^7$	1770	<i>Chin and Wine</i> (1994)
R <sub>o</sub> 00052	$\text{CH}_3\text{COOH} + \text{SO}_4^- \rightarrow \cdot\text{CH}_2\text{COOH} + \text{SO}_4^{2-} + \text{H}^+$	$2.00 \cdot 10^5$		<i>Reese et al.</i> (1997)
R <sub>o</sub> 00053	$\text{CH}_3\text{COO}^- + \text{SO}_4^- \rightarrow \cdot\text{CH}_3 + \text{CO}_2 + \text{SO}_4^{2-}$	$2.80 \cdot 10^7$	1210	<i>Huie and Clifton</i> (1990)
R <sub>o</sub> 00357*	$\text{CH}_3\text{COOH} + \text{NO}_3 \rightarrow \cdot\text{CH}_2\text{COOH} + \text{NO}_3^- + \text{H}^+$	$1.30 \cdot 10^4$	3800	<i>Exner et al.</i> (1994)
R <sub>o</sub> 00367*	$\text{CH}_3\text{COO}^- + \text{NO}_3 \rightarrow \cdot\text{CH}_3 + \text{CO}_2 + \text{NO}_3^-$	$2.90 \cdot 10^6$	3800	<i>Exner et al.</i> (1994)
R <sub>o</sub> 00054	$\text{CH}_3\text{COOH} + \text{Cl}_2^- \rightarrow \cdot\text{CH}_2\text{COOH} + 2 \text{Cl}^- + \text{H}^+$	$1.50 \cdot 10^3$	4930	<i>Jacob</i> (1999)
R <sub>o</sub> 00055	$\text{CH}_3\text{COO}^- + \text{Cl}_2^- \rightarrow \cdot\text{CH}_3 + \text{CO}_2 + 2 \text{Cl}^-$	$2.60 \cdot 10^5$	4800	<i>Jacobi et al.</i> (1996)
R <sub>o</sub> 00056	$\text{CH}_3\text{COOH} + \text{Br}_2^- \rightarrow \cdot\text{CH}_2\text{COOH} + 2 \text{Br}^- + \text{H}^+$	$1.00 \cdot 10^1$		<i>Reese et al.</i> (1999)
R <sub>o</sub> 00057	$\text{CH}_3\text{COO}^- + \text{Br}_2^- \rightarrow \cdot\text{CH}_3 + \text{CO}_2 + 2 \text{Br}^-$	$1.00 \cdot 10^2$		<i>Jacobi et al.</i> (1996)
R <sub>o</sub> 00058	$\text{CH}_3\text{COO}^- + \text{CO}_3^- \rightarrow \cdot\text{CH}_3 + \text{CO}_2 + \text{CO}_3^{2-}$	$5.80 \cdot 10^2$		<i>Zellner et al.</i> (1996)
R <sub>o</sub> 00059	$\cdot\text{CH}_2\text{COOH} + \text{O}_2 \rightarrow \cdot\text{OOCH}_2\text{COOH}$	$1.70 \cdot 10^9$		<i>Schuchmann et al.</i> (1985)
R <sub>o</sub> 00060	$\cdot\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{OO}\cdot$	$4.10 \cdot 10^9$		<i>Marchaj et al.</i> (1991)

**Table G.10** (continued) Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00061	$\text{CH}_3\text{OO}\cdot \xrightarrow{\text{RO}_2} 0.336 \text{CH}_3\text{OH} + 0.336 \text{HCHO} + 0.328 \text{CH}_3\text{O}\cdot + 0.5 \text{O}_2$	$1.10 \cdot 10^8$	2200	<i>Herrmann et al.</i> (1999)
R <sub>o</sub> 00062	$\text{CH}_3\text{CO}_3\cdot \xrightarrow{\text{RO}_2} \text{CH}_3\text{OO}\cdot + \text{CO}_2 - \text{O}_2$	$1.50 \cdot 10^8$		estimated equal as R <sub>o</sub> 00063
R <sub>o</sub> 00063	$\text{CH}_3\text{CH}_2\text{OO}\cdot \xrightarrow{\text{RO}_2} 0.624 \text{CH}_3\text{CH}_2\text{O}\cdot + 0.188 \text{CH}_3\text{CH}_2\text{OH} + 0.188 \text{CH}_3\text{CHO} + 0.5 \text{O}_2$	$1.60 \cdot 10^8$	-750	<i>Herrmann et al.</i> (1999)
R <sub>o</sub> 00064	$\text{CH}_3\text{CH}_2\text{O}\cdot + \text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2$	$6.00 \cdot 10^6$		estimated
R <sub>o</sub> 00065	$\text{CH}_3\text{CH}_2\text{O}\cdot \rightarrow \text{CH}_3\text{C}\cdot\text{H}(\text{OH})$	$1.00 \cdot 10^6$		estimated
R <sub>o</sub> 00379*	$\text{CO}(\text{OH})\text{COO}^- + \text{OH} \rightarrow \text{CO}(\text{O}^-)\text{CO}_2\cdot + \text{H}_2\text{O}$	$1.90 \cdot 10^8$	2800	<i>Ervens et al.</i> (2003b)
R <sub>o</sub> 00380*	$\text{CO}(\text{OH})\text{COO}^- + \text{NO}_3 \rightarrow \text{CO}(\text{O}^-)\text{CO}_2\cdot + \text{NO}_3^- + \text{H}^+$	$6.10 \cdot 10^7$	2180	Average of <i>Yang et al.</i> (2004) and <i>de Semainville et al.</i> (2010a) with $E_A/R$ of <i>Raabe</i> (1996)
R <sub>o</sub> 00066	$\text{CO}(\text{OH})\text{COO}^- + \text{Cl}_2^- \rightarrow \text{CO}(\text{O}^-)\text{CO}_2\cdot + 2 \text{Cl}^- + \text{H}^+$	$1.30 \cdot 10^6$		estimated (ETR)
R <sub>o</sub> 00067	$\text{CO}(\text{OH})\text{COO}^- + \text{Br}_2^- \rightarrow \text{CO}(\text{O}^-)\text{CO}_2\cdot + 2 \text{Br}^- + \text{H}^+$	$3.70 \cdot 10^3$		estimated (ETR)
R <sub>o</sub> 00068	$\text{CO}(\text{OH})\text{COO}^- + \text{SO}_4^- \rightarrow \text{CO}(\text{O}^-)\text{CO}_2\cdot + \text{SO}_4^{2-} + \text{H}^+$	$3.35 \cdot 10^5$		<i>Buxton et al.</i> (1999c)
R <sub>o</sub> 00069	$\text{CO}(\text{OH})\text{COO}^- + \text{SO}_5^- \rightarrow \text{CO}(\text{O}^-)\text{CO}_2\cdot + \text{HSO}_5^-$	$5.00 \cdot 10^3$		<i>Herrmann et al.</i> (2000)
R <sub>o</sub> 00070	$\text{CO}(\text{O}^-)\text{COO}^- + \text{OH} \rightarrow \text{CO}(\text{O}^-)\text{CO}_2\cdot + \text{OH}^-$	$1.60 \cdot 10^8$	4300	<i>Ervens et al.</i> (2003b)
R <sub>o</sub> 00071	$\text{CO}(\text{O}^-)\text{COO}^- + \text{NO}_3 \rightarrow \text{CO}(\text{O}^-)\text{CO}_2\cdot + \text{NO}_3^-$	$2.20 \cdot 10^8$		<i>Raabe</i> (1996)
R <sub>o</sub> 00072	$\text{CO}(\text{O}^-)\text{COO}^- + \text{Cl}_2^- \rightarrow \text{CO}(\text{O}^-)\text{CO}_2\cdot + 2 \text{Cl}^-$	$4.00 \cdot 10^6$		estimated (ETR)
R <sub>o</sub> 00073	$\text{CO}(\text{O}^-)\text{COO}^- + \text{Br}^- \rightarrow \text{CO}(\text{O}^-)\text{CO}_2\cdot + 2 \text{Br}^-$	$1.10 \cdot 10^4$		estimated (ETR)
R <sub>o</sub> 00074	$\text{CO}(\text{O}^-)\text{COO}^- + \text{SO}_4^- \rightarrow \text{CO}(\text{O}^-)\text{CO}_2\cdot + \text{SO}_4^{2-}$	$1.05 \cdot 10^6$		<i>Buxton et al.</i> (1999c)
R <sub>o</sub> 00075	$\text{CO}(\text{O}^-)\text{COO}^- + \text{SO}_5^- \xrightarrow{\text{H}_2\text{O}} \text{CO}(\text{O}^-)\text{CO}_2\cdot + \text{HSO}_5^- + \text{OH}^-$	$1.00 \cdot 10^4$		<i>Herrmann et al.</i> (2000)
R <sub>o</sub> 00076	$\text{CO}(\text{O}^-)\text{CO}_2\cdot + \text{O}_2 \rightarrow 2 \text{CO}_2 + \text{O}_2^-$	$2.00 \cdot 10^9$		estimated
R <sub>o</sub> 00336*	$\text{CH}(\text{OH})_2\text{CH}(\text{OH})_2 + \text{OH} \rightarrow \cdot\text{C}(\text{OH})_2\text{CH}(\text{OH})_2 + \text{H}_2\text{O} + \text{H}^+$	$1.10 \cdot 10^9$	1516	<i>Buxton et al.</i> (1997)

**Table G.10 (continued)** Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00337*	$\text{CH(OH)}_2\text{CH(OH)}_2 + \text{NO}_3^\cdot \rightarrow$ $\cdot\text{C(OH)}_2\text{CH(OH)}_2 + \text{NO}_3^- + \text{H}^+$	$1.10 \cdot 10^6$	3368	<i>Herrmann et al.</i> (1995b)
R <sub>o</sub> 00077	$\text{CH(OH)}_2\text{CH(OH)}_2 + \text{Cl}_2^- \rightarrow$ $\cdot\text{C(OH)}_2\text{CH(OH)}_2 + 2 \text{Cl}^- + \text{H}^+$	$4.00 \cdot 10^4$		<i>Herrmann et al.</i> (1995b)
R <sub>o</sub> 00078	$\text{CH(OH)}_2\text{CH(OH)}_2 + \text{Br}_2^- \rightarrow$ $\cdot\text{C(OH)}_2\text{CH(OH)}_2 + 2 \text{Br}^- + \text{H}^+$	$5.00 \cdot 10^2$		estimated (H-atom abstraction)
R <sub>o</sub> 00079	$\text{CH(OH)}_2\text{CH(OH)}_2 + \text{SO}_4^- \rightarrow$ $\cdot\text{C(OH)}_2\text{CH(OH)}_2 + \text{SO}_4^{2-} + \text{H}^+$	$2.35 \cdot 10^7$	1395	<i>Mirabel</i> (1996)
R <sub>o</sub> 00080	$\text{CH(OH)}_2\text{CH(OH)}_2 + \text{SO}_5^- \rightarrow \cdot\text{C(OH)}_2\text{CH(OH)}_2 + \text{HSO}_5^-$	$5.00 \cdot 10^5$		<i>Herrmann et al.</i> (2000)
R <sub>o</sub> 00081	$\cdot\text{C(OH)}_2\text{CH(OH)}_2 + \text{O}_2 \rightarrow \cdot\text{OOC(OH)}_2\text{CH(OH)}_2$	$1.38 \cdot 10^9$		<i>Mirabel</i> (1996)
R <sub>o</sub> 00082	$\cdot\text{OOC(OH)}_2\text{CH(OH)}_2 \rightarrow \text{CH(OH)}_2\text{COOH} + \text{HO}_2$	$1.00 \cdot 10^7$		estimated
R <sub>o</sub> 00368*	$\text{CH(OH)}_2\text{COOH} + \text{OH} \rightarrow \cdot\text{C(OH)}_2\text{COOH} + \text{H}_2\text{O}$	$3.60 \cdot 10^8$	1000	<i>Ervens et al.</i> (2003b)
R <sub>o</sub> 00369*	$\text{CH(OH)}_2\text{COOH} + \text{NO}_3 \rightarrow \cdot\text{C(OH)}_2\text{COOH} + \text{NO}_3^- + \text{H}^+$	$7.38 \cdot 10^6$	3368	estimated equal as R <sub>o</sub> 00334
R <sub>o</sub> 00083	$\text{CH(OH)}_2\text{COOH} + \text{Cl}_2^- \rightarrow \cdot\text{C(OH)}_2\text{COOH} + 2 \text{Cl}^- + \text{H}^+$	$4.00 \cdot 10^4$		estimated equal as R <sub>o</sub> 00072
R <sub>o</sub> 00084	$\text{CH(OH)}_2\text{COOH} + \text{Br}_2^- \rightarrow \cdot\text{C(OH)}_2\text{COOH} + 2 \text{Br}^- + \text{H}^+$	$5.00 \cdot 10^2$		estimated equal as R <sub>o</sub> 00073
R <sub>o</sub> 00085	$\text{CH(OH)}_2\text{COOH} + \text{SO}_4^- \rightarrow \cdot\text{C(OH)}_2\text{COOH} + \text{SO}_4^{2-} + \text{H}^+$	$2.35 \cdot 10^7$	1395	estimated equal as R <sub>o</sub> 00074
R <sub>o</sub> 00086	$\cdot\text{C(OH)}_2\text{COOH} + \text{O}_2 \rightarrow \cdot\text{OOC(OH)}_2\text{COOH}$	$2.00 \cdot 10^9$		estimated
R <sub>o</sub> 00087	$\cdot\text{OOC(OH)}_2\text{COOH} \rightarrow \text{CO(OH)CO(OH)} + \text{HO}_2$	$2.00 \cdot 10^9$		estimated
R <sub>o</sub> 00088	$\text{CH}_3\text{CO}^\cdot + \text{O}_2 \rightarrow \text{CH}_3\text{CO}_3^\cdot$	$2.00 \cdot 10^9$		estimated
R <sub>o</sub> 00089	$\text{CH}_3\text{CO}_3^\cdot + \text{O}_2^- \rightarrow \text{CH}_3\text{CO(OO}^-) + \text{O}_2$	$1.00 \cdot 10^9$		<i>Schuchmann and von Sonntag</i> (1988)
R <sub>o</sub> 00090	$\text{CH}_3\text{C}^\cdot(\text{OH})_2 + \text{O}_2 \rightarrow \text{CH}_3\text{C(OH)}_2\text{OO}^\cdot$	$2.00 \cdot 10^9$		estimated
R <sub>o</sub> 00091	$\text{CH}_3\text{C(OH)}_2\text{OO}^\cdot \rightarrow \text{CH}_3\text{COO}^- + 2 \text{H}^+ + \text{O}_2^-$	$1.00 \cdot 10^5$		estimated
R <sub>o</sub> 00092	$\text{CH}_3\text{O}^\cdot + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2$	$1.20 \cdot 10^6$		estimated same as gas phase
R <sub>o</sub> 00093	$\text{CH}_3\text{O}^\cdot \rightarrow \cdot\text{CH}_2(\text{OH})$	$1.00 \cdot 10^6$		estimated
R <sub>o</sub> 00094	$\cdot\text{CH}_2\text{COO}^- + \text{O}_2 \rightarrow \cdot\text{OOCH}_2\text{COO}^-$	$2.00 \cdot 10^9$		estimated

**Table G.10** (continued) Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00095	$\cdot\text{OOCH}_2\text{COO}^- \xrightarrow{\text{RO}_2} 0.567 \text{CH}(\text{OH})_2\text{COO}^- +$ $0.144 \text{CH}_2(\text{OH})\text{COO}^- + 0.289 \text{HCHO} + 0.298 \text{H}_2\text{O}_2 +$ $0.173 \text{OH}^- + 0.289 \text{CO}_2 + 0.115 \text{O}_2^- + 0.087 \text{O}_2 - 0.74 \text{H}_2\text{O}$	$6.51 \cdot 10^7$		<i>Schuchmann et al.</i> (1985)
R <sub>o</sub> 00096	$\cdot\text{COO}^- + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}_2^-$	$4.00 \cdot 10^9$		estimated
R <sub>o</sub> 00375*	$\text{CH}(\text{OH})_2\text{COO}^- + \text{OH} \rightarrow \cdot\text{C}(\text{OH})_2\text{COO}^- + \text{H}_2\text{O}$	$2.60 \cdot 10^9$	4330	<i>Ervens et al.</i> (2003b)
R <sub>o</sub> 00376*	$\text{CH}(\text{OH})_2\text{COO}^- + \text{NO}_3 \rightarrow \cdot\text{C}(\text{OH})_2\text{COO}^- + \text{NO}_3^- + \text{H}^+$	$2.00 \cdot 10^7$		calculated ( <i>Herrmann and Zellner</i> , 1998)
R <sub>o</sub> 00097	$\cdot\text{C}(\text{OH})_2\text{COO}^- + \text{O}_2 \rightarrow \cdot\text{OOC}(\text{OH})_2\text{COO}^-$	$2.00 \cdot 10^9$		estimated same as R <sub>o</sub> 00015
R <sub>o</sub> 00098	$\cdot\text{OOC}(\text{OH})_2\text{COO}^- \xrightarrow{\text{RO}_2} \cdot\text{COO}^- + \text{CO}_2 + \text{H}_2\text{O}_2$	$2.00 \cdot 10^7$		estimated in analogy to $\cdot\text{OOCH}_2\text{COO}^-$ recombination, ( <i>Schuchmann et al.</i> , 1985)
R <sub>o</sub> 00099	$\cdot\text{OOC}(\text{OH})_2\text{COO}^- \xrightarrow{\text{RO}_2}$ $0.5 \cdot \text{COO}^- + 1.5 \text{CO}_2 + 0.418 \text{OH}^- + 0.209 \text{H}_2\text{O}_2 +$ $0.082 \text{O}_2^- + 0.209 \text{O}_2 + 0.582 \text{H}_2\text{O}$	$4.55 \cdot 10^7$		estimated in analogy to ( <i>Schuchmann et al.</i> , 1985)
R <sub>o</sub> 00381*	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{C}\cdot\text{H}(\text{OH}) + \text{H}_2\text{O}$	$3.20 \cdot 10^9$	1000	<i>Ervens et al.</i> (2003b)
R <sub>o</sub> 00382*	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{NO}_3 \rightarrow$ $\text{CH}_3\text{CH}_2\text{C}\cdot\text{H}(\text{OH}) + \text{NO}_3^- + \text{H}^+$	$3.20 \cdot 10^6$		<i>Herrmann et al.</i> (1994)
R <sub>o</sub> 00100	$\text{CH}_3\text{CH}_2\text{C}\cdot\text{H}(\text{OH}) + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{OO}\cdot$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00101	$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{OO}\cdot + \text{OH}^- \rightarrow$ $\text{CH}_3\text{CH}_2\text{CHO} + \text{O}_2^- + \text{H}_2\text{O}$	$4.00 \cdot 10^9$		estimated
R <sub>o</sub> 00102	$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{OO}\cdot \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{HO}_2$	$5.20 \cdot 10^1$		estimated equal as R <sub>o</sub> 00023
R <sub>o</sub> 00764*	$\text{CH}_3\text{CH}_2\text{CHO} + \text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CO}\cdot + \text{H}_2\text{O}$	$2.80 \cdot 10^9$	1300	<i>Hesper and Herrmann</i> (2003)
R <sub>o</sub> 00765*	$\text{CH}_3\text{CH}_2\text{CHO} + \text{NO}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CO}\cdot + \text{NO}_3^- + \text{H}^+$	$3.90 \cdot 10^7$	505	in $\text{CH}_3\text{CN}$ ( <i>Ito et al.</i> , 1989b)
R <sub>o</sub> 00103	$\text{CH}_3\text{CH}_2\text{CO}\cdot + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CO}_3$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)



**Table G.10 (continued)** Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00104	$\text{CH}_3\text{CH}_2\text{CO}_3 \xrightarrow{\text{RO}_2} \text{CH}_3\text{CH}_2\text{CO}_2 + 0.5 \text{O}_2$	$1.50 \cdot 10^8$		estimated after the $\text{CH}_3\text{CO}_3$ recombination ( <i>Herrmann et al.</i> , 1999)
R <sub>o</sub> 00105	$\text{CH}_3\text{CH}_2\text{CO}_2 \rightarrow \text{CH}_3\text{CH}_2 + \text{CO}_2$	$2.00 \cdot 10^9$		<i>Hilborn and Pincock</i> (1991)
R <sub>o</sub> 00106	$\text{CH}_3\text{CH}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OO}\cdot$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00770*	$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})_2 + \text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{C}^*(\text{OH})_2 + \text{H}_2\text{O}$	$2.80 \cdot 10^9$	1300	<i>Hesper and Herrmann</i> (2003)
R <sub>o</sub> 00771*	$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})_2 + \text{NO}_3 \rightarrow$ $\text{CH}_3\text{CH}_2\text{C}^*(\text{OH})_2 + \text{NO}_3^- + \text{H}^+$	$2.80 \cdot 10^9$	1300	in $\text{CH}_3\text{CN}$ ( <i>Ito et al.</i> , 1989b)
R <sub>o</sub> 00107	$\text{CH}_3\text{CH}_2\text{C}^*(\text{OH})_2 + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{COO}\cdot$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00108	$\text{CH}_3\text{CH}_2\text{COO}\cdot \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{HO}_2$	$1.00 \cdot 10^3$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00778*	$\text{CH}_3\text{CH}_2\text{COOH} + \text{OH} \rightarrow \text{CH}_3\text{C}^*\text{HCOOH} + \text{H}_2\text{O}$	$3.20 \cdot 10^8$	2300	<i>Ervens et al.</i> (2003b)
R <sub>o</sub> 00779*	$\text{CH}_3\text{CH}_2\text{COOH} + \text{NO}_3 \rightarrow \text{CH}_3\text{C}^*\text{HCOOH} + \text{NO}_3^- + \text{H}^+$	$7.70 \cdot 10^4$		calculated <i>Rousse and George</i> (2004)
R <sub>o</sub> 00109	$\text{CH}_3\text{C}^*\text{HCOOH} + \text{O}_2 \rightarrow \text{CH}_3\text{CH}(\text{OO}\cdot)\text{COOH}$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00110	$\text{CH}_3\text{CH}(\text{OO}\cdot)\text{COOH} \xrightarrow{\text{RO}_2} \text{CH}_3\text{CH}_2\text{OO}\cdot + 2 \text{CO}_2$	$1.50 \cdot 10^8$		in analogy to $\text{CH}_3\text{CO}_3$ recombination
R <sub>o</sub> 00781*	$\text{CH}_3\text{CH}_2\text{COO}^- + \text{OH} \rightarrow \text{CH}_3\text{C}^*\text{HCOO}^- + \text{H}_2\text{O}$	$7.20 \cdot 10^8$	1800	<i>Ervens et al.</i> (2003b)
R <sub>o</sub> 00782*	$\text{CH}_3\text{CH}_2\text{COO}^- + \text{NO}_3 \rightarrow \text{CH}_3\text{C}^*\text{HCOO}^- + \text{NO}_3^- + \text{H}^+$	$2.00 \cdot 10^7$		calculated ( <i>Herrmann and Zellner</i> , 1998), BDEs derived after correlation reported in <i>Glorigovski and Herrmann</i> (2004)
R <sub>o</sub> 00111	$\text{CH}_3\text{C}^*\text{HCOO}^- + \text{O}_2 \rightarrow \text{CH}_3\text{CH}(\text{OO}\cdot)\text{COO}^-$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00112	$\text{CH}_3\text{CH}(\text{OO}\cdot)\text{COO}^- \xrightarrow{\text{RO}_2}$ $0.567 \text{CH}_3\text{COCOO}^- + 0.144 \text{CH}_3\text{CH}(\text{OH})\text{COO}^- +$ $0.289 \text{CH}_3\text{CHO} + 0.289 \text{CO}_2 + 0.298 \text{H}_2\text{O}_2 +$ $0.173 \text{OH}^- + 0.115 \text{O}_2^- + 0.087 \text{O}_2 - 0.173 \text{H}_2\text{O}$	$6.55 \cdot 10^7$		estimated in analogy to $\cdot\text{OOCH}_2\text{COO}^-$ recombination ( <i>Schuchmann et al.</i> , 1985)

**Table G.10** (continued) Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00784*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + \text{OH} \rightarrow \text{CH}_3\text{C}^*(\text{OH})\text{CH}_3 + \text{H}_2\text{O}$	$2.10 \cdot 10^9$	962	<i>Hesper</i> (2003)
R <sub>o</sub> 00785*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + \text{NO}_3 \rightarrow \text{CH}_3\text{C}^*(\text{OH})\text{CH}_3 + \text{NO}_3^- + \text{H}^+$	$3.70 \cdot 10^6$	1323	<i>Herrmann et al.</i> (1994) with $E_A/R$ of ( <i>Ito et al.</i> , 1989b)
R <sub>o</sub> 00113	$\text{CH}_3\text{C}^*(\text{OH})\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_3$	$1.60 \cdot 10^9$		estimated
R <sub>o</sub> 00114	$\text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_3 \rightarrow \text{CH}_3\text{COCH}_3 + \text{HO}_2$	$6.65 \cdot 10^2$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00789*	$\text{CH}_3\text{COCH}_3 + \text{OH} \rightarrow \text{CH}_3\text{COCH}_2\cdot + \text{H}_2\text{O}$	$1.70 \cdot 10^8$	1788	average of measurements within the MOST project
R <sub>o</sub> 00790*	$\text{CH}_3\text{COCH}_3 + \text{NO}_3 \rightarrow \text{CH}_3\text{COCH}_2\cdot + \text{NO}_3^- + \text{H}^+$	$3.70 \cdot 10^3$	4330	<i>Herrmann and Zellner</i> (1998)
R <sub>o</sub> 00115	$\text{CH}_3\text{COCH}_2\cdot + \text{O}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{OO}\cdot$	$3.10 \cdot 10^9$		<i>Zegota et al.</i> (1986)
R <sub>o</sub> 00116	$\text{CH}_3\text{COCH}_2\text{OO}\cdot \xrightarrow{\text{RO}_2}$ $0.399 \text{ CH}_3\text{COCHO} + 0.08 \text{ CH}_3\text{COCH}_2\text{OH} +$ $0.521 \text{ CH}_3\text{COCH}_2\text{O}\cdot + 0.16 \text{ H}_2\text{O}_2 + 0.34 \text{ O}_2$	$3.76 \cdot 10^8$		<i>Zegota et al.</i> (1986)
R <sub>o</sub> 00117	$\text{CH}_3\text{COCH}_2\text{O}\cdot \rightarrow \text{HCHO} + \text{CH}_3\text{CO}\cdot$	$1.60 \cdot 10^6$		estimated from the gas phase
R <sub>o</sub> 00404*	$\text{CH}_3\text{COCH}_2\text{OH} + \text{OH} \rightarrow \text{CH}_3\text{COC}^*\text{H}(\text{OH}) + \text{H}_2\text{O}$	$1.20 \cdot 10^9$	1082	<i>Gligorovski</i> (2005)
R <sub>o</sub> 00405*	$\text{CH}_3\text{COCH}_2\text{OH} + \text{NO}_3 \rightarrow \text{CH}_3\text{COC}^*\text{H}(\text{OH}) + \text{NO}_3^- + \text{H}^+$	$1.80 \cdot 10^7$	1564	<i>de Semainville et al.</i> (2007b)
R <sub>o</sub> 00118	$\text{CH}_3\text{COC}^*\text{H}(\text{OH}) + \text{O}_2 \rightarrow \text{CH}_3\text{COCH}(\text{OH})\text{OO}\cdot$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00119	$\text{CH}_3\text{COCH}(\text{OH})\text{OO}\cdot \rightarrow \text{CH}_3\text{COCHO} + \text{HO}_2$	$2.10 \cdot 10^2$	4990	estimated after $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{OO}\cdot$ ( <i>Bothe et al.</i> , 1978)
R <sub>o</sub> 00120	$\text{CH}_3\text{COCH}(\text{OH})\text{OO}\cdot \xrightarrow{\text{RO}_2} \text{CH}_3\text{COCO}(\text{OH})\text{OOH} + 0.5 \text{ H}_2\text{O}_2$	$3.50 \cdot 10^8$		estimated after the decay of $\text{CH}_3\text{CH}(\text{OH})\text{OO}\cdot$ ( <i>Bothe et al.</i> , 1983)
R <sub>o</sub> 00577*	$\text{CH}_3\text{COCH}(\text{OH})_2 + \text{OH} \rightarrow \text{CH}_3\text{COC}^*(\text{OH})_2 + \text{H}_2\text{O}$	$7.90 \cdot 10^8$	1589	average of measurements within the MOST project
R <sub>o</sub> 00578*	$\text{CH}_3\text{COCH}(\text{OH})_2 + \text{NO}_3 \rightarrow \text{CH}_3\text{COC}^*(\text{OH})_2 + \text{NO}_3^- + \text{H}^+$	$8.77 \cdot 10^6$		estimated

**Table G.10 (continued)** Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00121	$\text{CH}_3\text{COC}^*(\text{OH})_2 + \text{O}_2 \rightarrow \text{CH}_3\text{COC}(\text{OH})_2\text{OO}\cdot$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00122	$\text{CH}_3\text{COC}(\text{OH})_2\text{OO}\cdot \rightarrow \text{CH}_3\text{COCO}(\text{OH})_2 + \text{HO}_2$	$1.00 \cdot 10^7$		approximation in analogy with glyoxal, ( <i>Buxton et al.</i> , 1997)
R <sub>o</sub> 00703*	$\text{CO}(\text{OH})\text{CH}_2\text{COOH} + \text{OH} \rightarrow \text{CO}(\text{OH})\text{C}^*\text{HCOOH} + \text{H}_2\text{O}$	$2.00 \cdot 10^7$		<i>Buxton et al.</i> (1988a)
R <sub>o</sub> 00704*	$\text{CO}(\text{OH})\text{CH}_2\text{COOH} + \text{NO}_3 \rightarrow \text{CO}(\text{OH})\text{C}^*\text{HCOOH} + \text{NO}_3^- + \text{H}^+$	$5.10 \cdot 10^4$		<i>de Semainville et al.</i> (2010a)
R <sub>o</sub> 00123	$\text{CO}(\text{OH})\text{C}^*\text{HCOOH} + \text{O}_2 \rightarrow \text{CO}(\text{OH})\text{CH}(\text{OO}\cdot)\text{COOH}$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00124	$\text{CO}(\text{OH})\text{CH}(\text{OO}\cdot)\text{COOH} \xrightarrow{\text{RO}_2} 0.565 \text{CO}(\text{OH})\text{COCO}(\text{OH})_2 + 0.145 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{COOH} + 0.29 \text{CH}(\text{OH})_2\text{COOH} + 0.29 \text{CO}_2 + 0.298 \text{H}_2\text{O}_2 + 0.115 \text{O}_2^- - 0.115 \text{OH}^- + 0.088 \text{O}_2 - 0.176 \text{H}_2\text{O}$	$6.55 \cdot 10^7$		estimated in analogy to $\text{CO}(\text{O}^-)\text{CH}_2\text{O}\cdot$ recombination, ( <i>Schuchmann et al.</i> , 1985)
R <sub>o</sub> 00748*	$\text{CO}(\text{O}^-)\text{CH}_2\text{COO}^- + \text{OH} \rightarrow \text{CO}(\text{O}^-)\text{C}^*\text{HCOO}^- + \text{H}_2\text{O}$	$2.40 \cdot 10^8$		<i>Logan</i> (1989)
R <sub>o</sub> 00749*	$\text{CO}(\text{O}^-)\text{CH}_2\text{COO}^- + \text{NO}_3 \rightarrow \text{CO}(\text{O}^-)\text{C}^*\text{HCOO}^- + \text{NO}_3^- + \text{H}^+$	$1.10 \cdot 10^6$		calculated ( <i>Herrmann and Zellner</i> , 1998), <i>BDEs</i> derived after correlation reported in <i>Gligorovski and Herrmann</i> (2004)
R <sub>o</sub> 00125	$\text{CO}(\text{O}^-)\text{C}^*\text{HCOO}^- + \text{O}_2 \rightarrow \text{CO}(\text{O}^-)\text{CH}(\text{OO}\cdot)\text{COO}^-$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00126	$\text{CO}(\text{O}^-)\text{CH}(\text{OO}\cdot)\text{COO}^- \xrightarrow{\text{RO}_2} 0.565 \text{CO}(\text{O}^-)\text{COCO}(\text{O}^-) + 0.145 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COO}^- + 0.29 \text{CH}(\text{OH})_2\text{COO}^- + 0.29 \text{CO}_2 + 0.298 \text{H}_2\text{O}_2 + 0.115 \text{O}_2^- + 0.176 \text{OH}^- + 0.087 \text{O}_2 - 0.466 \text{H}_2\text{O}$	$6.55 \cdot 10^7$		estimated in analogy to $\cdot\text{OOCH}_2\text{COO}^-$ recombination ( <i>Schuchmann et al.</i> , 1985)
R <sub>o</sub> 00742*	$\text{CO}(\text{OH})\text{CH}_2\text{COO}^- + \text{OH} \rightarrow \text{CO}(\text{OH})\text{C}^*\text{HCOO}^- + \text{H}_2\text{O}$	$6.00 \cdot 10^7$	1300	<i>Ervens et al.</i> (2003b)
R <sub>o</sub> 00743*	$\text{CO}(\text{OH})\text{CH}_2\text{COO}^- + \text{NO}_3 \rightarrow \text{CO}(\text{OH})\text{C}^*\text{HCOO}^- + \text{NO}_3^- + \text{H}^+$	$5.60 \cdot 10^6$	3368	<i>de Semainville et al.</i> (2010a)
R <sub>o</sub> 00127	$\text{CO}(\text{OH})\text{C}^*\text{HCOO}^- + \text{O}_2 \rightarrow \text{CO}(\text{OH})\text{CH}(\text{OO}\cdot)\text{COO}^-$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)

**Table G.10** (continued) Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00128	$\text{CO(OH)CH(OO}\cdot\text{)COO}^- \xrightarrow{\text{RO}_2}$ $0.565 \text{ CO(OH)COCOO}^- + 0.145 \text{ CO(OH)CH(OH)COO}^- +$ $0.29 \text{ CH(OH)}_2\text{COOH} + 0.29 \text{ CO}_2 + 0.298 \text{ H}_2\text{O}_2 +$ $0.115 \text{ O}_2^- + 0.176 \text{ OH}^- + 0.087 \text{ O}_2 - 0.466 \text{ H}_2\text{O}$	$6.55 \cdot 10^7$		estimated in analogy to <i>Schuchmann et al.</i> (1985)
R <sub>o</sub> 00638*	$\text{CH}_3\text{COCOOH} + \text{OH} \rightarrow \cdot\text{CH}_2\text{COCOOH} + \text{H}_2\text{O}$	$1.20 \cdot 10^8$	2800	<i>Ervens et al.</i> (2003b)
R <sub>o</sub> 00639*	$\text{CH}_3\text{COCOOH} + \text{NO}_3 \rightarrow \cdot\text{CH}_2\text{COCOOH} + \text{NO}_3^- + \text{H}^+$	$2.40 \cdot 10^6$	1804	<i>de Semainville et al.</i> (2007b)
R <sub>o</sub> 00129	$\cdot\text{CH}_2\text{COCOOH} + \text{O}_2 \rightarrow \cdot\text{OOCH}_2\text{COCOOH}$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00130	$\cdot\text{OOCH}_2\text{COCOOH} \xrightarrow{\text{RO}_2}$ $0.565 \text{ CO(OH)COCHO} + 0.145 \text{ CH}_2(\text{OH})\text{COCOOH} +$ $0.29 \text{ CH}_3\text{CHO} + 0.29 \text{ CO}_2 + 0.298 \text{ H}_2\text{O}_2 + 0.114 \text{ O}_2^- -$ $0.114 \text{ OH}^- + 0.378 \text{ O}_2 - 0.176 \text{ H}_2\text{O}$	$6.55 \cdot 10^7$		estimated in analogy to <i>Schuchmann et al.</i> (1985)
R <sub>o</sub> 00663*	$\text{CH}_3\text{COCOO}^- + \text{OH} \rightarrow \cdot\text{CH}_2\text{COCOO}^- + \text{H}_2\text{O}$	$7.00 \cdot 10^8$	2285	<i>Ervens et al.</i> (2003b)
R <sub>o</sub> 00664*	$\text{CH}_3\text{COCOO}^- + \text{NO}_3 \rightarrow \cdot\text{CH}_2\text{COCOO}^- + \text{NO}_3^- + \text{H}^+$	$1.90 \cdot 10^7$	2887	<i>de Semainville et al.</i> (2007b)
R <sub>o</sub> 00131	$\cdot\text{CH}_2\text{COCOO}^- + \text{O}_2 \rightarrow \cdot\text{OOCH}_2\text{COCOO}^-$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00132	$\cdot\text{OOCH}_2\text{COCOO}^- \xrightarrow{\text{RO}_2}$ $0.565 \text{ CO(O}^-\text{)COCHO} + 0.145 \text{ CH}_2(\text{OH})\text{COCOO}^- +$ $0.29 \text{ CH}_3\text{CHO} + 0.29 \text{ CO}_2 + 0.298 \text{ H}_2\text{O}_2 + 0.115 \text{ O}_2^- +$ $0.176 \text{ OH}^- + 0.378 \text{ O}_2 - 0.466 \text{ H}_2\text{O}$	$6.55 \cdot 10^7$		estimated in analogy to <i>Schuchmann et al.</i> (1985)
R <sub>o</sub> 00791*	$\text{CO(OH)CH}_2\text{CH}_2\text{COOH} + \text{OH} \rightarrow$ $\text{CO(OH)CH}_2\text{C}\cdot\text{HCOOH} + \text{H}_2\text{O}$	$1.10 \cdot 10^8$	1278	<i>Ervens et al.</i> (2003b)
R <sub>o</sub> 00792*	$\text{CO(OH)CH}_2\text{CH}_2\text{COOH} + \text{NO}_3 \rightarrow$ $\text{CO(OH)CH}_2\text{C}\cdot\text{HCOOH} + \text{NO}_3^- + \text{H}^+$	$5.00 \cdot 10^3$		<i>de Semainville et al.</i> (2010a)
R <sub>o</sub> 00133	$\text{CO(OH)CH}_2\text{C}\cdot\text{HCOOH} + \text{O}_2 \rightarrow$ $\text{CO(OH)CH}_2\text{CH(OO}\cdot\text{)COOH}$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)

**Table G.10 (continued)** Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00134	$\text{CO(OH)CH}_2\text{CH(OO}\cdot\text{)COOH} \xrightarrow{\text{RO}_2}$ $0.565 \text{ CO(OH)CH}_2\text{COCOOH} +$ $0.145 \text{ CO(OH)CH}_2\text{CH(OH)COOH} +$ $0.29 \text{ CO(OH)CH}_2\text{CHO} + 0.29 \text{ CO}_2 + 0.298 \text{ H}_2\text{O}_2 +$ $0.115 \text{ O}_2^- - 0.115 \text{ OH}^- + 0.087 \text{ O}_2 + 0.115 \text{ H}_2\text{O}$	$6.55 \cdot 10^7$		estimated in analogy to ( <i>Schuchmann et al.</i> , 1985)
R <sub>o</sub> 00628*	$\text{CH(OH)}_2\text{CH}_2\text{COOH} + \text{OH}^- \rightarrow \cdot\text{C(OH)}_2\text{CH}_2\text{COOH} + \text{H}_2\text{O}$	$8.67 \cdot 10^8$		estimated after glycolic acid
R <sub>o</sub> 00629*	$\text{CH(OH)}_2\text{CH}_2\text{COOH} + \text{NO}_3^- \rightarrow$ $\cdot\text{C(OH)}_2\text{CH}_2\text{COOH} + \text{NO}_3^- + \text{H}^+$	$8.71 \cdot 10^6$		estimated after glycolic acid
R <sub>o</sub> 00135	$\cdot\text{C(OH)}_2\text{CH}_2\text{COOH} + \text{O}_2 \rightarrow \cdot\text{OOC(OH)}_2\text{CH}_2\text{COOH}$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00136	$\cdot\text{OOC(OH)}_2\text{CH}_2\text{COOH} \rightarrow \text{CO(OH)CH}_2\text{CO(OH)} + \text{HO}_2$	$1.00 \cdot 10^3$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00799*	$\text{CO(O}^-\text{)CH}_2\text{CH}_2\text{COO}^- + \text{OH}^- \rightarrow$ $\text{CO(O}^-\text{)CH}_2\text{C}^-\text{HCOO}^- + \text{H}_2\text{O}$	$5.00 \cdot 10^8$	1300	<i>Ervens et al.</i> (2003b)
R <sub>o</sub> 00800*	$\text{CO(O}^-\text{)CH}_2\text{CH}_2\text{COO}^- + \text{NO}_3^- \rightarrow$ $\text{CO(O}^-\text{)CH}_2\text{C}^-\text{HCOO}^- + \text{NO}_3^- + \text{H}^+$	$5.50 \cdot 10^7$		( <i>Herrmann and Zellner</i> , 1998), BDEs derived after correlation reported in <i>Gligorovski and</i> <i>Herrmann</i> (2004)
R <sub>o</sub> 00137	$\text{CO(O}^-\text{)CH}_2\text{C}^-\text{HCOO}^- + \text{O}_2 \rightarrow$ $\text{CO(O}^-\text{)CH}_2\text{CH(OO}\cdot\text{)COO}^-$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00138	$\text{CO(O}^-\text{)CH}_2\text{CH(OO}\cdot\text{)COO}^- \xrightarrow{\text{RO}_2}$ $0.565 \text{ CO(O}^-\text{)CH}_2\text{COCOO}^- +$ $0.145 \text{ CO(O}^-\text{)CH}_2\text{CH(OH)COO}^- +$ $0.29 \text{ CHOCH}_2\text{COO}^- + 0.29 \text{ CO}_2 + 0.298 \text{ H}_2\text{O}_2 + 0.115 \text{ O}_2^- +$ $0.176 \text{ OH}^- - 0.087 \text{ O}_2 - 0.176 \text{ H}_2\text{O}$	$6.55 \cdot 10^7$		estimated in analogy to ( <i>Schuchmann et al.</i> , 1985)
R <sub>o</sub> 00652*	$\text{CH(OH)}_2\text{CH}_2\text{COO}^- + \text{OH}^- \rightarrow \cdot\text{C(OH)}_2\text{CH}_2\text{COO}^- + \text{H}_2\text{O}$	$1.20 \cdot 10^9$		estimated after glycolic acid

**Table G.10** (continued) Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00653*	$\text{CH(OH)}_2\text{CH}_2\text{COO}^- + \text{NO}_3 \rightarrow$ $\cdot\text{C(OH)}_2\text{CH}_2\text{COO}^- + \text{NO}_3^- + \text{H}^+$	$1.10 \cdot 10^9$		estimated after glycolic acid
R <sub>o</sub> 00139	$\cdot\text{C(OH)}_2\text{CH}_2\text{COO}^- + \text{O}_2 \rightarrow \cdot\text{OOC(OH)}_2\text{CH}_2\text{COO}^-$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00140	$\cdot\text{OOC(OH)}_2\text{CH}_2\text{COO}^- \rightarrow \text{CO(OH)CH}_2\text{COO}^- + \text{HO}_2$	$1.00 \cdot 10^3$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00793*	$\text{CO(OH)CH}_2\text{CH}_2\text{COO}^- + \text{OH} \rightarrow$ $\text{CO(OH)C}^*\text{HCH}_2\text{COO}^- + \text{H}_2\text{O}$	$2.60 \cdot 10^8$	1808	TROPOS measurements
R <sub>o</sub> 00794*	$\text{CO(OH)CH}_2\text{CH}_2\text{COO}^- + \text{NO}_3 \rightarrow$ $\text{CO(OH)C}^*\text{HCH}_2\text{COO}^- + \text{NO}_3^- + \text{H}^+$	$1.10 \cdot 10^7$		<i>de Semainville et al.</i> (2010a)
R <sub>o</sub> 00141	$\text{CO(OH)C}^*\text{HCH}_2\text{COO}^- + \text{O}_2 \rightarrow$ $\text{CO(OH)CH(OO}\cdot\text{)CH}_2\text{COO}^-$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00142	$\text{CO(OH)CH(OO}\cdot\text{)CH}_2\text{COO}^- \xrightarrow{\text{RO}_2}$ $0.565 \text{CO(O}^-\text{)CH}_2\text{COCOOH} +$ $0.145 \text{CO(O}^-\text{)CH}_2\text{CH(OH)COOH} +$ $0.29 \text{CO(OH)CH}_2\text{CHO} + 0.29 \text{CO}_2 + 0.298 \text{H}_2\text{O}_2 +$ $0.115 \text{O}_2^- + 0.176 \text{OH}^- + 0.087 \text{O}_2 - 0.176 \text{H}_2\text{O}$	$6.55 \cdot 10^7$		estimated in analogy to ( <i>Schuchmann et al.</i> , 1985)
R <sub>o</sub> 00541*	$\text{CH}_3\text{CH(OH)COOH} + \text{OH} \rightarrow \text{CH}_3\text{C}^*(\text{OH})\text{COOH} + \text{H}_2\text{O}$	$5.24 \cdot 10^8$	1120	<i>Martin et al.</i> (2009)
R <sub>o</sub> 00542*	$\text{CH}_3\text{CH(OH)COOH} + \text{NO}_3 \rightarrow$ $\text{CH}_3\text{C}^*(\text{OH})\text{COOH} + \text{NO}_3^- + \text{H}^+$	$2.10 \cdot 10^6$	3248	<i>de Semainville et al.</i> (2007b)
R <sub>o</sub> 00143	$\text{CH}_3\text{C}^*(\text{OH})\text{COOH} + \text{O}_2 \rightarrow \text{CH}_3\text{C(OO}\cdot\text{)(OH)COOH}$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00144	$\text{CH}_3\text{C(OO}\cdot\text{)(OH)COOH} \rightarrow \text{CH}_3\text{COCOOH} + \text{HO}_2$	$6.65 \cdot 10^2$		estimated after isopropanol ( <i>von Sonntag</i> , 1987)
R <sub>o</sub> 00612*	$\text{CH}_3\text{CH(OH)COO}^- + \text{OH} \rightarrow \text{CH}_3\text{C}^*(\text{OH})\text{COO}^- + \text{H}_2\text{O}$	$7.77 \cdot 10^8$	1295	<i>Martin et al.</i> (2009)
R <sub>o</sub> 00613*	$\text{CH}_3\text{CH(OH)COO}^- + \text{NO}_3 \rightarrow$ $\text{CH}_3\text{C}^*(\text{OH})\text{COO}^- + \text{NO}_3^- + \text{H}^+$	$1.00 \cdot 10^7$	2646	<i>de Semainville et al.</i> (2007b)
R <sub>o</sub> 00145	$\text{CH}_3\text{C}^*(\text{OH})\text{COO}^- + \text{O}_2 \rightarrow \text{CH}_3\text{C(OO}\cdot\text{)(OH)COO}^-$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)

**Table G.10 (continued)** Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00146	$\text{CH}_3\text{C}(\text{OO}\cdot)(\text{OH})\text{COO}^- \rightarrow \text{CH}_3\text{COCOO}^- + \text{HO}_2$	$6.65 \cdot 10^2$		estimated after isopropanol ( <i>von Sonntag</i> , 1987)
R <sub>o</sub> 00351*	$\text{CH}_2(\text{OH})\text{COOH} + \text{OH} \rightarrow \cdot\text{CH}(\text{OH})\text{COOH} + \text{H}_2\text{O}$	$6.00 \cdot 10^8$		<i>Buxton et al.</i> (1988a)
R <sub>o</sub> 00352*	$\text{CH}_2(\text{OH})\text{COOH} + \text{NO}_3 \rightarrow \cdot\text{CH}(\text{OH})\text{COOH} + \text{NO}_3^- + \text{H}^+$	$9.10 \cdot 10^5$	3969	<i>de Semainville et al.</i> (2007b)
R <sub>o</sub> 00147	$\cdot\text{CH}(\text{OH})\text{COOH} + \text{O}_2 \rightarrow \cdot\text{OOCH}(\text{OH})\text{COOH}$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00148	$\cdot\text{OOCH}(\text{OH})\text{COOH} \xrightarrow{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{COOH} + \text{HO}_2$	$5.20 \cdot 10^1$		estimated after ethanol ( <i>von Sonntag</i> , 1987)
R <sub>o</sub> 00358*	$\text{CH}_2(\text{OH})\text{COO}^- + \text{OH} \rightarrow \cdot\text{CH}(\text{OH})\text{COO}^- + \text{H}_2\text{O}$	$1.20 \cdot 10^9$		<i>Logan</i> (1989)
R <sub>o</sub> 00359*	$\text{CH}_2(\text{OH})\text{COO}^- + \text{NO}_3 \rightarrow \cdot\text{CH}(\text{OH})\text{COO}^- + \text{NO}_3^- + \text{H}^+$	$1.00 \cdot 10^7$	3007	<i>de Semainville et al.</i> (2007b)
R <sub>o</sub> 00149	$\cdot\text{CH}(\text{OH})\text{COO}^- + \text{O}_2 \rightarrow \cdot\text{OOCH}(\text{OH})\text{COO}^-$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00150	$\cdot\text{OOCH}(\text{OH})\text{COO}^- \xrightarrow{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{COO}^- + \text{HO}_2$	$5.20 \cdot 10^1$		estimated after ethanol ( <i>von Sonntag</i> , 1987)
R <sub>o</sub> 00151	$\cdot\text{OOCH}_2\text{COOH} + \text{HO}_2 \rightarrow \text{CH}_2(\text{OOH})\text{COOH} + \text{O}_2$	$8.30 \cdot 10^5$	2720	$k = k_{\text{HO}_2+\text{HO}_2}$ ( <i>Bielski et al.</i> , 1985)
R <sub>o</sub> 00152	$\cdot\text{OOCH}_2\text{COOH} + \text{O}_2^- \rightarrow \text{CH}_2(\text{OOH})\text{COOH} + \text{O}_2^- - \text{H}^+$	$9.70 \cdot 10^7$	1060	$k = k_{\text{HO}_2+\text{O}_2^-}$ ( <i>Bielski et al.</i> , 1985)
R <sub>o</sub> 00153	$\cdot\text{OOCH}_2\text{COOH} + \text{HSO}_3^- \rightarrow \text{CH}_2(\text{OOH})\text{COOH} + \text{SO}_3^-$	$5.00 \cdot 10^5$		$k = k_{\text{CH}_3(\text{OO}\cdot)+\text{HSO}_3^-}$ ( <i>Herrmann et al.</i> , 1999)
R <sub>o</sub> 00154	$\cdot\text{OOCH}_2\text{COO}^- + \text{HO}_2 \rightarrow \text{CH}_2(\text{OOH})\text{COO}^- + \text{O}_2$	$8.30 \cdot 10^5$	2720	$k = k_{\text{HO}_2+\text{O}_2^-}$ ( <i>Bielski et al.</i> , 1985)
R <sub>o</sub> 00155	$\cdot\text{OOCH}_2\text{COO}^- + \text{O}_2^- \rightarrow \text{CH}_2(\text{OOH})\text{COO}^- + \text{O}_2^- - \text{H}^+$	$9.70 \cdot 10^7$	1060	$k = k_{\text{HO}_2+\text{O}_2^-}$ ( <i>Bielski et al.</i> , 1985)
R <sub>o</sub> 00156	$\cdot\text{OOCH}_2\text{COO}^- + \text{HSO}_3^- \rightarrow \text{CH}_2(\text{OOH})\text{COO}^- + \text{SO}_3^-$	$5.00 \cdot 10^5$		$k = k_{\text{CH}_3(\text{OO}\cdot)+\text{HSO}_3^-}$ ( <i>Herrmann et al.</i> , 1999)
R <sub>o</sub> 00157	$\text{CH}_2(\text{OOH})\text{COOH} + \text{OH} \rightarrow \cdot\text{OOCH}_2\text{COOH} + \text{H}_2\text{O}$	$3.00 \cdot 10^7$		$k = k_{\text{OH}+\text{H}_2\text{O}_2}$
R <sub>o</sub> 00158	$\text{CH}_2(\text{OOH})\text{COOH} + \text{NO}_3 \rightarrow \cdot\text{OOCH}_2\text{COOH} + \text{NO}_3^- + \text{H}^+$	$1.70 \cdot 10^6$		calculated ( <i>Herrmann and Zellner</i> , 1998), BDE's determined with Benson's incremental method

**Table G.10** (continued) Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00159	$\text{CH}_2(\text{OOH})\text{COOH} + \text{Fe}^{2+} \xrightarrow{\text{H}_2\text{O}}$ $\text{Fe}^{3+} + \text{CH}_2(\text{OH})\text{COOH} + \text{OH} + \text{OH}^-$	$5.00 \cdot 10^1$		$k = k_{\text{Fe}^{2+} + \text{H}_2\text{O}_2}$
R <sub>o</sub> 00160	$\text{CH}_2(\text{OOH})\text{COO}^- + \text{OH} \rightarrow \cdot\text{OOCH}_2\text{COO}^- + \text{H}_2\text{O}$	$3.00 \cdot 10^7$		$k = k_{\text{OH} + \text{H}_2\text{O}_2}$
R <sub>o</sub> 00161	$\text{CH}_2(\text{OOH})\text{COO}^- + \text{NO}_3 \rightarrow \cdot\text{OOCH}_2\text{COO}^- + \text{NO}_3^- + \text{H}^+$	$7.10 \cdot 10^6$		$k = k_{\text{NO}_3 + \text{H}_2\text{O}_2}$
R <sub>o</sub> 00162	$\text{CH}_2(\text{OOH})\text{COO}^- + \text{Fe}^{2+} \xrightarrow{\text{H}_2\text{O}}$ $\text{Fe}^{3+} + \text{CH}_2(\text{OH})\text{COO}^- + \text{OH} + \text{OH}^-$	$5.00 \cdot 10^1$		$k = k_{\text{Fe}^{2+} + \text{H}_2\text{O}_2}$
R <sub>o</sub> 00962*	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{OH} \rightarrow$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\cdot\text{H}(\text{OH}) + \text{H}_2\text{O}$	$3.96 \cdot 10^9$	1000	<i>Hesper</i> (2003)
R <sub>o</sub> 00963*	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{NO}_3 \rightarrow$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\cdot\text{H}(\text{OH}) + \text{NO}_3^- + \text{H}^+$	$1.90 \cdot 10^6$		<i>Shastri and Huie</i> (1990)
R <sub>o</sub> 00163	$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\cdot\text{H}(\text{OH}) + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{OO}\cdot$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00164	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{OO}\cdot \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} + \text{HO}_2$	$1.00 \cdot 10^3$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 02757*	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} + \text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CO}\cdot + \text{H}_2\text{O}$	$3.90 \cdot 10^9$	900	<i>Hesper and Herrmann</i> (2003)
R <sub>o</sub> 02758*	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} + \text{NO}_3 \rightarrow$ $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}\cdot + \text{NO}_3^- + \text{H}^+$	$5.60 \cdot 10^7$	2045	<i>de Semainville et al.</i> (2007b)
R <sub>o</sub> 00165	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}\cdot + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_3\cdot$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00166	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_3\cdot \xrightarrow{\text{RO}_2} \text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\cdot + 0.5 \text{O}_2$	$1.50 \cdot 10^8$		estimated after $\text{CH}_3\text{CO}_3\cdot$ recombination ( <i>Herrmann et al.</i> , 1999)
R <sub>o</sub> 00167	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\cdot \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\cdot + \text{CO}_2$	$2.00 \cdot 10^9$		estimated after $\text{CH}_3\text{CH}_2\text{CO}_2\cdot$ ( <i>Hilborn and Pincock</i> , 1991)
R <sub>o</sub> 00168	$\text{CH}_3\text{CH}_2\text{CH}_2\cdot + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OO}\cdot$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00169	$\text{CH}_3\text{CH}_2\text{CH}_2\text{OO}\cdot \xrightarrow{\text{RO}_2} 0.624 \text{CH}_3\text{CH}_2\text{CH}_2\text{O}\cdot +$ $0.188 \text{CH}_3\text{CH}_2\text{CHO} + 0.188 \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + 0.5 \text{O}_2$	$1.60 \cdot 10^8$	750	estimated after $\text{CH}_3\text{CH}_2\text{O}\cdot$ ( <i>Herrmann et al.</i> , 1999)
R <sub>o</sub> 00170	$\text{CH}_3\text{CH}_2\text{CH}_2\text{O}\cdot + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{HO}_2$	$6.00 \cdot 10^6$		estimated



**Table G.10 (continued)** Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 02766*	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OH})_2 + \text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{C}^*(\text{OH})_2 + \text{H}_2\text{O}$	$3.90 \cdot 10^9$	900	<i>Hesper and Herrmann (2003)</i>
R <sub>o</sub> 02767*	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OH})_2 + \text{NO}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{C}^*(\text{OH})_2 + \text{NO}_3^- + \text{H}^+$	$1.24 \cdot 10^7$		calculated ( <i>Herrmann and Zellner, 1998</i> ), BDE's determined with Benson's incremental method
R <sub>o</sub> 00171	$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}^*(\text{OH})_2 + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{C}^*(\text{OH})_2\text{OO}\cdot$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag (1987)</i>
R <sub>o</sub> 00172	$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}^*(\text{OH})_2\text{OO}\cdot \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{HO}_2$	$1.00 \cdot 10^3$		estimated after <i>von Sonntag (1987)</i>
R <sub>o</sub> 02775*	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{C}^*\text{HCOOH} + \text{H}_2\text{O}$	$2.20 \cdot 10^9$		<i>Scholes and Willson (1967)</i>
R <sub>o</sub> 02776*	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} + \text{NO}_3 \rightarrow \text{CH}_3\text{CH}_2\text{C}^*\text{HCOOH} + \text{NO}_3^- + \text{H}^+$	$2.94 \cdot 10^2$		calculated ( <i>Herrmann and Zellner, 1998</i> ), BDEs determined with Benson's incremental method
R <sub>o</sub> 00173	$\text{CH}_3\text{CH}_2\text{C}^*\text{HCOOH} + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}(\text{OO}\cdot)\text{COOH}$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag (1987)</i>
R <sub>o</sub> 00174	$\text{CH}_3\text{CH}_2\text{CH}(\text{OO}\cdot)\text{COOH} \xrightarrow{\text{RO}_3} 0.565 \text{CH}_3\text{CH}_2\text{COCO}\cdot\text{H} + 0.145 \text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{COOH} + 0.29 \text{CH}_3\text{CH}_2\text{CHO} + 0.29 \text{CO}_2 + 0.298 \text{H}_2\text{O}_2 + 0.115 \text{O}_2^- - 0.115 \text{OH}^- + 0.087 \text{O}_2 + 0.115 \text{H}_2\text{O}$	$6.55 \cdot 10^7$		estimated in analogy to ( <i>Schuchmann et al., 1985</i> )
R <sub>o</sub> 02779*	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^- + \text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{C}^*\text{HCOO}^- + \text{H}_2\text{O}$	$2.00 \cdot 10^9$		<i>Anbar et al. (1966a)</i>
R <sub>o</sub> 02780*	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^- + \text{NO}_3 \rightarrow \text{CH}_3\text{CH}_2\text{C}^*\text{HCOO}^- + \text{NO}_3^- + \text{H}^+$	$2.00 \cdot 10^7$		<i>Herrmann and Zellner (1998)</i> , BDEs derived after correlation reported in <i>Gligorovski and Herrmann (2004)</i>
R <sub>o</sub> 00175	$\text{CH}_3\text{CH}_2\text{C}^*\text{HCOO}^- + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}(\text{OO}\cdot)\text{COO}^-$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag (1987)</i>

**Table G.10** (continued) Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00176	$\text{CH}_3\text{CH}_2\text{CH}(\text{OO}\cdot)\text{COO}^- \xrightarrow{\text{RO}_2}$ $0.565 \text{CH}_3\text{CH}_2\text{COCOO}^- + 0.145 \text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{COO}^- +$ $0.29 \text{CH}_3\text{CH}_2\text{CHO} + 0.29 \text{CO}_2 + 0.298 \text{H}_2\text{O}_2 +$ $0.115 \text{O}_2^- - 0.176 \text{OH}^- + 0.087 \text{O}_2 + 0.176 \text{H}_2\text{O}$	$6.55 \cdot 10^7$		estimated in analogy to <i>Schuchmann et al.</i> (1985)
R <sub>o</sub> 02783*	$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3 + \text{OH} \rightarrow$ $\text{CH}_3\text{CH}_2\text{C}^*(\text{OH})\text{CH}_3 + \text{H}_2\text{O}$	$3.50 \cdot 10^9$	910	<i>Hesper and Herrmann</i> (2003)
R <sub>o</sub> 02784*	$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3 + \text{NO}_3 \rightarrow$ $\text{CH}_3\text{CH}_2\text{C}^*(\text{OH})\text{CH}_3 + \text{NO}_3^- + \text{H}^+$	$2.25 \cdot 10^6$		calculated ( <i>Herrmann and Zellner</i> , 1998), <i>BDEs</i> determined with Benson's incremental method
R <sub>o</sub> 00177	$\text{CH}_3\text{CH}_2\text{C}^*(\text{OH})\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2(\text{OO}\cdot)(\text{OH})\text{CH}_3$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00178	$\text{CH}_3\text{CH}_2(\text{OO}\cdot)(\text{OH})\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{COCH}_3 + \text{HO}_2$	$1.00 \cdot 10^3$		( <i>von Sonntag</i> , 1987)
R <sub>o</sub> 02803*	$\text{CH}_3\text{CH}_2\text{COCH}_3 + \text{OH} \rightarrow \text{CH}_3\text{C}^*\text{HCOCH}_3 + \text{H}_2\text{O}$	$1.17 \cdot 10^9$	1451	average of measurements within the MOST project
R <sub>o</sub> 00179 <sup>#</sup>	$\text{CH}_3\text{CH}_2\text{COCH}_3 + \text{OH} \rightarrow \cdot\text{CH}_2\text{COCH}_2\text{CH}_3 + \text{H}_2\text{O}$	$1.30 \cdot 10^8$	1451	average of measurements within the MOST project
R <sub>o</sub> 02804*	$\text{CH}_3\text{CH}_2\text{COCH}_3 + \text{NO}_3 \rightarrow \text{CH}_3\text{C}^*\text{HCOCH}_3 + \text{NO}_3^- + \text{H}^+$	$7.38 \cdot 10^5$		calculated ( <i>Herrmann and Zellner</i> , 1998), <i>BDE's</i> determined with Benson's incremental method
R <sub>o</sub> 00180 <sup>#</sup>	$\text{CH}_3\text{CH}_2\text{COCH}_3 + \text{NO}_3 \rightarrow \cdot\text{CH}_2\text{COCH}_2\text{CH}_3 + \text{NO}_3^- + \text{H}^+$	$8.20 \cdot 10^4$		calculated ( <i>Herrmann and Zellner</i> , 1998), <i>BDE's</i> determined with Benson's incremental method
R <sub>o</sub> 00181	$\text{CH}_3\text{C}^*\text{HCOCH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{CH}(\text{OO}\cdot)\text{COCH}_3$	$3.10 \cdot 10^9$		<i>Glowa et al.</i> (2000)
R <sub>o</sub> 00182	$\text{CH}_3\text{CH}(\text{OO}\cdot)\text{COCH}_3 \xrightarrow{\text{RO}_2}$ $0.9 \text{CH}_3\text{CH}(\text{O}\cdot)\text{COCH}_3 +$ $0.1 \text{CH}_3\text{COCOCH}_3 + 0.05 \text{H}_2\text{O}_2 + 0.45 \text{O}_2$	$7.30 \cdot 10^8$		<i>Schaefer et al.</i> (2012)

**Table G.10 (continued)** Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00183	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{COCH}_3 \rightarrow \text{CH}_3\text{CHO} + \text{CH}_3\text{CO}\cdot$	$1.30 \cdot 10^2$	-6441	changed from $1.3 \cdot 10^5$ due to considerations made in section 5.5
R <sub>o</sub> 00184	$\text{CH}_3\text{COCOCH}_3 + \text{OH} \rightarrow \text{CH}_3\text{COCOCH}_2\cdot + \text{H}_2\text{O}$	$1.40 \cdot 10^8$	2435	$k_{298}$ after ( <i>Gligorovski and Herrmann</i> , 2004) Branching ratio estimated based on the gas phase reaction ( <i>Christensen et al.</i> , 1998)
R <sub>o</sub> 00185	$\text{CH}_3\text{COCOCH}_3 + \text{OH} \rightarrow \text{CH}_3\text{COOH} + \text{CH}_3\text{CO}\cdot$	$1.40 \cdot 10^8$	2435	$k_{298}$ after ( <i>Gligorovski and Herrmann</i> , 2004) Branching ratio estimated based on the gas phase reaction ( <i>Christensen et al.</i> , 1998)
R <sub>o</sub> 00186	$\text{CH}_3\text{COCOCH}_3 + \text{NO}_3 \rightarrow \text{CH}_3\text{COCOCH}_2\cdot + \text{NO}_3^- + \text{H}^+$	$2.90 \cdot 10^3$		( <i>Herrmann and Zellner</i> , 1998), BDE's derived after correlation reported in <i>Gligorovski and Herrmann</i> (2004)
R <sub>o</sub> 00187	$\text{CH}_3\text{COCOCH}_3 + \text{NO}_3 \rightarrow \text{CH}_3\text{C}(=\text{O})\text{ONO}_2 + \text{CH}_3\text{CO}\cdot$	$2.90 \cdot 10^3$		( <i>Herrmann and Zellner</i> , 1998), BDE's derived after correlation reported in <i>Gligorovski and Herrmann</i> (2004)
R <sub>o</sub> 00188	$\text{CH}_3\text{COCOCH}_2\cdot + \text{O}_2 \rightarrow \text{CH}_3\text{COCOCH}_2\text{OO}\cdot$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00189	$\text{CH}_3\text{COCOCH}_2\text{OO}\cdot \xrightarrow{\text{RO}_2} \text{CH}_3\text{COCOCH}_2\text{O}\cdot + 0.5 \text{O}_2$	$1.50 \cdot 10^8$		$k_{298}$ estimated after the $\text{CH}_3\text{CO}(\text{OO}\cdot)$ recombination
R <sub>o</sub> 00190	$\text{CH}_3\text{COCOCH}_2\text{O}\cdot \rightarrow \text{CH}_3\text{CO}\cdot + \text{HCHO} + \text{CO}$	$1.30 \cdot 10^2$	-6441	$k_{1st}$ changed from $1.3 \cdot 10^5$ due to considerations made in section 5.5
R <sub>o</sub> 00191	$\cdot\text{CH}_2\text{COCH}_2\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{COCH}_2\text{OO}\cdot$	$3.10 \cdot 10^9$		by analogy with acetone
R <sub>o</sub> 00192	$\text{CH}_3\text{CH}_2\text{COCH}_2\text{OO}\cdot \xrightarrow{\text{RO}_2} \text{CH}_3\text{CH}_2\text{COCH}_2\text{O}\cdot + 0.5 \text{O}_2$	$7.30 \cdot 10^8$		<i>Schaefer et al.</i> (2012)

**Table G.10** (continued) Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00193	$\text{CH}_3\text{CH}_2\text{COCH}_2\text{O}\cdot \rightarrow \text{HCHO} + \text{CH}_3\text{CH}_2\text{CO}\cdot$	$1.30 \cdot 10^2$	-6441	changed from $1.3 \cdot 10^5$ due to considerations made in section 5.5
R <sub>o</sub> 02806*	$\text{CHOCH}=\text{CHCHO} + \text{OH} \rightarrow \text{CHOCH}(\text{OH})\text{C}\cdot\text{HCHO}$	$2.31 \cdot 10^{10}$		$k = k_{\text{Maleic acid}}$ , ( <i>Cabelli and Bielski</i> , 1985)
R <sub>o</sub> 00194	$\text{CHOCH}(\text{OH})\text{C}\cdot\text{HCHO} + \text{O}_2 \rightarrow \text{CHOCH}(\text{OH})\text{CH}(\text{OO}\cdot)\text{CHO}$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00195	$\text{CHOCH}(\text{OH})\text{CH}(\text{OO}\cdot)\text{CHO} \xrightarrow{\text{RO}_2} 0.5 \text{CHOCH}(\text{OH})\text{COCHO} + 0.5 \text{CHOCH}(\text{OH})\text{CH}(\text{OH})\text{CHO} + 0.5 \text{O}_2$	$1.60 \cdot 10^8$		Formation of keto and hydroxy species ( $k = k_{2\text{CH}_3\text{CH}_2\text{OO}\cdot}$ )
R <sub>o</sub> 01783*	$\text{CHOCH}(\text{OH})\text{COCHO} + \text{OH} \rightarrow \text{CHOCHOCH}(\text{OH})\text{CO}\cdot + \text{H}_2\text{O}$	$1.99 \cdot 10^9$		estimated after glyoxal, ( <i>Buxton et al.</i> , 1997)
R <sub>o</sub> 01784*	$\text{CHOCH}(\text{OH})\text{COCHO} + \text{NO}_3 \rightarrow \text{CHOCHOCH}(\text{OH})\text{CO}\cdot + \text{NO}_3^- + \text{H}^+$	$5.51 \cdot 10^6$		calculated ( <i>Herrmann and Zellner</i> , 1998), <i>BDEs</i> determined with Benson's incremental method
R <sub>o</sub> 00196	$\text{CHOCHOCH}(\text{OH})\text{CO}\cdot + \text{O}_2 \rightarrow \text{CHOCHOCH}(\text{OH})\text{CO}_3\cdot$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00197	$\text{CHOCHOCH}(\text{OH})\text{CO}_3\cdot \xrightarrow{\text{H}_2\text{O}} \text{CO}(\text{OH})\text{CH}(\text{OH})\text{COCHO} + \text{HO}_2$	$1.00 \cdot 10^3$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 02344*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{COCHO} + \text{OH} \rightarrow \text{CO}(\text{OH})\text{CH}(\text{OH})\text{COCO}\cdot + \text{H}_2\text{O}$	$4.31 \cdot 10^8$		$k = k_{\text{glyoxylic acid}}$ ( <i>Ervens et al.</i> , 2003b), $k_{298}$ is eventually overestimated, because $k$ was set according to the fully hydrated form
R <sub>o</sub> 02345*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{COCHO} + \text{NO}_3 \rightarrow \text{CO}(\text{OH})\text{CH}(\text{OH})\text{COCO}\cdot + \text{NO}_3^- + \text{H}^+$	$6.00 \cdot 10^6$		calculated ( <i>Herrmann and Zellner</i> , 1998), <i>BDEs</i> determined with Benson's incremental method

**Table G.10 (continued)** Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00198	$\text{CO(OH)CH(OH)COCO}^\bullet + \text{O}_2 \rightarrow \text{CO(OH)CH(OH)COCO}_3^\bullet$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00199	$\text{CO(OH)CH(OH)COCO}_3^\bullet \xrightarrow{\text{H}_2\text{O}} \text{CO(OH)CH(OH)COCOOH} + \text{HO}_2$	$1.00 \cdot 10^3$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00200	$\text{CO(OH)CH(OH)COCOOH} \rightarrow \text{CH}_2(\text{OH})\text{COCOOH} + \text{CO}_2$	$1.00 \cdot 10^{-5}$		estimated after ( <i>Guthrie</i> , 2002) and ( <i>Guthrie and Jordan</i> , 1972)
R <sub>o</sub> 02530*	$\text{CO(O}^-\text{)CH(OH)COCHO} + \text{OH} \rightarrow \text{CO(O}^-\text{)CH(OH)COCO}^\bullet + \text{H}_2\text{O}$	$5.41 \cdot 10^8$		$k = k_{\text{glyoxylate}}$ ( <i>Ervens et al.</i> , 2003b)
R <sub>o</sub> 02531*	$\text{CO(O}^-\text{)CH(OH)COCHO} + \text{NO}_3 \rightarrow \text{CO(O}^-\text{)CH(OH)COCO}^\bullet + \text{NO}_3^- + \text{H}^+$	$2.00 \cdot 10^7$		$k = k_{\text{glyoxylate}}$
R <sub>o</sub> 00201	$\text{CO(O}^-\text{)CH(OH)COCO}^\bullet + \text{O}_2 \rightarrow \text{CO(O}^-\text{)CH(OH)COCO}_3^\bullet$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00202	$\text{CO(O}^-\text{)CH(OH)COCO}_3^\bullet \xrightarrow{\text{H}_2\text{O}} \text{CO(O}^-\text{)CH(OH)COCOOH} + \text{HO}_2$	$1.00 \cdot 10^3$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00203	$\text{CO(O}^-\text{)CH(OH)COCOOH} \rightarrow \text{CH}_2(\text{OH})\text{COCOO}^- + \text{CO}_2$	$1.00 \cdot 10^{-5}$		estimated after ( <i>Guthrie</i> , 2002) and ( <i>Guthrie and Jordan</i> , 1972)
R <sub>o</sub> 01793*	$\text{CHOCH(OH)CH(OH)CHO} + \text{OH} \rightarrow \text{CHOCH(OH)CH(OH)CO}^\bullet + \text{H}_2\text{O}$	$2.39 \cdot 10^9$		estimated after glyoxal ( <i>Buxton et al.</i> , 1997)
R <sub>o</sub> 01794*	$\text{CHOCH(OH)CH(OH)CHO} + \text{NO}_3 \rightarrow \text{CHOCH(OH)CH(OH)CO}^\bullet + \text{NO}_3^- + \text{H}^+$	$1.39 \cdot 10^7$		calculated ( <i>Herrmann and Zellner</i> , 1998), <i>BDEs</i> determined with Benson's incremental method
R <sub>o</sub> 00204	$\text{CHOCH(OH)CH(OH)CO}^\bullet + \text{O}_2 \rightarrow \text{CHOCH(OH)CH(OH)CO}_3^\bullet$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00205	$\text{CHOCH(OH)CH(OH)CO}_3^\bullet \xrightarrow{\text{H}_2\text{O}} \text{CO(OH)CH(OH)CH(OH)CHO} + \text{HO}_2$	$1.00 \cdot 10^3$		estimated after <i>von Sonntag</i> (1987)

**Table G.10** (continued) Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 02348*	CO(OH)CH(OH)CH(OH)CHO + OH → CO(OH)CH(OH)CH(OH)CO· + H <sub>2</sub> O	$1.23 \cdot 10^9$		estimated after malic acid ( <i>Gligorovski and Herrmann, 2004</i> )
R <sub>o</sub> 02349*	CO(OH)CH(OH)CH(OH)CHO + NO <sub>3</sub> → CO(OH)CH(OH)CH(OH)CO· + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	$1.54 \cdot 10^7$		calculated ( <i>Herrmann and Zellner, 1998</i> ), <i>BDEs</i> determined with Benson's incremental method
R <sub>o</sub> 00206	CO(OH)CH(OH)CH(OH)CO· + O <sub>2</sub> → CO(OH)CH(OH)CH(OH)CO <sub>3</sub> ·	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00207	CO(OH)CH(OH)CH(OH)CO <sub>3</sub> · $\xrightarrow{H_2O}$ CO(OH)CH(OH)CH(OH)COOH + HO <sub>2</sub>	$1.00 \cdot 10^3$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 02538*	CO(O <sup>-</sup> )CH(OH)CH(OH)CHO + OH → CO(O <sup>-</sup> )CH(OH)CH(OH)CO· + H <sub>2</sub> O	$1.45 \cdot 10^9$		estimated after malate ( <i>Gligorovski and Herrmann, 2004</i> )
R <sub>o</sub> 02539*	CO(O <sup>-</sup> )CH(OH)CH(OH)CHO + NO <sub>3</sub> → CO(O <sup>-</sup> )CH(OH)CH(OH)CO· + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	$2.00 \cdot 10^7$		( <i>Herrmann and Zellner, 1998</i> ), <i>BDEs</i> derived after correlation reported in <i>Gligorovski and Herrmann (2004)</i>
R <sub>o</sub> 00208	CO(O <sup>-</sup> )CH(OH)CH(OH)CO· + O <sub>2</sub> → CO(O <sup>-</sup> )CH(OH)CH(OH)CO <sub>3</sub> ·	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00209	CO(O <sup>-</sup> )CH(OH)CH(OH)CO <sub>3</sub> · $\xrightarrow{H_2O}$ CO(O <sup>-</sup> )CH(OH)CH(OH)COOH + HO <sub>2</sub>	$1.00 \cdot 10^3$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00316*	CH <sub>2</sub> (OH)CH <sub>2</sub> OH + OH → CH <sub>2</sub> (OH)C·H(OH) + H <sub>2</sub> O	$1.70 \cdot 10^9$	1191	<i>Hoffmann et al. (2009)</i>
R <sub>o</sub> 00317*	CH <sub>2</sub> (OH)CH <sub>2</sub> OH + NO <sub>3</sub> → CH <sub>2</sub> (OH)C·H(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	$6.60 \cdot 10^6$	2117	<i>Hoffmann et al. (2009)</i>
R <sub>o</sub> 00210	CH <sub>2</sub> (OH)C·H(OH) + O <sub>2</sub> → CH <sub>2</sub> (OH)CH(OH)OO·	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00211	CH <sub>2</sub> (OH)CH(OH)OO· → CH <sub>2</sub> (OH)CHO + HO <sub>2</sub>	$1.90 \cdot 10^2$		<i>von Sonntag</i> (1987)

**Table G.10 (continued)** Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00318*	$\text{CH}_2(\text{OH})\text{CHO} + \text{OH} \rightarrow \text{CH}_2(\text{OH})\text{CO}^\cdot + \text{H}_2\text{O}$	$1.29 \cdot 10^9$		$k = k_{\text{CH}_3\text{CHO}}$ ( <i>Schuchmann and von Sonntag</i> , 1988)
R <sub>o</sub> 00319*	$\text{CH}_2(\text{OH})\text{CHO} + \text{NO}_3 \rightarrow \text{CH}_2(\text{OH})\text{CO}^\cdot + \text{NO}_3^- + \text{H}^+$	$5.72 \cdot 10^6$		estimated
R <sub>o</sub> 00212	$\text{CH}_2(\text{OH})\text{CO}^\cdot + \text{O}_2 \rightarrow \text{CH}_2(\text{OH})\text{CO}_3^\cdot$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00213	$\text{CH}_2(\text{OH})\text{CO}_3^\cdot \xrightarrow{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{COOH} + \text{HO}_2$	$1.90 \cdot 10^2$		estimated after ethylene glycol ( <i>von Sonntag</i> , 1987)
R <sub>o</sub> 00323*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})_2 + \text{OH} \rightarrow \text{CH}_2(\text{OH})\text{C}^\cdot(\text{OH})_2 + \text{H}_2\text{O}$	$9.74 \cdot 10^8$		$k = k_{\text{CH}_3\text{CH}(\text{OH})_2}$ ( <i>Schuchmann and von Sonntag</i> , 1988)
R <sub>o</sub> 00324*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})_2 + \text{NO}_3 \rightarrow$ $\text{CH}_2(\text{OH})\text{C}^\cdot(\text{OH})_2 + \text{NO}_3^- + \text{H}^+$	$9.51 \cdot 10^6$		estimated
R <sub>o</sub> 00214	$\text{CH}_2(\text{OH})\text{C}^\cdot(\text{OH})_2 + \text{O}_2 \rightarrow \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{OO}^\cdot$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00215	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{OO}^\cdot \rightarrow \text{CH}_2(\text{OH})\text{COOH} + \text{HO}_2$	$1.90 \cdot 10^2$		estimated after ethylene glycol ( <i>von Sonntag</i> , 1987)
R <sub>o</sub> 00546*	$\text{CH}_2(\text{OH})\text{COCOOH} + \text{OH} \rightarrow \cdot\text{CH}(\text{OH})\text{COCOOH} + \text{H}_2\text{O}$	$2.95 \cdot 10^8$		$k = k_{\text{glycolic acid}}$ ( <i>Scholes and Willson</i> , 1967)
R <sub>o</sub> 00547*	$\text{CH}_2(\text{OH})\text{COCOOH} + \text{NO}_3 \rightarrow$ $\cdot\text{CH}(\text{OH})\text{COCOOH} + \text{NO}_3^- + \text{H}^+$	$1.93 \cdot 10^5$		calculated ( <i>Herrmann and Zellner</i> , 1998), <i>BDEs</i> determined with Benson's incremental method
R <sub>o</sub> 00216	$\cdot\text{CH}(\text{OH})\text{COCOOH} + \text{O}_2 \rightarrow \cdot\text{OOCH}(\text{OH})\text{COCOOH}$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00217	$\cdot\text{OOCH}(\text{OH})\text{COCOOH} \rightarrow \text{CO}(\text{OH})\text{COCHO} + \text{HO}_2$	$6.65 \cdot 10^2$		estimated after isopropanol ( <i>von Sonntag</i> , 1987)
R <sub>o</sub> 00218	$\text{CO}(\text{OH})\text{COCHO} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CHO} + \text{CO}_2 + \text{O}_2$	$1.00 \cdot 10^{-5}$		estimated after ( <i>Guthrie</i> , 2002) and ( <i>Guthrie and Jordan</i> , 1972)
R <sub>o</sub> 00624*	$\text{CH}_2(\text{OH})\text{COCOO}^- + \text{OH} \rightarrow \cdot\text{CH}(\text{OH})\text{COCOO}^- + \text{H}_2\text{O}$	$4.18 \cdot 10^8$		$k = k_{\text{glycolate}}$ ( <i>Logan</i> , 1989)

**Table G.10** (continued) Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00625*	$\text{CH}_2(\text{OH})\text{COCOO}^- + \text{NO}_3 \rightarrow$ $\cdot\text{CH}(\text{OH})\text{COCOO}^- + \text{NO}_3^- + \text{H}^+$	$2.00 \cdot 10^7$		<i>Herrmann and Zellner</i> (1998), <i>BDEs</i> derived after correlation reported in <i>Gligorovski and</i> <i>Herrmann</i> (2004), <i>BDE</i> = <i>BDE</i> (glycolate)
R <sub>o</sub> 00219	$\cdot\text{CH}(\text{OH})\text{COCOO}^- + \text{O}_2 \rightarrow \cdot\text{OOCH}(\text{OH})\text{COCOO}^-$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00220	$\cdot\text{OOCH}(\text{OH})\text{COCOO}^- \rightarrow \text{CO}(\text{O}^-)\text{COCHO} + \text{HO}_2$	$6.65 \cdot 10^2$		estimated after isopropanol ( <i>von</i> <i>Sonntag</i> , 1987)
R <sub>o</sub> 00221	$\text{CO}(\text{O}^-)\text{COCHO} \xrightarrow{\text{H}_2\text{O}} \text{CHOCHO} + \text{CO}_2 + \text{OH}^-$	$1.00 \cdot 10^{-6}$		estimated after ( <i>Guthrie</i> , 2002) and ( <i>Guthrie and Jordan</i> , 1972)
R <sub>o</sub> 00645*	$\text{CO}(\text{OH})\text{COCHO} + \text{OH} \rightarrow \text{CO}(\text{OH})\text{COCO}^\cdot + \text{H}_2\text{O}$	$2.18 \cdot 10^8$		$k = k_{\text{lyoxylic acid}}$ ( <i>Ervens et al.</i> , 2003b), additional source of mesoxalic acid
R <sub>o</sub> 00646*	$\text{CO}(\text{OH})\text{COCHO} + \text{NO}_3 \rightarrow \text{CO}(\text{OH})\text{COCO}^\cdot + \text{NO}_3^- + \text{H}^+$	$3.40 \cdot 10^6$		calculated ( <i>Herrmann and Zellner</i> , 1998), <i>BDEs</i> determined with Benson's incremental method
R <sub>o</sub> 00222	$\text{CO}(\text{OH})\text{COCO}^\cdot + \text{O}_2 \rightarrow \text{CO}(\text{OH})\text{COCO}_3^\cdot$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00223	$\text{CO}(\text{OH})\text{COCO}_3^\cdot \xrightarrow{\text{H}_2\text{O}} \text{CO}(\text{OH})\text{COCO}_3\text{OOH} + \text{HO}_2$	$6.65 \cdot 10^2$		estimated after isopropanol ( <i>von</i> <i>Sonntag</i> , 1987)
R <sub>o</sub> 00665*	$\text{CO}(\text{O}^-)\text{COCHO} + \text{OH} \rightarrow \text{CO}(\text{O}^-)\text{COCO}^\cdot + \text{H}_2\text{O}$	$3.83 \cdot 10^8$		$k = k_{\text{glyoxylate}}$ ( <i>Ervens et al.</i> , 2003b), additional source of mesoxalate



**Table G.10 (continued)** Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00666*	$\text{CO}(\text{O}^-)\text{COCHO} + \text{NO}_3 \rightarrow \text{CO}(\text{O}^-)\text{COCO}^\bullet + \text{NO}_3^- + \text{H}^+$	$2.00 \cdot 10^7$		<i>Herrmann and Zellner</i> (1998), <i>BDEs</i> derived after correlation reported in <i>Gligorovski and</i> <i>Herrmann</i> (2004), <i>BDE</i> = <i>BDE</i> (glyoxylate)
R <sub>o</sub> 00224	$\text{CO}(\text{O}^-)\text{COCO}^\bullet + \text{O}_2 \rightarrow \text{CO}(\text{O}^-)\text{COCO}_3^\bullet$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00225	$\text{CO}(\text{O}^-)\text{COCO}_3^\bullet \xrightarrow{\text{H}_2\text{O}} \text{CO}(\text{O}^-)\text{COCO}^\bullet\text{OOH} + \text{HO}_2$	$6.65 \cdot 10^2$		estimated after isopropanol ( <i>von</i> <i>Sonntag</i> , 1987)
R <sub>o</sub> 00857*	$\text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{COOH} + \text{OH} \rightarrow$ $\text{CO}(\text{OH})\text{CH}_2\text{C}^\bullet(\text{OH})\text{COOH} + \text{H}_2\text{O}$	$3.60 \cdot 10^8$	1575	<i>Gligorovski et al.</i> (2009)
R <sub>o</sub> 00858*	$\text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{COOH} + \text{NO}_3 \rightarrow$ $\text{CO}(\text{OH})\text{CH}_2\text{C}^\bullet(\text{OH})\text{COOH} + \text{NO}_3^- + \text{H}^+$	$7.20 \cdot 10^3$		calculated ( <i>Herrmann and Zellner</i> , 1998), <i>BDEs</i> determined with Benson's incremental method
R <sub>o</sub> 00226	$\text{CO}(\text{OH})\text{CH}_2\text{C}^\bullet(\text{OH})\text{COOH} + \text{O}_2 \rightarrow$ $\text{CO}(\text{OH})\text{CH}_2\text{C}(\text{OH})(\text{OO}^\bullet)\text{COOH}$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00227	$\text{CO}(\text{OH})\text{CH}_2\text{C}(\text{OH})(\text{OO}^\bullet)\text{COOH} \rightarrow$ $\text{CO}(\text{OH})\text{CH}_2\text{COCO}^\bullet\text{OOH} + \text{HO}_2$	$1.00 \cdot 10^3$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00849*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CH}(\text{OH})\text{COOH} + \text{OH} \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}_2\text{C}^\bullet(\text{OH})\text{COOH} + \text{H}_2\text{O}$	$9.70 \cdot 10^8$	1700	<i>Gligorovski et al.</i> (2009)
R <sub>o</sub> 00850*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CH}(\text{OH})\text{COOH} + \text{NO}_3 \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}_2\text{C}^\bullet(\text{OH})\text{COOH} + \text{NO}_3^- + \text{H}^+$	$2.50 \cdot 10^7$		<i>Herrmann and Zellner</i> (1998), <i>BDEs</i> derived after correlation reported in <i>Gligorovski and</i> <i>Herrmann</i> (2004)
R <sub>o</sub> 00228	$\text{CO}(\text{O}^-)\text{CH}_2\text{C}^\bullet(\text{OH})\text{COOH} + \text{O}_2 \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}_2\text{C}(\text{OH})(\text{OO}^\bullet)\text{COOH}$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)

**Table G.10** (continued) Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00229	$\text{CO}(\text{O}^-)\text{CH}_2\text{C}(\text{OH})(\text{OO}\cdot)\text{COOH} \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}_2\text{COCO}(\text{OH}) + \text{HO}_2$	$1.00 \cdot 10^3$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00855*	$\text{CO}(\text{OH})\text{CH}_2\text{COCO}(\text{OH}) + \text{OH} \rightarrow$ $\text{CO}(\text{OH})\text{C}'\text{HCOCO}(\text{OH}) + \text{H}_2\text{O}$	$6.82 \cdot 10^6$		$k = k_{\text{CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CO}(\text{OH})}$ ( <i>Ervens et al.</i> , 2003b)
R <sub>o</sub> 00856*	$\text{CO}(\text{OH})\text{CH}_2\text{COCO}(\text{OH}) + \text{NO}_3 \rightarrow$ $\text{CO}(\text{OH})\text{C}'\text{HCOCO}(\text{OH}) + \text{NO}_3^- + \text{H}^+$	$1.66 \cdot 10^5$		calculated ( <i>Herrmann and Zellner</i> , 1998), <i>BDEs</i> determined with Benson's incremental method
R <sub>o</sub> 00230	$\text{CO}(\text{OH})\text{C}'\text{HCOCO}(\text{OH}) + \text{O}_2 \rightarrow$ $\text{CO}(\text{OH})\text{CH}(\text{OO}\cdot)\text{COCO}(\text{OH})$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00231	$\text{CO}(\text{OH})\text{CH}(\text{OO}\cdot)\text{COCO}(\text{OH}) \xrightarrow{\text{RO}_2}$ $0.5 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{OH}) +$ $0.5 \text{CO}(\text{OH})\text{COCOCO}(\text{OH}) + 0.5 \text{O}_2$	$1.60 \cdot 10^8$		formation from keto- and hydroxyacids, $k = k_{2\text{CH}_3\text{CH}_2\text{OO}\cdot}$
R <sub>o</sub> 00232	$\text{CO}(\text{OH})\text{COCOCO}(\text{OH}) \rightarrow \text{CO}(\text{OH})\text{COCHO} + \text{CO}_2$	$1.00 \cdot 10^{-5}$		estimated after ( <i>Guthrie</i> , 2002) and ( <i>Guthrie and Jordan</i> , 1972)
R <sub>o</sub> 00233	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{OH}) \rightarrow$ $\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CHO} + \text{CO}_2$	$1.00 \cdot 10^{-5}$		estimated after ( <i>Guthrie</i> , 2002) and ( <i>Guthrie and Jordan</i> , 1972)
R <sub>o</sub> 00640*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CHO} + \text{OH} \rightarrow$ $\text{CO}(\text{OH})\text{C}'(\text{OH})\text{CHO} + \text{H}_2\text{O}$	$7.23 \cdot 10^8$		estimated after lactic acid
R <sub>o</sub> 00641*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CHO} + \text{NO}_3 \rightarrow$ $\text{CO}(\text{OH})\text{C}'(\text{OH})\text{CHO} + \text{NO}_3^- + \text{H}^+$	$6.17 \cdot 10^6$		estimated after lactic acid
R <sub>o</sub> 00234#	$\text{CO}(\text{OH})\text{C}'(\text{OH})\text{CHO} + \text{O}_2 \rightarrow \text{CO}(\text{OH})\text{C}(\text{OO}\cdot)(\text{OH})\text{CHO}$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00235#	$\text{CO}(\text{OH})\text{C}(\text{OO}\cdot)(\text{OH})\text{CHO} \rightarrow \text{CO}(\text{OH})\text{COCHO} + \text{HO}_2$	$1.00 \cdot 10^3$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00833*	$\text{CO}(\text{O}^-)\text{CH}_2\text{COCO}(\text{OH}) + \text{OH} \rightarrow$ $\text{CO}(\text{O}^-)\text{C}'\text{HCOCO}(\text{OH}) + \text{H}_2\text{O}$	$1.93 \cdot 10^7$		$k = k_{\text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2\text{COO}^-}$ ( <i>Ervens et al.</i> , 2003b)
R <sub>o</sub> 00834*	$\text{CO}(\text{O}^-)\text{CH}_2\text{COCO}(\text{OH}) + \text{NO}_3 \rightarrow$ $\text{CO}(\text{O}^-)\text{C}'\text{HCOCO}(\text{OH}) + \text{NO}_3^- + \text{H}^+$	$2.50 \cdot 10^7$		$k = k_{\text{CO}(\text{OH})\text{CH}_2\text{CH}_2\text{COO}^-}$

**Table G.10 (continued)** Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00236	$\text{CO}(\text{O}^-)\text{C}'\text{HCOCO}(\text{OH}) + \text{O}_2 \rightarrow \text{CO}(\text{O}^-)\text{CH}(\text{OO}\cdot)\text{COCO}(\text{OH})$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00237	$\text{CO}(\text{O}^-)\text{CH}(\text{OO}\cdot)\text{COCO}(\text{OH}) \xrightarrow{\text{RO}_2} 0.5 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCO}(\text{OH}) + 0.5 \text{CO}(\text{OH})\text{COCOCOO}^- + 0.5 \text{O}_2$	$1.60 \cdot 10^8$		formation from keto- und hydroxyacids, $k = k_2 \text{CH}_3\text{CH}_2\text{OO}\cdot$
R <sub>o</sub> 00238	$\text{CO}(\text{OH})\text{COCOCO}(\text{O}^-) \rightarrow \text{CO}(\text{O}^-)\text{COCHO} + \text{CO}_2$	$1.00 \cdot 10^{-6}$		estimated after ( <i>Guthrie</i> , 2002) and ( <i>Guthrie and Jordan</i> , 1972)
R <sub>o</sub> 00239	$\text{CO}(\text{OH})\text{COCOCOO}^- \rightarrow \text{CO}(\text{O}^-)\text{COCHO} + \text{CO}_2$	$1.00 \cdot 10^{-6}$		estimated after ( <i>Guthrie</i> , 2002) and ( <i>Guthrie and Jordan</i> , 1972)
R <sub>o</sub> 00667*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CHO} + \text{OH} \rightarrow \text{CO}(\text{O}^-)\text{C}'(\text{OH})\text{CHO} + \text{H}_2\text{O}$	$1.29 \cdot 10^9$		estimated after lactate
R <sub>o</sub> 00668*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CHO} + \text{NO}_3 \rightarrow \text{CO}(\text{O}^-)\text{C}'(\text{OH})\text{CHO} + \text{NO}_3^- + \text{H}^+$	$2.00 \cdot 10^7$		estimated after lactate
R <sub>o</sub> 00240	$\text{CO}(\text{O}^-)\text{C}'(\text{OH})\text{CHO} + \text{O}_2 \rightarrow \text{CO}(\text{O}^-)\text{C}(\text{OO}\cdot)(\text{OH})\text{CHO}$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00241	$\text{CO}(\text{O}^-)\text{C}(\text{OO}\cdot)(\text{OH})\text{CHO} \rightarrow \text{CO}(\text{O}^-)\text{COCHO} + \text{HO}_2$	$1.00 \cdot 10^3$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00698*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{COOH} + \text{OH} \rightarrow \text{CO}(\text{OH})\text{C}'(\text{OH})\text{COOH} + \text{H}_2\text{O}$	$3.40 \cdot 10^8$	1112	TROPOS measurements
R <sub>o</sub> 00699*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{COOH} + \text{NO}_3 \rightarrow \text{CO}(\text{OH})\text{C}'(\text{OH})\text{COOH} + \text{NO}_3^- + \text{H}^+$	$1.40 \cdot 10^5$		calculated ( <i>Herrmann and Zellner</i> , 1998), <i>BDEs</i> determined with Benson's incremental method
R <sub>o</sub> 00242	$\text{CO}(\text{OH})\text{C}'(\text{OH})\text{COOH} + \text{O}_2 \rightarrow \text{CO}(\text{OH})\text{C}(\text{OO}\cdot)(\text{OH})\text{COOH}$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00243	$\text{CO}(\text{OH})\text{C}(\text{OO}\cdot)(\text{OH})\text{COOH} \rightarrow \text{CO}(\text{OH})\text{COCOOH} + \text{HO}_2$	$6.65 \cdot 10^2$		estimated after isopropanal ( <i>von Sonntag</i> , 1987)

**Table G.10** (continued) Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00244	$\text{CO(OH)COCOOH} \xrightarrow{\text{H}_2\text{O}} \text{CH(OH)}_2\text{COOH} + \text{CO}_2$	$1.00 \cdot 10^{-5}$		estimated after (Guthrie, 2002) and (Guthrie and Jordan, 1972)
R <sub>o</sub> 00738*	$\text{CO(OH)CH(OH)COO}^- + \text{OH} \rightarrow \text{CO(OH)C}^*(\text{OH})\text{COO}^- + \text{H}_2\text{O}$	$3.60 \cdot 10^8$		Schuchmann et al. (1995)
R <sub>o</sub> 00739*	$\text{CO(OH)CH(OH)COO}^- + \text{NO}_3 \rightarrow \text{CO(OH)C}^*(\text{OH})\text{COO}^- + \text{NO}_3^- + \text{H}^+$	$2.50 \cdot 10^7$		$k = k_{\text{CO(OH)CH}_2\text{CO(O}^-)}$
R <sub>o</sub> 00245	$\text{CO(OH)C}^*(\text{OH})\text{COO}^- + \text{O}_2 \rightarrow \text{CO(OH)C(OO}\cdot)(\text{OH})\text{COO}^-$	$2.00 \cdot 10^9$		estimated after von Sonntag (1987)
R <sub>o</sub> 00246	$\text{CO(OH)C(OO}\cdot)(\text{OH})\text{COO}^- \rightarrow \text{CO(OH)COCOO}^- + \text{HO}_2$	$6.65 \cdot 10^2$		estimated after isopropanal (von Sonntag, 1987)
R <sub>o</sub> 00247	$\text{CO(OH)COCOO}^- \xrightarrow{\text{H}_2\text{O}} \text{CH(OH)}_2\text{COO}^- + \text{CO}_2$	$1.00 \cdot 10^{-6}$		estimated after (Guthrie, 2002) and (Guthrie and Jordan, 1972)
R <sub>o</sub> 00248	$\text{CH}_3\text{COCH}_2\text{CH(CH}_3)_2 + \text{OH} \rightarrow \text{CH}_3\text{COC}^*\text{HCH(CH}_3)_2 + \text{H}_2\text{O}$	$2.38 \cdot 10^9$	1360	average of measurements within the MOST project
R <sub>o</sub> 00249	$\text{CH}_3\text{COCH}_2\text{CH(CH}_3)_2 + \text{OH} \rightarrow \text{CH}_3\text{COCH}_2\text{C}^*(\text{CH}_3)_2 + \text{H}_2\text{O}$	$1.02 \cdot 10^9$	1360	average of measurements within the MOST project
R <sub>o</sub> 00250	$\text{CH}_3\text{COCH}_2\text{CH(CH}_3)_2 + \text{NO}_3 \rightarrow \text{CH}_3\text{COC}^*\text{HCH(CH}_3)_2 + \text{NO}_3^- + \text{H}^+$	$1.05 \cdot 10^5$		(Herrmann and Zellner, 1998), BDEs derived after correlation reported in Gligorovski and Herrmann (2004)
R <sub>o</sub> 00251	$\text{CH}_3\text{COCH}_2\text{CH(CH}_3)_2 + \text{NO}_3 \rightarrow \text{CH}_3\text{COCH}_2\text{C}^*(\text{CH}_3)_2 + \text{NO}_3^- + \text{H}^+$	$4.50 \cdot 10^4$		(Herrmann and Zellner, 1998), BDEs derived after correlation reported in Gligorovski and Herrmann (2004)

**Table G.10 (continued)** Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00252	$\text{CH}_3\text{COC}\cdot\text{HCH}(\text{CH}_3)_2 + \text{O}_2 \rightarrow$ $\text{CH}_3\text{COCH}(\text{OO}\cdot)\text{CH}(\text{CH}_3)_2$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00253	$\text{CH}_3\text{COCH}(\text{OO}\cdot)\text{CH}(\text{CH}_3)_2 \xrightarrow{\text{RO}_2}$ $0.4 \text{ CH}_3\text{COCH}(\text{O}\cdot)\text{CH}(\text{CH}_3)_2 +$ $0.45 \text{ CH}_3\text{COCOCH}(\text{CH}_3)_2 +$ $0.15 \text{ CH}_3\text{COCH}(\text{OH})\text{CH}(\text{CH}_3)_2 + 0.15 \text{ H}_2\text{O}_2 + 0.35 \text{ O}_2$	$7.30 \cdot 10^8$		<i>Schaefer et al.</i> (2012)
R <sub>o</sub> 00254	$\text{CH}_3\text{COCH}(\text{O}\cdot)\text{CH}(\text{CH}_3)_2 \rightarrow \text{CH}_3\text{CO}\cdot + \text{CHOCH}(\text{CH}_3)_2$	$1.60 \cdot 10^2$		changed from $1.6 \cdot 10^6$ due to considerations made in section 5.5
R <sub>o</sub> 00255	$\text{CH}_3\text{COCH}_2\text{C}\cdot(\text{CH}_3)_2 + \text{O}_2 \rightarrow \text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{OO}\cdot$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00256	$\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{OO}\cdot \xrightarrow{\text{RO}_2}$ $\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{O}\cdot + 0.5 \text{ O}_2$	$7.30 \cdot 10^8$		<i>Schaefer et al.</i> (2012)
R <sub>o</sub> 00257	$\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{O}\cdot \rightarrow \text{CH}_3\text{COCH}_3 + \text{CH}_3\text{COCH}_2\cdot$	$1.28 \cdot 10^2$		changed from $1.28 \cdot 10^6$ due to considerations made in section 5.5
R <sub>o</sub> 00258	$\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2\text{O}\cdot \rightarrow \cdot\text{CH}_2\text{COCH}_2\text{C}(\text{CH}_3)_2\text{OH}$	$3.20 \cdot 10^5$		by analogy with the gas phase, ( <i>Mellouki et al.</i> , 2003)
R <sub>o</sub> 00259	$\cdot\text{CH}_2\text{COCH}_2\text{C}(\text{CH}_3)_2\text{OH} + \text{O}_2 \rightarrow$ $\cdot\text{OOCH}_2\text{COCH}_2\text{C}(\text{CH}_3)_2\text{OH}$	$3.10 \cdot 10^9$		by analogy with acetone
R <sub>o</sub> 00260	$\cdot\text{OOCH}_2\text{COCH}_2\text{C}(\text{CH}_3)_2\text{OH} \xrightarrow{\text{RO}_2}$ $0.399 \text{ CHOCOCH}_2\text{C}(\text{CH}_3)_2\text{OH} +$ $0.08 \text{ CH}_2(\text{OH})\text{COCH}_2\text{C}(\text{CH}_3)_2\text{OH} + 0.521 \cdot$ $\text{OCH}_2\text{COCH}_2\text{C}(\text{CH}_3)_2\text{OH} + 0.34 \text{ O}_2 + 0.16 \text{ H}_2\text{O}_2$	$3.76 \cdot 10^8$		by analogy with acetone
R <sub>o</sub> 00261	$2 \cdot \text{OCH}_2\text{COCH}_2\text{C}(\text{CH}_3)_2\text{OH} \rightarrow$ $\text{CHOCOCH}_2\text{C}(\text{CH}_3)_2\text{OH} + \text{CH}_2(\text{OH})\text{COCH}_2\text{C}(\text{CH}_3)_2\text{OH}$	$1.00 \cdot 10^6$		by analogy with acetone

**Table G.10** (continued) Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00262	$\cdot\text{OCH}_2\text{COCH}_2\text{C}(\text{CH}_3)_2\text{OH} \rightarrow \text{HCHO} + \cdot\text{COCH}_2\text{C}(\text{CH}_3)_2\text{OH}$	$1.60 \cdot 10^6$		by analogy with acetone by analogy with the gas phase ( <i>Mellouki et al.</i> , 2003)
R <sub>o</sub> 00263	$\cdot\text{COCH}_2\text{C}(\text{CH}_3)_2\text{OH} \rightarrow \text{CHOCH}_2\text{C}(\text{OH})(\text{CH}_3)\text{CH}_2\cdot$	$3.20 \cdot 10^5$		by analogy with $\text{CH}_3\text{COCH}_2\text{C}(\text{CH}_3)_2(\text{O}\cdot)$
R <sub>o</sub> 00264	$\text{CHOCH}_2\text{C}(\text{OH})(\text{CH}_3)\text{CH}_2\cdot + \text{O}_2 \rightarrow \text{CHOCH}_2\text{C}(\text{OH})(\text{CH}_3)\text{CH}_2\text{OO}\cdot$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00265	$\text{CHOCH}_2\text{C}(\text{OH})(\text{CH}_3)\text{CH}_2\text{OO}\cdot \xrightarrow{\text{RO}_2} 0.5 \text{CHOCH}_2\text{C}(\text{OH})(\text{CH}_3)\text{CH}_2\text{OH} + 0.5 \text{CHOCH}_2\text{C}(\text{OH})(\text{CH}_3)\text{CHO} + 0.5 \text{O}_2$	$6.00 \cdot 10^7$		estimated after $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{COCH}_2\text{OO}\cdot$
R <sub>o</sub> 00266	$\text{CH}_3\text{CH}_2\text{--O--CHO} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{HCOOH}$	$4.7 \cdot 10^{-6}$	11 000	<i>Mata-Segreda</i> (2000)
R <sub>o</sub> 00267	$\text{CH}_3\text{CH}_2\text{--O--CHO} + \text{H}^+ \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{OH} + \text{HCOOH} + \text{H}^+$	$2.60 \cdot 10^{-3}$	7220	<i>Mata-Segreda</i> (2000)
R <sub>o</sub> 00268	$\text{CH}_3\text{CH}_2\text{--O--CHO} + \text{OH} \rightarrow \text{CH}_3\text{CH}_2\text{--O--CO}\cdot + \text{H}_2\text{O}$	$3.34 \cdot 10^8$	2106	average of measurements within the MOST project
R <sub>o</sub> 00269	$\text{CH}_3\text{CH}_2\text{--O--CHO} + \text{OH} \rightarrow \text{CH}_3\text{C}\cdot\text{H--O--CHO} + \text{H}_2\text{O}$	$4.56 \cdot 10^7$	2106	average of measurements within the MOST project
R <sub>o</sub> 00270	$\text{CH}_3\text{CH}_2\text{--O--CHO} + \text{NO}_3 \rightarrow \text{CH}_3\text{CH}_2\text{--O--CO}\cdot + \text{NO}_3^- + \text{H}^+$	$8.40 \cdot 10^4$		calculated ( <i>Herrmann and Zellner</i> , 1998), <i>BDEs</i> determined with Benson's incremental method
R <sub>o</sub> 00271	$\text{CH}_3\text{CH}_2\text{--O--CHO} + \text{NO}_3 \rightarrow \text{CH}_3\text{C}\cdot\text{H--O--CHO} + \text{NO}_3^- + \text{H}^+$	$1.10 \cdot 10^4$		calculated ( <i>Herrmann and Zellner</i> , 1998), <i>BDEs</i> determined with Benson's incremental method
R <sub>o</sub> 00272	$\text{CH}_3\text{CH}_2\text{--O--CO}\cdot + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{--O--CO}_3\cdot$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00273	$\text{CH}_3\text{CH}_2\text{--O--CO}_3\cdot + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{CO}_2 + \text{HO}_2$	$4.70 \cdot 10^{-6}$	11 000	estimated after reaction R <sub>o</sub> 00274

**Table G.10 (continued)** Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00274	$\text{CH}_3\text{CH}_2\text{-O-CO}_3^\cdot + \text{H}^+ \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{OH} + \text{CO}_2 + \text{HO}_2 + \text{H}^+$	$2.60 \cdot 10^{-3}$	7220	estimated after reaction R <sub>o</sub> 00275
R <sub>o</sub> 00275	$\text{CH}_3\text{CH}_2\text{-O-CO}_3^\cdot \xrightarrow{\text{RO}_2} \text{CH}_3\text{CH}_2\text{-O-CO}_2^\cdot + 0.5 \text{O}_2$	$6.51 \cdot 10^{-3}$		estimated based on product studies carried out within MOST by Poulain et al.
R <sub>o</sub> 00276	$\text{CH}_3\text{CH}_2\text{-O-CO}_2^\cdot \rightarrow \text{CH}_3\text{CH}_2\text{O}^\cdot + \text{CO}_2$	$1.00 \cdot 10^9$		see <i>Tilgner and Herrmann</i> (2010)
R <sub>o</sub> 00277	$\text{CH}_3\text{CH}_2\text{-O-CO}_2^\cdot \rightarrow \cdot\text{CH}_2\text{CH}_2\text{-O-COOH}$	$3.00 \cdot 10^{-3}$		estimated
R <sub>o</sub> 00278	$\text{CH}_3\text{CH(OH)OO}^\cdot \xrightarrow{\text{RO}_2} \text{CH}_3\text{COOH} + 0.5 \text{H}_2\text{O}_2$	$3.50 \cdot 10^8$		<i>Neta et al.</i> (1990)
R <sub>o</sub> 00279	$\cdot\text{CH}_2\text{CH}_2\text{-O-COOH} + \text{O}_2 \rightarrow \cdot\text{OOCH}_2\text{CH}_2\text{-O-COOH}$	$2.00 \cdot 10^9$		estimated
R <sub>o</sub> 00280	$\cdot\text{OOCH}_2\text{CH}_2\text{-O-COOH} \xrightarrow{\text{RO}_2} \cdot\text{OCH}_2\text{CH}_2\text{-O-COOH} + 0.5 \text{O}_2$	$5.00 \cdot 10^8$		estimated
R <sub>o</sub> 00281	$\cdot\text{OCH}_2\text{CH}_2\text{-O-COOH} \rightarrow \text{HCHO} + \cdot\text{CH}_2\text{-O-COOH}$	$1.60 \cdot 10^2$		changed from $1.6 \cdot 10^6$ due to considerations made in section 5.5
R <sub>o</sub> 00282	$\cdot\text{CH}_2\text{-O-COOH} \rightarrow \text{HCHO} + \cdot\text{COOH}$	$1.60 \cdot 10^6$		estimated in analogy with $\text{CH}_3\text{COCH}_2\text{O}^\cdot$
R <sub>o</sub> 00283	$\text{CH}_3\text{C}^\cdot\text{H-O-CHO} + \text{O}_2 \rightarrow \text{CH}_3\text{CH(OO}^\cdot\text{)-O-CHO}$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00284	$\text{CH}_3\text{CH(OO}^\cdot\text{)-O-CHO} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH(OH)OO}^\cdot + \text{HCOOH}$	$4.70 \cdot 10^{-6}$	11 000	in analogy with ethyl formate, ( <i>Mata-Segreda</i> , 2000)
R <sub>o</sub> 00285	$\text{CH}_3\text{CH(OO}^\cdot\text{)-O-CHO} + \text{H}^+ \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CH(OH)OO}^\cdot + \text{HCOOH} + \text{H}^+$	$2.60 \cdot 10^{-3}$	7220	in analogy with ethyl formate ( <i>Mata-Segreda</i> , 2000)
R <sub>o</sub> 00286	$\text{C}_1\text{H}_2\text{CH}_2\text{N(CH}_3\text{)COC}_1\text{H}_2 + \text{OH} \rightarrow \text{C}_1\text{H}_2\text{C}^\cdot\text{HN(CH}_3\text{)COC}_1\text{H}_2 + \text{H}_2\text{O}$	$6.21 \cdot 10^9$		average of measurements within the MOST project
R <sub>o</sub> 00287	$\text{C}_1\text{H}_2\text{CH}_2\text{N(CH}_3\text{)COC}_1\text{H}_2 + \text{OH} \rightarrow \text{C}_1\text{H}_2\text{CH}_2\text{N(CH}_2\text{)COC}_1\text{H}_2 + \text{H}_2\text{O}$	$6.90 \cdot 10^8$		average of measurements within the MOST project

**Table G.10** (continued) Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00288	$C_1H_2CH_2N(CH_3)COC_1H_2 + NO_3 \rightarrow$ $C_1H_2C\dot{H}N(CH_3)COC_1H_2 + NO_3^- + H^+$	$7.40 \cdot 10^5$		(Herrmann and Zellner, 1998), BDEs derived after correlation reported in Gligorovski and Herrmann (2004)
R <sub>o</sub> 00289	$C_1H_2CH_2N(CH_3)COC_1H_2 + NO_3 \rightarrow$ $C_1H_2CH_2N(CH_2)COC_1H_2 + NO_3^- + H^+$	$8.20 \cdot 10^4$		(Herrmann and Zellner, 1998), BDEs derived after correlation reported in Gligorovski and Herrmann (2004)
R <sub>o</sub> 00290	$C_1H_2C\dot{H}N(CH_3)COC_1H_2 + O_2 \rightarrow$ $C_1H_2CH(OO\cdot)N(CH_3)COC_1H_2$	$2.00 \cdot 10^9$		estimated after von Sonntag (1987)
R <sub>o</sub> 00291	$C_1H_2CH(OO\cdot)N(CH_3)COC_1H_2 \xrightarrow{RO_2}$ $C_1H_2CH(O\cdot)N(CH_3)COC_1H_2 + 0.5 O_2$	$1.00 \cdot 10^8$		$k_{298}$ estimated after the ethyl peroxy radical (Herrmann et al., 1999)
R <sub>o</sub> 00292	$C_1H_2CH(O\cdot)N(CH_3)COC_1H_2 + O_2 \rightarrow$ $C_1H_2CON(CH_3)COC_1H_2 + HO_2$	$6.00 \cdot 10^6$		$k_{298}$ estimated after reaction R <sub>o</sub> 00214
R <sub>o</sub> 00293	$C_1H_2CON(CH_3)COC_1H_2 + OH \rightarrow$ $C_1H_2CON(CH_2)COC_1H_2 + H_2O$	$6.90 \cdot 10^9$		estimated after NMP
R <sub>o</sub> 00294	$C_1H_2CON(CH_3)COC_1H_2 + NO_3 \rightarrow$ $C_1H_2CON(CH_2)COC_1H_2 + NO_3^- + H^+$	$2.60 \cdot 10^7$		calculated (Herrmann and Zellner, 1998), BDEs derived after correlation reported in Gligorovski and Herrmann (2004)
R <sub>o</sub> 00295	$C_1H_2CON(CH_2)COC_1H_2 + O_2 \rightarrow$ $C_1H_2CON(CH_2OO\cdot)COC_1H_2$	$2.00 \cdot 10^9$		estimated after von Sonntag (1987)
R <sub>o</sub> 00296	$C_1H_2CON(CH_2OO\cdot)COC_1H_2 \xrightarrow{RO_2}$ $C_1H_2CONHCOC_1H_2 + CO_2 + 0.5 H_2O_2 - 0.5 O_2$	$1.00 \cdot 10^8$		estimated after the ethyl peroxy radical (Herrmann et al., 1999)



**Table G.10** (continued) Irreversible organic reactions in CAPRAM 3.0o

	Reaction	$k_{298}^{(a)}$	$E_A/R^{(b)}$	Reference/comment
R <sub>o</sub> 00297	$C_1H_2CH_2N(CH_2)COC_1H_2 + O_2 \rightarrow C_1H_2CH_2N(CH_2OO\cdot)COC_1H_2$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00298	$C_1H_2CH_2N(CH_2OO\cdot)COC_1H_2 \xrightarrow{RO_2} C_1H_2CH_2NHCOC_1H_2 + CO_2 + \nu, 0.5 H_2O_2 - 0.5 O_2$	$1.00 \cdot 10^8$		estimated after the ethyl peroxy radical ( <i>Herrmann et al.</i> , 1999)
R <sub>o</sub> 00299	$C_1H_2CH_2NHCOC_1H_2 + OH \rightarrow C_1H_2C\cdot H NHCOC_1H_2 + H_2O$	$6.90 \cdot 10^9$		estimated after NMP
R <sub>o</sub> 00300	$C_1H_2CH_2NHCOC_1H_2 + NO_3 \rightarrow C_1H_2C\cdot H NHCOC_1H_2 + NO_3^- + H^+$	$8.20 \cdot 10^5$		estimated after NMP
R <sub>o</sub> 00301	$C_1H_2C\cdot H NHCOC_1H_2 + O_2 \rightarrow C_1H_2CH(OO\cdot)NHCOC_1H_2$	$2.00 \cdot 10^9$		estimated after <i>von Sonntag</i> (1987)
R <sub>o</sub> 00302	$C_1H_2CH(OO\cdot)NHCOC_1H_2 \xrightarrow{RO_2} C_1H_2CH(O\cdot)NHCOC_1H_2 + 0.5 O_2$	$1.00 \cdot 10^8$		estimated after the ethyl peroxy radical ( <i>Herrmann et al.</i> , 1999)
R <sub>o</sub> 00303	$C_1H_2CH(O\cdot)NHCOC_1H_2 + O_2 \rightarrow C_1H_2CONHCOC_1H_2 + HO_2$	$6.00 \cdot 10^6$		estimated after reaction R <sub>o</sub> 00064
R <sub>o</sub> 00304	$CH_3C(OH)_2OO\cdot \rightarrow CH_3COOH + HO_2$	$1.00 \cdot 10^3$		estimated after <i>von Sonntag</i> (1987)

\*Reaction label taken from the self-generated mechanism CAPRAM 3.5, where branching ratios are introduced; #obsolete from CAPRAM 3.5 on;

<sup>(a)</sup>in M<sup>-(order-1)</sup> s<sup>-1</sup>; <sup>(b)</sup>in K

**Table G.11** Organic equilibria in CAPRAM 3.0o.

	Equilibrium	$K^{(a)}$	$k_f^{(b)}$	$\frac{E_A^{(c)}}{R}$	$k_b^{(b)}$	Reference/comment
E <sub>o</sub> 0001	$HCOOH \rightleftharpoons H^+ + HCOO^-$	$1.77 \cdot 10^{-4}$	$8.85 \cdot 10^6$	-12	$5.00 \cdot 10^{10}$	$k_{for}$ after <i>Harned and Owen</i> (1958) and $k_{back}$ after <i>Graedel and Weschler</i> (1981)

**Table G.11** (continued) Organic equilibria in CAPRAM 3.0o.

	Equilibrium	$K^{(a)}$	$k_f^{(b)}$	$\frac{E_A^{(c)}}{R}$	$k_b^{(b)}$	Reference/comment
E <sub>o</sub> 0002	$\text{HCHO} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2(\text{OH})_2$	$3.60 \cdot 10^1$	$1.80 \cdot 10^{-1}$	4030	$5.10 \cdot 10^{-3}$	$k_{for}$ after <i>Olson and Hoffmann</i> (1989) and $k_{back}$ after <i>Bell et al.</i> (1956)
E <sub>o</sub> 0003	$\text{CH}_3\text{CO}(\text{OOH}) \rightleftharpoons \text{H}^+ + \text{CH}_3\text{CO}(\text{OO}-)$	$6.30 \cdot 10^{-9}$	$3.15 \cdot 10^2$		$5.00 \cdot 10^{10}$	$K$ after <i>Bell et al.</i> (1956)
E <sub>o</sub> 0004	$\text{CH}_3\text{CO}\cdot + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{C}\cdot(\text{OH})_2$	$1.20 \cdot 10^{-2}$	$2.00 \cdot 10^4$		$3.00 \cdot 10^4$	<i>Schuchmann and von Sonntag</i> (1988)
E <sub>o</sub> 0005	$\cdot\text{OOCH}_2\text{COOH} \rightleftharpoons \text{H}^+ + \cdot\text{OOCH}_2\text{COO}^-$	$1.75 \cdot 10^{-5}$	$8.75 \cdot 10^5$	46	$5.00 \cdot 10^{10}$	estimated equal as acetic acid
E <sub>o</sub> 0006	$\text{CH}_3\text{CO}_3\cdot + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{C}(\text{OH})_2\text{OO}\cdot$	$3.67 \cdot 10^2$	$1.10 \cdot 10^7$		$3.00 \cdot 10^4$	estimated in analogy to the acetyl radical
E <sub>o</sub> 0007	$\text{CH}_2(\text{OOH})\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_2(\text{OOH})\text{COO}^-$	$1.74 \cdot 10^{-5}$	$8.70 \cdot 10^5$		$5.00 \cdot 10^{10}$	estimated in analogy to acetic acid ( <i>Lide and Frederikse</i> , 1995)
E <sub>o</sub> 0008	$\text{CO}(\text{OH})\text{COCO}(\text{OOH}) \rightleftharpoons \text{H}^+ + \text{CO}(\text{OH})\text{COCO}(\text{OO})^-$	$3.16 \cdot 10^{-3}$	$1.58 \cdot 10^8$		$5.00 \cdot 10^{10}$	<i>Albalat et al.</i> (1989)
E <sub>o</sub> 0009	$\text{CO}(\text{OH})\text{COCOCO}(\text{OOH}) \rightleftharpoons \text{H}^+ + \text{CO}(\text{OH})\text{COCOCO}(\text{OO})^-$	$3.16 \cdot 10^{-3}$	$1.58 \cdot 10^8$		$5.00 \cdot 10^{10}$	estimated after mesoxalic acid ( <i>Albalat et al.</i> , 1989)
E <sub>o</sub> 0010	$\text{CO}(\text{OH})\text{COCO}(\text{OO})^- \rightleftharpoons \text{H}^+ + \text{CO}(\text{O}^-)\text{COCO}(\text{OO})^-$	$1.64 \cdot 10^{-4}$	$8.20 \cdot 10^6$		$5.00 \cdot 10^{10}$	estimated after acetaldehyde
E <sub>o</sub> 0011	$\text{CO}(\text{OH})\text{CH}_2\text{CHO} \rightleftharpoons \text{H}^+ + \text{CO}(\text{O}^-)\text{CH}_2\text{CHO}$	$1.35 \cdot 10^{-5}$	$6.75 \cdot 10^5$	-60	$5.00 \cdot 10^{10}$	estimated after propanic acid
E <sub>o</sub> 0012	$\text{CO}(\text{OH})\text{CH}_2\text{CHO} + \text{H}_2\text{O} \rightleftharpoons \text{CH}(\text{OH})_2\text{CH}_2\text{COOH}$	$1.84 \cdot 10^{-2}$	$1.02 \cdot 10^{-3}$		$5.69 \cdot 10^{-3}$	( <i>Betterton and Hoffmann</i> , 1988)
E <sub>o</sub> 0013	$\text{CHOCH}_2\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}(\text{OH})_2\text{CH}_2\text{COO}^-$	$1.84 \cdot 10^{-2}$	$1.05 \cdot 10^{-4}$		$5.69 \cdot 10^{-3}$	$k_{back}$ estimated after acetaldehyde estimated after acetaldehyde

**Table G.11 (continued)** Organic equilibria in CAPRAM 3.0o.

	Equilibrium	$K^{(a)}$	$k_f^{(b)}$	$\frac{E_A^{(c)}}{R}$	$k_b^{(b)}$	Reference/comment
E <sub>o</sub> 0014	$\text{CH}_3\text{CH}_2\text{COCOOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{CH}_2\text{COCOO}^-$	$3.16 \cdot 10^{-3}$	$1.58 \cdot 10^8$		$5.00 \cdot 10^{10}$	see <i>Tilgner and Herrmann</i> (2010)
E <sub>o</sub> 0018*	$\text{CH}_2(\text{OH})\text{CHO} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2(\text{OH})\text{CH}(\text{OH})_2$	$1.64 \cdot 10^{-1}$	$1.57 \cdot 10^{-3}$		$9.6 \cdot 10^{-3}$	<i>Betterton and Hoffmann</i> (1988), $k_{\text{back}}$ see <i>Tilgner and Herrmann</i> (2010)
E <sub>o</sub> 0019*	$\text{CHOCHO} + 2\text{H}_2\text{O} \rightleftharpoons \text{CH}(\text{OH})_2\text{CH}(\text{OH})_2$	$3.90 \cdot 10^3$	$2.15 \cdot 10^1$		$5.50 \cdot 10^{-3}$	<i>Betterton and Hoffmann</i> (1988)
E <sub>o</sub> 0020*	$\text{CH}_3\text{CHO} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CH}(\text{OH})_2$	$2.46 \cdot 10^{-2}$	$1.40 \cdot 10^{-4}$	-2500	$5.69 \cdot 10^{-3}$	$k_{\text{for}}$ after <i>Bell et al.</i> (1956) and $k_{\text{back}}$ after <i>Bell and Evans</i> (1966)
E <sub>o</sub> 0022*	$\text{CH}_2(\text{OH})\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_2(\text{OH})\text{COO}^-$	$1.48 \cdot 10^{-4}$	$7.40 \cdot 10^6$		$5.00 \cdot 10^{10}$	<i>Lide and Frederikse</i> (1995)
E <sub>o</sub> 0025*	$\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^-$	$1.75 \cdot 10^{-5}$	$8.75 \cdot 10^5$	-46	$5.00 \cdot 10^{10}$	$k_{\text{for}}$ after <i>Harned and Owen</i> (1958) and $k_{\text{back}}$ after <i>Graedel and Weschler</i> (1981)
E <sub>o</sub> 0027*	$\text{CH}(\text{OH})_2\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}(\text{OH})_2\text{COO}^-$	$3.16 \cdot 10^{-4}$	$6.32 \cdot 10^6$		$2.00 \cdot 10^{10}$	<i>Buxton et al.</i> (1997)
E <sub>o</sub> 0028*	$\text{CO}(\text{OH})\text{COOH} \rightleftharpoons \text{H}^+ + \text{CO}(\text{OH})\text{COO}^-$	$6.40 \cdot 10^{-2}$	$3.20 \cdot 10^9$		$5.00 \cdot 10^{10}$	<i>Meyerstein</i> (1971)
E <sub>o</sub> 0029*	$\text{CO}(\text{OH})\text{COO}^- \rightleftharpoons \text{H}^+ + \text{CO}(\text{O}^-)\text{COO}^-$	$6.25 \cdot 10^{-5}$	$2.60 \cdot 10^6$		$5.00 \cdot 10^{10}$	<i>Meyerstein</i> (1971)
E <sub>o</sub> 0039*	$\text{CH}_3\text{COCHO} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COCH}(\text{OH})_2$	$4.86 \cdot 10^2$	$2.15 \cdot 10^2$		$5.43 \cdot 10^{-1}$	<i>Betterton and Hoffmann</i> (1988), $k_f$ as for glyoxal

**Table G.11** (continued) Organic equilibria in CAPRAM 3.0o.

	Equilibrium	$K^{(a)}$	$k_f^{(b)}$	$\frac{E_A^{(c)}}{R}$	$k_b^{(b)}$	Reference/comment
E <sub>o</sub> 0045*	$\text{CH}_3\text{CH}(\text{OH})\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{CH}(\text{OH})\text{COO}^-$	$1.35 \cdot 10^{-5}$	$6.75 \cdot 10^5$		$5.00 \cdot 10^{10}$	lactate is formed by the recombination of the propionate peroxy radical; no sinks implemented until CAPRAM 3.5, estimated same as propionate
E <sub>o</sub> 0047*	$\text{CH}_2(\text{OH})\text{COCOOH} \rightleftharpoons \text{H}^+ + \text{CH}_2(\text{OH})\text{COCOO}^-$	$3.55 \cdot 10^{-3}$	$1.80 \cdot 10^8$		$5.00 \cdot 10^{10}$	estimated after pyruvic acid ( <i>Lide and Frederikse</i> , 1995)
E <sub>o</sub> 0058*	$\text{CH}_3\text{COCOOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COCOO}^-$	$3.55 \cdot 10^{-3}$	$1.80 \cdot 10^8$		$5.00 \cdot 10^{10}$	Lit.: Handbook of Organic Compounds
E <sub>o</sub> 0060*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CHO} \rightleftharpoons \text{H}^+ + \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CHO}$	$1.35 \cdot 10^{-5}$	$6.75 \cdot 10^5$		$5.00 \cdot 10^{10}$	estimated after Propanoic acid
E <sub>o</sub> 0062*	$\text{CO}(\text{OH})\text{COCHO} \rightleftharpoons \text{H}^+ + \text{CO}(\text{O}^-)\text{COCHO}$	$3.55 \cdot 10^{-3}$	$1.80 \cdot 10^8$		$5.00 \cdot 10^{10}$	estimated after pyruvic acid ( <i>Lide and Frederikse</i> , 1995)
E <sub>o</sub> 0075*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{COOH} \rightleftharpoons \text{H}^+ + \text{CO}(\text{OH})\text{CH}(\text{OH})\text{COO}^-$	$9.55 \cdot 10^{-3}$	$4.77 \cdot 10^8$		$5.00 \cdot 10^{10}$	<i>Campi</i> (1963)
E <sub>o</sub> 0076*	$\text{CO}(\text{OH})\text{CH}_2\text{COOH} \rightleftharpoons \text{H}^+ + \text{CO}(\text{OH})\text{CH}_2\text{COO}^-$	$1.40 \cdot 10^{-3}$	$7.10 \cdot 10^7$		$5.00 \cdot 10^{10}$	see <i>Tilgner and Herrmann</i> (2010)
E <sub>o</sub> 0078*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{COO}^- \rightleftharpoons \text{H}^+ + \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COO}^-$	$5.75 \cdot 10^{-5}$	$2.88 \cdot 10^6$		$5.00 \cdot 10^{10}$	<i>Campi</i> (1963)
E <sub>o</sub> 0080*	$\text{CO}(\text{OH})\text{CH}_2\text{COO}^- \rightleftharpoons \text{H}^+ + \text{CO}(\text{O}^-)\text{CH}_2\text{COO}^-$	$2.04 \cdot 10^{-6}$	$1.02 \cdot 10^5$	117	$5.00 \cdot 10^{10}$	Lit.: Handbook of Organic Compounds, T-dependency between 0 and 30°C
E <sub>o</sub> 0083*	$\text{CH}_3\text{CH}_2\text{CHO} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CH}_2\text{CH}(\text{OH})_2$	$1.84 \cdot 10^{-2}$	$1.05 \cdot 10^{-4}$		$5.69 \cdot 10^{-3}$	see <i>Tilgner and Herrmann</i> (2010), $k_{\text{back}}$ estimated after acetaldehyde

**Table G.11 (continued)** Organic equilibria in CAPRAM 3.0o.

	Equilibrium	$K^{(a)}$	$k_f^{(b)}$	$\frac{E_A^{(c)}}{R}$	$k_b^{(b)}$	Reference/comment
E <sub>o</sub> 0084*	$\text{CH}_3\text{CH}_2\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{CH}_2\text{COO}^-$	$1.35 \cdot 10^{-5}$	$6.75 \cdot 10^5$	-60	$5.00 \cdot 10^{10}$	T-dependency between 5 and 20°C
E <sub>o</sub> 0085*	$\text{CO(OH)CH}_2\text{CH}_2\text{COOH} \rightleftharpoons \text{H}^+ + \text{CO(OH)CH}_2\text{CH}_2\text{COO}^-$	$6.46 \cdot 10^{-5}$	$3.20 \cdot 10^6$		$5.00 \cdot 10^{10}$	
E <sub>o</sub> 0086*	$\text{CO(OH)CH}_2\text{CH}_2\text{COO}^- \rightleftharpoons \text{H}^+ + \text{CO(O}^-\text{)CH}_2\text{CH}_2\text{COO}^-$	$2.29 \cdot 10^{-6}$	$1.15 \cdot 10^5$		$5.00 \cdot 10^{10}$	
E <sub>o</sub> 0088*	$\text{CO(OH)CH}_2\text{CH(OH)COOH} \rightleftharpoons \text{H}^+ + \text{CO(O}^-\text{)CH}_2\text{CH(OH)COOH}$	$1.48 \cdot 10^{-3}$	$7.40 \cdot 10^7$		$5.00 \cdot 10^{10}$	<i>Lide and Frederikse (1995)</i>
E <sub>o</sub> 0091*	$\text{CO(OH)CH}_2\text{COCOOH} \rightleftharpoons \text{H}^+ + \text{CO(O}^-\text{)CH}_2\text{COCOOH}$	$2.80 \cdot 10^{-3}$	$3.02 \cdot 10^8$		$5.00 \cdot 10^{10}$	<i>Lide and Frederikse (1995)</i>
E <sub>o</sub> 0093*	$\text{CO(O}^-\text{)CH}_2\text{CH(OH)COOH} \rightleftharpoons \text{H}^+ + \text{CO(O}^-\text{)CH(OH)CH}_2\text{COO}^-$	$8.00 \cdot 10^{-6}$	$4.00 \cdot 10^5$		$5.00 \cdot 10^{10}$	<i>Lide and Frederikse (1995)</i>
E <sub>o</sub> 0096*	$\text{CO(OH)CH(OH)COCOOH} \rightleftharpoons \text{H}^+ + \text{CO(O}^-\text{)CH(OH)COCOOH}$	$6.03 \cdot 10^{-3}$	$3.01 \cdot 10^8$		$5.00 \cdot 10^{10}$	estimated after oxaloacetic acid ( <i>Lide and Frederikse, 1995</i> )
E <sub>o</sub> 0098*	$\text{CO(O}^-\text{)CH}_2\text{COCOOH} \rightleftharpoons \text{H}^+ + \text{CO(O}^-\text{)COCH}_2\text{COO}^-$	$4.30 \cdot 10^{-5}$	$2.15 \cdot 10^6$		$5.00 \cdot 10^{10}$	<i>Lide and Frederikse (1995)</i>
E <sub>o</sub> 0101*	$\text{CO(OH)CH(OH)CH(OH)COOH} \rightleftharpoons \text{H}^+ + \text{CO(O}^-\text{)CH(OH)CH(OH)COOH}$	$1.05 \cdot 10^{-3}$	$5.25 \cdot 10^7$		$5.00 \cdot 10^{10}$	<i>Lide and Frederikse (1995)</i>
E <sub>o</sub> 0300*	$\text{CO(OH)CH(OH)COCHO} \rightleftharpoons \text{H}^+ + \text{CO(O}^-\text{)CH(OH)COCHO}$	$4.57 \cdot 10^{-5}$	$2.29 \cdot 10^6$		$5.00 \cdot 10^{10}$	estimated after the second dissociation step of tartaric acid ( <i>Lide and Frederikse, 1995</i> )
E <sub>o</sub> 0302*	$\text{CO(OH)CH(OH)CH(OH)CHO} \rightleftharpoons \text{H}^+ + \text{CO(O}^-\text{)CH(OH)CH(OH)CHO}$	$4.57 \cdot 10^{-5}$	$2.29 \cdot 10^6$		$5.00 \cdot 10^{10}$	estimated after the second dissociation step of tartaric acid ( <i>Lide and Frederikse, 1995</i> )

**Table G.11** (continued) Organic equilibria in CAPRAM 3.0o.

	Equilibrium	$K^{(a)}$	$k_f^{(b)}$	$\frac{E_A^{(c)}}{R}$	$k_b^{(b)}$	Reference/comment
E <sub>o</sub> 0365*	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OH})_2$	$9.01 \cdot 10^{-3}$	$5.13 \cdot 10^{-5}$		$5.69 \cdot 10^{-3}$	see <i>Tilgner and Herrmann</i> (2010), $k_{\text{back}}$ estimated after acetaldehyde
E <sub>o</sub> 0366*	$\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{CH}_2\text{CH}_2\text{COO}^-$	$1.54 \cdot 10^{-5}$	$7.70 \cdot 10^5$	500	$5.00 \cdot 10^{10}$	<i>Lide and Frederikse</i> (1995)

\*Reaction label taken from the self-generated mechanism CAPRAM 3.5, where branching ratios are introduced

(<sup>a</sup>) in  $\text{M}^{\text{order}(k_b - k_f)}$ ; (<sup>b</sup>) in  $\text{M}^{-(\text{order}-1)} \text{s}^{-1}$ ; (<sup>c</sup>) in K

**Table G.12** Additional processes in CAPRAM 3.0p

	Process	$k_{298} / K / j_{\text{max}}^a$	Reference/comment
R <sub>o</sub> 00305	$\text{WSOC} + \text{OH} \longrightarrow \text{WSOC} + \text{HO}_2$	$3.8 \cdot 10^8$	estimated after <i>Arakaki et al.</i> (2013)
R <sub>o</sub> 00306	$\text{HULIS} + \text{OH} \longrightarrow \text{HULIS} + \text{HO}_2$	$3.8 \cdot 10^8$	estimated after <i>Arakaki et al.</i> (2013)
R <sub>o</sub> 00307	$\text{HULIS}^- + \text{OH} \longrightarrow \text{HULIS}^- + \text{HO}_2$	$3.8 \cdot 10^8$	estimated after <i>Arakaki et al.</i> (2013)
R <sub>o</sub> 00308	$\text{WSOC} + \text{NO}_3 \longrightarrow \text{WSOC} + \text{NO}_3^-$	$1.0 \cdot 10^7$	estimated (see subsection 5.5.1)
R <sub>o</sub> 00309	$\text{HULIS} + \text{NO}_3 \longrightarrow \text{HULIS} + \text{NO}_3^-$	$1.0 \cdot 10^7$	estimated (see subsection 5.5.1)
R <sub>o</sub> 00310	$\text{HULIS}^- + \text{NO}_3 \longrightarrow \text{HULIS}^- + \text{NO}_3^-$	$5.0 \cdot 10^7$	estimated (see subsection 5.5.1)
E <sub>o</sub> 00015	$\text{HULIS} \rightleftharpoons \text{HULIS}^- + \text{H}^+$	$3.98 \cdot 10^{-4(b)}$	estimated with the $pK_a$ of fulvic acid after <i>Salma and Láng</i> (2008)
E <sub>o</sub> 00016	$\text{Fe}^{3+} + \text{HULIS}^- \rightleftharpoons [\text{FeHULIS}]^{2+}$	$1.0 \cdot 10^{9(c)}$	estimated after iron-oxalato complex formation
E <sub>o</sub> 00017	$\text{Fe}^{2+} + \text{HULIS}^- \rightleftharpoons [\text{FeHULIS}]^+$	$1.0 \cdot 10^{5(c)}$	estimated after iron-oxalato complex formation
P <sub>o</sub> 0003	$[\text{FeHULIS}]^{2+} \xrightarrow{h\nu} \text{Fe}^{2+} + \text{HULIS}$	$2.0 \cdot 10^{-2}$	estimated after iron-hydroxy complex photolysis (see <i>Arakaki et al.</i> , 2010)

<sup>a</sup> $k_{298}$  is given for non-reversible reactions (labelled with R<sub>o</sub>XXXXX in the first column) in  $\text{M}^{-1} \text{s}^{-1}$ ,  $K$  is given for equilibria (labelled with E<sub>o</sub>XXXX in the first column) in  $\text{M}^{-1}$ . For more convenience,  $K$  values are printed italic. For photolysis (indicated by P<sub>o</sub>XXXX in the first column),  $j_{\text{max}}$  is given in  $\text{s}^{-1}$ . (<sup>b</sup>)  $k_b = 5 \cdot 10^{10} \text{M}^{-1} \text{s}^{-1}$ ; (<sup>c</sup>)  $k_b = 3 \cdot 10^{-3} \text{s}^{-1}$

**Table G.13** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00311	*	*	CH <sub>3</sub> CH <sub>2</sub> (OH) + OH $\rightarrow$ 0.089 CH <sub>2</sub> (OH)CH <sub>2</sub> (OO $\cdot$ ) + 0.865 CH <sub>3</sub> CH(OH)(OO $\cdot$ ) + 0.047 CH <sub>3</sub> CH <sub>2</sub> (O $\cdot$ ) + H <sub>2</sub> O – 0.953 O <sub>2</sub>	$2.1 \cdot 10^{+09}$	–1200.0	<i>Ervens et al.</i> (2003b)
R <sub>o</sub> 00312	*		CH <sub>3</sub> CH <sub>2</sub> (OH) + NO <sub>3</sub> $\rightarrow$ 0.089 CH <sub>2</sub> (OH)CH <sub>2</sub> (OO $\cdot$ ) + 0.865 CH <sub>3</sub> CH(OH)(OO $\cdot$ ) + 0.047 CH <sub>3</sub> CH <sub>2</sub> (O $\cdot$ ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.953 O <sub>2</sub>	$2.2 \cdot 10^{+06}$	–3300.0	<i>Herrmann and Zellner</i> (1998)
R <sub>o</sub> 00313	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> (OO $\cdot$ ) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH <sub>2</sub> (O $\cdot$ ) + 0.550 CH <sub>2</sub> (OH)CHO + 0.250 CH <sub>2</sub> (OH)CH <sub>2</sub> (OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00314	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> (O $\cdot$ ) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00315	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> (O $\cdot$ ) $\rightarrow$ CH <sub>2</sub> (OH) $\cdot$ + CH <sub>2</sub> O	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00316	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> (OH) + OH $\rightarrow$ 0.888 CH <sub>2</sub> (OH)CH(OH)(OO $\cdot$ ) + 0.112 CH <sub>2</sub> (OH)CH <sub>2</sub> (O $\cdot$ ) + H <sub>2</sub> O – 0.888 O <sub>2</sub>	$1.7 \cdot 10^{+09}$	–1191.0	<i>Hoffmann et al.</i> (2009)
R <sub>o</sub> 00317	*		CH <sub>2</sub> (OH)CH <sub>2</sub> (OH) + NO <sub>3</sub> $\rightarrow$ 0.888 CH <sub>2</sub> (OH)CH(OH)(OO $\cdot$ ) + 0.112 CH <sub>2</sub> (OH)CH <sub>2</sub> (O $\cdot$ ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.888 O <sub>2</sub>	$6.6 \cdot 10^{+06}$	–2117.0	<i>Hoffmann et al.</i> (2009)
E <sub>o</sub> 00018	*	*	CH <sub>2</sub> (OH)CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)CH(OH) <sub>2</sub>	$7.4 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00318	*	*	CH <sub>2</sub> (OH)CHO + OH $\rightarrow$ 0.220 CHOCH(OH)(OO $\cdot$ ) + 0.725 CH <sub>2</sub> (OH)CO(OO $\cdot$ ) + 0.055 CHOCH <sub>2</sub> (O $\cdot$ ) + H <sub>2</sub> O – 0.945 O <sub>2</sub>	$1.4 \cdot 10^{+09}$		
R <sub>o</sub> 00319	*		CH <sub>2</sub> (OH)CHO + NO <sub>3</sub> $\rightarrow$ 0.220 CHOCH(OH)(OO $\cdot$ ) + 0.725 CH <sub>2</sub> (OH)CO(OO $\cdot$ ) + 0.055 CHOCH <sub>2</sub> (O $\cdot$ ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.945 O <sub>2</sub>	$5.7 \cdot 10^{+06}$		
R <sub>o</sub> 00320	*	*	CHOCH(OH)(OO $\cdot$ ) $\rightarrow$ CHOCHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00321	*	*	CHOCH <sub>2</sub> (O $\cdot$ ) $\xrightarrow{O_2}$ CHOCHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00322	*	*	CHOCH <sub>2</sub> (O $\cdot$ ) $\rightarrow$ CH $\cdot$ (OH) <sub>2</sub> + CH <sub>2</sub> O – H <sub>2</sub> O	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00323	*	*	CH <sub>2</sub> (OH)CH(OH) <sub>2</sub> + OH $\rightarrow$ 0.261 CH(OH) <sub>2</sub> CH(OH)(OO $\cdot$ ) + 0.304 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.078 CH(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) + 0.356 CH <sub>2</sub> (OH)CH(OH)(O $\cdot$ ) + H <sub>2</sub> O – 0.566 O <sub>2</sub>	$1.1 \cdot 10^{+09}$		
R <sub>o</sub> 00324	*		CH <sub>2</sub> (OH)CH(OH) <sub>2</sub> + NO <sub>3</sub> $\rightarrow$ 0.261 CH(OH) <sub>2</sub> CH(OH)(OO $\cdot$ ) + 0.304 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.078 CH(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) + 0.356 CH <sub>2</sub> (OH)CH(OH)(O $\cdot$ ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.566 O <sub>2</sub>	$9.5 \cdot 10^{+06}$		
R <sub>o</sub> 00325	*	*	CH(OH) <sub>2</sub> CH(OH)(OO $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> CHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00326	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00327	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) $\rightarrow$ CH $\cdot$ (OH) <sub>2</sub> + CH <sub>2</sub> O	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00328	*	*	CH <sub>2</sub> (OH)CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CO(OH) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00329	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\cdot + \text{CHO}(\text{OH})$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00019	*	*	$\text{CHOCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{CH}(\text{OH})_2$	$9.1 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00330	*	*	$\text{CHOCHO} + \text{OH} \rightarrow \text{CHOCO}(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$6.6 \cdot 10^{+07}$		<i>Buxton et al.</i> (1988a)
R <sub>o</sub> 00331	*	*	$\text{CHOCHO} + \text{NO}_3 \rightarrow \text{CHOCO}(\text{OO}\cdot) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$1.1 \cdot 10^{+06}$	-3368.0	TROPOS measurements
R <sub>o</sub> 00332	*	*	$\text{CHOCO}(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CHO} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
E <sub>o</sub> 00020	*	*	$\text{CH}_3\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{CH}(\text{OH})_2$	$1.2 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00333	*	*	$\text{CH}_3\text{CHO} + \text{OH} \rightarrow 0.030 \text{CHOCH}_2(\text{OO}\cdot) + 0.970 \text{CH}_3\text{CO}(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$3.1 \cdot 10^{+09}$		Average of <i>Schuchmann and von Sonntag</i> (1988) and <i>Monod et al.</i> (2005)
R <sub>o</sub> 00334	*		$\text{CH}_3\text{CHO} + \text{NO}_3 \rightarrow$ $0.030 \text{CHOCH}_2(\text{OO}\cdot) + 0.970 \text{CH}_3\text{CO}(\text{OO}\cdot) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$1.9 \cdot 10^{+06}$		<i>Zellner et al.</i> (1996)
R <sub>o</sub> 00335	*	*	$\text{CHOCH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2} 0.200 \text{CHOCH}_2(\text{O}\cdot) + 0.550 \text{CHOCHO} +$ $0.250 \text{CH}_2(\text{OH})\text{CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00336	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OH})_2 + \text{OH} \rightarrow$ $0.266 \text{CH}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.734 \text{CH}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.266 \text{O}_2$	$1.1 \cdot 10^{+09}$	-1516.0	<i>Buxton et al.</i> (1997)
R <sub>o</sub> 00337	*		$\text{CH}(\text{OH})_2\text{CH}(\text{OH})_2 + \text{NO}_3 \rightarrow 0.266 \text{CH}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.734 \text{CH}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.266 \text{O}_2$	$1.1 \cdot 10^{+06}$	-3368.0	<i>Tilgner and Herrmann</i> (2010)
R <sub>o</sub> 00338	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00339	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CH}\cdot(\text{OH})_2 + \text{CHO}(\text{OH})$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00340	*	*	$\text{CH}_3\text{CH}(\text{OH})_2 + \text{OH} \rightarrow 0.056 \text{CH}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) +$ $0.631 \text{CH}_3\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.314 \text{CH}_3\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.686 \text{O}_2$	$1.3 \cdot 10^{+09}$		<i>Schuchmann and von Sonntag</i> (1988)
R <sub>o</sub> 00341	*		$\text{CH}_3\text{CH}(\text{OH})_2 + \text{NO}_3 \rightarrow 0.056 \text{CH}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) +$ $0.631 \text{CH}_3\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.314 \text{CH}_3\text{CH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.686 \text{O}_2$	$2.0 \cdot 10^{+06}$		Average of <i>Zellner et al.</i> (1996) and <i>Rousse and George</i> (2004)
R <sub>o</sub> 00342	*	*	$\text{CH}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2} 0.200 \text{CH}(\text{OH})_2\text{CH}_2(\text{O}\cdot) + 0.550 \text{CH}(\text{OH})_2\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{CH}(\text{OH})_2 + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00343	*	*	$\text{CH}_3\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_3\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00344	*	*	$\text{CH}_3\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CH}_3(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00021	*	*	$\text{CH}(\text{OH})_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{CH}(\text{OH})_2$	$9.1 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00345	*	*	$\text{CH}(\text{OH})_2\text{CHO} + \text{OH} \rightarrow 0.163 \text{CHOC}(\text{OH})_2(\text{OO}\cdot) +$ $0.461 \text{CH}(\text{OH})_2\text{CO}(\text{OO}\cdot) + 0.377 \text{CHOCH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.623 \text{O}_2$	$8.7 \cdot 10^{+08}$		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00346	*		CH(OH) <sub>2</sub> CHO + NO <sub>3</sub> → 0.163 CHOC(OH) <sub>2</sub> (OO·) + 0.461 CH(OH) <sub>2</sub> CO(OO·) + 0.377 CHOCH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.623 O <sub>2</sub>	7.3 · 10 <sup>+06</sup>		
R <sub>o</sub> 00347	*	*	CHOC(OH) <sub>2</sub> (OO·) → CO(OH)CHO + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 00348	*	*	CH(OH) <sub>2</sub> CO(OO·) → CH(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 00349	*	*	CHOCH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 00350	*	*	CHOCH(OH)(O·) → CH·(OH) <sub>2</sub> + CHO(OH) - H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00022	*	*	CH <sub>2</sub> (OH)CO(OH) ⇌ CH <sub>2</sub> (OH)CO(O <sup>-</sup> ) + H <sup>+</sup>	4.5 · 10 <sup>-05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00351	*	*	CH <sub>2</sub> (OH)CO(OH) + OH → 0.620 CO(OH)CH(OH)(OO·) + 0.380 CO(OH)CH <sub>2</sub> (O·) + H <sub>2</sub> O - 0.620 O <sub>2</sub>	6.0 · 10 <sup>+08</sup>		Buxton et al. (1988a)
R <sub>o</sub> 00352	*		CH <sub>2</sub> (OH)CO(OH) + NO <sub>3</sub> → 0.620 CO(OH)CH(OH)(OO·) + 0.380 CO(OH)CH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.620 O <sub>2</sub>	9.1 · 10 <sup>+05</sup>	-3969.0	de Semainville et al. (2007a)
E <sub>o</sub> 00023	*	*	CO(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CO(OH)	5.2 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00024	*	*	CO(OH)CHO ⇌ CO(O <sup>-</sup> )CHO + H <sup>+</sup>	4.4 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00353	*	*	CO(OH)CHO + OH → CO(OH)CO(OO·) + H <sub>2</sub> O - O <sub>2</sub>	1.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 00354	*		CO(OH)CHO + NO <sub>3</sub> → CO(OH)CO(OO·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	2.2 · 10 <sup>+06</sup>		
R <sub>o</sub> 00355	*	*	CO(OH)CO(OO·) → CO(OH)CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
E <sub>o</sub> 00025	*	*	CH <sub>3</sub> CO(OH) ⇌ CH <sub>3</sub> CO(O <sup>-</sup> ) + H <sup>+</sup>	1.6 · 10 <sup>-05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00356	*	*	CH <sub>3</sub> CO(OH) + OH → CO(OH)CH <sub>2</sub> (OO·) + H <sub>2</sub> O - O <sub>2</sub>	1.7 · 10 <sup>+07</sup>	-1330.0	Chin and Wine (1994)
R <sub>o</sub> 00357	*		CH <sub>3</sub> CO(OH) + NO <sub>3</sub> → CO(OH)CH <sub>2</sub> (OO·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	1.3 · 10 <sup>+04</sup>	-3800.0	Exner et al. (1994)
R <sub>o</sub> 00358	*	*	CH <sub>2</sub> (OH)CO(O <sup>-</sup> ) + OH → 0.761 CO(O <sup>-</sup> )CH(OH)(OO·) + 0.239 CO(O <sup>-</sup> )CH <sub>2</sub> (O·) + H <sub>2</sub> O - 0.761 O <sub>2</sub>	1.2 · 10 <sup>+09</sup>		Logan (1989)
R <sub>o</sub> 00359	*		CH <sub>2</sub> (OH)CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>2</sub> (OH)CO(O·) + NO <sub>3</sub> <sup>-</sup>	1.0 · 10 <sup>+07</sup>	-3007.0	de Semainville et al. (2007a)
R <sub>o</sub> 00360	*	*	CO(O <sup>-</sup> )CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(O <sup>-</sup> )CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 00361	*	*	CO(O <sup>-</sup> )CH <sub>2</sub> (O·) → ·CO(O <sup>-</sup> ) + CH <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00026	*	*	CO(O <sup>-</sup> )CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CO(O <sup>-</sup> )	1.2 · 10 <sup>+00</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00362	*	*	CO(O <sup>-</sup> )CHO + OH → CO(O <sup>-</sup> )CO(OO·) + H <sub>2</sub> O - O <sub>2</sub>	4.5 · 10 <sup>+08</sup>		
R <sub>o</sub> 00363	*		CO(O <sup>-</sup> )CHO + NO <sub>3</sub> → CHOCO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 00364	*	*	CO(O <sup>-</sup> )CO(OO·) → CO(OH)CO(O <sup>-</sup> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 00365	*		CHOCO(O·) → CH·(OH) <sub>2</sub> + CO <sub>2</sub> - H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00366	*	*	CH <sub>3</sub> CO(O <sup>-</sup> ) + OH → CO(O <sup>-</sup> )CH <sub>2</sub> (OO·) + H <sub>2</sub> O - O <sub>2</sub>	7.3 · 10 <sup>+07</sup>	-1770.0	Chin and Wine (1994)
R <sub>o</sub> 00367	*		CH <sub>3</sub> CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>3</sub> CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.9 · 10 <sup>+06</sup>	-3800.0	Exner et al. (1994)

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A/R^b$	Reference/comment
E <sub>o</sub> 00027	*	*	$\text{CH(OH)}_2\text{CO(OH)} \rightleftharpoons \text{CH(OH)}_2\text{CO(O}^-) + \text{H}^+$	$1.0 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00368	*	*	$\text{CH(OH)}_2\text{CO(OH)} + \text{OH} \rightarrow$ $0.150 \text{ CO(OH)C(OH)}_2(\text{OO}\cdot) + 0.850 \text{ CO(OH)CH(OH)(O}\cdot) + \text{H}_2\text{O} - 0.150 \text{ O}_2$	$3.6 \cdot 10^{+08}$	-1000.0	<i>Ervens et al.</i> (2003b)
R <sub>o</sub> 00369	*		$\text{CH(OH)}_2\text{CO(OH)} + \text{NO}_3 \rightarrow 0.150 \text{ CO(OH)C(OH)}_2(\text{OO}\cdot) +$ $0.850 \text{ CO(OH)CH(OH)(O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.150 \text{ O}_2$	$7.4 \cdot 10^{+06}$		
R <sub>o</sub> 00370	*	*	$\text{CO(OH)CH(OH)(O}\cdot) \xrightarrow{\text{O}_2} \text{CO(OH)CO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00371	*	*	$\text{CO(OH)CH(OH)(O}\cdot) \rightarrow \cdot\text{CO(OH)} + \text{CHO(OH)}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00028	*	*	$\text{CO(OH)CO(OH)} \rightleftharpoons \text{CO(OH)CO(O}^-) + \text{H}^+$	$2.5 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00372	*	*	$\text{CO(OH)CO(OH)} + \text{OH} \rightarrow \text{CO(OH)CO(O}\cdot) + \text{H}_2\text{O}$	$1.4 \cdot 10^{+06}$		<i>Getoff et al.</i> (1971)
R <sub>o</sub> 00373	*		$\text{CO(OH)CO(OH)} + \text{NO}_3 \rightarrow \text{CO(OH)CO(O}\cdot) + \text{NO}_3^- + \text{H}^+$	$2.4 \cdot 10^{+04}$		<i>Yang et al.</i> (2004)
R <sub>o</sub> 00374	*	*	$\text{CO(OH)CO(O}\cdot) \rightarrow \cdot\text{CO(OH)} + \text{CO}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00375	*	*	$\text{CH(OH)}_2\text{CO(O}^-) + \text{OH} \rightarrow$ $0.256 \text{ CO(O}^-)\text{C(OH)}_2(\text{OO}\cdot) + 0.744 \text{ CO(O}^-)\text{CH(OH)(O}\cdot) + \text{H}_2\text{O} - 0.256 \text{ O}_2$	$2.6 \cdot 10^{+09}$	-4330.0	<i>Ervens et al.</i> (2003b)
R <sub>o</sub> 00376	*		$\text{CH(OH)}_2\text{CO(O}^-) + \text{NO}_3 \rightarrow \text{CH(OH)}_2\text{CO(O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 00377	*	*	$\text{CO(O}^-)\text{CH(OH)(O}\cdot) \xrightarrow{\text{O}_2} \text{CO(OH)CO(O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00378	*	*	$\text{CO(O}^-)\text{CH(OH)(O}\cdot) \rightarrow \cdot\text{CO(O}^-) + \text{CHO(OH)}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00029	*	*	$\text{CO(OH)CO(O}^-) \rightleftharpoons \text{CO(O}^-)\text{CO(O}^-) + \text{H}^+$	$2.2 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00379	*	*	$\text{CO(OH)CO(O}^-) + \text{OH} \rightarrow \text{CO(O}^-)\text{CO(O}\cdot) + \text{H}_2\text{O}$	$1.9 \cdot 10^{+08}$	-2800.0	<i>Ervens et al.</i> (2003b)
R <sub>o</sub> 00380	*		$\text{CO(OH)CO(O}^-) + \text{NO}_3 \rightarrow \text{CO(OH)CO(O}\cdot) + \text{NO}_3^-$	$6.1 \cdot 10^{+07}$		Average of <i>Yang et al.</i> (2004) and <i>de Semainville et al.</i> (2010b) and <i>Raabe</i> (1996)
R <sub>o</sub> 00381	*	*	$\text{CH}_3\text{CH}_2\text{CH}_2(\text{OH}) + \text{OH} \rightarrow$ $0.158 \text{ CH}_2(\text{OH})\text{CH}_2\text{CH}_2(\text{OO}\cdot) + 0.156 \text{ CH}_3\text{CH}(\text{OO}\cdot)\text{CH}_2(\text{OH}) +$ $0.655 \text{ CH}_3\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) + 0.031 \text{ CH}_3\text{CH}_2\text{CH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.969 \text{ O}_2$	$3.2 \cdot 10^{+09}$	-1000.0	<i>Ervens et al.</i> (2003b)
R <sub>o</sub> 00382	*		$\text{CH}_3\text{CH}_2\text{CH}_2(\text{OH}) + \text{NO}_3 \rightarrow 0.158 \text{ CH}_2(\text{OH})\text{CH}_2\text{CH}_2(\text{OO}\cdot) +$ $0.156 \text{ CH}_3\text{CH}(\text{OO}\cdot)\text{CH}_2(\text{OH}) + 0.655 \text{ CH}_3\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.031 \text{ CH}_3\text{CH}_2\text{CH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.969 \text{ O}_2$	$3.2 \cdot 10^{+06}$		<i>Herrmann et al.</i> (1994)
R <sub>o</sub> 00383	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CH}_2(\text{OH})\text{CH}_2\text{CH}_2(\text{O}\cdot) + 0.550 \text{ CH}_2(\text{OH})\text{CH}_2\text{CHO} +$ $0.250 \text{ CH}_2(\text{OH})\text{CH}_2\text{CH}_2(\text{OH}) + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00384	*	*	$\text{CH}_3\text{CH}(\text{OO}\cdot)\text{CH}_2(\text{OH}) \xrightarrow{RO_2}$ 0.200 $\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) + 0.550 \text{CH}_3\text{COCH}_2(\text{OH}) +$ 0.250 $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00385	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2(\text{O}\cdot) \xrightarrow{O_2} \text{CH}_2(\text{OH})\text{CH}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00386	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00387	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) \xrightarrow{O_2} \text{CH}_3\text{COCH}_2(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00388	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) \rightarrow 0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CH}_2(\text{OH})\text{CHO} +$ 0.500 $\text{CH}_3\text{CHO} + 0.500 \text{CH}_2(\text{OH})\cdot - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00389	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2(\text{OH}) + \text{OH} \rightarrow 0.101 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) +$ 0.377 $\text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2(\text{OH}) + 0.421 \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ 0.053 $\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) + 0.047 \text{CH}_3\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.900 \text{O}_2$	$1.7 \cdot 10^{+09}$	-1383.0	Hoffmann et al. (2009)
R <sub>o</sub> 00390	*		$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2(\text{OH}) + \text{NO}_3 \rightarrow$ 0.101 $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) + 0.377 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2(\text{OH}) +$ 0.421 $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) + 0.053 \text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) +$ 0.047 $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.900 \text{O}_2$	$9.9 \cdot 10^{+06}$	-2622.0	Hoffmann et al. (2009)
R <sub>o</sub> 00391	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) \xrightarrow{RO_2}$ 0.200 $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) + 0.550 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CHO} +$ 0.250 $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00392	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2(\text{OH}) \rightarrow \text{CH}_3\text{COCH}_2(\text{OH}) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00393	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00394	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \xrightarrow{O_2} \text{CH}_3\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00395	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00396	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \xrightarrow{O_2} \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00397	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00398	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2(\text{OH}) + \text{OH} \rightarrow$ 0.908 $\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) + 0.046 \text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{CH}_2(\text{OH}) +$ 0.046 $\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.954 \text{O}_2$	$2.7 \cdot 10^{+09}$	-1371.0	Hoffmann et al. (2009)
R <sub>o</sub> 00399	*		$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2(\text{OH}) + \text{NO}_3 \rightarrow$ 0.908 $\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) + 0.046 \text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{CH}_2(\text{OH}) +$ 0.046 $\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.954 \text{O}_2$	$1.8 \cdot 10^{+06}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00400	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00401	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{CH}_2(\text{OH}) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) + 0.550 \text{CH}_2(\text{OH})\text{COCH}_2(\text{OH}) +$ $0.250 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00402	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCH}_2(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00403	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) \rightarrow \text{CH}_2(\text{OH})\cdot + \text{CH}_2(\text{OH})\text{CHO}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00404	*	*	$\text{CH}_3\text{COCH}_2(\text{OH}) + \text{OH} \rightarrow 0.166 \text{CH}_2(\text{OH})\text{COCH}_2(\text{OO}\cdot) +$ $0.687 \text{CH}_3\text{COCH}(\text{OH})(\text{OO}\cdot) + 0.147 \text{CH}_3\text{COCH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.853 \text{O}_2$	$1.2 \cdot 10^{+09}$	-1082.0	<i>Gligorovski (2005)</i>
R <sub>o</sub> 00405	*	*	$\text{CH}_3\text{COCH}_2(\text{OH}) + \text{NO}_3 \rightarrow 0.166 \text{CH}_2(\text{OH})\text{COCH}_2(\text{OO}\cdot) +$ $0.687 \text{CH}_3\text{COCH}(\text{OH})(\text{OO}\cdot) + 0.147 \text{CH}_3\text{COCH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.853 \text{O}_2$	$1.8 \cdot 10^{+07}$	-1564.0	<i>de Semainville et al. (2007a)</i>
R <sub>o</sub> 00406	*	*	$\text{CH}_2(\text{OH})\text{COCH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_2(\text{OH})\text{COCH}_2(\text{O}\cdot) + 0.550 \text{CH}_2(\text{OH})\text{COCHO} +$ $0.250 \text{CH}_2(\text{OH})\text{COCH}_2(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00407	*	*	$\text{CH}_2(\text{OH})\text{COCH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00408	*	*	$\text{CH}_2(\text{OH})\text{COCH}_2(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00030	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})_2$	$2.5 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00409	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CHO} + \text{OH} \rightarrow$ $0.375 \text{CHOCH}_2\text{CH}(\text{OH})(\text{OO}\cdot) + 0.625 \text{CH}_2(\text{OH})\text{CH}_2\text{CO}(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$4.0 \cdot 10^{+09}$		
R <sub>o</sub> 00410	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CHO} + \text{NO}_3 \rightarrow 0.375 \text{CHOCH}_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.625 \text{CH}_2(\text{OH})\text{CH}_2\text{CO}(\text{OO}\cdot) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$1.4 \cdot 10^{+07}$		
R <sub>o</sub> 00411	*	*	$\text{CHOCH}_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CHOCH}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00412	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CO}(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}_2\text{CO}(\text{OH}) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00413	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})_2 + \text{OH} \rightarrow$ $0.581 \text{CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) + 0.286 \text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.134 \text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.866 \text{O}_2$	$3.0 \cdot 10^{+09}$		
R <sub>o</sub> 00414	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})_2 + \text{NO}_3 \rightarrow$ $0.581 \text{CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) + 0.286 \text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.134 \text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.866 \text{O}_2$	$1.1 \cdot 10^{+07}$		
R <sub>o</sub> 00415	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CH}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00416	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}_2\text{CO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00417	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{CH}_2\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00418	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}_2(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00419	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OH}) + \text{OH} \rightarrow$ $0.728 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.139 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2(\text{OH}) + 0.087 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) +$ $0.046 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) + \text{H}_2\text{O} - 0.867 \text{O}_2$	$1.9 \cdot 10^{+09}$	-1479.0	Hoffmann et al. (2009)
R <sub>o</sub> 00420	*		$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OH}) + \text{NO}_3 \rightarrow$ $0.728 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.139 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2(\text{OH}) + 0.087 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) +$ $0.046 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) + \text{NO}_3^- + \text{H}^+ - 0.867 \text{O}_2$	$1.3 \cdot 10^{+07}$	-3452.0	Hoffmann et al. (2009)
R <sub>o</sub> 00421	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00422	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2(\text{OH}) \rightarrow \text{CH}_2(\text{OH})\text{COCH}_2(\text{OH}) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
E <sub>o</sub> 00031	*	*	$\text{CH}_2(\text{OH})\text{COCH}_2(\text{OH}) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{OH})$	$1.4 \cdot 10^{-01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00423	*	*	$\text{CH}_2(\text{OH})\text{COCH}_2(\text{OH}) + \text{OH} \rightarrow 0.815 \text{CH}_2(\text{OH})\text{COCH}(\text{OH})(\text{OO}\cdot) +$ $0.185 \text{CH}_2(\text{OH})\text{COCH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.815 \text{O}_2$	$8.1 \cdot 10^{+08}$		
R <sub>o</sub> 00424	*		$\text{CH}_2(\text{OH})\text{COCH}_2(\text{OH}) + \text{NO}_3 \rightarrow 0.815 \text{CH}_2(\text{OH})\text{COCH}(\text{OH})(\text{OO}\cdot) +$ $0.185 \text{CH}_2(\text{OH})\text{COCH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.815 \text{O}_2$	$1.4 \cdot 10^{+06}$		
R <sub>o</sub> 00425	*	*	$\text{CH}_2(\text{OH})\text{COCH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
E <sub>o</sub> 00032	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})_2$	$7.4 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00426	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CHO} + \text{OH} \rightarrow$ $0.097 \text{CHOCH}(\text{OH})\text{CH}_2(\text{OO}\cdot) + 0.182 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CHO} +$ $0.670 \text{CH}_3\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) + 0.051 \text{CH}_3\text{CH}(\text{O}\cdot)\text{CHO} + \text{H}_2\text{O} - 0.949 \text{O}_2$	$1.6 \cdot 10^{+09}$		
R <sub>o</sub> 00427	*		$\text{CH}_3\text{CH}(\text{OH})\text{CHO} + \text{NO}_3 \rightarrow 0.097 \text{CHOCH}(\text{OH})\text{CH}_2(\text{OO}\cdot) +$ $0.182 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CHO} + 0.670 \text{CH}_3\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) +$ $0.051 \text{CH}_3\text{CH}(\text{O}\cdot)\text{CHO} + \text{NO}_3^- + \text{H}^+ - 0.949 \text{O}_2$	$1.5 \cdot 10^{+07}$		
R <sub>o</sub> 00428	*	*	$\text{CHOCH}(\text{OH})\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CHOCH}(\text{OH})\text{CH}_2(\text{O}\cdot) + 0.550 \text{CHOCH}(\text{OH})\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00429	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CHO} \rightarrow \text{CH}_3\text{COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00430	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CO}(\text{OH}) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00431	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CHO} \xrightarrow{\text{O}_2} \text{CH}_3\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00432	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CHO} \rightarrow 0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CHOCHO} + 0.500 \text{CH}_3\text{CHO} + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{O}_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00433	*	*	$\text{CHOCH}(\text{OH})\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CHOCH}(\text{OH})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00434	*	*	$\text{CHOCH}(\text{OH})\text{CH}_2(\text{O}\cdot) \rightarrow \text{CHOCH}(\text{OH})(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00033	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})_2$	$1.5 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00435	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CHO} + \text{OH} \rightarrow 0.319 \text{CHOCH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) + 0.062 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CHO} + 0.532 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) + 0.047 \text{CHOCH}(\text{OH})\text{CH}_2(\text{O}\cdot) + 0.040 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CHO} + \text{H}_2\text{O} - 0.913 \text{O}_2$	$1.9 \cdot 10^{+09}$		
R <sub>o</sub> 00436	*		$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CHO} + \text{NO}_3 \rightarrow 0.319 \text{CHOCH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) + 0.062 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CHO} + 0.532 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) + 0.047 \text{CHOCH}(\text{OH})\text{CH}_2(\text{O}\cdot) + 0.040 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CHO} + \text{NO}_3^- + \text{H}^+ - 0.913 \text{O}_2$	$1.5 \cdot 10^{+07}$		
R <sub>o</sub> 00437	*	*	$\text{CHOCH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CHOCH}(\text{OH})\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00438	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CHO} \rightarrow \text{CH}_2(\text{OH})\text{COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00439	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{OH}) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00440	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CHO} \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00441	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CHO} \rightarrow 0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CHOCHO} + 0.500 \text{CH}_2(\text{OH})\text{CHO} + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00034	*	*	$\text{CH}_2(\text{OH})\text{COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{COCH}(\text{OH})_2$	$9.7 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00035	*	*	$\text{CH}_2(\text{OH})\text{COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})_2$	$1.4 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00442	*	*	$\text{CH}_2(\text{OH})\text{COCHO} + \text{OH} \rightarrow 0.340 \text{CHOCOCH}(\text{OH})(\text{OO}\cdot) + 0.566 \text{CH}_2(\text{OH})\text{COCO}(\text{OO}\cdot) + 0.094 \text{CHOCOCH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.906 \text{O}_2$	$8.0 \cdot 10^{+08}$		
R <sub>o</sub> 00443	*		$\text{CH}_2(\text{OH})\text{COCHO} + \text{NO}_3 \rightarrow 0.340 \text{CHOCOCH}(\text{OH})(\text{OO}\cdot) + 0.566 \text{CH}_2(\text{OH})\text{COCO}(\text{OO}\cdot) + 0.094 \text{CHOCOCH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.906 \text{O}_2$	$5.6 \cdot 10^{+06}$		
R <sub>o</sub> 00444	*	*	$\text{CHOCOCH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CHOCOCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00445	*	*	$\text{CH}_2(\text{OH})\text{COCO}(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{COCO}(\text{OH}) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00446	*	*	$\text{CHOCOCH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CHOCOCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00447	*	*	$\text{CHOCOCH}_2(\text{O}\cdot) \rightarrow \text{CHOCO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00036	*	*	$\text{CHOCH}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{CH}_2\text{CHO}$	$3.0 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00037	*	*	$\text{CHOCH}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{CH}_2\text{CH(OH)}_2$	$1.5 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00448	*	*	$\text{CHOCH}_2\text{CHO} + \text{OH} \rightarrow \text{CHOCH}_2\text{CO(OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$4.1 \cdot 10^{+09}$		
R <sub>o</sub> 00449	*	*	$\text{CHOCH}_2\text{CHO} + \text{NO}_3 \rightarrow \text{CHOCH}_2\text{CO(OO}\cdot) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$5.4 \cdot 10^{+06}$		
R <sub>o</sub> 00450	*	*	$\text{CHOCH}_2\text{CO(OO}\cdot) \rightarrow \text{CO(OH)CH}_2\text{CHO} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
E <sub>o</sub> 00038	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CO(OH)} \rightleftharpoons \text{CH}_2(\text{OH})\text{CH}_2\text{CO(O}^-) + \text{H}^+$	$2.5 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00451	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CO(OH)} + \text{OH} \rightarrow 0.926 \text{ CO(OH)CH}_2\text{CH(OH)(OO}\cdot) + 0.074 \text{ CO(OH)CH}_2\text{CH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.926 \text{ O}_2$	$1.2 \cdot 10^{+09}$		
R <sub>o</sub> 00452	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CO(OH)} + \text{NO}_3 \rightarrow 0.926 \text{ CO(OH)CH}_2\text{CH(OH)(OO}\cdot) + 0.074 \text{ CO(OH)CH}_2\text{CH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.926 \text{ O}_2$	$8.3 \cdot 10^{+03}$		
R <sub>o</sub> 00453	*	*	$\text{CO(OH)CH}_2\text{CH(OH)(OO}\cdot) \rightarrow \text{CO(OH)CH}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00454	*	*	$\text{CO(OH)CH}_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO(OH)CH}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00455	*	*	$\text{CO(OH)CH}_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CO(OH)CH}_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00456	*	*	$\text{CH(OH)}_2\text{CH}_2\text{CH(OH)}_2 + \text{OH} \rightarrow 0.671 \text{ CH(OH)}_2\text{CH}_2\text{C(OH)}_2(\text{OO}\cdot) + 0.329 \text{ CH(OH)}_2\text{CH}_2\text{CH(OH)(O}\cdot) + \text{H}_2\text{O} - 0.671 \text{ O}_2$	$2.4 \cdot 10^{+09}$		
R <sub>o</sub> 00457	*	*	$\text{CH(OH)}_2\text{CH}_2\text{CH(OH)}_2 + \text{NO}_3 \rightarrow 0.671 \text{ CH(OH)}_2\text{CH}_2\text{C(OH)}_2(\text{OO}\cdot) + 0.329 \text{ CH(OH)}_2\text{CH}_2\text{CH(OH)(O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.671 \text{ O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 00458	*	*	$\text{CH(OH)}_2\text{CH}_2\text{C(OH)}_2(\text{OO}\cdot) \rightarrow \text{CH(OH)}_2\text{CH}_2\text{CO(OH)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00459	*	*	$\text{CH(OH)}_2\text{CH}_2\text{CH(OH)(O}\cdot) \xrightarrow{\text{O}_2} \text{CH(OH)}_2\text{CH}_2\text{CO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00460	*	*	$\text{CH(OH)}_2\text{CH}_2\text{CH(OH)(O}\cdot) \rightarrow \text{CH(OH)}_2\text{CH}_2(\text{OO}\cdot) + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00461	*	*	$\text{CH}_2(\text{OH})\text{C(OH)}_2\text{CH(OH)}_2 + \text{OH} \rightarrow 0.224 \text{ CH(OH)}_2\text{C(OH)}_2\text{CH(OH)(OO}\cdot) + 0.110 \text{ CH}_2(\text{OH})\text{C(OH)}_2\text{C(OH)}_2(\text{OO}\cdot) + 0.067 \text{ CH(OH)}_2\text{C(OH)}_2\text{CH}_2(\text{O}\cdot) + 0.305 \text{ CH}_2(\text{OH})\text{C(OH)(O}\cdot)\text{CH(OH)}_2 + 0.293 \text{ CH}_2(\text{OH})\text{C(OH)}_2\text{CH(OH)(O}\cdot) + \text{H}_2\text{O} - 0.334 \text{ O}_2$	$1.2 \cdot 10^{+09}$		
R <sub>o</sub> 00462	*	*	$\text{CH}_2(\text{OH})\text{C(OH)}_2\text{CH(OH)}_2 + \text{NO}_3 \rightarrow 0.224 \text{ CH(OH)}_2\text{C(OH)}_2\text{CH(OH)(OO}\cdot) + 0.110 \text{ CH}_2(\text{OH})\text{C(OH)}_2\text{C(OH)}_2(\text{OO}\cdot) + 0.067 \text{ CH(OH)}_2\text{C(OH)}_2\text{CH}_2(\text{O}\cdot) + 0.305 \text{ CH}_2(\text{OH})\text{C(OH)(O}\cdot)\text{CH(OH)}_2 + 0.293 \text{ CH}_2(\text{OH})\text{C(OH)}_2\text{CH(OH)(O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.334 \text{ O}_2$	$9.7 \cdot 10^{+06}$		
R <sub>o</sub> 00463	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)(OO}\cdot) \rightarrow \text{CH(OH)}_2\text{C(OH)}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00464	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00465	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00466	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00467	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})_2 \rightarrow 0.500 \text{CH}_2(\text{OH})\cdot +$ $0.500 \text{CH}(\text{OH})_2\text{CO}(\text{OH}) + 0.500 \text{CH}_2(\text{OH})\text{CO}(\text{OH}) + 0.500 \text{CH}\cdot(\text{OH})_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00468	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00469	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00470	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})_2 + \text{OH} \rightarrow$ $0.138 \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) + 0.216 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})_2 +$ $0.281 \text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.072 \text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})_2 +$ $0.292 \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.635 \text{O}_2$	$1.3 \cdot 10^{+09}$		
R <sub>o</sub> 00471	*		$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})_2 + \text{NO}_3 \rightarrow$ $0.138 \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) + 0.216 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})_2 +$ $0.281 \text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.072 \text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})_2 +$ $0.292 \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.635 \text{O}_2$	$1.1 \cdot 10^{+07}$		
R <sub>o</sub> 00472	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) + 0.550 \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})_2 + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00473	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})_2 \rightarrow \text{CH}_3\text{COCH}(\text{OH})_2 + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00474	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00475	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})_2 \xrightarrow{\text{O}_2} \text{CH}_3\text{COCH}(\text{OH})_2 + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00476	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})_2 \rightarrow 0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CH}(\text{OH})_2\text{CHO} +$ $0.500 \text{CH}_3\text{CHO} + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00477	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_3\text{CH}(\text{OH})\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00478	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00479	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00480	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00481	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OH) <sub>2</sub> + OH → 0.408 CH(OH) <sub>2</sub> CH(OH)CH(OH)(OO·) + 0.066 CH <sub>2</sub> (OH)C(OH)(OO·)CH(OH) <sub>2</sub> + 0.201 CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> (OO·) + 0.051 CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) + 0.052 CH <sub>2</sub> (OH)CH(O·)CH(OH) <sub>2</sub> + 0.222 CH <sub>2</sub> (OH)CH(OH)CH(OH)(O·) + H <sub>2</sub> O – 0.675 O <sub>2</sub>	1.7 · 10 <sup>+09</sup>		
R <sub>o</sub> 00482	*		CH <sub>2</sub> (OH)CH(OH)CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.408 CH(OH) <sub>2</sub> CH(OH)CH(OH)(OO·) + 0.066 CH <sub>2</sub> (OH)C(OH)(OO·)CH(OH) <sub>2</sub> + 0.201 CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> (OO·) + 0.051 CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) + 0.052 CH <sub>2</sub> (OH)CH(O·)CH(OH) <sub>2</sub> + 0.222 CH <sub>2</sub> (OH)CH(OH)CH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.675 O <sub>2</sub>	1.2 · 10 <sup>+07</sup>		
R <sub>o</sub> 00483	*	*	CH(OH) <sub>2</sub> CH(OH)CH(OH)(OO·) → CH(OH) <sub>2</sub> CH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00484	*	*	CH <sub>2</sub> (OH)C(OH)(OO·)CH(OH) <sub>2</sub> → CH <sub>2</sub> (OH)COCH(OH) <sub>2</sub> + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00485	*	*	CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)CH(OH)CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 00486	*	*	CH <sub>2</sub> (OH)CH(O·)CH(OH) <sub>2</sub> $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCH(OH) <sub>2</sub> + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 00487	*	*	CH <sub>2</sub> (OH)CH(O·)CH(OH) <sub>2</sub> → 0.500 CH <sub>2</sub> (OH)· + 0.500 CH(OH) <sub>2</sub> CHO + 0.500 CH <sub>2</sub> (OH)CHO + 0.500 CH·(OH) <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00488	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(OH)CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 00489	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OH)(O·) → CH <sub>2</sub> (OH)CH(OH)(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00490	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH <sub>2</sub> (OH) + OH → 0.508 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)(OO·) + 0.146 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.346 CH <sub>2</sub> (OH)C(OH)(O·)CH <sub>2</sub> (OH) + H <sub>2</sub> O – 0.508 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 00491	*		CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH <sub>2</sub> (OH) + NO <sub>3</sub> → 0.508 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)(OO·) + 0.146 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.346 CH <sub>2</sub> (OH)C(OH)(O·)CH <sub>2</sub> (OH) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.508 O <sub>2</sub>	1.1 · 10 <sup>+07</sup>		
R <sub>o</sub> 00492	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)(OO·) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00493	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 00494	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00495	*	*	CH <sub>2</sub> (OH)C(OH)(O·)CH <sub>2</sub> (OH) → CH <sub>2</sub> (OH)· + CH <sub>2</sub> (OH)CO(OH)	5.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00496	*	*	$\text{CH}_2(\text{OH})\text{COCH}(\text{OH})_2 + \text{OH} \rightarrow 0.361 \text{CH}(\text{OH})_2\text{COCH}(\text{OH})(\text{OO}\cdot) + 0.178 \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2(\text{OO}\cdot) + 0.086 \text{CH}(\text{OH})_2\text{COCH}_2(\text{O}\cdot) + 0.375 \text{CH}_2(\text{OH})\text{COCH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.539 \text{O}_2$	$8.7 \cdot 10^{+08}$		
R <sub>o</sub> 00497	*		$\text{CH}_2(\text{OH})\text{COCH}(\text{OH})_2 + \text{NO}_3 \rightarrow 0.361 \text{CH}(\text{OH})_2\text{COCH}(\text{OH})(\text{OO}\cdot) + 0.178 \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2(\text{OO}\cdot) + 0.086 \text{CH}(\text{OH})_2\text{COCH}_2(\text{O}\cdot) + 0.375 \text{CH}_2(\text{OH})\text{COCH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.539 \text{O}_2$	$9.6 \cdot 10^{+06}$		
R <sub>o</sub> 00498	*	*	$\text{CH}(\text{OH})_2\text{COCH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00499	*	*	$\text{CH}_2(\text{OH})\text{COC}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{COCO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00500	*	*	$\text{CH}(\text{OH})_2\text{COCH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00501	*	*	$\text{CH}(\text{OH})_2\text{COCH}_2(\text{O}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00502	*	*	$\text{CH}_2(\text{OH})\text{COCH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00503	*	*	$\text{CH}_2(\text{OH})\text{COCH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CO}(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00504	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{CHO} + \text{OH} \rightarrow 0.202 \text{CHOCH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.683 \text{CH}(\text{OH})_2\text{CH}_2\text{CO}(\text{OO}\cdot) + 0.115 \text{CHOCH}_2\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.885 \text{O}_2$	$3.5 \cdot 10^{+09}$		
R <sub>o</sub> 00505	*		$\text{CH}(\text{OH})_2\text{CH}_2\text{CHO} + \text{NO}_3 \rightarrow 0.202 \text{CHOCH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.683 \text{CH}(\text{OH})_2\text{CH}_2\text{CO}(\text{OO}\cdot) + 0.115 \text{CHOCH}_2\text{CH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.885 \text{O}_2$	$8.5 \cdot 10^{+06}$		
R <sub>o</sub> 00506	*	*	$\text{CHOCH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}_2\text{CHO} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00507	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{CO}(\text{OO}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CH}_2\text{CO}(\text{OH}) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00508	*	*	$\text{CHOCH}_2\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{CH}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00509	*	*	$\text{CHOCH}_2\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CHOCH}_2(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00039	*	*	$\text{CH}_3\text{COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{COCH}(\text{OH})_2$	$1.4 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00040	*	*	$\text{CH}_3\text{COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C}(\text{OH})_2\text{CH}(\text{OH})_2$	$3.3 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00510	*	*	$\text{CH}_3\text{COCHO} + \text{OH} \rightarrow 0.126 \text{CHOCOCH}_2(\text{OO}\cdot) + 0.874 \text{CH}_3\text{COCO}(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$8.6 \cdot 10^{+08}$	-1350.0	Average of <i>Monod et al.</i> (2005), <i>Park et al.</i> (2003), <i>Stefan and Bolton</i> (1999), and TROPOS measurements
R <sub>o</sub> 00511	*		$\text{CH}_3\text{COCHO} + \text{NO}_3 \rightarrow 0.126 \text{CHOCOCH}_2(\text{OO}\cdot) + 0.874 \text{CH}_3\text{COCO}(\text{OO}\cdot) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$5.8 \cdot 10^{+06}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00512	*	*	$\text{CHOCOCH}_2(\text{OO}\cdot) \xrightarrow{RO_2} 0.200 \text{CHOCOCH}_2(\text{O}\cdot) + 0.550 \text{CHOCOCHO} + 0.250 \text{CH}_2(\text{OH})\text{COCHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00513	*	*	$\text{CH}_3\text{COCO}(\text{OO}\cdot) \rightarrow \text{CH}_3\text{COCO}(\text{OH}) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
E <sub>o</sub> 00041	*	*	$\text{CHOCOCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{COCH}(\text{OH})_2$	$2.5 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00042	*	*	$\text{CHOCOCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})_2$	$2.7 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00514	*	*	$\text{CHOCOCHO} \rightarrow 0.500 \text{CHO}(\text{OO}\cdot) + 0.500 \text{CHOCO}(\text{OO}\cdot)$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 00515	*	*	$\text{CHOCOCHO} + \text{OH} \rightarrow \text{CHOCOCO}(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$7.4 \cdot 10^{+08}$		
R <sub>o</sub> 00516	*		$\text{CHOCOCHO} + \text{NO}_3 \rightarrow \text{CHOCOCO}(\text{OO}\cdot) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$2.1 \cdot 10^{+06}$		
R <sub>o</sub> 00517	*	*	$\text{CHOCOCO}(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{COCHO} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
E <sub>o</sub> 00043	*	*	$\text{CHOCH}(\text{OH})\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})_2$	$6.3 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00518	*	*	$\text{CHOCH}(\text{OH})\text{CHO} + \text{OH} \rightarrow 0.963 \text{CHOCH}(\text{OH})\text{CO}(\text{OO}\cdot) + 0.037 \text{CHOCH}(\text{O}\cdot)\text{CHO} + \text{H}_2\text{O} - 0.963 \text{O}_2$	$1.7 \cdot 10^{+09}$		
R <sub>o</sub> 00519	*		$\text{CHOCH}(\text{OH})\text{CHO} + \text{NO}_3 \rightarrow 0.963 \text{CHOCH}(\text{OH})\text{CO}(\text{OO}\cdot) + 0.037 \text{CHOCH}(\text{O}\cdot)\text{CHO} + \text{NO}_3^- + \text{H}^+ - 0.963 \text{O}_2$	$5.7 \cdot 10^{+06}$		
R <sub>o</sub> 00520	*	*	$\text{CHOCH}(\text{OH})\text{CO}(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CHO} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00521	*	*	$\text{CHOCH}(\text{O}\cdot)\text{CHO} \xrightarrow{\text{O}_2} \text{CHOCOCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00522	*	*	$\text{CHOCH}(\text{O}\cdot)\text{CHO} \rightarrow \text{CH}\cdot(\text{OH})_2 + \text{CHOCHO} - \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00523	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CO}(\text{O}^-) + \text{OH} \rightarrow 0.921 \text{CO}(\text{O}^-)\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) + 0.038 \text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) + 0.042 \text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.958 \text{O}_2$	$2.2 \cdot 10^{+09}$		
R <sub>o</sub> 00524	*		$\text{CH}_2(\text{OH})\text{CH}_2\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow \text{CH}_2(\text{OH})\text{CH}_2\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 00525	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{CH}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00526	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) \rightarrow 2.000 \text{CH}_2(\text{OH})\text{CHO} + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 00527	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) \xrightarrow{RO_2} 0.200 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) + 0.550 \text{CH}_2(\text{OH})\text{COCO}(\text{O}^-) + 0.250 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00528	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{CH}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00529	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{CH}_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00530	*		$\text{CH}_2(\text{OH})\text{CH}_2\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00531	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00532	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CO}(\text{O}^-)\text{CHO} + 0.500 \text{CH}_2(\text{OH})\text{CHO} + 0.500 \cdot\text{CO}(\text{O}^-)$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00044	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{OH}) \rightleftharpoons \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{H}^+$	$5.9 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00533	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{OH}) + \text{OH} \rightarrow 0.718 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.057 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{OH}) + 0.135 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) +$ $0.091 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{OH}) + \text{H}_2\text{O} - 0.774 \text{O}_2$	$6.5 \cdot 10^{+08}$		
R <sub>o</sub> 00534	*		$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{OH}) + \text{NO}_3 \rightarrow$ $0.718 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.057 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{OH}) + 0.135 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) +$ $0.091 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{OH}) + \text{NO}_3^- + \text{H}^+ - 0.774 \text{O}_2$	$7.8 \cdot 10^{+03}$		
R <sub>o</sub> 00535	*	*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00536	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{OH}) \rightarrow \text{CH}_2(\text{OH})\text{COCO}(\text{OH}) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00537	*	*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00538	*	*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00539	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{OH}) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00540	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{OH}) \rightarrow 0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CO}(\text{OH})\text{CHO} +$ $0.500 \text{CH}_2(\text{OH})\text{CHO} + 0.500 \cdot\text{CO}(\text{OH})$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00045	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CO}(\text{OH}) \rightleftharpoons \text{CH}_3\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{H}^+$	$4.1 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00541	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CO}(\text{OH}) + \text{OH} \rightarrow$ $0.436 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) + 0.335 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{OH}) +$ $0.229 \text{CH}_3\text{CH}(\text{O}\cdot)\text{CO}(\text{OH}) + \text{H}_2\text{O} - 0.771 \text{O}_2$	$5.2 \cdot 10^{+08}$	-1120.0	<i>Martin et al.</i> (2009)
R <sub>o</sub> 00542	*		$\text{CH}_3\text{CH}(\text{OH})\text{CO}(\text{OH}) + \text{NO}_3 \rightarrow$ $0.436 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) + 0.335 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{OH}) +$ $0.229 \text{CH}_3\text{CH}(\text{O}\cdot)\text{CO}(\text{OH}) + \text{NO}_3^- + \text{H}^+ - 0.771 \text{O}_2$	$2.1 \cdot 10^{+06}$	-3248.0	<i>de Semainville et al.</i> (2007a)
R <sub>o</sub> 00543	*	*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) + 0.550 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00544	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CO}(\text{OH}) \xrightarrow{\text{O}_2} \text{CH}_3\text{COCO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00545	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CO}(\text{OH}) \rightarrow 0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CHO} +$ $0.500 \text{CH}_3\text{CHO} + 0.500 \cdot\text{CO}(\text{OH}) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00046	*	*	$\text{CH}_2(\text{OH})\text{COCO}(\text{OH}) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OH})$	$9.9 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00047	*	*	$\text{CH}_2(\text{OH})\text{COCO}(\text{OH}) \rightleftharpoons \text{CH}_2(\text{OH})\text{COCO}(\text{O}^-) + \text{H}^+$	$4.7 \cdot 10^{-02}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00546	*	*	$\text{CH}_2(\text{OH})\text{COCO}(\text{OH}) + \text{OH} \rightarrow 0.737 \text{ CO}(\text{OH})\text{COCH}(\text{OH})(\text{OO}\cdot) +$ $0.263 \text{ CO}(\text{OH})\text{COCH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.737 \text{ O}_2$	$2.9 \cdot 10^{+08}$		
R <sub>o</sub> 00547	*		$\text{CH}_2(\text{OH})\text{COCO}(\text{OH}) + \text{NO}_3 \rightarrow 0.737 \text{ CO}(\text{OH})\text{COCH}(\text{OH})(\text{OO}\cdot) +$ $0.263 \text{ CO}(\text{OH})\text{COCH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.737 \text{ O}_2$	$1.9 \cdot 10^{+05}$		
R <sub>o</sub> 00548	*	*	$\text{CO}(\text{OH})\text{COCH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00549	*	*	$\text{CO}(\text{OH})\text{COCH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{OH})\text{CO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00550	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})_2 \rightarrow$ $0.500 \text{ CHO}(\text{OH}) + 0.500 \text{ HO}_2 + 0.500 \text{ CH}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot)$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 00551	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})_2 + \text{OH} \rightarrow$ $0.194 \text{ CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.539 \text{ CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) +$ $0.268 \text{ CH}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})_2 + \text{H}_2\text{O} - 0.194 \text{ O}_2$	$1.3 \cdot 10^{+09}$		
R <sub>o</sub> 00552	*		$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})_2 + \text{NO}_3 \rightarrow$ $0.194 \text{ CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.539 \text{ CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) +$ $0.268 \text{ CH}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})_2 + \text{NO}_3^- + \text{H}^+ - 0.194 \text{ O}_2$	$8.8 \cdot 10^{+06}$		
R <sub>o</sub> 00553	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00554	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00555	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00556	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})_2 \rightarrow \text{CH}\cdot(\text{OH})_2 + \text{CH}(\text{OH})_2\text{CO}(\text{OH})$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00557	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{CH}(\text{OH})_2 + \text{OH} \rightarrow 0.073 \text{ CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) +$ $0.148 \text{ CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.409 \text{ CH}_3\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})_2 +$ $0.370 \text{ CH}_3\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.221 \text{ O}_2$	$9.8 \cdot 10^{+08}$		
R <sub>o</sub> 00558	*		$\text{CH}_3\text{C}(\text{OH})_2\text{CH}(\text{OH})_2 + \text{NO}_3 \rightarrow 0.073 \text{ CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) +$ $0.148 \text{ CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.409 \text{ CH}_3\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})_2 +$ $0.370 \text{ CH}_3\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.221 \text{ O}_2$	$8.9 \cdot 10^{+06}$		
R <sub>o</sub> 00559	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) + 0.550 \text{ CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CHO} +$ $0.250 \text{ CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})_2 + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00560	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CH}_3\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00561	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})_2 \rightarrow 0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CH}(\text{OH})_2\text{CO}(\text{OH}) + 0.500 \text{CH}_3\text{CO}(\text{OH}) + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00562	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_3\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00563	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CH}_3\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00564	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})_2 + \text{OH} \rightarrow 0.437 \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.507 \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) + 0.056 \text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})_2 + \text{H}_2\text{O} - 0.437 \text{O}_2$	$1.5 \cdot 10^{+09}$		
R <sub>o</sub> 00565	*		$\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})_2 + \text{NO}_3 \rightarrow 0.437 \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.507 \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) + 0.056 \text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})_2 + \text{NO}_3^- + \text{H}^+ - 0.437 \text{O}_2$	$1.1 \cdot 10^{+07}$		
R <sub>o</sub> 00566	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00567	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00568	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00569	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})_2 \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{COCH}(\text{OH})_2 + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00570	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})_2 \rightarrow \text{CH}\cdot(\text{OH})_2 + \text{CH}(\text{OH})_2\text{CHO}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00571	*	*	$\text{CH}(\text{OH})_2\text{COCH}(\text{OH})_2 \rightarrow 0.500 \text{CHO}(\text{OH}) + 0.500 \text{HO}_2 + 0.500 \text{CH}(\text{OH})_2\text{CO}(\text{OO}\cdot)$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 00572	*	*	$\text{CH}(\text{OH})_2\text{COCH}(\text{OH})_2 + \text{OH} \rightarrow 0.312 \text{CH}(\text{OH})_2\text{COC}(\text{OH})_2(\text{OO}\cdot) + 0.688 \text{CH}(\text{OH})_2\text{COCH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.312 \text{O}_2$	$9.5 \cdot 10^{+08}$		
R <sub>o</sub> 00573	*		$\text{CH}(\text{OH})_2\text{COCH}(\text{OH})_2 + \text{NO}_3 \rightarrow 0.312 \text{CH}(\text{OH})_2\text{COC}(\text{OH})_2(\text{OO}\cdot) + 0.688 \text{CH}(\text{OH})_2\text{COCH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.312 \text{O}_2$	$8.8 \cdot 10^{+06}$		
R <sub>o</sub> 00574	*	*	$\text{CH}(\text{OH})_2\text{COC}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{COCO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00575	*	*	$\text{CH}(\text{OH})_2\text{COCH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{COCO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00576	*	*	$\text{CH}(\text{OH})_2\text{COCH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CO}(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00577	*	*	$\text{CH}_3\text{COCH}(\text{OH})_2 + \text{OH} \rightarrow 0.141 \text{CH}(\text{OH})_2\text{COCH}_2(\text{OO}\cdot) + 0.288 \text{CH}_3\text{COC}(\text{OH})_2(\text{OO}\cdot) + 0.570 \text{CH}_3\text{COCH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.430 \text{O}_2$	$7.9 \cdot 10^{+08}$	-1589.0	Average of measurements within MOST
R <sub>o</sub> 00578	*		$\text{CH}_3\text{COCH}(\text{OH})_2 + \text{NO}_3 \rightarrow 0.141 \text{CH}(\text{OH})_2\text{COCH}_2(\text{OO}\cdot) + 0.288 \text{CH}_3\text{COC}(\text{OH})_2(\text{OO}\cdot) + 0.570 \text{CH}_3\text{COCH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.430 \text{O}_2$	$8.8 \cdot 10^{+06}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00579	*	*	$\text{CH(OH)}_2\text{COCH}_2(\text{OO}\cdot) \xrightarrow{RO_2}$ 0.200 $\text{CH(OH)}_2\text{COCH}_2(\text{O}\cdot) + 0.550 \text{CH(OH)}_2\text{COCHO} +$ 0.250 $\text{CH}_2(\text{OH})\text{COCH(OH)}_2 + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00580	*	*	$\text{CH}_3\text{COCH(OH)(O}\cdot) \xrightarrow{O_2} \text{CH}_3\text{COCO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00581	*	*	$\text{CH}_3\text{COCH(OH)(O}\cdot) \rightarrow \text{CH}_3\text{CO(OO}\cdot) + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00048	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{CHO} \xrightleftharpoons{H_2O} \text{CH(OH)}_2\text{COCH(OH)}_2$	$2.5 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00049	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{CHO} \xrightleftharpoons{H_2O} \text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)}_2$	$2.7 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00582	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{CHO} \rightarrow 0.250 \text{CHO(OH)} + 0.250 \text{HO}_2 +$ 0.250 $\text{CHOC(OH)}_2(\text{OO}\cdot) + 0.250 \text{CH(OH)}_2\text{C(OH)}_2(\text{OO}\cdot) + 0.250 \text{CHO(OO}\cdot)$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 00583	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{CHO} + \text{OH} \rightarrow 0.096 \text{CHOC(OH)}_2\text{C(OH)}_2(\text{OO}\cdot) +$ 0.325 $\text{CH(OH)}_2\text{C(OH)}_2\text{CO(OO}\cdot) + 0.312 \text{CHOC(OH)}_2\text{CH(OH)(O}\cdot) +$ 0.266 $\text{CH(OH)}_2\text{C(OH)(O}\cdot)\text{CHO} + \text{H}_2\text{O} - 0.422 \text{O}_2$	$1.2 \cdot 10^{+09}$		
R <sub>o</sub> 00584	*		$\text{CH(OH)}_2\text{C(OH)}_2\text{CHO} + \text{NO}_3 \rightarrow 0.096 \text{CHOC(OH)}_2\text{C(OH)}_2(\text{OO}\cdot) +$ 0.325 $\text{CH(OH)}_2\text{C(OH)}_2\text{CO(OO}\cdot) + 0.312 \text{CHOC(OH)}_2\text{CH(OH)(O}\cdot) +$ 0.266 $\text{CH(OH)}_2\text{C(OH)(O}\cdot)\text{CHO} + \text{NO}_3^- + \text{H}^+ - 0.422 \text{O}_2$	$7.3 \cdot 10^{+06}$		
R <sub>o</sub> 00585	*	*	$\text{CHOC(OH)}_2\text{C(OH)}_2(\text{OO}\cdot) \rightarrow \text{CO(OH)C(OH)}_2\text{CHO} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00586	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{CO(OO}\cdot) \rightarrow \text{CH(OH)}_2\text{C(OH)}_2\text{CO(OH)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00587	*	*	$\text{CHOC(OH)}_2\text{CH(OH)(O}\cdot) \xrightarrow{O_2} \text{CO(OH)C(OH)}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00588	*	*	$\text{CHOC(OH)}_2\text{CH(OH)(O}\cdot) \rightarrow \text{CHOC(OH)}_2(\text{OO}\cdot) + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00589	*	*	$\text{CH(OH)}_2\text{C(OH)(O}\cdot)\text{CHO} \rightarrow 0.500 \text{CH}\cdot(\text{OH})_2 + 0.500 \text{CO(OH)CHO} +$ 0.500 $\text{CH(OH)}_2\text{CO(OH)} + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00050	*	*	$\text{CH}_2(\text{OH})\text{C(OH)}_2\text{CHO} \xrightleftharpoons{H_2O} \text{CH}_2(\text{OH})\text{COCH(OH)}_2$	$9.7 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00051	*	*	$\text{CH}_2(\text{OH})\text{C(OH)}_2\text{CHO} \xrightleftharpoons{H_2O} \text{CH}_2(\text{OH})\text{C(OH)}_2\text{CH(OH)}_2$	$1.4 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00590	*	*	$\text{CH}_2(\text{OH})\text{C(OH)}_2\text{CHO} + \text{OH} \rightarrow 0.228 \text{CHOC(OH)}_2\text{CH(OH)(OO}\cdot) +$ 0.380 $\text{CH}_2(\text{OH})\text{C(OH)}_2\text{CO(OO}\cdot) + 0.080 \text{CHOC(OH)}_2\text{CH}_2(\text{O}\cdot) +$ 0.311 $\text{CH}_2(\text{OH})\text{C(OH)(O}\cdot)\text{CHO} + \text{H}_2\text{O} - 0.609 \text{O}_2$	$1.0 \cdot 10^{+09}$		
R <sub>o</sub> 00591	*		$\text{CH}_2(\text{OH})\text{C(OH)}_2\text{CHO} + \text{NO}_3 \rightarrow 0.228 \text{CHOC(OH)}_2\text{CH(OH)(OO}\cdot) +$ 0.380 $\text{CH}_2(\text{OH})\text{C(OH)}_2\text{CO(OO}\cdot) + 0.080 \text{CHOC(OH)}_2\text{CH}_2(\text{O}\cdot) +$ 0.311 $\text{CH}_2(\text{OH})\text{C(OH)(O}\cdot)\text{CHO} + \text{NO}_3^- + \text{H}^+ - 0.609 \text{O}_2$	$8.0 \cdot 10^{+06}$		
R <sub>o</sub> 00592	*	*	$\text{CHOC(OH)}_2\text{CH(OH)(OO}\cdot) \rightarrow \text{CHOC(OH)}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00593	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00594	*	*	$\text{CHOC}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CHOC}(\text{OH})_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00595	*	*	$\text{CHOC}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CHOC}(\text{OH})_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00596	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CHO} \rightarrow 0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CO}(\text{OH})\text{CHO} + 0.500 \text{CH}_2(\text{OH})\text{CO}(\text{OH}) + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00052	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})_2$	$6.3 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00597	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CHO} + \text{OH} \rightarrow 0.167 \text{CHOCH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.565 \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) + 0.226 \text{CHOCH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) + 0.043 \text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CHO} + \text{H}_2\text{O} - 0.732 \text{O}_2$	$1.7 \cdot 10^{+09}$		
R <sub>o</sub> 00598	*		$\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CHO} + \text{NO}_3 \rightarrow 0.167 \text{CHOCH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.565 \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) + 0.226 \text{CHOCH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) + 0.043 \text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CHO} + \text{NO}_3^- + \text{H}^+ - 0.732 \text{O}_2$	$9.4 \cdot 10^{+06}$		
R <sub>o</sub> 00599	*	*	$\text{CHOCH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00600	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{OH}) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00601	*	*	$\text{CHOCH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00602	*	*	$\text{CHOCH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CHOCH}(\text{OH})(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00603	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CHO} \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00604	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CHO} \rightarrow 0.500 \text{CH}\cdot(\text{OH})_2 + 0.500 \text{CHOCHO} + 0.500 \text{CH}(\text{OH})_2\text{CHO} + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00053	*	*	$\text{CH}(\text{OH})_2\text{COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{COCH}(\text{OH})_2$	$2.5 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00054	*	*	$\text{CH}(\text{OH})_2\text{COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})_2$	$2.7 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00605	*	*	$\text{CH}(\text{OH})_2\text{COCHO} \rightarrow 0.250 \text{CHO}(\text{OH}) + 0.250 \text{HO}_2 + 0.250 \text{CHOCO}(\text{OO}\cdot) + 0.250 \text{CH}(\text{OH})_2\text{CO}(\text{OO}\cdot) + 0.250 \text{CHO}(\text{OO}\cdot)$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 00606	*	*	$\text{CH}(\text{OH})_2\text{COCHO} + \text{OH} \rightarrow 0.144 \text{CHOCOC}(\text{OH})_2(\text{OO}\cdot) + 0.486 \text{CH}(\text{OH})_2\text{COCO}(\text{OO}\cdot) + 0.370 \text{CHOCOCH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.630 \text{O}_2$	$8.8 \cdot 10^{+08}$		
R <sub>o</sub> 00607	*		$\text{CH}(\text{OH})_2\text{COCHO} + \text{NO}_3 \rightarrow 0.144 \text{CHOCOC}(\text{OH})_2(\text{OO}\cdot) + 0.486 \text{CH}(\text{OH})_2\text{COCO}(\text{OO}\cdot) + 0.370 \text{CHOCOCH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.630 \text{O}_2$	$7.2 \cdot 10^{+06}$		
R <sub>o</sub> 00608	*	*	$\text{CHOCOC}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{COCHO} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00609	*	*	$\text{CH(OH)}_2\text{COCO(OO}\cdot\text{)} \rightarrow \text{CH(OH)}_2\text{COCO(OH)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00610	*	*	$\text{CHOCOCH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CO(OH)COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00611	*	*	$\text{CHOCOCH(OH)(O}\cdot\text{)} \rightarrow \text{CHOCO(OO}\cdot\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00612	*	*	$\text{CH}_3\text{CH(OH)CO(O}^-\text{)} + \text{OH} \rightarrow 0.331 \text{CO(O}^-\text{)CH(OH)CH}_2\text{(OO}\cdot\text{)} +$ $0.496 \text{CH}_3\text{C(OH)(OO}\cdot\text{)CO(O}^-\text{)} + 0.173 \text{CH}_3\text{CH(O}\cdot\text{)CO(O}^-\text{)} + \text{H}_2\text{O} - 0.827 \text{O}_2$	$7.8 \cdot 10^{+08}$	-1295.0	Martin et al. (2009)
R <sub>o</sub> 00613	*		$\text{CH}_3\text{CH(OH)CO(O}^-\text{)} + \text{NO}_3 \rightarrow \text{CH}_3\text{CH(OH)CO(O}\cdot\text{)} + \text{NO}_3^-$	$1.0 \cdot 10^{+07}$	-2646.0	de Semainville et al. (2007a)
R <sub>o</sub> 00614	*	*	$\text{CO(O}^-\text{)CH(OH)CH}_2\text{(OO}\cdot\text{)} \xrightarrow{\text{RO}_2}$ $0.200 \text{CO(O}^-\text{)CH(OH)CH}_2\text{(O}\cdot\text{)} + 0.550 \text{CO(O}^-\text{)CH(OH)CHO} +$ $0.250 \text{CH}_2\text{(OH)CH(OH)CO(O}^-\text{)} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00615	*	*	$\text{CH}_3\text{CH(O}\cdot\text{)CO(O}^-\text{)} \xrightarrow{\text{O}_2} \text{CH}_3\text{COCO(O}^-\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00616	*	*	$\text{CH}_3\text{CH(O}\cdot\text{)CO(O}^-\text{)} \rightarrow 0.500 \text{CH}_3\text{(OO}\cdot\text{)} + 0.500 \text{CO(O}^-\text{)CHO} +$ $0.500 \text{CH}_3\text{CHO} + 0.500 \cdot \text{CO(O}^-\text{)} - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00617	*	*	$\text{CO(O}^-\text{)CH(OH)CH}_2\text{(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CO(O}^-\text{)CH(OH)CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00618	*	*	$\text{CO(O}^-\text{)CH(OH)CH}_2\text{(O}\cdot\text{)} \rightarrow \text{CO(O}^-\text{)CH(OH)(OO}\cdot\text{)} + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00619	*	*	$\text{CH}_2\text{(OH)CH(OH)CO(O}^-\text{)} + \text{OH} \rightarrow 0.721 \text{CO(O}^-\text{)CH(OH)CH(OH)(OO}\cdot\text{)} +$ $0.111 \text{CH}_2\text{(OH)C(OH)(OO}\cdot\text{)CO(O}^-\text{)} + 0.077 \text{CO(O}^-\text{)CH(OH)CH}_2\text{(O}\cdot\text{)} +$ $0.091 \text{CH}_2\text{(OH)CH(O}\cdot\text{)CO(O}^-\text{)} + \text{H}_2\text{O} - 0.832 \text{O}_2$	$1.1 \cdot 10^{+09}$		
R <sub>o</sub> 00620	*		$\text{CH}_2\text{(OH)CH(OH)CO(O}^-\text{)} + \text{NO}_3 \rightarrow \text{CH}_2\text{(OH)CH(OH)CO(O}\cdot\text{)} + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 00621	*	*	$\text{CO(O}^-\text{)CH(OH)CH(OH)(OO}\cdot\text{)} \rightarrow \text{CO(O}^-\text{)CH(OH)CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00622	*	*	$\text{CH}_2\text{(OH)C(OH)(OO}\cdot\text{)CO(O}^-\text{)} \rightarrow \text{CH}_2\text{(OH)COCO(O}^-\text{)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00623	*		$\text{CH}_2\text{(OH)CH(OH)CO(O}\cdot\text{)} \rightarrow \text{CH}_2\text{(OH)CH(OH)(OO}\cdot\text{)} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00624	*	*	$\text{CH}_2\text{(OH)COCO(O}^-\text{)} + \text{OH} \rightarrow 0.831 \text{CO(O}^-\text{)COCH(OH)(OO}\cdot\text{)} +$ $0.169 \text{CO(O}^-\text{)COCH}_2\text{(O}\cdot\text{)} + \text{H}_2\text{O} - 0.831 \text{O}_2$	$4.4 \cdot 10^{+08}$		
R <sub>o</sub> 00625	*		$\text{CH}_2\text{(OH)COCO(O}^-\text{)} + \text{NO}_3 \rightarrow \text{CH}_2\text{(OH)COCO(O}\cdot\text{)} + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 00626	*	*	$\text{CO(O}^-\text{)COCH}_2\text{(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CO(O}^-\text{)COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00627	*	*	$\text{CO(O}^-\text{)COCH}_2\text{(O}\cdot\text{)} \rightarrow \text{CO(O}^-\text{)CO(OO}\cdot\text{)} + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00055	*	*	$\text{CH(OH)}_2\text{CH}_2\text{CO(OH)} \rightleftharpoons \text{CH(OH)}_2\text{CH}_2\text{CO(O}^-\text{)} + \text{H}^+$	$3.7 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00628	*	*	$\text{CH(OH)}_2\text{CH}_2\text{CO(OH)} + \text{OH} \rightarrow 0.576 \text{CO(OH)CH}_2\text{C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.424 \text{CO(OH)CH}_2\text{CH(OH)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.576 \text{O}_2$	$9.4 \cdot 10^{+08}$		
R <sub>o</sub> 00629	*		$\text{CH(OH)}_2\text{CH}_2\text{CO(OH)} + \text{NO}_3 \rightarrow 0.576 \text{CO(OH)CH}_2\text{C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.424 \text{CO(OH)CH}_2\text{CH(OH)(O}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - 0.576 \text{O}_2$	$8.7 \cdot 10^{+06}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00630	*	*	$\text{CO(OH)CH}_2\text{CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CO(OH)CH}_2\text{CO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00631	*	*	$\text{CO(OH)CH}_2\text{CH(OH)(O}\cdot\text{)} \rightarrow \text{CO(OH)CH}_2\text{(OO}\cdot\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00056	*	*	$\text{CH}_2\text{(OH)C(OH)}_2\text{CO(OH)} \rightleftharpoons \text{CH}_2\text{(OH)C(OH)}_2\text{CO(O}^-) + \text{H}^+$	$1.3 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00632	*	*	$\text{CH}_2\text{(OH)C(OH)}_2\text{CO(OH)} + \text{OH} \rightarrow$ $0.356 \text{ CO(OH)C(OH)}_2\text{CH(OH)(OO}\cdot\text{)} + 0.160 \text{ CO(OH)C(OH)}_2\text{CH}_2\text{(O}\cdot\text{)} +$ $0.484 \text{ CH}_2\text{(OH)C(OH)(O}\cdot\text{)CO(OH)} + \text{H}_2\text{O} - 0.356 \text{ O}_2$	$5.2 \cdot 10^{+08}$		
R <sub>o</sub> 00633	*		$\text{CH}_2\text{(OH)C(OH)}_2\text{CO(OH)} + \text{NO}_3 \rightarrow$ $0.356 \text{ CO(OH)C(OH)}_2\text{CH(OH)(OO}\cdot\text{)} + 0.160 \text{ CO(OH)C(OH)}_2\text{CH}_2\text{(O}\cdot\text{)} +$ $0.484 \text{ CH}_2\text{(OH)C(OH)(O}\cdot\text{)CO(OH)} + \text{NO}_3^- + \text{H}^+ - 0.356 \text{ O}_2$	$8.1 \cdot 10^{+06}$		
R <sub>o</sub> 00634	*	*	$\text{CO(OH)C(OH)}_2\text{CH(OH)(OO}\cdot\text{)} \rightarrow \text{CO(OH)C(OH)}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00635	*	*	$\text{CO(OH)C(OH)}_2\text{CH}_2\text{(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CO(OH)C(OH)}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00636	*	*	$\text{CO(OH)C(OH)}_2\text{CH}_2\text{(O}\cdot\text{)} \rightarrow \text{CO(OH)C(OH)}_2\text{(OO}\cdot\text{)} + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00637	*	*	$\text{CH}_2\text{(OH)C(OH)(O}\cdot\text{)CO(OH)} \rightarrow 0.500 \text{ CH}_2\text{(OH)}\cdot +$ $0.500 \text{ CO(OH)CO(OH)} + 0.500 \text{ CH}_2\text{(OH)CO(OH)} + 0.500 \cdot \text{CO(OH)}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00057	*	*	$\text{CH}_3\text{COCO(OH)} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C(OH)}_2\text{CO(OH)}$	$1.6 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00058	*	*	$\text{CH}_3\text{COCO(OH)} \rightleftharpoons \text{CH}_3\text{COCO(O}^-) + \text{H}^+$	$1.9 \cdot 10^{-02}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00638	*	*	$\text{CH}_3\text{COCO(OH)} + \text{OH} \rightarrow \text{CO(OH)COCH}_2\text{(OO}\cdot\text{)} + \text{H}_2\text{O} - \text{O}_2$	$1.2 \cdot 10^{+08}$	-2800.0	<i>Ervens et al. (2003b)</i>
R <sub>o</sub> 00639	*		$\text{CH}_3\text{COCO(OH)} + \text{NO}_3 \rightarrow \text{CO(OH)COCH}_2\text{(OO}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$2.4 \cdot 10^{+06}$	-1804.0	<i>de Semainville et al. (2007a)</i>
E <sub>o</sub> 00059	*	*	$\text{CO(OH)CH(OH)CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{CH(OH)CO(OH)}$	$8.3 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00060	*	*	$\text{CO(OH)CH(OH)CHO} \rightleftharpoons \text{CO(O}^-)\text{CH(OH)CHO} + \text{H}^+$	$1.5 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00640	*	*	$\text{CO(OH)CH(OH)CHO} + \text{OH} \rightarrow 0.929 \text{ CO(OH)CH(OH)CO(OO}\cdot\text{)} +$ $0.071 \text{ CO(OH)CH(O}\cdot\text{)CHO} + \text{H}_2\text{O} - 0.929 \text{ O}_2$	$6.8 \cdot 10^{+08}$		
R <sub>o</sub> 00641	*		$\text{CO(OH)CH(OH)CHO} + \text{NO}_3 \rightarrow 0.929 \text{ CO(OH)CH(OH)CO(OO}\cdot\text{)} +$ $0.071 \text{ CO(OH)CH(O}\cdot\text{)CHO} + \text{NO}_3^- + \text{H}^+ - 0.929 \text{ O}_2$	$6.2 \cdot 10^{+06}$		
R <sub>o</sub> 00642	*	*	$\text{CO(OH)CH(OH)CO(OO}\cdot\text{)} \rightarrow \text{CO(OH)CH(OH)CO(OH)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00643	*	*	$\text{CO(OH)CH(O}\cdot\text{)CHO} \xrightarrow{\text{O}_2} \text{CO(OH)COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00644	*	*	$\text{CO(OH)CH(O}\cdot\text{)CHO} \rightarrow 0.500 \cdot \text{CO(OH)} + 0.500 \text{ CHOCHO} +$ $0.500 \text{ CO(OH)CHO} + 0.500 \text{ CH}\cdot\text{(OH)}_2 - 0.500 \text{ H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00061	*	*	$\text{CO(OH)COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)}_2\text{CO(OH)}$	$1.5 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00062	*	*	$\text{CO(OH)COCHO} \rightleftharpoons \text{CO(O}^-)\text{COCHO} + \text{H}^+$	$4.6 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00645	*	*	$\text{CO(OH)COCHO} + \text{OH} \rightarrow \text{CO(OH)COCO(OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$2.9 \cdot 10^{+08}$		
R <sub>o</sub> 00646	*		$\text{CO(OH)COCHO} + \text{NO}_3 \rightarrow \text{CO(OH)COCO(OO}\cdot) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$2.2 \cdot 10^{+06}$		
E <sub>o</sub> 00063	*	*	$\text{CHOC(OH)}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{COCH(OH)}_2$	$2.5 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00064	*	*	$\text{CHOC(OH)}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)}_2$	$2.7 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00647	*	*	$\text{CHOC(OH)}_2\text{CHO} \rightarrow 0.500 \text{ CHO(OO}\cdot) + 0.500 \text{ CHOC(OH)}_2\text{(OO}\cdot)$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 00648	*	*	$\text{CHOC(OH)}_2\text{CHO} + \text{OH} \rightarrow$ $0.710 \text{ CHOC(OH)}_2\text{CO(OO}\cdot) + 0.290 \text{ CHOC(OH)(O}\cdot\text{)CHO} + \text{H}_2\text{O} - 0.710 \text{ O}_2$	$9.1 \cdot 10^{+08}$		
R <sub>o</sub> 00649	*		$\text{CHOC(OH)}_2\text{CHO} + \text{NO}_3 \rightarrow 0.710 \text{ CHOC(OH)}_2\text{CO(OO}\cdot) +$ $0.290 \text{ CHOC(OH)(O}\cdot\text{)CHO} + \text{NO}_3^- + \text{H}^+ - 0.710 \text{ O}_2$	$6.1 \cdot 10^{+06}$		
R <sub>o</sub> 00650	*	*	$\text{CHOC(OH)}_2\text{CO(OO}\cdot) \rightarrow \text{CO(OH)C(OH)}_2\text{CHO} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00651	*	*	$\text{CHOC(OH)(O}\cdot\text{)CHO} \rightarrow \text{CH}\cdot\text{(OH)}_2 + \text{CO(OH)CHO} - \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00652	*	*	$\text{CH(OH)}_2\text{CH}_2\text{CO(O}^-) + \text{OH} \rightarrow 0.705 \text{ CO(O}^-)\text{CH}_2\text{C(OH)}_2\text{(OO}\cdot) +$ $0.295 \text{ CO(O}^-)\text{CH}_2\text{CH(OH)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.705 \text{ O}_2$	$1.4 \cdot 10^{+09}$		
R <sub>o</sub> 00653	*		$\text{CH(OH)}_2\text{CH}_2\text{CO(O}^-) + \text{NO}_3 \rightarrow \text{CH(OH)}_2\text{CH}_2\text{CO(O}\cdot\text{)} + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 00654	*	*	$\text{CO(O}^-)\text{CH}_2\text{CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CO(OH)CH}_2\text{CO(O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00655	*	*	$\text{CO(O}^-)\text{CH}_2\text{CH(OH)(O}\cdot\text{)} \rightarrow \text{CO(O}^-)\text{CH}_2\text{(OO}\cdot) + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00656	*	*	$\text{CH}_2\text{(OH)C(OH)}_2\text{CO(O}^-) + \text{OH} \rightarrow$ $0.382 \text{ CO(O}^-)\text{C(OH)}_2\text{CH(OH)(OO}\cdot) + 0.098 \text{ CO(O}^-)\text{C(OH)}_2\text{CH}_2\text{(O}\cdot\text{)} +$ $0.520 \text{ CH}_2\text{(OH)C(OH)(O}\cdot\text{)CO(O}^-) + \text{H}_2\text{O} - 0.382 \text{ O}_2$	$8.5 \cdot 10^{+08}$		
R <sub>o</sub> 00657	*		$\text{CH}_2\text{(OH)C(OH)}_2\text{CO(O}^-) + \text{NO}_3 \rightarrow \text{CH}_2\text{(OH)C(OH)}_2\text{CO(O}\cdot\text{)} + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 00658	*	*	$\text{CO(O}^-)\text{C(OH)}_2\text{CH(OH)(OO}\cdot) \rightarrow \text{CO(O}^-)\text{C(OH)}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00659	*	*	$\text{CO(O}^-)\text{C(OH)}_2\text{CH}_2\text{(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CO(O}^-)\text{C(OH)}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00660	*	*	$\text{CO(O}^-)\text{C(OH)}_2\text{CH}_2\text{(O}\cdot\text{)} \rightarrow \text{CO(O}^-)\text{C(OH)}_2\text{(OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00661	*	*	$\text{CH}_2\text{(OH)C(OH)(O}\cdot\text{)CO(O}^-) \rightarrow 0.500 \text{ CH}_2\text{(OH)}\cdot + 0.500 \text{ CO(OH)CO(O}^-) +$ $0.500 \text{ CH}_2\text{(OH)CO(OH)} + 0.500 \cdot \text{CO(O}^-)$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00662	*		$\text{CH}_2\text{(OH)C(OH)}_2\text{CO(O}\cdot\text{)} \rightarrow \text{CH}_2\text{(OH)C(OH)}_2\text{(OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00663	*	*	$\text{CH}_3\text{COCO(O}^-) + \text{OH} \rightarrow \text{CO(O}^-)\text{COCH}_2\text{(OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$7.0 \cdot 10^{+08}$	-2300.0	<i>Ervens et al.</i> (2003b)
R <sub>o</sub> 00664	*		$\text{CH}_3\text{COCO(O}^-) + \text{NO}_3 \rightarrow \text{CH}_3\text{COCO(O}\cdot\text{)} + \text{NO}_3^-$	$1.9 \cdot 10^{+07}$	-2887.0	<i>de Semainville et al.</i> (2007a)
E <sub>o</sub> 00065	*	*	$\text{CO(O}^-)\text{COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{COCO(O}^-)$	$1.4 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00066	*	*	$\text{CO(O}^-)\text{COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)}_2\text{CO(O}^-)$	$3.3 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00665	*	*	$\text{CO}(\text{O}^-)\text{COCHO} + \text{OH} \rightarrow \text{CO}(\text{O}^-)\text{COCO}(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+08}$		
R <sub>o</sub> 00666	*		$\text{CO}(\text{O}^-)\text{COCHO} + \text{NO}_3 \rightarrow \text{CHOCOCO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
E <sub>o</sub> 00067	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}^-)$	$7.4 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00667	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CHO} + \text{OH} \rightarrow$ $0.042 \text{ CO}(\text{O}^-)\text{C}(\text{OH})(\text{OO}\cdot)\text{CHO} + 0.891 \text{ CO}(\text{O}^-)\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) +$ $0.068 \text{ CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{CHO} + \text{H}_2\text{O} - 0.932 \text{ O}_2$	$1.3 \cdot 10^{+09}$		
R <sub>o</sub> 00668	*		$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CHO} + \text{NO}_3 \rightarrow \text{CHOCH}(\text{OH})\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 00669	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00670	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{CHO} \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00671	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{CHO} \rightarrow 0.500 \cdot \text{CO}(\text{O}^-) + 0.500 \text{ CHOCHO} +$ $0.500 \text{ CO}(\text{O}^-)\text{CHO} + 0.500 \text{ CH}\cdot(\text{OH})_2 - 0.500 \text{ H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00068	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{CO}(\text{OH}) \rightleftharpoons \text{CH}_3\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{H}^+$	$8.0 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00672	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{OH} \rightarrow 0.150 \text{ CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) +$ $0.850 \text{ CH}_3\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) + \text{H}_2\text{O} - 0.150 \text{ O}_2$	$3.2 \cdot 10^{+08}$		
R <sub>o</sub> 00673	*		$\text{CH}_3\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{NO}_3 \rightarrow 0.150 \text{ CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) +$ $0.850 \text{ CH}_3\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) + \text{NO}_3^- + \text{H}^+ - 0.150 \text{ O}_2$	$7.5 \cdot 10^{+06}$		
R <sub>o</sub> 00674	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) + 0.550 \text{ CO}(\text{OH})\text{C}(\text{OH})_2\text{CHO} +$ $0.250 \text{ CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OH}) + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00675	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) \rightarrow 0.500 \text{ CH}_3(\text{OO}\cdot) + 0.500 \text{ CO}(\text{OH})\text{CO}(\text{OH}) +$ $0.500 \text{ CH}_3\text{CO}(\text{OH}) + 0.500 \cdot \text{CO}(\text{OH}) - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00069	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) \rightleftharpoons \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{H}^+$	$2.0 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00676	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{OH} \rightarrow$ $0.126 \text{ CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.526 \text{ CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) +$ $0.348 \text{ CH}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) + \text{H}_2\text{O} - 0.126 \text{ O}_2$	$6.9 \cdot 10^{+08}$		
R <sub>o</sub> 00677	*		$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{NO}_3 \rightarrow$ $0.126 \text{ CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.526 \text{ CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) +$ $0.348 \text{ CH}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) + \text{NO}_3^- + \text{H}^+ - 0.126 \text{ O}_2$	$7.4 \cdot 10^{+06}$		
R <sub>o</sub> 00678	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00679	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00680	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CO}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00681	*	*	CH(OH) <sub>2</sub> C(OH)(O·)CO(OH) → 0.500 CH·(OH) <sub>2</sub> + 0.500 CO(OH)CO(OH) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500·CO(OH)	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00070	*	*	CH(OH) <sub>2</sub> CH(OH)CO(OH) ⇌ CH(OH) <sub>2</sub> CH(OH)CO(O <sup>-</sup> ) + H <sup>+</sup>	$8.6 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00682	*	*	CH(OH) <sub>2</sub> CH(OH)CO(OH) + OH → 0.334 CO(OH)CH(OH)C(OH) <sub>2</sub> (OO·) + 0.580 CO(OH)CH(OH)CH(OH)(O·) + 0.086 CH(OH) <sub>2</sub> CH(O·)CO(OH) + H <sub>2</sub> O - 0.334 O <sub>2</sub>	$6.6 \cdot 10^{+08}$		
R <sub>o</sub> 00683	*		CH(OH) <sub>2</sub> CH(OH)CO(OH) + NO <sub>3</sub> → 0.334 CO(OH)CH(OH)C(OH) <sub>2</sub> (OO·) + 0.580 CO(OH)CH(OH)CH(OH)(O·) + 0.086 CH(OH) <sub>2</sub> CH(O·)CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.334 O <sub>2</sub>	$9.6 \cdot 10^{+06}$		
R <sub>o</sub> 00684	*	*	CO(OH)CH(OH)C(OH) <sub>2</sub> (OO·) → CO(OH)CH(OH)CO(OH) + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00685	*	*	CO(OH)CH(OH)CH(OH)(O·) $\xrightarrow{\text{O}_2}$ CO(OH)CH(OH)CO(OH) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00686	*	*	CO(OH)CH(OH)CH(OH)(O·) → CO(OH)CH(OH)(OO·) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00687	*	*	CH(OH) <sub>2</sub> CH(O·)CO(OH) $\xrightarrow{\text{O}_2}$ CH(OH) <sub>2</sub> COCO(OH) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00688	*	*	CH(OH) <sub>2</sub> CH(O·)CO(OH) → 0.500 CH·(OH) <sub>2</sub> + 0.500 CO(OH)CHO + 0.500 CH(OH) <sub>2</sub> CHO + 0.500·CO(OH)	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00071	*	*	CH(OH) <sub>2</sub> COCO(OH) $\xrightleftharpoons{\text{H}_2\text{O}}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH)	$1.5 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00072	*	*	CH(OH) <sub>2</sub> COCO(OH) ⇌ CH(OH) <sub>2</sub> COCO(O <sup>-</sup> ) + H <sup>+</sup>	$1.2 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00689	*	*	CH(OH) <sub>2</sub> COCO(OH) + OH → 0.232 CO(OH)COC(OH) <sub>2</sub> (OO·) + 0.768 CO(OH)COCH(OH)(O·) + H <sub>2</sub> O - 0.232 O <sub>2</sub>	$4.3 \cdot 10^{+08}$		
R <sub>o</sub> 00690	*		CH(OH) <sub>2</sub> COCO(OH) + NO <sub>3</sub> → 0.232 CO(OH)COC(OH) <sub>2</sub> (OO·) + 0.768 CO(OH)COCH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.232 O <sub>2</sub>	$7.3 \cdot 10^{+06}$		
R <sub>o</sub> 00691	*	*	CO(OH)COC(OH) <sub>2</sub> (OO·) → CO(OH)COCO(OH) + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00692	*	*	CO(OH)COCH(OH)(O·) $\xrightarrow{\text{O}_2}$ CO(OH)COCO(OH) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00693	*	*	CO(OH)COCH(OH)(O·) → CO(OH)CO(OO·) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00073	*	*	CO(OH)C(OH) <sub>2</sub> CHO $\xrightleftharpoons{\text{H}_2\text{O}}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH)	$1.5 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00074	*	*	CO(OH)C(OH) <sub>2</sub> CHO ⇌ CO(O <sup>-</sup> )C(OH) <sub>2</sub> CHO + H <sup>+</sup>	$4.0 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00694	*	*	CO(OH)C(OH) <sub>2</sub> CHO + OH → 0.550 CO(OH)C(OH) <sub>2</sub> CO(OO·) + 0.450 CO(OH)C(OH)(O·)CHO + H <sub>2</sub> O - 0.550 O <sub>2</sub>	$4.6 \cdot 10^{+08}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00695	*		$\text{CO(OH)C(OH)}_2\text{CHO} + \text{NO}_3 \rightarrow 0.550 \text{CO(OH)C(OH)}_2\text{CO(OO}\cdot\text{)} + 0.450 \text{CO(OH)C(OH)(O}\cdot\text{)CHO} + \text{NO}_3^- + \text{H}^+ - 0.550 \text{O}_2$	$6.2 \cdot 10^{+06}$		
R <sub>o</sub> 00696	*	*	$\text{CO(OH)C(OH)}_2\text{CO(OO}\cdot\text{)} \rightarrow \text{CO(OH)C(OH)}_2\text{CO(OH)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00697	*	*	$\text{CO(OH)C(OH)(O}\cdot\text{)CHO} \rightarrow 0.500 \cdot \text{CO(OH)} + 0.500 \text{CO(OH)CHO} + 0.500 \text{CO(OH)CO(OH)} + 0.500 \text{CH} \cdot (\text{OH})_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00075	*	*	$\text{CO(OH)CH(OH)CO(OH)} \rightleftharpoons \text{CO(OH)CH(OH)CO(O}^-\text{)} + \text{H}^+$	$7.1 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00698	*	*	$\text{CO(OH)CH(OH)CO(OH)} + \text{OH} \rightarrow 0.111 \text{CO(OH)C(OH)(OO}\cdot\text{)CO(OH)} + 0.857 \text{CO(OH)CH(O}\cdot\text{)CO(OH)} + 0.032 \text{CO(OH)CH(OH)CO(O}\cdot\text{)} + \text{H}_2\text{O} - 0.111 \text{O}_2$	$3.4 \cdot 10^{+08}$	-1112.0	TROPOS measurements
R <sub>o</sub> 00699	*		$\text{CO(OH)CH(OH)CO(OH)} + \text{NO}_3 \rightarrow 0.111 \text{CO(OH)C(OH)(OO}\cdot\text{)CO(OH)} + 0.857 \text{CO(OH)CH(O}\cdot\text{)CO(OH)} + 0.032 \text{CO(OH)CH(OH)CO(O}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - 0.111 \text{O}_2$	$1.4 \cdot 10^{+05}$		
R <sub>o</sub> 00700	*	*	$\text{CO(OH)CH(O}\cdot\text{)CO(OH)} \xrightarrow{\text{O}_2} \text{CO(OH)COCO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00701	*	*	$\text{CO(OH)CH(O}\cdot\text{)CO(OH)} \rightarrow \cdot\text{CO(OH)} + \text{CO(OH)CHO}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00702	*	*	$\text{CO(OH)CH(OH)CO(O}\cdot\text{)} \rightarrow \text{CO(OH)CH(OH)(OO}\cdot\text{)} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00076	*	*	$\text{CO(OH)CH}_2\text{CO(OH)} \rightleftharpoons \text{CO(OH)CH}_2\text{CO(O}^-\text{)} + \text{H}^+$	$3.1 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00703	*	*	$\text{CO(OH)CH}_2\text{CO(OH)} + \text{OH} \rightarrow 0.695 \text{CO(OH)CH(OO}\cdot\text{)CO(OH)} + 0.305 \text{CO(OH)CH}_2\text{CO(O}\cdot\text{)} + \text{H}_2\text{O} - 0.695 \text{O}_2$	$2.0 \cdot 10^{+07}$		Buxton <i>et al.</i> (1988a)
R <sub>o</sub> 00704	*		$\text{CO(OH)CH}_2\text{CO(OH)} + \text{NO}_3 \rightarrow 0.695 \text{CO(OH)CH(OO}\cdot\text{)CO(OH)} + 0.305 \text{CO(OH)CH}_2\text{CO(O}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - 0.695 \text{O}_2$	$5.1 \cdot 10^{+04}$		de Semainville <i>et al.</i> (2007a)
R <sub>o</sub> 00705	*	*	$\text{CO(OH)CH}_2\text{CO(O}\cdot\text{)} \rightarrow \text{CO(OH)CH}_2\text{(OO}\cdot\text{)} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00706	*	*	$\text{CH}_3\text{C(OH)}_2\text{CO(O}^-\text{)} + \text{OH} \rightarrow 0.150 \text{CO(O}^-\text{)C(OH)}_2\text{CH}_2\text{(OO}\cdot\text{)} + 0.850 \text{CH}_3\text{C(OH)(O}\cdot\text{)CO(O}^-\text{)} + \text{H}_2\text{O} - 0.150 \text{O}_2$	$5.5 \cdot 10^{+08}$		
R <sub>o</sub> 00707	*		$\text{CH}_3\text{C(OH)}_2\text{CO(O}^-\text{)} + \text{NO}_3 \rightarrow \text{CH}_3\text{C(OH)}_2\text{CO(O}\cdot\text{)} + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 00708	*	*	$\text{CO(O}^-\text{)C(OH)}_2\text{CH}_2\text{(OO}\cdot\text{)} \xrightarrow{\text{RO}_2} 0.200 \text{CO(O}^-\text{)C(OH)}_2\text{CH}_2\text{(O}\cdot\text{)} + 0.550 \text{CO(O}^-\text{)C(OH)}_2\text{CHO} + 0.250 \text{CH}_2\text{(OH)C(OH)}_2\text{CO(O}^-\text{)} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00709	*	*	$\text{CH}_3\text{C(OH)(O}\cdot\text{)CO(O}^-\text{)} \rightarrow 0.500 \text{CH}_3\text{(OO}\cdot\text{)} + 0.500 \text{CO(OH)CO(O}^-\text{)} + 0.500 \text{CH}_3\text{CO(OH)} + 0.500 \cdot \text{CO(O}^-\text{)} - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00710	*		$\text{CH}_3\text{C(OH)}_2\text{CO(O}\cdot\text{)} \rightarrow \text{CH}_3\text{C(OH)}_2\text{(OO}\cdot\text{)} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00711	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + OH → 0.163 CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.387 CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)(O·) + 0.450 CH(OH) <sub>2</sub> C(OH)(O·)CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.163 O <sub>2</sub>	9.4 · 10 <sup>+08</sup>		
R <sub>o</sub> 00712	*		CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 00713	*	*	CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CO(OH)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 00714	*	*	CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 00715	*	*	CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)(O·) → CO(O <sup>-</sup> )C(OH) <sub>2</sub> (OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00716	*	*	CH(OH) <sub>2</sub> C(OH)(O·)CO(O <sup>-</sup> ) → 0.500 CH·(OH) <sub>2</sub> + 0.500 CO(OH)CO(O <sup>-</sup> ) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 · CO(O <sup>-</sup> )	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00717	*		CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O·) → CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00718	*	*	CH(OH) <sub>2</sub> CH(OH)CO(O <sup>-</sup> ) + OH → 0.421 CO(O <sup>-</sup> )CH(OH)C(OH) <sub>2</sub> (OO·) + 0.056 CH(OH) <sub>2</sub> C(OH)(OO·)CO(O <sup>-</sup> ) + 0.416 CO(O <sup>-</sup> )CH(OH)CH(OH)(O·) + 0.108 CH(OH) <sub>2</sub> CH(O·)CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.476 O <sub>2</sub>	9.2 · 10 <sup>+08</sup>		
R <sub>o</sub> 00719	*		CH(OH) <sub>2</sub> CH(OH)CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH(OH) <sub>2</sub> CH(OH)CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 00720	*	*	CO(O <sup>-</sup> )CH(OH)C(OH) <sub>2</sub> (OO·) → CO(OH)CH(OH)CO(O <sup>-</sup> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 00721	*	*	CH(OH) <sub>2</sub> C(OH)(OO·)CO(O <sup>-</sup> ) → CH(OH) <sub>2</sub> COCO(O <sup>-</sup> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00722	*	*	CO(O <sup>-</sup> )CH(OH)CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH(OH)CO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 00723	*	*	CO(O <sup>-</sup> )CH(OH)CH(OH)(O·) → CO(O <sup>-</sup> )CH(OH)(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00724	*	*	CH(OH) <sub>2</sub> CH(O·)CO(O <sup>-</sup> ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 00725	*	*	CH(OH) <sub>2</sub> CH(O·)CO(O <sup>-</sup> ) → 0.500 CH·(OH) <sub>2</sub> + 0.500 CO(O <sup>-</sup> )CHO + 0.500 CH(OH) <sub>2</sub> CHO + 0.500 · CO(O <sup>-</sup> )	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00726	*		CH(OH) <sub>2</sub> CH(OH)CO(O·) → CH(OH) <sub>2</sub> CH(OH)(OO·) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00727	*	*	CH(OH) <sub>2</sub> COCO(O <sup>-</sup> ) + OH → 0.347 CO(O <sup>-</sup> )COC(OH) <sub>2</sub> (OO·) + 0.653 CO(O <sup>-</sup> )COCH(OH)(O·) + H <sub>2</sub> O - 0.347 O <sub>2</sub>	5.0 · 10 <sup>+08</sup>		
R <sub>o</sub> 00728	*		CH(OH) <sub>2</sub> COCO(O <sup>-</sup> ) + NO <sub>3</sub> → CH(OH) <sub>2</sub> COCO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 00729	*	*	CO(O <sup>-</sup> )COC(OH) <sub>2</sub> (OO·) → CO(OH)COCO(O <sup>-</sup> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 00730	*	*	CO(O <sup>-</sup> )COCH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)COCO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 00731	*	*	CO(O <sup>-</sup> )COCH(OH)(O·) → CO(O <sup>-</sup> )CO(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00732	*		CH(OH) <sub>2</sub> COCO(O·) → CH(OH) <sub>2</sub> CO(OO·) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00077	*	*	CO(O <sup>-</sup> )C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> COCO(O <sup>-</sup> )	1.4 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00078	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}^-)$	$3.3 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00733	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CHO} + \text{OH} \rightarrow 0.550 \text{ CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) + 0.450 \text{ CO}(\text{O}^-)\text{C}(\text{OH})(\text{O}\cdot)\text{CHO} + \text{H}_2\text{O} - 0.550 \text{ O}_2$	$8.0 \cdot 10^{+08}$		
R <sub>o</sub> 00734	*		$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CHO} + \text{NO}_3 \rightarrow \text{CHOC}(\text{OH})_2\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 00735	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 00736	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{O}\cdot)\text{CHO} \rightarrow 0.500 \cdot \text{CO}(\text{O}^-) + 0.500 \text{ CO}(\text{OH})\text{CHO} + 0.500 \text{ CO}(\text{OH})\text{CO}(\text{O}^-) + 0.500 \text{ CH} \cdot (\text{OH})_2 - 0.500 \text{ H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00737	*		$\text{CHOC}(\text{OH})_2\text{CO}(\text{O}\cdot) \rightarrow \text{CHOC}(\text{OH})_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00079	*	*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^-) \rightleftharpoons \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{H}^+$	$4.1 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00738	*	*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{OH} \rightarrow 0.201 \text{ CO}(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{O}^-) + 0.799 \text{ CO}(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) + \text{H}_2\text{O} - 0.201 \text{ O}_2$	$3.6 \cdot 10^{+08}$		Schuchmann et al. (1995)
R <sub>o</sub> 00739	*		$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 00740	*	*	$\text{CO}(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{COCO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00741	*	*	$\text{CO}(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) \rightarrow 0.500 \cdot \text{CO}(\text{OH}) + 0.500 \text{ CO}(\text{O}^-)\text{CHO} + 0.500 \text{ CO}(\text{OH})\text{CHO} + 0.500 \cdot \text{CO}(\text{O}^-)$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00080	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{CO}(\text{O}^-) \rightleftharpoons \text{CO}(\text{O}^-)\text{CH}_2\text{CO}(\text{O}^-) + \text{H}^+$	$1.7 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00742	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{CO}(\text{O}^-) + \text{OH} \rightarrow 0.940 \text{ CO}(\text{OH})\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) + 0.060 \text{ CO}(\text{O}^-)\text{CH}_2\text{CO}(\text{O}\cdot) + \text{H}_2\text{O} - 0.940 \text{ O}_2$	$6.0 \cdot 10^{+07}$	-1300.0	Ervens et al. (2003b)
R <sub>o</sub> 00743	*		$\text{CO}(\text{OH})\text{CH}_2\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow \text{CO}(\text{OH})\text{CH}_2\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$5.6 \cdot 10^{+06}$	-3368.0	de Semainville et al. (2007a)
R <sub>o</sub> 00744	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CO}(\text{O}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{CH}_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00081	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OH}) \rightleftharpoons \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{H}^+$	$1.9 \cdot 10^{-03}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00745	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{OH} \rightarrow \text{CO}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) + \text{H}_2\text{O}$	$1.6 \cdot 10^{+08}$		
R <sub>o</sub> 00746	*		$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{NO}_3 \rightarrow \text{CO}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) + \text{NO}_3^- + \text{H}^+$	$6.2 \cdot 10^{+06}$		
R <sub>o</sub> 00747	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) \rightarrow \cdot\text{CO}(\text{OH}) + \text{CO}(\text{OH})\text{CO}(\text{OH})$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00748	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CO}(\text{O}^-) + \text{OH} \rightarrow \text{CO}(\text{O}^-)\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{H}_2\text{O} - \text{O}_2$	$2.7 \cdot 10^{+08}$		Average of Logan (1989) and Adams et al. (1965a)
R <sub>o</sub> 00749	*		$\text{CO}(\text{O}^-)\text{CH}_2\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow 0.500 \text{ CO}(\text{O}^-)\text{CH}_2\text{CO}(\text{O}\cdot) + 0.500 \text{ CO}(\text{O}^-)\text{CH}_2\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.3 \cdot 10^{+07}$	-3007.0	de Semainville et al. (2007a)
R <sub>o</sub> 00750	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{OH} \rightarrow 0.329 \text{ CO}(\text{O}^-)\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{O}^-) + 0.671 \text{ CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) + \text{H}_2\text{O} - 0.329 \text{ O}_2$	$4.4 \cdot 10^{+08}$		Schuchmann et al. (1995)



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00751	*		$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CO}(\text{O}^\cdot) + 0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CO}(\text{O}^\cdot) + \text{NO}_3^-$	$7.8 \cdot 10^{+07}$		
R <sub>o</sub> 00752	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{OO}^\cdot)\text{CO}(\text{O}^-) \rightarrow \text{CO}(\text{O}^-)\text{COCO}(\text{O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00753	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{O}^\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{COCO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00754	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{O}^\cdot)\text{CO}(\text{O}^-) \rightarrow \cdot\text{CO}(\text{O}^-) + \text{CO}(\text{O}^-)\text{CHO}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00755	*		$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CO}(\text{O}^\cdot) \rightarrow \text{CO}(\text{O}^-)\text{CH}(\text{OH})(\text{OO}^\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00082	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{O}^-) \rightleftharpoons \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{H}^+$	$8.0 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00756	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{OH} \rightarrow \text{CO}(\text{OH})\text{C}(\text{OH})(\text{O}^\cdot)\text{CO}(\text{O}^-) + \text{H}_2\text{O}$	$2.8 \cdot 10^{+08}$		
R <sub>o</sub> 00757	*		$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{O}^\cdot) + \text{NO}_3^-$	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 00758	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})(\text{O}^\cdot)\text{CO}(\text{O}^-) \rightarrow 0.500 \cdot \text{CO}(\text{OH}) + 0.500 \text{CO}(\text{OH})\text{CO}(\text{O}^-) +$ $0.500 \text{CO}(\text{OH})\text{CO}(\text{OH}) + 0.500 \cdot \text{CO}(\text{O}^-)$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00759	*		$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{O}^\cdot) \rightarrow \text{CO}(\text{OH})\text{C}(\text{OH})_2(\text{OO}^\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00760	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{OH} \rightarrow \text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{O}^\cdot)\text{CO}(\text{O}^-) + \text{H}_2\text{O}$	$4.9 \cdot 10^{+08}$		
R <sub>o</sub> 00761	*		$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $0.500 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CO}(\text{O}^\cdot) + 0.500 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CO}(\text{O}^\cdot) + \text{NO}_3^-$	$7.8 \cdot 10^{+07}$		
R <sub>o</sub> 00762	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{O}^\cdot)\text{CO}(\text{O}^-) \rightarrow \cdot\text{CO}(\text{O}^-) + \text{CO}(\text{OH})\text{CO}(\text{O}^-)$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00763	*		$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CO}(\text{O}^\cdot) \rightarrow \text{CO}(\text{O}^-)\text{C}(\text{OH})_2(\text{OO}^\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00083	*	*	$\text{CH}_3\text{CH}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{CH}(\text{OH})_2$	$1.2 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00764	*	*	$\text{CH}_3\text{CH}_2\text{CHO} + \text{OH} \rightarrow 0.119 \text{CHOCH}_2\text{CH}_2(\text{OO}^\cdot) +$ $0.059 \text{CH}_3\text{CH}(\text{OO}^\cdot)\text{CHO} + 0.822 \text{CH}_3\text{CH}_2\text{CO}(\text{OO}^\cdot) + \text{H}_2\text{O} - \text{O}_2$	$2.8 \cdot 10^{+09}$	-1300.0	<i>Hesper</i> (2003)
R <sub>o</sub> 00765	*		$\text{CH}_3\text{CH}_2\text{CHO} + \text{NO}_3 \rightarrow 0.119 \text{CHOCH}_2\text{CH}_2(\text{OO}^\cdot) +$ $0.059 \text{CH}_3\text{CH}(\text{OO}^\cdot)\text{CHO} + 0.822 \text{CH}_3\text{CH}_2\text{CO}(\text{OO}^\cdot) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$5.8 \cdot 10^{+07}$	-2646.0	<i>de Semainville et al.</i> (2007a)
R <sub>o</sub> 00766	*	*	$\text{CHOCH}_2\text{CH}_2(\text{OO}^\cdot) \xrightarrow{\text{RO}_2} 0.200 \text{CHOCH}_2\text{CH}_2(\text{O}^\cdot) + 0.550 \text{CHOCH}_2\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{CH}_2\text{CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00767	*	*	$\text{CH}_3\text{CH}(\text{OO}^\cdot)\text{CHO} \xrightarrow{\text{RO}_2} 0.200 \text{CH}_3\text{CH}(\text{O}^\cdot)\text{CHO} + 0.550 \text{CH}_3\text{COCHO} +$ $0.250 \text{CH}_3\text{CH}(\text{OH})\text{CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00768	*	*	$\text{CHOCH}_2\text{CH}_2(\text{O}^\cdot) \xrightarrow{\text{O}_2} \text{CHOCH}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00769	*	*	$\text{CHOCH}_2\text{CH}_2(\text{O}^\cdot) \rightarrow \text{CHOCH}_2(\text{OO}^\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00770	*	*	$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})_2 + \text{OH} \rightarrow$ $0.229 \text{CH}(\text{OH})_2\text{CH}_2\text{CH}_2(\text{OO}^\cdot) + 0.096 \text{CH}_3\text{CH}(\text{OO}^\cdot)\text{CH}(\text{OH})_2 +$ $0.469 \text{CH}_3\text{CH}_2\text{C}(\text{OH})_2(\text{OO}^\cdot) + 0.206 \text{CH}_3\text{CH}_2\text{CH}(\text{OH})(\text{O}^\cdot) + \text{H}_2\text{O} - 0.794 \text{O}_2$	$1.9 \cdot 10^{+09}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00771	*		$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})_2 + \text{NO}_3 \rightarrow 0.229 \text{CH}(\text{OH})_2\text{CH}_2\text{CH}_2(\text{OO}\cdot) +$ $0.096 \text{CH}_3\text{CH}(\text{OO}\cdot)\text{CH}(\text{OH})_2 + 0.469 \text{CH}_3\text{CH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.206 \text{CH}_3\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.794 \text{O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 00772	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}(\text{OH})_2\text{CH}_2\text{CH}_2(\text{O}\cdot) + 0.550 \text{CH}(\text{OH})_2\text{CH}_2\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})_2 + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00773	*	*	$\text{CH}_3\text{CH}(\text{OO}\cdot)\text{CH}(\text{OH})_2 \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})_2 + 0.550 \text{CH}_3\text{COCH}(\text{OH})_2 +$ $0.250 \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})_2 + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00774	*	*	$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_3\text{CH}_2\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00775	*	*	$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CH}_3\text{CH}_2(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00776	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{CH}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00777	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00084	*	*	$\text{CH}_3\text{CH}_2\text{CO}(\text{OH}) \rightleftharpoons \text{CH}_3\text{CH}_2\text{CO}(\text{O}^-) + \text{H}^+$	$1.7 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00778	*	*	$\text{CH}_3\text{CH}_2\text{CO}(\text{OH}) + \text{OH} \rightarrow$ $0.830 \text{CO}(\text{OH})\text{CH}_2\text{CH}_2(\text{OO}\cdot) + 0.170 \text{CH}_3\text{CH}(\text{OO}\cdot)\text{CO}(\text{OH}) + \text{H}_2\text{O} - \text{O}_2$	$3.2 \cdot 10^{+08}$	-2300.0	<i>Ervens et al.</i> (2003b)
R <sub>o</sub> 00779	*		$\text{CH}_3\text{CH}_2\text{CO}(\text{OH}) + \text{NO}_3 \rightarrow 0.830 \text{CO}(\text{OH})\text{CH}_2\text{CH}_2(\text{OO}\cdot) +$ $0.170 \text{CH}_3\text{CH}(\text{OO}\cdot)\text{CO}(\text{OH}) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$7.7 \cdot 10^{+04}$		<i>Rousse and George</i> (2004)
R <sub>o</sub> 00780	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CO}(\text{OH})\text{CH}_2\text{CH}_2(\text{O}\cdot) + 0.550 \text{CO}(\text{OH})\text{CH}_2\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{CH}_2\text{CO}(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00781	*	*	$\text{CH}_3\text{CH}_2\text{CO}(\text{O}^-) + \text{OH} \rightarrow$ $0.715 \text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2(\text{OO}\cdot) + 0.285 \text{CH}_3\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{H}_2\text{O} - \text{O}_2$	$7.2 \cdot 10^{+08}$	-1800.0	<i>Ervens et al.</i> (2003b)
R <sub>o</sub> 00782	*		$\text{CH}_3\text{CH}_2\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 00783	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2(\text{O}\cdot) + 0.550 \text{CO}(\text{O}^-)\text{CH}_2\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{CH}_2\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00784	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + \text{OH} \rightarrow 0.178 \text{CH}_3\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) +$ $0.776 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_3 + 0.047 \text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}_3 + \text{H}_2\text{O} - 0.953 \text{O}_2$	$2.1 \cdot 10^{+09}$	-962.0	<i>Hesper</i> (2003)
R <sub>o</sub> 00785	*		$\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + \text{NO}_3 \rightarrow 0.178 \text{CH}_3\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) +$ $0.776 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_3 + 0.047 \text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}_3 + \text{NO}_3^- + \text{H}^+ - 0.953 \text{O}_2$	$3.7 \cdot 10^{+06}$	-1323.0	<i>Herrmann et al.</i> (1994) with <i>Ito et al.</i> (1989b)

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00786	*	*	CH <sub>3</sub> CH(OH)CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>3</sub> CH(OH)CH <sub>2</sub> (O·) + 0.550 CH <sub>3</sub> CH(OH)CHO + 0.250 CH <sub>3</sub> CH(OH)CH <sub>2</sub> (OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 00787	*	*	CH <sub>3</sub> CH(O·)CH <sub>3</sub> $\xrightarrow{O_2}$ CH <sub>3</sub> COCH <sub>3</sub> + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 00788	*	*	CH <sub>3</sub> CH(O·)CH <sub>3</sub> → CH <sub>3</sub> (OO·) + CH <sub>3</sub> CHO – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00789	*	*	CH <sub>3</sub> COCH <sub>3</sub> + OH → CH <sub>3</sub> COCH <sub>2</sub> (OO·) + H <sub>2</sub> O – O <sub>2</sub>	1.7 · 10 <sup>+08</sup>	–1788.0	Average of measurements within MOST
R <sub>o</sub> 00790	*		CH <sub>3</sub> COCH <sub>3</sub> + NO <sub>3</sub> → CH <sub>3</sub> COCH <sub>2</sub> (OO·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – O <sub>2</sub>	3.7 · 10 <sup>+03</sup>	–4330.0	Herrmann and Zellner (1998)
E <sub>o</sub> 00085	*	*	CO(OH)CH <sub>2</sub> CH <sub>2</sub> CO(OH) ⇌ CO(OH)CH <sub>2</sub> CH <sub>2</sub> CO(O <sup>–</sup> ) + H <sup>+</sup>	1.4 · 10 <sup>–04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00791	*	*	CO(OH)CH <sub>2</sub> CH <sub>2</sub> CO(OH) + OH → CO(OH)CH <sub>2</sub> CH(OO·)CO(OH) + H <sub>2</sub> O – O <sub>2</sub>	1.1 · 10 <sup>+08</sup>	–1278.0	Ervens et al. (2003b)
R <sub>o</sub> 00792	*		CO(OH)CH <sub>2</sub> CH <sub>2</sub> CO(OH) + NO <sub>3</sub> → CO(OH)CH <sub>2</sub> CH(OO·)CO(OH) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – O <sub>2</sub>	5.0 · 10 <sup>+03</sup>		de Semainville et al. (2007a)
E <sub>o</sub> 00086	*	*	CO(OH)CH <sub>2</sub> CH <sub>2</sub> CO(O <sup>–</sup> ) ⇌ CO(O <sup>–</sup> )CH <sub>2</sub> CH <sub>2</sub> CO(O <sup>–</sup> ) + H <sup>+</sup>	1.7 · 10 <sup>–05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00793	*	*	CO(OH)CH <sub>2</sub> CH <sub>2</sub> CO(O <sup>–</sup> ) + OH → 0.339 CO(OH)CH(OO·)CH <sub>2</sub> CO(O <sup>–</sup> ) + 0.661 CO(OH)CH <sub>2</sub> CH(OO·)CO(O <sup>–</sup> ) + H <sub>2</sub> O – O <sub>2</sub>	2.6 · 10 <sup>+08</sup>	–1808.0	TROPOS measurements
R <sub>o</sub> 00794	*		CO(OH)CH <sub>2</sub> CH <sub>2</sub> CO(O <sup>–</sup> ) + NO <sub>3</sub> → CO(OH)CH <sub>2</sub> CH <sub>2</sub> CO(O·) + NO <sub>3</sub> <sup>–</sup>	1.1 · 10 <sup>+07</sup>		de Semainville et al. (2007a)
R <sub>o</sub> 00795	*	*	CO(OH)CH <sub>2</sub> CH(OO·)CO(O <sup>–</sup> ) + CO(OH)CH <sub>2</sub> CH(OO·)CO(O <sup>–</sup> ) → 2.000 CO(OH)CH <sub>2</sub> CHO + 2.000 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2.000 OH <sup>–</sup> – 2.000 H <sub>2</sub> O	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 00796	*	*	CO(OH)CH <sub>2</sub> CH(OO·)CO(O <sup>–</sup> ) $\xrightarrow{RO_2}$ 0.200 CO(OH)CH <sub>2</sub> CH(O·)CO(O <sup>–</sup> ) + 0.550 CO(OH)CH <sub>2</sub> COCO(O <sup>–</sup> ) + 0.250 CO(OH)CH <sub>2</sub> CH(OH)CO(O <sup>–</sup> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 00797	*	*	CO(OH)CH <sub>2</sub> CH(O·)CO(O <sup>–</sup> ) $\xrightarrow{O_2}$ CO(OH)CH <sub>2</sub> COCO(O <sup>–</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 00798	*	*	CO(OH)CH <sub>2</sub> CH(O·)CO(O <sup>–</sup> ) → 0.500 CO(OH)CH <sub>2</sub> (OO·) + 0.500 CO(O <sup>–</sup> )CHO + 0.500 CO(OH)CH <sub>2</sub> CHO + 0.500 · CO(O <sup>–</sup> ) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00799	*	*	CO(O <sup>–</sup> )CH <sub>2</sub> CH <sub>2</sub> CO(O <sup>–</sup> ) + OH → CO(O <sup>–</sup> )CH <sub>2</sub> CH(OO·)CO(O <sup>–</sup> ) + H <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+08</sup>	–1413.0	Ervens et al. (2003b)
R <sub>o</sub> 00800	*		CO(O <sup>–</sup> )CH <sub>2</sub> CH <sub>2</sub> CO(O <sup>–</sup> ) + NO <sub>3</sub> → 0.500 CO(O <sup>–</sup> )CH <sub>2</sub> CH <sub>2</sub> CO(O·) + 0.500 CO(O <sup>–</sup> )CH <sub>2</sub> CH <sub>2</sub> CO(O·) + NO <sub>3</sub> <sup>–</sup>	1.8 · 10 <sup>+07</sup>	–3127.0	de Semainville et al. (2007a)
E <sub>o</sub> 00087	*	*	CO(OH)CH <sub>2</sub> CH(OH)CO(O <sup>–</sup> ) ⇌ CO(O <sup>–</sup> )CH <sub>2</sub> CH(OH)CO(O <sup>–</sup> ) + H <sup>+</sup>	2.5 · 10 <sup>–05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
E <sub>o</sub> 00088	*	*	CO(OH)CH <sub>2</sub> CH(OH)CO(OH) ⇌ CO(OH)CH(OH)CH <sub>2</sub> CO(O <sup>–</sup> ) + H <sup>+</sup>	2.5 · 10 <sup>–05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00089	*	*	$\text{CO(OH)CH}_2\text{CH(OH)CO(OH)} \rightleftharpoons \text{CO(OH)CH}_2\text{CH(OH)CO(O}^-) + \text{H}^+$	$6.7 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00801	*	*	$\text{CO(OH)CH}_2\text{CH(OH)CO(O}^-) + \text{OH} \rightarrow$ $0.082 \text{ CO(OH)CH(OO}\cdot\text{)CH(OH)CO(O}^-) +$ $0.605 \text{ CO(OH)CH}_2\text{C(OH)(OO}\cdot\text{)CO(O}^-) +$ $0.313 \text{ CO(OH)CH}_2\text{CH(O}\cdot\text{)CO(O}^-) + \text{H}_2\text{O} - 0.687 \text{ O}_2$	$3.3 \cdot 10^{+08}$		
R <sub>o</sub> 00802	*		$\text{CO(OH)CH}_2\text{CH(OH)CO(O}^-) + \text{NO}_3 \rightarrow$ $\text{CO(OH)CH}_2\text{CH(OH)CO(O}\cdot\text{) + NO}_3^-$	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 00803	*	*	$\text{CO(OH)CH(OO}\cdot\text{)CH(OH)CO(O}^-) + \text{CO(OH)CH(OO}\cdot\text{)CH(OH)CO(O}^-) \rightarrow$ $2.000 \text{ CO(O}^-)\text{CH(OH)CHO} + 2.000 \text{ CO}_2 + -\text{O}_2-$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 00804	*	*	$\text{CO(OH)CH(OO}\cdot\text{)CH(OH)CO(O}^-) \xrightarrow{RO_2}$ $0.200 \text{ CO(OH)CH(O}\cdot\text{)CH(OH)CO(O}^-) +$ $0.550 \text{ CO(OH)COCH(OH)CO(O}^-) +$ $0.250 \text{ CO(OH)CH(OH)CH(OH)CO(O}^-) + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00805	*	*	$\text{CO(OH)CH}_2\text{C(OH)(OO}\cdot\text{)CO(O}^-) \rightarrow \text{CO(OH)CH}_2\text{COCO(O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00806	*		$\text{CO(OH)CH}_2\text{CH(OH)CO(O}\cdot\text{) } \rightarrow \text{CO(OH)CH}_2\text{CH(OH)(OO}\cdot\text{) + CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00807	*	*	$\text{CO(OH)CH(O}\cdot\text{)CH(OH)CO(O}^-) \xrightarrow{O_2} \text{CO(OH)COCH(OH)CO(O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00808	*	*	$\text{CO(OH)CH(O}\cdot\text{)CH(OH)CO(O}^-) \rightarrow$ $0.500 \cdot \text{CO(OH)} + 0.500 \text{ CO(O}^-)\text{CH(OH)CHO} + 0.500 \text{ CO(OH)CHO} +$ $0.500 \text{ CO(O}^-)\text{CH(OH)(OO}\cdot\text{) - 0.500 O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00090	*	*	$\text{CO(OH)CH}_2\text{COCO(O}^-) \rightleftharpoons \text{CO(O}^-)\text{CH}_2\text{COCO(O}^-) + \text{H}^+$	$5.3 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
E <sub>o</sub> 00091	*	*	$\text{CO(OH)CH}_2\text{COCO(OH)} \rightleftharpoons \text{CO(OH)COCH}_2\text{CO(O}^-) + \text{H}^+$	$5.3 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
E <sub>o</sub> 00092	*	*	$\text{CO(OH)CH}_2\text{COCO(OH)} \rightleftharpoons \text{CO(OH)CH}_2\text{COCO(O}^-) + \text{H}^+$	$6.5 \cdot 10^{-02}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00809	*	*	$\text{CO(OH)CH}_2\text{COCO(O}^-) + \text{OH} \rightarrow 0.946 \text{ CO(OH)CH(OO}\cdot\text{)COCO(O}^-) +$ $0.054 \text{ CO(O}^-)\text{COCH}_2\text{CO(O}\cdot\text{) + H}_2\text{O} - 0.946 \text{ O}_2$	$1.3 \cdot 10^{+07}$		
R <sub>o</sub> 00810	*		$\text{CO(OH)CH}_2\text{COCO(O}^-) + \text{NO}_3 \rightarrow \text{CO(OH)CH}_2\text{COCO(O}\cdot\text{) + NO}_3^-$	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 00811	*	*	$\text{CO(OH)CH(OO}\cdot\text{)COCO(O}^-) + \text{CO(OH)CH(OO}\cdot\text{)COCO(O}^-) \rightarrow$ $2.000 \text{ CO(O}^-)\text{COCHO} + 2.000 \text{ CO}_2 + -\text{O}_2-$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 00812	*	*	$\text{CO(OH)CH(OO}\cdot\text{)COCO(O}^-) \xrightarrow{RO_2}$ $0.200 \text{ CO(OH)CH(O}\cdot\text{)COCO(O}^-) + 0.550 \text{ CO(OH)COCOCO(O}^-) +$ $0.250 \text{ CO(OH)CH(OH)COCO(O}^-) + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00813	*	*	$\text{CO(O}^-)\text{COCH}_2\text{CO(O}\cdot\text{) } \rightarrow \text{CO(O}^-)\text{COCH}_2\text{(OO}\cdot\text{) + CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00814	*	*	$\text{CO(OH)CH}_2\text{COCO(O}\cdot\text{)} \rightarrow \text{CO(OH)CH}_2\text{CO(OO}\cdot\text{)} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00815	*	*	$\text{CO(OH)CH(O}\cdot\text{)COCO(O}^-) \xrightarrow{\text{O}_2} \text{CO(OH)COCOCO(O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00816	*	*	$\text{CO(OH)CH(O}\cdot\text{)COCO(O}^-) \rightarrow 0.500 \cdot \text{CO(OH)} + 0.500 \text{CO(O}^-)\text{COCHO} +$ $0.500 \text{CO(OH)CHO} + 0.500 \text{CO(O}^-)\text{CO(OO}\cdot\text{)} - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00817	*	*	$\text{CO(OH)CH}_2\text{CO(OO}\cdot\text{)} \rightarrow \text{CO(OH)CH}_2\text{CO(OH)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
E <sub>o</sub> 00093	*	*	$\text{CO(OH)CH(OH)CH}_2\text{CO(O}^-) \rightleftharpoons \text{CO(O}^-)\text{CH}_2\text{CH(OH)CO(O}^-) + \text{H}^+$	$2.3 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00818	*	*	$\text{CO(O}^-)\text{CH}_2\text{CH(OH)CO(O}^-) + \text{OH} \rightarrow$ $0.170 \text{CO(O}^-)\text{CH(OH)CH(OO}\cdot\text{)CO(O}^-) +$ $0.641 \text{CO(O}^-)\text{CH}_2\text{C(OH)(OO}\cdot\text{)CO(O}^-) +$ $0.188 \text{CO(O}^-)\text{CH}_2\text{CH(O}\cdot\text{)CO(O}^-) + \text{H}_2\text{O} - 0.812 \text{O}_2$	$8.5 \cdot 10^{+08}$	-1449.0	<i>Gligorovski et al.</i> (2009)
R <sub>o</sub> 00819	*		$\text{CO(O}^-)\text{CH}_2\text{CH(OH)CO(O}^-) + \text{NO}_3 \rightarrow$ $0.500 \text{CO(O}^-)\text{CH(OH)CH}_2\text{CO(O}\cdot\text{)} + 0.500 \text{CO(O}^-)\text{CH}_2\text{CH(OH)CO(O}\cdot\text{)} +$ $\text{NO}_3^-$	$7.8 \cdot 10^{+07}$		
R <sub>o</sub> 00820	*	*	$\text{CO(O}^-)\text{CH(OH)CH(OO}\cdot\text{)CO(O}^-) + \text{CO(O}^-)\text{CH(OH)CH(OO}\cdot\text{)CO(O}^-) \rightarrow$ $2.000 \text{CO(O}^-)\text{CH(OH)CHO} + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 00821	*	*	$\text{CO(O}^-)\text{CH(OH)CH(OO}\cdot\text{)CO(O}^-) \xrightarrow{\text{RO}_2}$ $0.200 \text{CO(O}^-)\text{CH(OH)CH(O}\cdot\text{)CO(O}^-) + 0.550 \text{CO(O}^-)\text{CH(OH)COCO(O}^-) +$ $0.250 \text{CO(O}^-)\text{CH(OH)CH(OH)CO(O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00822	*	*	$\text{CO(O}^-)\text{CH}_2\text{C(OH)(OO}\cdot\text{)CO(O}^-) \rightarrow \text{CO(O}^-)\text{CH}_2\text{COCO(O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00823	*	*	$\text{CO(O}^-)\text{CH}_2\text{CH(O}\cdot\text{)CO(O}^-) \xrightarrow{\text{O}_2} \text{CO(O}^-)\text{CH}_2\text{COCO(O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00824	*	*	$\text{CO(O}^-)\text{CH}_2\text{CH(O}\cdot\text{)CO(O}^-) \rightarrow 0.500 \text{CO(O}^-)\text{CH}_2\text{(OO}\cdot\text{)} +$ $0.500 \text{CO(O}^-)\text{CHO} + 0.500 \text{CO(O}^-)\text{CH}_2\text{CHO} + 0.500 \cdot \text{CO(O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00825	*		$\text{CO(O}^-)\text{CH(OH)CH}_2\text{CO(O}\cdot\text{)} \rightarrow \text{CO(O}^-)\text{CH(OH)CH}_2\text{(OO}\cdot\text{)} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00826	*		$\text{CO(O}^-)\text{CH}_2\text{CH(OH)CO(O}\cdot\text{)} \rightarrow \text{CO(O}^-)\text{CH}_2\text{CH(OH)(OO}\cdot\text{)} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00827	*	*	$\text{CO(O}^-)\text{CH(OH)CH(O}\cdot\text{)CO(O}^-) \xrightarrow{\text{O}_2} \text{CO(O}^-)\text{CH(OH)COCO(O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00828	*	*	$\text{CO(O}^-)\text{CH(OH)CH(O}\cdot\text{)CO(O}^-) \rightarrow 0.500 \text{CO(O}^-)\text{CH(OH)(OO}\cdot\text{)} +$ $0.500 \text{CO(O}^-)\text{CHO} + 0.500 \text{CO(O}^-)\text{CH(OH)CHO} + 0.500 \cdot \text{CO(O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00094	*	*	$\text{CO(OH)CH(OH)COCO(O}^-) \xrightarrow{\text{H}_2\text{O}} \text{CO(OH)CH(OH)C(OH)}_2\text{CO(O}^-)$	$2.6 \cdot 10^{-01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00095	*	*	$\text{CO(OH)CH(OH)COCO(O}^-) \rightleftharpoons \text{CO(O}^-)\text{CH(OH)COCO(O}^-) + \text{H}^+$	$1.2 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
E <sub>o</sub> 00096	*	*	$\text{CO(OH)CH(OH)COCO(OH)} \rightleftharpoons \text{CO(OH)COCH(OH)CO(O}^-) + \text{H}^+$	$1.2 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A/R^b$	Reference/comment
E <sub>o</sub> 00097	*	*	$\text{CO(OH)CH(OH)COCO(OH)} \rightleftharpoons \text{CO(OH)CH(OH)COCO(O}^-) + \text{H}^+$	$1.6 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00829	*	*	$\text{CO(OH)CH(OH)COCO(O}^-) + \text{OH} \rightarrow$ $0.279 \text{ CO(OH)C(OH)(OO}\cdot\text{)COCO(O}^-) +$ $0.721 \text{ CO(OH)CH(O}\cdot\text{)COCO(O}^-) + \text{H}_2\text{O} - 0.279 \text{ O}_2$	$6.7 \cdot 10^{+07}$		
R <sub>o</sub> 00830	*		$\text{CO(OH)CH(OH)COCO(O}^-) + \text{NO}_3 \rightarrow \text{CO(OH)CH(OH)COCO(O}\cdot\text{) + NO}_3^-$	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 00831	*	*	$\text{CO(OH)C(OH)(OO}\cdot\text{)COCO(O}^-) \rightarrow \text{CO(OH)COCOCO(O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00832	*		$\text{CO(OH)CH(OH)COCO(O}\cdot\text{)} \rightarrow \text{CO(OH)CH(OH)CO(OO}\cdot\text{) + CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00098	*	*	$\text{CO(OH)COCH}_2\text{CO(O}^-) \xrightleftharpoons{\text{H}_2\text{O}} \text{CO(OH)C(OH)}_2\text{CH}_2\text{CO(O}^-)$	$1.6 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00099	*	*	$\text{CO(OH)COCH}_2\text{CO(O}^-) \rightleftharpoons \text{CO(O}^-)\text{CH}_2\text{COCO(O}^-) + \text{H}^+$	$1.9 \cdot 10^{-02}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00833	*	*	$\text{CO(OH)COCH}_2\text{CO(O}^-) + \text{OH} \rightarrow$ $\text{CO(OH)COCH(OO}\cdot\text{)CO(O}^-) + \text{H}_2\text{O} - \text{O}_2$	$2.4 \cdot 10^{+07}$		
R <sub>o</sub> 00834	*		$\text{CO(OH)COCH}_2\text{CO(O}^-) + \text{NO}_3 \rightarrow \text{CO(OH)COCH}_2\text{CO(O}\cdot\text{) + NO}_3^-$	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 00835	*	*	$\text{CO(OH)COCH}_2\text{CO(O}\cdot\text{)} \rightarrow \text{CO(OH)COCH}_2\text{(OO}\cdot\text{) + CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00100	*	*	$\text{CO(OH)CH(OH)CH(OH)CO(O}^-) \rightleftharpoons$ $\text{CO(O}^-)\text{CH(OH)CH(OH)CO(O}^-) + \text{H}^+$	$5.9 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
E <sub>o</sub> 00101	*	*	$\text{CO(OH)CH(OH)CH(OH)CO(OH)} \rightleftharpoons$ $\text{CO(OH)CH(OH)CH(OH)CO(O}^-) + \text{H}^+$	$2.9 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00836	*	*	$\text{CO(OH)CH(OH)CH(OH)CO(O}^-) + \text{OH} \rightarrow$ $0.149 \text{ CO(OH)C(OH)(OO}\cdot\text{)CH(OH)CO(O}^-) +$ $0.292 \text{ CO(OH)CH(OH)C(OH)(OO}\cdot\text{)CO(O}^-) +$ $0.203 \text{ CO(OH)CH(O}\cdot\text{)CH(OH)CO(O}^-) +$ $0.356 \text{ CO(OH)CH(OH)CH(O}\cdot\text{)CO(O}^-) + \text{H}_2\text{O} - 0.441 \text{ O}_2$	$2.8 \cdot 10^{+08}$		
R <sub>o</sub> 00837	*		$\text{CO(OH)CH(OH)CH(OH)CO(O}^-) + \text{NO}_3 \rightarrow$ $\text{CO(OH)CH(OH)CH(OH)CO(O}\cdot\text{) + NO}_3^-$	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 00838	*	*	$\text{CO(OH)C(OH)(OO}\cdot\text{)CH(OH)CO(O}^-) \rightarrow$ $\text{CO(OH)COCH(OH)CO(O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00839	*	*	$\text{CO(OH)CH(OH)C(OH)(OO}\cdot\text{)CO(O}^-) \rightarrow$ $\text{CO(OH)CH(OH)COCO(O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00840	*	*	$\text{CO(OH)CH(OH)CH(O}\cdot\text{)CO(O}^-) \xrightarrow{\text{O}_2} \text{CO(OH)CH(OH)COCO(O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00841	*	*	$\text{CO(OH)CH(OH)CH(O}\cdot\text{)CO(O}^-) \rightarrow 0.500 \text{ CO(OH)CH(OH)(OO}\cdot\text{) +}$ $0.500 \text{ CO(O}^-)\text{CHO} + 0.500 \text{ CO(OH)CH(OH)CHO} + 0.500 \cdot \text{CO(O}^-) - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00842	*		CO(OH)CH(OH)CH(OH)CO(O $\cdot$ ) $\rightarrow$ CO(OH)CH(OH)CH(OH)(OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00102	*	*	CO(OH)COCH(OH)CO(O $^-$ ) $\xrightleftharpoons{H_2O}$ CO(OH)C(OH) <sub>2</sub> CH(OH)CO(O $^-$ )	9.9 · 10 <sup>+00</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00103	*	*	CO(OH)COCH(OH)CO(O $^-$ ) $\rightleftharpoons$ CO(O $^-$ )CH(OH)COCO(O $^-$ ) + H $^+$	4.7 · 10 <sup>-02</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00843	*	*	CO(OH)COCH(OH)CO(O $^-$ ) + OH $\rightarrow$ 0.301 CO(OH)COC(OH)(OO $\cdot$ )CO(O $^-$ ) + 0.699 CO(OH)COCH(O $\cdot$ )CO(O $^-$ ) + H <sub>2</sub> O - 0.301 O <sub>2</sub>	1.2 · 10 <sup>+08</sup>		
R <sub>o</sub> 00844	*		CO(OH)COCH(OH)CO(O $^-$ ) + NO <sub>3</sub> $\rightarrow$ CO(OH)COCH(OH)CO(O $\cdot$ ) + NO <sub>3</sub> $^-$	2.5 · 10 <sup>+07</sup>		
R <sub>o</sub> 00845	*	*	CO(OH)COC(OH)(OO $\cdot$ )CO(O $^-$ ) $\rightarrow$ CO(OH)COCOCO(O $^-$ ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00846	*	*	CO(OH)COCH(O $\cdot$ )CO(O $^-$ ) $\xrightarrow{O_2}$ CO(OH)COCOCO(O $^-$ ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 00847	*	*	CO(OH)COCH(O $\cdot$ )CO(O $^-$ ) $\rightarrow$ 0.500 CO(OH)CO(OO $\cdot$ ) + 0.500 CO(O $^-$ )CHO + 0.500 CO(OH)COCHO + 0.500 · CO(O $^-$ ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00848	*		CO(OH)COCH(OH)CO(O $\cdot$ ) $\rightarrow$ CO(OH)COCH(OH)(OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00849	*	*	CO(OH)CH(OH)CH <sub>2</sub> CO(O $^-$ ) + OH $\rightarrow$ 0.478 CO(OH)C(OH)(OO $\cdot$ )CH <sub>2</sub> CO(O $^-$ ) + 0.248 CO(OH)CH(OH)CH(OO $\cdot$ )CO(O $^-$ ) + 0.274 CO(OH)CH(O $\cdot$ )CH <sub>2</sub> CO(O $^-$ ) + H <sub>2</sub> O - 0.726 O <sub>2</sub>	9.7 · 10 <sup>+08</sup>	-1701.0	Gligorovski et al. (2009)
R <sub>o</sub> 00850	*		CO(OH)CH(OH)CH <sub>2</sub> CO(O $^-$ ) + NO <sub>3</sub> $\rightarrow$ CO(OH)CH(OH)CH <sub>2</sub> CO(O $\cdot$ ) + NO <sub>3</sub> $^-$	2.5 · 10 <sup>+07</sup>		
R <sub>o</sub> 00851	*	*	CO(OH)CH(OH)CH(OO $\cdot$ )CO(O $^-$ ) + CO(OH)CH(OH)CH(OO $\cdot$ )CO(O $^-$ ) $\rightarrow$ 2.000 CO(OH)CH(OH)CHO + 2.000 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2.000 OH $^-$ - 2.000 H <sub>2</sub> O	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 00852	*	*	CO(OH)CH(OH)CH(OO $\cdot$ )CO(O $^-$ ) $\xrightarrow{RO_2}$ 0.200 CO(OH)CH(OH)CH(O $\cdot$ )CO(O $^-$ ) + 0.550 CO(OH)CH(OH)COCO(O $^-$ ) + 0.250 CO(OH)CH(OH)CH(OH)CO(O $^-$ ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 00853	*	*	CO(OH)CH(O $\cdot$ )CH <sub>2</sub> CO(O $^-$ ) $\xrightarrow{O_2}$ CO(OH)COCH <sub>2</sub> CO(O $^-$ ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 00854	*	*	CO(OH)CH(O $\cdot$ )CH <sub>2</sub> CO(O $^-$ ) $\rightarrow$ 0.500 · CO(OH) + 0.500 CO(O $^-$ )CH <sub>2</sub> CHO + 0.500 CO(OH)CHO + 0.500 CO(O $^-$ )CH <sub>2</sub> (OO $\cdot$ ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00104	*	*	CO(OH)CH <sub>2</sub> COCO(OH) $\xrightleftharpoons{H_2O}$ CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CO(OH)	1.8 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00855	*	*	CO(OH)CH <sub>2</sub> COCO(OH) + OH $\rightarrow$ 0.833 CO(OH)COCH(OO $\cdot$ )CO(OH) + 0.083 CO(OH)COCH <sub>2</sub> CO(O $\cdot$ ) + 0.083 CO(OH)CH <sub>2</sub> COCO(O $\cdot$ ) + H <sub>2</sub> O - 0.833 O <sub>2</sub>	$8.4 \cdot 10^{+06}$		
R <sub>o</sub> 00856	*		CO(OH)CH <sub>2</sub> COCO(OH) + NO <sub>3</sub> $\rightarrow$ 0.833 CO(OH)COCH(OO $\cdot$ )CO(OH) + 0.083 CO(OH)COCH <sub>2</sub> CO(O $\cdot$ ) + 0.083 CO(OH)CH <sub>2</sub> COCO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.833 O <sub>2</sub>	$1.7 \cdot 10^{+05}$		
R <sub>o</sub> 00857	*	*	CO(OH)CH <sub>2</sub> CH(OH)CO(OH) + OH $\rightarrow$ 0.117 CO(OH)CH(OH)CH(OO $\cdot$ )CO(OH) + 0.440 CO(OH)CH <sub>2</sub> C(OH)(OO $\cdot$ )CO(OH) + 0.443 CO(OH)CH <sub>2</sub> CH(O $\cdot$ )CO(OH) + H <sub>2</sub> O - 0.557 O <sub>2</sub>	$3.6 \cdot 10^{+08}$	-1575.0	<i>Glignowski et al. (2009)</i>
R <sub>o</sub> 00858	*		CO(OH)CH <sub>2</sub> CH(OH)CO(OH) + NO <sub>3</sub> $\rightarrow$ 0.117 CO(OH)CH(OH)CH(OO $\cdot$ )CO(OH) + 0.440 CO(OH)CH <sub>2</sub> C(OH)(OO $\cdot$ )CO(OH) + 0.443 CO(OH)CH <sub>2</sub> CH(O $\cdot$ )CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.557 O <sub>2</sub>	$7.2 \cdot 10^{+03}$		
R <sub>o</sub> 00859	*	*	CO(OH)CH(OH)CH(OO $\cdot$ )CO(OH) + CO(OH)CH(OH)CH(OO $\cdot$ )CO(OH) $\rightarrow$ 2.000 CO(OH)CH(OH)CHO + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 00860	*	*	CO(OH)CH(OH)CH(OO $\cdot$ )CO(OH) $\xrightarrow{RO_2}$ 0.200 CO(OH)CH(OH)CH(O $\cdot$ )CO(OH) + 0.550 CO(OH)CH(OH)COCO(OH) + 0.250 CO(OH)CH(OH)CH(OH)CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00861	*	*	CO(OH)CH <sub>2</sub> CH(O $\cdot$ )CO(OH) $\xrightarrow{O_2}$ CO(OH)CH <sub>2</sub> COCO(OH) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00862	*	*	CO(OH)CH <sub>2</sub> CH(O $\cdot$ )CO(OH) $\rightarrow$ 0.500 CO(OH)CH <sub>2</sub> (OO $\cdot$ ) + 0.500 CO(OH)CHO + 0.500 CO(OH)CH <sub>2</sub> CHO + 0.500 $\cdot$ CO(OH) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00863	*	*	CO(OH)CH(OH)CH(O $\cdot$ )CO(OH) $\xrightarrow{O_2}$ CO(OH)CH(OH)COCO(OH) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00864	*	*	CO(OH)CH(OH)CH(O $\cdot$ )CO(OH) $\rightarrow$ 0.500 CO(OH)CH(OH)(OO $\cdot$ ) + 0.500 CO(OH)CHO + 0.500 CO(OH)CH(OH)CHO + 0.500 $\cdot$ CO(OH) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00865	*	*	CO(O <sup>-</sup> )CH(OH)CH(OH)CO(O <sup>-</sup> ) + OH $\rightarrow$ 0.590 CO(O <sup>-</sup> )CH(OH)C(OH)(OO $\cdot$ )CO(O <sup>-</sup> ) + 0.410 CO(O <sup>-</sup> )CH(OH)CH(O $\cdot$ )CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.590 O <sub>2</sub>	$1.0 \cdot 10^{+08}$		Average of <i>Kraljic (1967)</i> and <i>Logan (1989)</i>



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00866	*		$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^\cdot) +$ $0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^\cdot) + \text{NO}_3^-$	$7.8 \cdot 10^{+07}$		
R <sub>o</sub> 00867	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})(\text{OO}^\cdot)\text{CO}(\text{O}^-) \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCO}(\text{O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00868	*		$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}^\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00869	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCO}(\text{O}^-) + \text{OH} \rightarrow$ $0.431 \text{CO}(\text{O}^-)\text{COC}(\text{OH})(\text{OO}^\cdot)\text{CO}(\text{O}^-) + 0.569 \text{CO}(\text{O}^-)\text{COCH}(\text{O}^\cdot)\text{CO}(\text{O}^-) +$ $\text{H}_2\text{O} - 0.431 \text{O}_2$	$1.5 \cdot 10^{+08}$		
R <sub>o</sub> 00870	*		$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $0.500 \text{CO}(\text{O}^-)\text{COCH}(\text{OH})\text{CO}(\text{O}^\cdot) + 0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCO}(\text{O}^\cdot) + \text{NO}_3^-$	$7.8 \cdot 10^{+07}$		
R <sub>o</sub> 00871	*	*	$\text{CO}(\text{O}^-)\text{COC}(\text{OH})(\text{OO}^\cdot)\text{CO}(\text{O}^-) \rightarrow \text{CO}(\text{O}^-)\text{COCOCO}(\text{O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00872	*	*	$\text{CO}(\text{O}^-)\text{COCH}(\text{O}^\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{COCOCO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00873	*	*	$\text{CO}(\text{O}^-)\text{COCH}(\text{O}^\cdot)\text{CO}(\text{O}^-) \rightarrow 0.500 \text{CO}(\text{O}^-)\text{CO}(\text{OO}^\cdot) +$ $0.500 \text{CO}(\text{O}^-)\text{CHO} + 0.500 \text{CO}(\text{O}^-)\text{COCHO} + 0.500 \cdot \text{CO}(\text{O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00874	*		$\text{CO}(\text{O}^-)\text{COCH}(\text{OH})\text{CO}(\text{O}^\cdot) \rightarrow \text{CO}(\text{O}^-)\text{COCH}(\text{OH})(\text{OO}^\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00875	*		$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCO}(\text{O}^\cdot) \rightarrow \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CO}(\text{OO}^\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00105	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}^-) \rightleftharpoons \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{H}^+$	$1.3 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
E <sub>o</sub> 00106	*	*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OH}) \rightleftharpoons \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{H}^+$	$1.5 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
E <sub>o</sub> 00107	*	*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OH}) \rightleftharpoons \text{CO}(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{H}^+$	$1.2 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00876	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{OH} \rightarrow$ $0.088 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{OO}^\cdot)\text{CO}(\text{O}^-) +$ $0.656 \text{CO}(\text{OH})\text{C}(\text{OH})(\text{O}^\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) +$ $0.257 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{O}^\cdot)\text{CO}(\text{O}^-) + \text{H}_2\text{O} - 0.088 \text{O}_2$	$3.7 \cdot 10^{+08}$		
R <sub>o</sub> 00877	*		$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}^\cdot) + \text{NO}_3^-$	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 00878	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{OO}^\cdot)\text{CO}(\text{O}^-) \rightarrow \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{COCO}(\text{O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00879	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})(\text{O}^\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) \rightarrow$ $0.500 \cdot \text{CO}(\text{OH}) + 0.500 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^-) +$ $0.500 \text{CO}(\text{OH})\text{CO}(\text{OH}) + 0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})(\text{OO}^\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A/R^b$	Reference/comment
R <sub>o</sub> 00880	*	*	$\text{CO(OH)C(OH)}_2\text{CH(O}\cdot\text{)CO(O}^-) \xrightarrow{\text{O}_2} \text{CO(OH)C(OH)}_2\text{COCO(O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00881	*	*	$\text{CO(OH)C(OH)}_2\text{CH(O}\cdot\text{)CO(O}^-) \rightarrow 0.500 \text{CO(OH)C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.500 \text{CO(O}^-)\text{CHO} + 0.500 \text{CO(OH)C(OH)}_2\text{CHO} + 0.500 \cdot \text{CO(O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00882	*		$\text{CO(OH)C(OH)}_2\text{CH(OH)CO(O}\cdot\text{)} \rightarrow$ $\text{CO(OH)C(OH)}_2\text{CH(OH)(OO}\cdot\text{)} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00108	*	*	$\text{CO(OH)C(OH)}_2\text{CH}_2\text{CO(O}^-) \rightleftharpoons \text{CO(O}^-)\text{CH}_2\text{C(OH)}_2\text{CO(O}^-) + \text{H}^+$	$8.0 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
E <sub>o</sub> 00109	*	*	$\text{CO(OH)CH}_2\text{C(OH)}_2\text{CO(OH)} \rightleftharpoons \text{CO(OH)C(OH)}_2\text{CH}_2\text{CO(O}^-) + \text{H}^+$	$1.2 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
E <sub>o</sub> 00110	*	*	$\text{CO(OH)CH}_2\text{C(OH)}_2\text{CO(OH)} \rightleftharpoons \text{CO(OH)CH}_2\text{C(OH)}_2\text{CO(O}^-) + \text{H}^+$	$3.7 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00883	*	*	$\text{CO(OH)C(OH)}_2\text{CH}_2\text{CO(O}^-) + \text{OH} \rightarrow$ $0.077 \text{CO(OH)C(OH)}_2\text{CH(OO}\cdot\text{)CO(O}^-) +$ $0.923 \text{CO(OH)C(OH)(O}\cdot\text{)CH}_2\text{CO(O}^-) + \text{H}_2\text{O} - 0.077 \text{O}_2$	$2.7 \cdot 10^{+08}$		
R <sub>o</sub> 00884	*		$\text{CO(OH)C(OH)}_2\text{CH}_2\text{CO(O}^-) + \text{NO}_3 \rightarrow$ $\text{CO(OH)C(OH)}_2\text{CH}_2\text{CO(O}\cdot\text{)} + \text{NO}_3^-$	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 00885	*	*	$\text{CO(OH)C(OH)}_2\text{CH(OO}\cdot\text{)CO(O}^-) + \text{CO(OH)C(OH)}_2\text{CH(OO}\cdot\text{)CO(O}^-) \rightarrow$ $2.000 \text{CO(OH)C(OH)}_2\text{CHO} + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 00886	*	*	$\text{CO(OH)C(OH)}_2\text{CH(OO}\cdot\text{)CO(O}^-) \xrightarrow{\text{RO}_2}$ $0.200 \text{CO(OH)C(OH)}_2\text{CH(O}\cdot\text{)CO(O}^-) + 0.550 \text{CO(OH)C(OH)}_2\text{COCO(O}^-) +$ $0.250 \text{CO(OH)C(OH)}_2\text{CH(OH)CO(O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00887	*	*	$\text{CO(OH)C(OH)(O}\cdot\text{)CH}_2\text{CO(O}^-) \rightarrow$ $0.500 \cdot \text{CO(OH)} + 0.500 \text{CO(OH)CH}_2\text{CO(O}^-) + 0.500 \text{CO(OH)CO(OH)} +$ $0.500 \text{CO(O}^-)\text{CH}_2\text{(OO}\cdot\text{)} - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00888	*		$\text{CO(OH)C(OH)}_2\text{CH}_2\text{CO(O}\cdot\text{)} \rightarrow \text{CO(OH)C(OH)}_2\text{CH}_2\text{(OO}\cdot\text{)} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00111	*	*	$\text{CO(OH)CH(OH)C(OH)}_2\text{CO(O}^-) \rightleftharpoons \text{CO(O}^-)\text{CH(OH)C(OH)}_2\text{CO(O}^-) + \text{H}^+$	$8.6 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00889	*	*	$\text{CO(OH)CH(OH)C(OH)}_2\text{CO(O}^-) + \text{OH} \rightarrow$ $0.033 \text{CO(OH)C(OH)(OO}\cdot\text{)C(OH)}_2\text{CO(O}^-) +$ $0.109 \text{CO(OH)CH(O}\cdot\text{)C(OH)}_2\text{CO(O}^-) +$ $0.858 \text{CO(OH)CH(OH)C(OH)(O}\cdot\text{)CO(O}^-) + \text{H}_2\text{O} - 0.033 \text{O}_2$	$4.9 \cdot 10^{+08}$		
R <sub>o</sub> 00890	*		$\text{CO(OH)CH(OH)C(OH)}_2\text{CO(O}^-) + \text{NO}_3 \rightarrow$ $\text{CO(OH)CH(OH)C(OH)}_2\text{CO(O}\cdot\text{)} + \text{NO}_3^-$	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 00891	*	*	$\text{CO(OH)C(OH)(OO}\cdot\text{)C(OH)}_2\text{CO(O}^-) \rightarrow \text{CO(OH)COC(OH)}_2\text{CO(O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00892	*	*	$\text{CO(OH)CH(O}\cdot\text{)C(OH)}_2\text{CO(O}^-) \xrightarrow{\text{O}_2} \text{CO(OH)COC(OH)}_2\text{CO(O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00893	*	*	CO(OH)CH(O $\cdot$ )C(OH) <sub>2</sub> CO(O $^-$ ) $\rightarrow$ 0.500 $\cdot$ CO(OH) + 0.500 CO(O $^-$ )C(OH) <sub>2</sub> CHO + 0.500 CO(OH)CHO + 0.500 CO(O $^-$ )C(OH) <sub>2</sub> (OO $\cdot$ ) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00894	*	*	CO(OH)CH(OH)C(OH)(O $\cdot$ )CO(O $^-$ ) $\rightarrow$ 0.500 CO(OH)CH(OH)(OO $\cdot$ ) + 0.500 CO(OH)CO(O $^-$ ) + 0.500 CO(OH)CH(OH)CO(OH) + 0.500 $\cdot$ CO(O $^-$ ) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00895	*		CO(OH)CH(OH)C(OH) <sub>2</sub> CO(O $\cdot$ ) $\rightarrow$ CO(OH)CH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00896	*	*	CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + OH $\rightarrow$ CO(OH)CH <sub>2</sub> C(OH)(O $\cdot$ )CO(OH) + H <sub>2</sub> O	$2.5 \cdot 10^{+08}$		
R <sub>o</sub> 00897	*		CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + NO <sub>3</sub> $\rightarrow$ CO(OH)CH <sub>2</sub> C(OH)(O $\cdot$ )CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	$7.4 \cdot 10^{+06}$		
R <sub>o</sub> 00898	*	*	CO(OH)CH <sub>2</sub> C(OH)(O $\cdot$ )CO(OH) $\rightarrow$ 0.500 CO(OH)CH <sub>2</sub> (OO $\cdot$ ) + 0.500 CO(OH)CO(OH) + 0.500 CO(OH)CH <sub>2</sub> CO(OH) + 0.500 $\cdot$ CO(OH) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00899	*	*	CO(OH)CH(OH)CH(OH)CO(OH) + OH $\rightarrow$ 0.296 CO(OH)CH(OH)C(OH)(OO $\cdot$ )CO(OH) + 0.704 CO(OH)CH(OH)CH(O $\cdot$ )CO(OH) + H <sub>2</sub> O - 0.296 O <sub>2</sub>	$1.1 \cdot 10^{+09}$		Average of Scholes and Willson (1967) and Moore <i>et al.</i> (1979)
R <sub>o</sub> 00900	*		CO(OH)CH(OH)CH(OH)CO(OH) + NO <sub>3</sub> $\rightarrow$ 0.296 CO(OH)CH(OH)C(OH)(OO $\cdot$ )CO(OH) + 0.704 CO(OH)CH(OH)CH(O $\cdot$ )CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.296 O <sub>2</sub>	$6.8 \cdot 10^{+03}$		
R <sub>o</sub> 00901	*	*	CO(OH)CH(OH)C(OH)(OO $\cdot$ )CO(OH) $\rightarrow$ CO(OH)CH(OH)COCO(OH) + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
E <sub>o</sub> 00112	*	*	CO(OH)CH(OH)COCO(OH) $\xrightleftharpoons{H_2O}$ CO(OH)CH(OH)C(OH) <sub>2</sub> CO(OH)	$1.1 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00902	*	*	CO(OH)CH(OH)COCO(OH) + OH $\rightarrow$ 0.181 CO(OH)COC(OH)(OO $\cdot$ )CO(OH) + 0.819 CO(OH)COCH(O $\cdot$ )CO(OH) + H <sub>2</sub> O - 0.181 O <sub>2</sub>	$5.9 \cdot 10^{+07}$		
R <sub>o</sub> 00903	*		CO(OH)CH(OH)COCO(OH) + NO <sub>3</sub> $\rightarrow$ 0.181 CO(OH)COC(OH)(OO $\cdot$ )CO(OH) + 0.819 CO(OH)COCH(O $\cdot$ )CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.181 O <sub>2</sub>	$1.5 \cdot 10^{+05}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00904	*	*	$\text{CO(OH)COC(OH)(OO}\cdot\text{)CO(OH)} \rightarrow \text{CO(OH)COCOCO(OH)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00905	*	*	$\text{CO(OH)COCH(O}\cdot\text{)CO(OH)} \xrightarrow{\text{O}_2} \text{CO(OH)COCOCO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00906	*	*	$\text{CO(OH)COCH(O}\cdot\text{)CO(OH)} \rightarrow 0.500 \text{CO(OH)CO(OO}\cdot\text{)} +$ $0.500 \text{CO(OH)CHO} + 0.500 \text{CO(OH)COCHO} + 0.500 \cdot \text{CO(OH)} - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00113	*	*	$\text{CO(OH)CH}_2\text{C(OH)}_2\text{CO(O}^-) \rightleftharpoons \text{CO(O}^-)\text{CH}_2\text{C(OH)}_2\text{CO(O}^-) + \text{H}^+$	$3.7 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00907	*	*	$\text{CO(O}^-)\text{CH}_2\text{C(OH)}_2\text{CO(O}^-) + \text{OH} \rightarrow$ $0.077 \text{CO(O}^-)\text{C(OH)}_2\text{CH(OO}\cdot\text{)CO(O}^-) +$ $0.923 \text{CO(O}^-)\text{CH}_2\text{C(OH)(O}\cdot\text{)CO(O}^-) + \text{H}_2\text{O} - 0.077 \text{O}_2$	$4.8 \cdot 10^{+08}$		
R <sub>o</sub> 00908	*		$\text{CO(O}^-)\text{CH}_2\text{C(OH)}_2\text{CO(O}^-) + \text{NO}_3 \rightarrow 0.500 \text{CO(O}^-)\text{C(OH)}_2\text{CH}_2\text{CO(O}\cdot\text{)} +$ $0.500 \text{CO(O}^-)\text{CH}_2\text{C(OH)}_2\text{CO(O}\cdot\text{)} + \text{NO}_3^-$	$7.8 \cdot 10^{+07}$		
R <sub>o</sub> 00909	*	*	$\text{CO(O}^-)\text{C(OH)}_2\text{CH(OO}\cdot\text{)CO(O}^-) + \text{CO(O}^-)\text{C(OH)}_2\text{CH(OO}\cdot\text{)CO(O}^-) \rightarrow$ $2.000 \text{CO(O}^-)\text{C(OH)}_2\text{CHO} + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 00910	*	*	$\text{CO(O}^-)\text{C(OH)}_2\text{CH(OO}\cdot\text{)CO(O}^-) \xrightarrow{\text{RO}_2}$ $0.200 \text{CO(O}^-)\text{C(OH)}_2\text{CH(O}\cdot\text{)CO(O}^-) + 0.550 \text{CO(O}^-)\text{C(OH)}_2\text{COCO(O}^-) +$ $0.250 \text{CO(O}^-)\text{CH(OH)C(OH)}_2\text{CO(O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00911	*	*	$\text{CO(O}^-)\text{CH}_2\text{C(OH)(O}\cdot\text{)CO(O}^-) \rightarrow$ $0.500 \text{CO(O}^-)\text{CH}_2(\text{OO}\cdot) + 0.500 \text{CO(OH)CO(O}^-) +$ $0.500 \text{CO(OH)CH}_2\text{CO(O}^-) + 0.500 \cdot \text{CO(O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00912	*		$\text{CO(O}^-)\text{C(OH)}_2\text{CH}_2\text{CO(O}\cdot\text{)} \rightarrow \text{CO(O}^-)\text{C(OH)}_2\text{CH}_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00913	*		$\text{CO(O}^-)\text{CH}_2\text{C(OH)}_2\text{CO(O}\cdot\text{)} \rightarrow \text{CO(O}^-)\text{CH}_2\text{C(OH)}_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00914	*	*	$\text{CO(O}^-)\text{C(OH)}_2\text{CH(O}\cdot\text{)CO(O}^-) \xrightarrow{\text{O}_2} \text{CO(O}^-)\text{C(OH)}_2\text{COCO(O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00915	*	*	$\text{CO(O}^-)\text{C(OH)}_2\text{CH(O}\cdot\text{)CO(O}^-) \rightarrow 0.500 \text{CO(O}^-)\text{C(OH)}_2(\text{OO}\cdot) +$ $0.500 \text{CO(O}^-)\text{CHO} + 0.500 \text{CO(O}^-)\text{C(OH)}_2\text{CHO} + 0.500 \cdot \text{CO(O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00916	*	*	$\text{CO(O}^-)\text{CH(OH)C(OH)}_2\text{CO(O}^-) + \text{OH} \rightarrow$ $0.098 \text{CO(O}^-)\text{C(OH)}_2\text{C(OH)(OO}\cdot\text{)CO(O}^-) +$ $0.164 \text{CO(O}^-)\text{C(OH)}_2\text{CH(O}\cdot\text{)CO(O}^-) +$ $0.737 \text{CO(O}^-)\text{CH(OH)C(OH)(O}\cdot\text{)CO(O}^-) + \text{H}_2\text{O} - 0.098 \text{O}_2$	$5.7 \cdot 10^{+08}$		
R <sub>o</sub> 00917	*		$\text{CO(O}^-)\text{CH(OH)C(OH)}_2\text{CO(O}^-) + \text{NO}_3 \rightarrow$ $0.500 \text{CO(O}^-)\text{C(OH)}_2\text{CH(OH)CO(O}\cdot\text{)} +$ $0.500 \text{CO(O}^-)\text{CH(OH)C(OH)}_2\text{CO(O}\cdot\text{)} + \text{NO}_3^-$	$7.8 \cdot 10^{+07}$		
R <sub>o</sub> 00918	*	*	$\text{CO(O}^-)\text{C(OH)}_2\text{C(OH)(OO}\cdot\text{)CO(O}^-) \rightarrow \text{CO(O}^-)\text{C(OH)}_2\text{COCO(O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00919	*	*	CO(O <sup>-</sup> )CH(OH)C(OH)(O $\cdot$ )CO(O <sup>-</sup> ) $\rightarrow$ 0.500 CO(O <sup>-</sup> )CH(OH)(OO $\cdot$ ) + 0.500 CO(OH)CO(O <sup>-</sup> ) + 0.500 CO(OH)CH(OH)CO(O <sup>-</sup> ) + 0.500 $\cdot$ CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00920	*		CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)CO(O $\cdot$ ) $\rightarrow$ CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)(OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00921	*		CO(O <sup>-</sup> )CH(OH)C(OH) <sub>2</sub> CO(O $\cdot$ ) $\rightarrow$ CO(O <sup>-</sup> )CH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00114	*	*	CO(O <sup>-</sup> )COCOCO(O <sup>-</sup> ) $\xrightleftharpoons{H_2O}$ CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCO(O <sup>-</sup> )	$1.5 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00115	*	*	CO(O <sup>-</sup> )COCOCO(O <sup>-</sup> ) $\xrightleftharpoons{H_2O}$ CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>-</sup> )	$2.1 \cdot 10^{-01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00116	*	*	CO(OH)COCOCO(O <sup>-</sup> ) $\rightleftharpoons$ CO(O <sup>-</sup> )COCOCO(O <sup>-</sup> ) + H <sup>+</sup>	$2.8 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00922	*	*	CO(O <sup>-</sup> )COCOCO(O <sup>-</sup> ) + NO <sub>3</sub> $\rightarrow$ 0.500 CO(O <sup>-</sup> )COCOCO(O $\cdot$ ) + 0.500 CO(O <sup>-</sup> )COCOCO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	$0.0 \cdot 10^{+00}$		
R <sub>o</sub> 00923	*	*	CO(O <sup>-</sup> )COCOCO(O $\cdot$ ) $\rightarrow$ CO(O <sup>-</sup> )COCO(OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00117	*	*	CO(OH)COC(OH) <sub>2</sub> CO(O <sup>-</sup> ) $\xrightleftharpoons{H_2O}$ CO(OH)C(OH) <sub>2</sub> COCO(O <sup>-</sup> )	$8.5 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00118	*	*	CO(OH)COC(OH) <sub>2</sub> CO(O <sup>-</sup> ) $\xrightleftharpoons{H_2O}$ CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>-</sup> )	$1.3 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00119	*	*	CO(OH)COC(OH) <sub>2</sub> CO(O <sup>-</sup> ) $\rightleftharpoons$ CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCO(O <sup>-</sup> ) + H <sup>+</sup>	$1.2 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
E <sub>o</sub> 00120	*	*	CO(OH)C(OH) <sub>2</sub> COCO(OH) $\rightleftharpoons$ CO(OH)COC(OH) <sub>2</sub> CO(O <sup>-</sup> ) + H <sup>+</sup>	$5.9 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
E <sub>o</sub> 00121	*	*	CO(OH)C(OH) <sub>2</sub> COCO(OH) $\rightleftharpoons$ CO(OH)C(OH) <sub>2</sub> COCO(O <sup>-</sup> ) + H <sup>+</sup>	$1.2 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00924	*	*	CO(OH)COC(OH) <sub>2</sub> CO(O <sup>-</sup> ) + OH $\rightarrow$ CO(OH)COC(OH)(O $\cdot$ )CO(O <sup>-</sup> ) + H <sub>2</sub> O	$3.6 \cdot 10^{+08}$		
R <sub>o</sub> 00925	*		CO(OH)COC(OH) <sub>2</sub> CO(O <sup>-</sup> ) + NO <sub>3</sub> $\rightarrow$ CO(OH)COC(OH) <sub>2</sub> CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 00926	*	*	CO(OH)COC(OH)(O $\cdot$ )CO(O <sup>-</sup> ) $\rightarrow$ 0.500 CO(OH)CO(OO $\cdot$ ) + 0.500 CO(OH)CO(O <sup>-</sup> ) + 0.500 CO(OH)COCO(OH) + 0.500 $\cdot$ CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00927	*		CO(OH)COC(OH) <sub>2</sub> CO(O $\cdot$ ) $\rightarrow$ CO(OH)COC(OH) <sub>2</sub> (OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00928	*	*	CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + OH $\rightarrow$ CO(OH)CH <sub>2</sub> C(OH)(O $\cdot$ )CO(O <sup>-</sup> ) + H <sub>2</sub> O	$4.4 \cdot 10^{+08}$		
R <sub>o</sub> 00929	*		CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + NO <sub>3</sub> $\rightarrow$ CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	$2.5 \cdot 10^{+07}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00930	*	*	CO(OH)CH <sub>2</sub> C(OH)(O·)CO(O <sup>-</sup> ) → 0.500 CO(OH)CH <sub>2</sub> (OO·) + 0.500 CO(OH)CO(O <sup>-</sup> ) + 0.500 CO(OH)CH <sub>2</sub> CO(OH) + 0.500 ·CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00931	*		CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CO(O·) → CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
E <sub>o</sub> 00122	*	*	CO(OH)C(OH) <sub>2</sub> COCO(O <sup>-</sup> ) ⇌ CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCO(O <sup>-</sup> ) + H <sup>+</sup>	3.1 · 10 <sup>-04</sup>		
R <sub>o</sub> 00932	*	*	CO(OH)C(OH) <sub>2</sub> COCO(O <sup>-</sup> ) + OH → CO(OH)C(OH)(O·)COCO(O <sup>-</sup> ) + H <sub>2</sub> O	2.1 · 10 <sup>+08</sup>		
R <sub>o</sub> 00933	*		CO(OH)C(OH) <sub>2</sub> COCO(O <sup>-</sup> ) + NO <sub>3</sub> → CO(OH)C(OH) <sub>2</sub> COCO(O·) + NO <sub>3</sub> <sup>-</sup>	2.5 · 10 <sup>+07</sup>		
R <sub>o</sub> 00934	*	*	CO(OH)C(OH)(O·)COCO(O <sup>-</sup> ) → 0.500 ·CO(OH) + 0.500 CO(OH)COCO(O <sup>-</sup> ) + 0.500 CO(OH)CO(OH) + 0.500 CO(O <sup>-</sup> )CO(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00935	*		CO(OH)C(OH) <sub>2</sub> COCO(O·) → CO(OH)C(OH) <sub>2</sub> CO(OO·) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00936	*	*	CO(OH)CH(OH)C(OH) <sub>2</sub> CO(OH) + OH → 0.031 CO(OH)C(OH) <sub>2</sub> C(OH)(OO·)CO(OH) + 0.177 CO(OH)C(OH) <sub>2</sub> CH(O·)CO(OH) + 0.792 CO(OH)CH(OH)C(OH)(O·)CO(OH) + H <sub>2</sub> O - 0.031 O <sub>2</sub>	3.0 · 10 <sup>+08</sup>		
R <sub>o</sub> 00937	*		CO(OH)CH(OH)C(OH) <sub>2</sub> CO(OH) + NO <sub>3</sub> → 0.031 CO(OH)C(OH) <sub>2</sub> C(OH)(OO·)CO(OH) + 0.177 CO(OH)C(OH) <sub>2</sub> CH(O·)CO(OH) + 0.792 CO(OH)CH(OH)C(OH)(O·)CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.031 O <sub>2</sub>	8.1 · 10 <sup>+06</sup>		
R <sub>o</sub> 00938	*	*	CO(OH)C(OH) <sub>2</sub> C(OH)(OO·)CO(OH) → CO(OH)C(OH) <sub>2</sub> COCO(OH) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00939	*	*	CO(OH)C(OH) <sub>2</sub> CH(O·)CO(OH) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> COCO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 00940	*	*	CO(OH)C(OH) <sub>2</sub> CH(O·)CO(OH) → 0.500 CO(OH)C(OH) <sub>2</sub> (OO·) + 0.500 CO(OH)CHO + 0.500 CO(OH)C(OH) <sub>2</sub> CHO + 0.500 ·CO(OH) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00941	*	*	CO(OH)CH(OH)C(OH)(O·)CO(OH) → 0.500 CO(OH)CH(OH)(OO·) + 0.500 CO(OH)CO(OH) + 0.500 CO(OH)CH(OH)CO(OH) + 0.500 ·CO(OH) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00123	*	*	CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>-</sup> ) ⇌ CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + H <sup>+</sup>	2.0 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00942	*	*	CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + OH → CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH)(O·)CO(O <sup>-</sup> ) + H <sub>2</sub> O	8.0 · 10 <sup>+08</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00943	*		CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + NO <sub>3</sub> → 0.500 CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>·</sup> ) + 0.500 CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>·</sup> ) + NO <sub>3</sub> <sup>-</sup>	7.8 · 10 <sup>+07</sup>		
R <sub>o</sub> 00944	*	*	CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH)(O <sup>·</sup> )CO(O <sup>-</sup> ) → 0.500 CO(O <sup>-</sup> )C(OH) <sub>2</sub> (OO <sup>·</sup> ) + 0.500 CO(OH)CO(O <sup>-</sup> ) + 0.500 CO(OH)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + 0.500 ·CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00945	*		CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>·</sup> ) → CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO <sup>·</sup> ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00946	*	*	CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCO(O <sup>-</sup> ) + OH → CO(O <sup>-</sup> )COC(OH)(O <sup>·</sup> )CO(O <sup>-</sup> ) + H <sub>2</sub> O	3.6 · 10 <sup>+08</sup>		
R <sub>o</sub> 00947	*		CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCO(O <sup>-</sup> ) + NO <sub>3</sub> → 0.500 CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CO(O <sup>·</sup> ) + 0.500 CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCO(O <sup>·</sup> ) + NO <sub>3</sub> <sup>-</sup>	7.8 · 10 <sup>+07</sup>		
R <sub>o</sub> 00948	*	*	CO(O <sup>-</sup> )COC(OH)(O <sup>·</sup> )CO(O <sup>-</sup> ) → 0.500 CO(O <sup>-</sup> )CO(OO <sup>·</sup> ) + 0.500 CO(OH)CO(O <sup>-</sup> ) + 0.500 CO(OH)COCO(O <sup>-</sup> ) + 0.500 ·CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00949	*		CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CO(O <sup>·</sup> ) → CO(O <sup>-</sup> )COC(OH) <sub>2</sub> (OO <sup>·</sup> ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00950	*		CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCO(O <sup>·</sup> ) → CO(O <sup>-</sup> )C(OH) <sub>2</sub> CO(OO <sup>·</sup> ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00124	*	*	CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH) ⇌ CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + H <sup>+</sup>	1.0 · 10 <sup>-03</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 00951	*	*	CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + OH → 0.363 CO(OH)C(OH)(O <sup>·</sup> )C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + 0.637 CO(OH)C(OH) <sub>2</sub> C(OH)(O <sup>·</sup> )CO(O <sup>-</sup> ) + H <sub>2</sub> O	6.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 00952	*		CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + NO <sub>3</sub> → CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>·</sup> ) + NO <sub>3</sub> <sup>-</sup>	2.5 · 10 <sup>+07</sup>		
R <sub>o</sub> 00953	*	*	CO(OH)C(OH)(O <sup>·</sup> )C(OH) <sub>2</sub> CO(O <sup>-</sup> ) → 0.500 ·CO(OH) + 0.500 CO(OH)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + 0.500 CO(OH)CO(OH) + 0.500 CO(O <sup>-</sup> )C(OH) <sub>2</sub> (OO <sup>·</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00954	*	*	CO(OH)C(OH) <sub>2</sub> C(OH)(O <sup>·</sup> )CO(O <sup>-</sup> ) → 0.500 CO(OH)C(OH) <sub>2</sub> (OO <sup>·</sup> ) + 0.500 CO(OH)CO(O <sup>-</sup> ) + 0.500 CO(OH)C(OH) <sub>2</sub> CO(OH) + 0.500 ·CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 00955	*		CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>·</sup> ) → CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO <sup>·</sup> ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00125	*	*	$\text{CO(OH)C(OH)}_2\text{COCO(OH)} \xrightleftharpoons{\text{H}_2\text{O}} \text{CO(OH)C(OH)}_2\text{C(OH)}_2\text{CO(OH)}$	$1.4 \cdot 10^{+03}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 00956	*	*	$\text{CO(OH)C(OH)}_2\text{COCO(OH)} + \text{OH} \rightarrow$ $\text{CO(OH)COC(OH)(O}\cdot\text{)CO(OH)} + \text{H}_2\text{O}$	$2.1 \cdot 10^{+08}$		
R <sub>o</sub> 00957	*		$\text{CO(OH)C(OH)}_2\text{COCO(OH)} + \text{NO}_3 \rightarrow$ $\text{CO(OH)COC(OH)(O}\cdot\text{)CO(OH)} + \text{NO}_3^- + \text{H}^+$	$6.2 \cdot 10^{+06}$		
R <sub>o</sub> 00958	*	*	$\text{CO(OH)COC(OH)(O}\cdot\text{)CO(OH)} \rightarrow$ $0.500 \text{ CO(OH)CO(OO}\cdot\text{)} + 0.500 \text{ CO(OH)CO(OH)} +$ $0.500 \text{ CO(OH)COCO(OH)} + 0.500 \cdot \text{CO(OH)} - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00959	*	*	$\text{CO(OH)C(OH)}_2\text{C(OH)}_2\text{CO(OH)} + \text{OH} \rightarrow$ $\text{CO(OH)C(OH)}_2\text{C(OH)(O}\cdot\text{)CO(OH)} + \text{H}_2\text{O}$	$4.6 \cdot 10^{+08}$		
R <sub>o</sub> 00960	*		$\text{CO(OH)C(OH)}_2\text{C(OH)}_2\text{CO(OH)} + \text{NO}_3 \rightarrow$ $\text{CO(OH)C(OH)}_2\text{C(OH)(O}\cdot\text{)CO(OH)} + \text{NO}_3^- + \text{H}^+$	$6.2 \cdot 10^{+06}$		
R <sub>o</sub> 00961	*	*	$\text{CO(OH)C(OH)}_2\text{C(OH)(O}\cdot\text{)CO(OH)} \rightarrow$ $0.500 \text{ CO(OH)C(OH)}_2\text{(OO}\cdot\text{)} + 0.500 \text{ CO(OH)CO(OH)} +$ $0.500 \text{ CO(OH)C(OH)}_2\text{CO(OH)} + 0.500 \cdot \text{CO(OH)} - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00962	*	*	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{(OH)} + \text{OH} \rightarrow 0.119 \text{ CH}_2\text{(OH)CH}_2\text{CH}_2\text{CH}_2\text{(OO}\cdot\text{)} +$ $0.293 \text{ CH}_3\text{CH(OO}\cdot\text{)CH}_2\text{CH}_2\text{(OH)} + 0.125 \text{ CH}_3\text{CH}_2\text{CH(OO}\cdot\text{)CH}_2\text{(OH)} +$ $0.463 \text{ CH}_3\text{CH}_2\text{CH}_2\text{CH(OH)(OO}\cdot\text{)} + \text{H}_2\text{O} - \text{O}_2$	$4.0 \cdot 10^{+09}$	-1000.0	Hesper (2003)
R <sub>o</sub> 00963	*		$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{(OH)} + \text{NO}_3 \rightarrow 0.119 \text{ CH}_2\text{(OH)CH}_2\text{CH}_2\text{CH}_2\text{(OO}\cdot\text{)} +$ $0.293 \text{ CH}_3\text{CH(OO}\cdot\text{)CH}_2\text{CH}_2\text{(OH)} + 0.125 \text{ CH}_3\text{CH}_2\text{CH(OO}\cdot\text{)CH}_2\text{(OH)} +$ $0.463 \text{ CH}_3\text{CH}_2\text{CH}_2\text{CH(OH)(OO}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$1.9 \cdot 10^{+06}$		Shastri and Huie (1990)
R <sub>o</sub> 00964	*	*	$\text{CH}_2\text{(OH)CH}_2\text{CH}_2\text{CH}_2\text{(OO}\cdot\text{)} \xrightarrow{\text{RO}_2}$ $0.200 \text{ CH}_2\text{(OH)CH}_2\text{CH}_2\text{CH}_2\text{(O}\cdot\text{)} + 0.550 \text{ CH}_2\text{(OH)CH}_2\text{CH}_2\text{CHO} +$ $0.250 \text{ CH}_2\text{(OH)CH}_2\text{CH}_2\text{CH}_2\text{(OH)} + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00965	*	*	$\text{CH}_3\text{CH(OO}\cdot\text{)CH}_2\text{CH}_2\text{(OH)} \xrightarrow{\text{RO}_2}$ $0.200 \text{ CH}_3\text{CH(O}\cdot\text{)CH}_2\text{CH}_2\text{(OH)} + 0.550 \text{ CH}_3\text{COCH}_2\text{CH}_2\text{(OH)} +$ $0.250 \text{ CH}_3\text{CH(OH)CH}_2\text{CH}_2\text{(OH)} + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00966	*	*	$\text{CH}_3\text{CH}_2\text{CH}(\text{OO}\cdot)\text{CH}_2(\text{OH}) \xrightarrow{RO_2}$ 0.200 $\text{CH}_3\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH})$ + 0.550 $\text{CH}_3\text{CH}_2\text{COCH}_2(\text{OH})$ + 0.250 $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OH})$ + 0.350 $\text{O}_2$ + 0.150 $\text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00967	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2(\text{O}\cdot) \xrightarrow{O_2} \text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00968	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00969	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}_2\text{CH}_2(\text{OH}) \xrightarrow{O_2} \text{CH}_3\text{COCH}_2\text{CH}_2(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00970	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}_2\text{CH}_2(\text{OH}) \rightarrow 0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CH}_2(\text{OH})\text{CH}_2\text{CHO} +$ $0.500 \text{CH}_3\text{CHO} + 0.500 \text{CH}_2(\text{OH})\text{CH}_2(\text{OO}\cdot) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00971	*	*	$\text{CH}_3\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) \xrightarrow{O_2} \text{CH}_3\text{CH}_2\text{COCH}_2(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00972	*	*	$\text{CH}_3\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) \rightarrow 0.500 \text{CH}_3\text{CH}_2(\text{OO}\cdot) + 0.500 \text{CH}_2(\text{OH})\text{CHO} +$ $0.500 \text{CH}_3\text{CH}_2\text{CHO} + 0.500 \text{CH}_2(\text{OH})\cdot - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00973	*	*	$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OH}) + \text{OH} \rightarrow$ 0.173 $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CH}_2(\text{OO}\cdot) +$ 0.181 $\text{CH}_3\text{CH}(\text{OO}\cdot)\text{CH}(\text{OH})\text{CH}_2(\text{OH}) +$ 0.290 $\text{CH}_3\text{CH}_2\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2(\text{OH}) +$ 0.286 $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) + 0.036 \text{CH}_3\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) +$ 0.034 $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.930 \text{O}_2$	$2.3 \cdot 10^{+09}$	-1600.0	Hoffmann et al. (2009)
R <sub>o</sub> 00974	*		$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OH}) + \text{NO}_3 \rightarrow$ 0.173 $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CH}_2(\text{OO}\cdot) +$ 0.181 $\text{CH}_3\text{CH}(\text{OO}\cdot)\text{CH}(\text{OH})\text{CH}_2(\text{OH}) +$ 0.290 $\text{CH}_3\text{CH}_2\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2(\text{OH}) +$ 0.286 $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) + 0.036 \text{CH}_3\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) +$ 0.034 $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.930 \text{O}_2$	$2.2 \cdot 10^{+06}$		
R <sub>o</sub> 00975	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{RO_2}$ 0.200 $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CH}_2(\text{O}\cdot) + 0.550 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CHO} +$ 0.250 $\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00976	*	*	$\text{CH}_3\text{CH}(\text{OO}\cdot)\text{CH}(\text{OH})\text{CH}_2(\text{OH}) \xrightarrow{RO_2}$ 0.200 $\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CH}_2(\text{OH}) + 0.550 \text{CH}_3\text{COCH}(\text{OH})\text{CH}_2(\text{OH}) +$ 0.250 $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00977	*	*	$\text{CH}_3\text{CH}_2\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2(\text{OH}) \rightarrow \text{CH}_3\text{CH}_2\text{COCH}_2(\text{OH}) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00978	*	*	$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00979	*	*	$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00980	*	*	$\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \rightarrow \text{CH}_3\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00981	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00982	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00983	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CH}_2(\text{OH}) \xrightarrow{\text{O}_2} \text{CH}_3\text{COCH}(\text{OH})\text{CH}_2(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00984	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CH}_2(\text{OH}) \rightarrow$ $0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CHO} + 0.500 \text{CH}_3\text{CHO} +$ $0.500 \text{CH}_2(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00985	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2(\text{OH}) + \text{OH} \rightarrow$ $0.049 \text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) +$ $0.452 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2\text{CH}_2(\text{OH}) +$ $0.051 \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OO}\cdot)\text{CH}_2(\text{OH}) +$ $0.448 \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$1.8 \cdot 10^{+09}$		Average of <i>Anbar et al.</i> (1966a) and <i>Adams et al.</i> (1965a)
R <sub>o</sub> 00986	*		$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2(\text{OH}) + \text{NO}_3 \rightarrow$ $0.049 \text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) +$ $0.452 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2\text{CH}_2(\text{OH}) +$ $0.051 \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OO}\cdot)\text{CH}_2(\text{OH}) +$ $0.448 \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$2.2 \cdot 10^{+06}$		
R <sub>o</sub> 00987	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) + 0.550 \text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00988	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2\text{CH}_2(\text{OH}) \rightarrow \text{CH}_3\text{COCH}_2\text{CH}_2(\text{OH}) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00989	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OO}\cdot)\text{CH}_2(\text{OH}) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) + 0.550 \text{CH}_3\text{CH}(\text{OH})\text{COCH}_2(\text{OH}) +$ $0.250 \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00990	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00991	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00992	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 00993	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) \xrightarrow{\text{O}_2} \text{CH}_3\text{CH}(\text{OH})\text{COCH}_2(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 00994	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) \rightarrow 0.500 \text{CH}_3\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.500 \text{CH}_2(\text{OH})\text{CHO} + 0.500 \text{CH}_3\text{CH}(\text{OH})\text{CHO} + 0.500 \text{CH}_2(\text{OH})\cdot - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 00995	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2(\text{OH}) + \text{OH} \rightarrow$ $0.767 \text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.194 \text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OO}\cdot)\text{CH}_2(\text{OH}) + 0.039 \text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2(\text{O}\cdot) +$ $\text{H}_2\text{O} - 0.961 \text{O}_2$	$3.5 \cdot 10^{+09}$	-1203.0	Hoffmann et al. (2009)
R <sub>o</sub> 00996	*		$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2(\text{OH}) + \text{NO}_3 \rightarrow$ $0.767 \text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.194 \text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OO}\cdot)\text{CH}_2(\text{OH}) + 0.039 \text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2(\text{O}\cdot) +$ $\text{NO}_3^- + \text{H}^+ - 0.961 \text{O}_2$	$2.2 \cdot 10^{+06}$		
R <sub>o</sub> 00997	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 00998	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OO}\cdot)\text{CH}_2(\text{OH}) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) + 0.550 \text{CH}_2(\text{OH})\text{CH}_2\text{COCH}_2(\text{OH}) +$ $0.250 \text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 00999	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{CH}_2\text{COCH}_2(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01000	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) \rightarrow 0.500 \text{CH}_2(\text{OH})\text{CH}_2(\text{OO}\cdot) +$ $0.500 \text{CH}_2(\text{OH})\text{CHO} + 0.500 \text{CH}_2(\text{OH})\text{CH}_2\text{CHO} + 0.500 \text{CH}_2(\text{OH})\cdot - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01001	*	*	$\text{CH}_3\text{CH}_2\text{COCH}_2(\text{OH}) + \text{OH} \rightarrow 0.383 \text{CH}_2(\text{OH})\text{COCH}_2\text{CH}_2(\text{OO}\cdot) +$ $0.210 \text{CH}_3\text{CH}(\text{OO}\cdot)\text{COCH}_2(\text{OH}) + 0.332 \text{CH}_3\text{CH}_2\text{COCH}(\text{OH})(\text{OO}\cdot) +$ $0.075 \text{CH}_3\text{CH}_2\text{COCH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.925 \text{O}_2$	$1.0 \cdot 10^{+09}$		
R <sub>o</sub> 01002	*		$\text{CH}_3\text{CH}_2\text{COCH}_2(\text{OH}) + \text{NO}_3 \rightarrow 0.383 \text{CH}_2(\text{OH})\text{COCH}_2\text{CH}_2(\text{OO}\cdot) +$ $0.210 \text{CH}_3\text{CH}(\text{OO}\cdot)\text{COCH}_2(\text{OH}) + 0.332 \text{CH}_3\text{CH}_2\text{COCH}(\text{OH})(\text{OO}\cdot) +$ $0.075 \text{CH}_3\text{CH}_2\text{COCH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.925 \text{O}_2$	$1.8 \cdot 10^{+06}$		
R <sub>o</sub> 01003	*	*	$\text{CH}_2(\text{OH})\text{COCH}_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_2(\text{OH})\text{COCH}_2\text{CH}_2(\text{O}\cdot) + 0.550 \text{CH}_2(\text{OH})\text{COCH}_2\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{CH}_2\text{COCH}_2(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01004	*	*	$\text{CH}_3\text{CH}(\text{OO}\cdot)\text{COCH}_2(\text{OH}) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_3\text{CH}(\text{O}\cdot)\text{COCH}_2(\text{OH}) + 0.550 \text{CH}_3\text{COCOCH}_2(\text{OH}) +$ $0.250 \text{CH}_3\text{CH}(\text{OH})\text{COCH}_2(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01005	*	*	$\text{CH}_3\text{CH}_2\text{COCH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_3\text{CH}_2\text{COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01006	*	*	$\text{CH}_2(\text{OH})\text{COCH}_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCH}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01007	*	*	$\text{CH}_2(\text{OH})\text{COCH}_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{COCH}_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01008	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{COCH}_2(\text{OH}) \xrightarrow{\text{O}_2} \text{CH}_3\text{COCOCH}_2(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01009	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{COCH}_2(\text{OH}) \rightarrow 0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CH}_2(\text{OH})\text{COCHO} + 0.500 \text{CH}_3\text{CHO} + 0.500 \text{CH}_2(\text{OH})\text{CO}(\text{OO}\cdot) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01010	*	*	$\text{CH}_3\text{COCH}_2\text{CH}_2(\text{OH}) + \text{OH} \rightarrow 0.048 \text{CH}_2(\text{OH})\text{CH}_2\text{COCH}_2(\text{OO}\cdot) + 0.051 \text{CH}_3\text{COCH}(\text{OO}\cdot)\text{CH}_2(\text{OH}) + 0.848 \text{CH}_3\text{COCH}_2\text{CH}(\text{OH})(\text{OO}\cdot) + 0.052 \text{CH}_3\text{COCH}_2\text{CH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.948 \text{O}_2$	$1.8 \cdot 10^{+09}$		
R <sub>o</sub> 01011	*		$\text{CH}_3\text{COCH}_2\text{CH}_2(\text{OH}) + \text{NO}_3 \rightarrow 0.048 \text{CH}_2(\text{OH})\text{CH}_2\text{COCH}_2(\text{OO}\cdot) + 0.051 \text{CH}_3\text{COCH}(\text{OO}\cdot)\text{CH}_2(\text{OH}) + 0.848 \text{CH}_3\text{COCH}_2\text{CH}(\text{OH})(\text{OO}\cdot) + 0.052 \text{CH}_3\text{COCH}_2\text{CH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.948 \text{O}_2$	$1.8 \cdot 10^{+06}$		
R <sub>o</sub> 01012	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{COCH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_2(\text{OH})\text{CH}_2\text{COCH}_2(\text{O}\cdot) + 0.550 \text{CH}_2(\text{OH})\text{CH}_2\text{COCHO} + 0.250 \text{CH}_2(\text{OH})\text{CH}_2\text{COCH}_2(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01013	*	*	$\text{CH}_3\text{COCH}(\text{OO}\cdot)\text{CH}_2(\text{OH}) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_3\text{COCH}(\text{O}\cdot)\text{CH}_2(\text{OH}) + 0.550 \text{CH}_3\text{COCOCH}_2(\text{OH}) + 0.250 \text{CH}_3\text{COCH}(\text{OH})\text{CH}_2(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01014	*	*	$\text{CH}_3\text{COCH}_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_3\text{COCH}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01015	*	*	$\text{CH}_3\text{COCH}_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_3\text{COCH}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01016	*	*	$\text{CH}_3\text{COCH}_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CH}_3\text{COCH}_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01017	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{COCH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{CH}_2\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01018	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{COCH}_2(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}_2\text{CO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01019	*	*	$\text{CH}_3\text{COCH}(\text{O}\cdot)\text{CH}_2(\text{OH}) \xrightarrow{\text{O}_2} \text{CH}_3\text{COCOCH}_2(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01020	*	*	$\text{CH}_3\text{COCH}(\text{O}\cdot)\text{CH}_2(\text{OH}) \rightarrow 0.500 \text{CH}_3\text{CO}(\text{OO}\cdot) + 0.500 \text{CH}_2(\text{OH})\text{CHO} + 0.500 \text{CH}_3\text{COCHO} + 0.500 \text{CH}_2(\text{OH})\cdot - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00126	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CH}(\text{OH})_2$	$1.6 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01021	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CHO} + \text{OH} \rightarrow 0.374 \text{CHOCH}_2\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) + 0.078 \text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{CH}_2\text{CHO} + 0.039 \text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OO}\cdot)\text{CHO} + 0.509 \text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CO}(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$4.9 \cdot 10^{+09}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01022	*		CH <sub>2</sub> (OH)CH <sub>2</sub> CH <sub>2</sub> CHO + NO <sub>3</sub> → 0.374 CHOCH <sub>2</sub> CH <sub>2</sub> CH(OH)(OO·) + 0.078 CH <sub>2</sub> (OH)CH(OO·)CH <sub>2</sub> CHO + 0.039 CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OO·)CHO + 0.509 CH <sub>2</sub> (OH)CH <sub>2</sub> CH <sub>2</sub> CO(OO·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	3.8 · 10 <sup>+07</sup>		
R <sub>o</sub> 01023	*	*	CHOCH <sub>2</sub> CH <sub>2</sub> CH(OH)(OO·) → CHOCH <sub>2</sub> CH <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01024	*	*	CH <sub>2</sub> (OH)CH(OO·)CH <sub>2</sub> CHO $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(O·)CH <sub>2</sub> CHO + 0.550 CH <sub>2</sub> (OH)COCH <sub>2</sub> CHO + 0.250 CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01025	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OO·)CHO $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH <sub>2</sub> CH(O·)CHO + 0.550 CH <sub>2</sub> (OH)CH <sub>2</sub> COCHO + 0.250 CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01026	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH <sub>2</sub> CO(OO·) → CH <sub>2</sub> (OH)CH <sub>2</sub> CH <sub>2</sub> CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01027	*	*	CH <sub>2</sub> (OH)CH(O·)CH <sub>2</sub> CHO $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCH <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01028	*	*	CH <sub>2</sub> (OH)CH(O·)CH <sub>2</sub> CHO → 0.500 CH <sub>2</sub> (OH)· + 0.500 CHOCH <sub>2</sub> CHO + 0.500 CH <sub>2</sub> (OH)CHO + 0.500 CHOCH <sub>2</sub> (OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01029	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH(O·)CHO $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH <sub>2</sub> COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01030	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH(O·)CHO → 0.500 CH <sub>2</sub> (OH)CH <sub>2</sub> (OO·) + 0.500 CHOCHO + 0.500 CH <sub>2</sub> (OH)CH <sub>2</sub> CHO + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01031	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH <sub>2</sub> CH(OH) <sub>2</sub> + OH → 0.492 CH(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OH)(OO·) + 0.119 CH <sub>2</sub> (OH)CH(OO·)CH <sub>2</sub> CH(OH) <sub>2</sub> + 0.050 CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OO·)CH(OH) <sub>2</sub> + 0.231 CH <sub>2</sub> (OH)CH <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.108 CH <sub>2</sub> (OH)CH <sub>2</sub> CH <sub>2</sub> CH(OH)(O·) + H <sub>2</sub> O - 0.892 O <sub>2</sub>	3.7 · 10 <sup>+09</sup>		
R <sub>o</sub> 01032	*		CH <sub>2</sub> (OH)CH <sub>2</sub> CH <sub>2</sub> CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.492 CH(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OH)(OO·) + 0.119 CH <sub>2</sub> (OH)CH(OO·)CH <sub>2</sub> CH(OH) <sub>2</sub> + 0.050 CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OO·)CH(OH) <sub>2</sub> + 0.231 CH <sub>2</sub> (OH)CH <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.108 CH <sub>2</sub> (OH)CH <sub>2</sub> CH <sub>2</sub> CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.892 O <sub>2</sub>	1.3 · 10 <sup>+07</sup>		
R <sub>o</sub> 01033	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OH)(OO·) → CH(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01034	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{CH}_2\text{CH}(\text{OH})_2 \xrightarrow{RO_2}$ $0.200 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2\text{CH}(\text{OH})_2 + 0.550 \text{CH}_2(\text{OH})\text{COCH}_2\text{CH}(\text{OH})_2 +$ $0.250 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CH}(\text{OH})_2 + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01035	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OO}\cdot)\text{CH}(\text{OH})_2 \xrightarrow{RO_2}$ $0.200 \text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})_2 + 0.550 \text{CH}_2(\text{OH})\text{CH}_2\text{COCH}(\text{OH})_2 +$ $0.250 \text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CH}(\text{OH})_2 + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01036	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01037	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{O_2} \text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01038	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01039	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2\text{CH}(\text{OH})_2 \xrightarrow{O_2} \text{CH}_2(\text{OH})\text{COCH}_2\text{CH}(\text{OH})_2 + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01040	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2\text{CH}(\text{OH})_2 \rightarrow$ $0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CH}(\text{OH})_2\text{CH}_2\text{CHO} + 0.500 \text{CH}_2(\text{OH})\text{CHO} +$ $0.500 \text{CH}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01041	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})_2 \xrightarrow{O_2} \text{CH}_2(\text{OH})\text{CH}_2\text{COCH}(\text{OH})_2 + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01042	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})_2 \rightarrow 0.500 \text{CH}_2(\text{OH})\text{CH}_2(\text{OO}\cdot) +$ $0.500 \text{CH}(\text{OH})_2\text{CHO} + 0.500 \text{CH}_2(\text{OH})\text{CH}_2\text{CHO} + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01043	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OH}) + \text{OH} \rightarrow$ $0.083 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) +$ $0.327 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})\text{CH}_2(\text{OH}) +$ $0.139 \text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2(\text{OH}) +$ $0.325 \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.044 \text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CH}_2(\text{OH}) + 0.041 \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) +$ $0.041 \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.875 \text{O}_2$	$2.2 \cdot 10^{+09}$		
R <sub>o</sub> 01044	*		$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OH}) + \text{NO}_3 \rightarrow$ $0.083 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) +$ $0.327 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})\text{CH}_2(\text{OH}) +$ $0.139 \text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2(\text{OH}) +$ $0.325 \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.044 \text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CH}_2(\text{OH}) + 0.041 \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) +$ $0.041 \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.875 \text{O}_2$	$2.2 \cdot 10^{+06}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01045	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OH)CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(OH)CH(OH)CH <sub>2</sub> (O·) + 0.550 CH <sub>2</sub> (OH)CH(OH)CH(OH)CHO + 0.250 CH <sub>2</sub> (OH)CH(OH)CH(OH)CH <sub>2</sub> (OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01046	*	*	CH <sub>3</sub> C(OH)(OO·)CH(OH)CH <sub>2</sub> (OH) → CH <sub>3</sub> COCH(OH)CH <sub>2</sub> (OH) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01047	*	*	CH <sub>3</sub> CH(OH)C(OH)(OO·)CH <sub>2</sub> (OH) → CH <sub>3</sub> CH(OH)COCH <sub>2</sub> (OH) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01048	*	*	CH <sub>3</sub> CH(OH)CH(OH)CH(OH)(OO·) → CH <sub>3</sub> CH(OH)CH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01049	*	*	CH <sub>3</sub> CH(OH)CH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>3</sub> CH(OH)CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01050	*	*	CH <sub>3</sub> CH(OH)CH(OH)CH <sub>2</sub> (O·) → CH <sub>3</sub> CH(OH)CH(OH)(OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01051	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(OH)CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01052	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OH)CH <sub>2</sub> (O·) → CH <sub>2</sub> (OH)CH(OH)CH(OH)(OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01053	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CH <sub>2</sub> (OH) + OH → 0.517 CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> CH(OH)(OO·) + 0.055 CH <sub>2</sub> (OH)CH(OH)CH(OO·)CH <sub>2</sub> (OH) + 0.209 CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH)(OO·)CH <sub>2</sub> (OH) + 0.219 CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CH(OH)(OO·) + H <sub>2</sub> O – O <sub>2</sub>	3.4 · 10 <sup>+09</sup>		
R <sub>o</sub> 01054	*		CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CH <sub>2</sub> (OH) + NO <sub>3</sub> → 0.517 CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> CH(OH)(OO·) + 0.055 CH <sub>2</sub> (OH)CH(OH)CH(OO·)CH <sub>2</sub> (OH) + 0.209 CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH)(OO·)CH <sub>2</sub> (OH) + 0.219 CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CH(OH)(OO·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – O <sub>2</sub>	2.2 · 10 <sup>+06</sup>		
R <sub>o</sub> 01055	*	*	CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> CH(OH)(OO·) → CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01056	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OO·)CH <sub>2</sub> (OH) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(OH)CH(O·)CH <sub>2</sub> (OH) + 0.550 CH <sub>2</sub> (OH)CH(OH)COCH <sub>2</sub> (OH) + 0.250 CH <sub>2</sub> (OH)CH(OH)CH(OH)CH <sub>2</sub> (OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01057	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH)(OO·)CH <sub>2</sub> (OH) → CH <sub>2</sub> (OH)CH <sub>2</sub> COCH <sub>2</sub> (OH) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01058	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CH(OH)(OO·) → CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01059	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) \xrightarrow{\text{O}_2}$ $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCH}_2(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01060	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) + 0.500 \text{CH}_2(\text{OH})\text{CHO} +$ $0.500 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CHO} + 0.500 \text{CH}_2(\text{OH})\cdot - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01061	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{COCH}_2(\text{OH}) + \text{OH} \rightarrow 0.719 \text{CH}_2(\text{OH})\text{COCH}_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.041 \text{CH}_2(\text{OH})\text{COCH}(\text{OO}\cdot)\text{CH}_2(\text{OH}) +$ $0.160 \text{CH}_2(\text{OH})\text{CH}_2\text{COCH}(\text{OH})(\text{OO}\cdot) + 0.044 \text{CH}_2(\text{OH})\text{COCH}_2\text{CH}_2(\text{O}\cdot) +$ $0.036 \text{CH}_2(\text{OH})\text{CH}_2\text{COCH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.919 \text{O}_2$	$2.1 \cdot 10^{+09}$		
R <sub>o</sub> 01062	*		$\text{CH}_2(\text{OH})\text{CH}_2\text{COCH}_2(\text{OH}) + \text{NO}_3 \rightarrow$ $0.719 \text{CH}_2(\text{OH})\text{COCH}_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.041 \text{CH}_2(\text{OH})\text{COCH}(\text{OO}\cdot)\text{CH}_2(\text{OH}) +$ $0.160 \text{CH}_2(\text{OH})\text{CH}_2\text{COCH}(\text{OH})(\text{OO}\cdot) + 0.044 \text{CH}_2(\text{OH})\text{COCH}_2\text{CH}_2(\text{O}\cdot) +$ $0.036 \text{CH}_2(\text{OH})\text{CH}_2\text{COCH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.919 \text{O}_2$	$1.8 \cdot 10^{+06}$		
R <sub>o</sub> 01063	*	*	$\text{CH}_2(\text{OH})\text{COCH}_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{COCH}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01064	*	*	$\text{CH}_2(\text{OH})\text{COCH}(\text{OO}\cdot)\text{CH}_2(\text{OH}) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_2(\text{OH})\text{COCH}(\text{O}\cdot)\text{CH}_2(\text{OH}) + 0.550 \text{CH}_2(\text{OH})\text{COCOCH}_2(\text{OH}) +$ $0.250 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCH}_2(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01065	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{COCH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}_2\text{COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01066	*	*	$\text{CH}_2(\text{OH})\text{COCH}(\text{O}\cdot)\text{CH}_2(\text{OH}) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCOCH}_2(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01067	*	*	$\text{CH}_2(\text{OH})\text{COCH}(\text{O}\cdot)\text{CH}_2(\text{OH}) \rightarrow 0.500 \text{CH}_2(\text{OH})\text{CO}(\text{OO}\cdot) +$ $0.500 \text{CH}_2(\text{OH})\text{CHO} + 0.500 \text{CH}_2(\text{OH})\text{COCHO} + 0.500 \text{CH}_2(\text{OH})\cdot - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00127	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{COCH}_2(\text{OH}) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{OH})$	$1.4 \cdot 10^{-01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01068	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{COCH}_2(\text{OH}) + \text{OH} \rightarrow$ $0.163 \text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{CH}_2(\text{OO}\cdot) + 0.337 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{COCH}_2(\text{OH}) +$ $0.335 \text{CH}_3\text{CH}(\text{OH})\text{COCH}(\text{OH})(\text{OO}\cdot) + 0.086 \text{CH}_3\text{CH}(\text{O}\cdot)\text{COCH}_2(\text{OH}) +$ $0.080 \text{CH}_3\text{CH}(\text{OH})\text{COCH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.835 \text{O}_2$	$9.4 \cdot 10^{+08}$		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01069	*		CH <sub>3</sub> CH(OH)COCH <sub>2</sub> (OH) + NO <sub>3</sub> → 0.163 CH <sub>2</sub> (OH)COCH(OH)CH <sub>2</sub> (OO·) + 0.337 CH <sub>3</sub> C(OH)(OO·)COCH <sub>2</sub> (OH) + 0.335 CH <sub>3</sub> CH(OH)COCH(OH)(OO·) + 0.086 CH <sub>3</sub> CH(O·)COCH <sub>2</sub> (OH) + 0.080 CH <sub>3</sub> CH(OH)COCH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.835 O <sub>2</sub>	1.8 · 10 <sup>+06</sup>		
R <sub>o</sub> 01070	*	*	CH <sub>2</sub> (OH)COCH(OH)CH <sub>2</sub> (OO·) $\xrightarrow{RO_2^-}$ 0.200 CH <sub>2</sub> (OH)COCH(OH)CH <sub>2</sub> (O·) + 0.550 CH <sub>2</sub> (OH)COCH(OH)CHO + 0.250 CH <sub>2</sub> (OH)CH(OH)COCH <sub>2</sub> (OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01071	*	*	CH <sub>3</sub> C(OH)(OO·)COCH <sub>2</sub> (OH) → CH <sub>3</sub> COCOCH <sub>2</sub> (OH) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01072	*	*	CH <sub>3</sub> CH(OH)COCH(OH)(OO·) → CH <sub>3</sub> CH(OH)COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01073	*	*	CH <sub>3</sub> CH(OH)COCH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>3</sub> CH(OH)COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01074	*	*	CH <sub>3</sub> CH(OH)COCH <sub>2</sub> (O·) → CH <sub>3</sub> CH(OH)CO(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01075	*	*	CH <sub>2</sub> (OH)COCH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01076	*	*	CH <sub>2</sub> (OH)COCH(OH)CH <sub>2</sub> (O·) → CH <sub>2</sub> (OH)COCH(OH)(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01077	*	*	CH <sub>3</sub> COCH(OH)CH <sub>2</sub> (OH) + OH → 0.083 CH <sub>2</sub> (OH)CH(OH)COCH <sub>2</sub> (OO·) + 0.138 CH <sub>3</sub> COC(OH)(OO·)CH <sub>2</sub> (OH) + 0.612 CH <sub>3</sub> COCH(OH)CH(OH)(OO·) + 0.077 CH <sub>3</sub> COCH(O·)CH <sub>2</sub> (OH) + 0.089 CH <sub>3</sub> COCH(OH)CH <sub>2</sub> (O·) + H <sub>2</sub> O - 0.833 O <sub>2</sub>	9.8 · 10 <sup>+08</sup>		
R <sub>o</sub> 01078	*		CH <sub>3</sub> COCH(OH)CH <sub>2</sub> (OH) + NO <sub>3</sub> → 0.083 CH <sub>2</sub> (OH)CH(OH)COCH <sub>2</sub> (OO·) + 0.138 CH <sub>3</sub> COC(OH)(OO·)CH <sub>2</sub> (OH) + 0.612 CH <sub>3</sub> COCH(OH)CH(OH)(OO·) + 0.077 CH <sub>3</sub> COCH(O·)CH <sub>2</sub> (OH) + 0.089 CH <sub>3</sub> COCH(OH)CH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.833 O <sub>2</sub>	1.8 · 10 <sup>+06</sup>		
R <sub>o</sub> 01079	*	*	CH <sub>2</sub> (OH)CH(OH)COCH <sub>2</sub> (OO·) $\xrightarrow{RO_2^-}$ 0.200 CH <sub>2</sub> (OH)CH(OH)COCH <sub>2</sub> (O·) + 0.550 CH <sub>2</sub> (OH)CH(OH)COCHO + 0.250 CH <sub>2</sub> (OH)CH(OH)COCH <sub>2</sub> (OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01080	*	*	CH <sub>3</sub> COC(OH)(OO·)CH <sub>2</sub> (OH) → CH <sub>3</sub> COCOCH <sub>2</sub> (OH) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01081	*	*	CH <sub>3</sub> COCH(OH)CH(OH)(OO·) → CH <sub>3</sub> COCH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01082	*	*	CH <sub>3</sub> COCH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>3</sub> COCH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01083	*	*	CH <sub>3</sub> COCH(OH)CH <sub>2</sub> (O·) → CH <sub>3</sub> COCH(OH)(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01084	*	*	CH <sub>2</sub> (OH)CH(OH)COCH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(OH)COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01085	*	*	CH <sub>2</sub> (OH)CH(OH)COCH <sub>2</sub> (O·) → CH <sub>2</sub> (OH)CH(OH)CO(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00128	*	*	$\text{CH}_3\text{COCOCH}_2(\text{OH}) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C}(\text{OH})_2\text{COCH}_2(\text{OH})$	$1.5 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00129	*	*	$\text{CH}_3\text{COCOCH}_2(\text{OH}) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{COC}(\text{OH})_2\text{CH}_2(\text{OH})$	$4.5 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00130	*	*	$\text{CH}_3\text{COCOCH}_2(\text{OH}) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{OH})$	$1.3 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01086	*	*	$\text{CH}_3\text{COCOCH}_2(\text{OH}) + \text{OH} \rightarrow 0.167 \text{CH}_2(\text{OH})\text{COCOCH}_2(\text{OO}\cdot) +$ $0.652 \text{CH}_3\text{COCOCH}(\text{OH})(\text{OO}\cdot) + 0.181 \text{CH}_3\text{COCOCH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.819 \text{O}_2$	$4.1 \cdot 10^{+08}$		
R <sub>o</sub> 01087	*		$\text{CH}_3\text{COCOCH}_2(\text{OH}) + \text{NO}_3 \rightarrow$ $0.167 \text{CH}_2(\text{OH})\text{COCOCH}_2(\text{OO}\cdot) + 0.652 \text{CH}_3\text{COCOCH}(\text{OH})(\text{OO}\cdot) +$ $0.181 \text{CH}_3\text{COCOCH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.819 \text{O}_2$	$1.4 \cdot 10^{+06}$		
R <sub>o</sub> 01088	*	*	$\text{CH}_2(\text{OH})\text{COCOCH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_2(\text{OH})\text{COCOCH}_2(\text{O}\cdot) + 0.550 \text{CH}_2(\text{OH})\text{COCOCHO} +$ $0.250 \text{CH}_2(\text{OH})\text{COCOCH}_2(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01089	*	*	$\text{CH}_3\text{COCOCH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_3\text{COCOCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01090	*	*	$\text{CH}_2(\text{OH})\text{COCOCH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCOCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01091	*	*	$\text{CH}_2(\text{OH})\text{COCOCH}_2(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{COCO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00131	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}(\text{OH})_2$	$2.5 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01092	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO} + \text{OH} \rightarrow$ $0.047 \text{CHOCH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) + 0.359 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2\text{CHO} +$ $0.594 \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CO}(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$4.0 \cdot 10^{+09}$		
R <sub>o</sub> 01093	*		$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CHO} + \text{NO}_3 \rightarrow$ $0.047 \text{CHOCH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) + 0.359 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2\text{CHO} +$ $0.594 \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CO}(\text{OO}\cdot) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$3.8 \cdot 10^{+07}$		
R <sub>o</sub> 01094	*	*	$\text{CHOCH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CHOCH}_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) + 0.550 \text{CHOCH}_2\text{CH}(\text{OH})\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01095	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2\text{CHO} \rightarrow \text{CH}_3\text{COCH}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01096	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CO}(\text{OO}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CO}(\text{OH}) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01097	*	*	$\text{CHOCH}_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CHOCH}_2\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01098	*	*	$\text{CHOCH}_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \rightarrow \text{CHOCH}_2\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00132	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CH}(\text{OH})_2$	$9.8 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01099	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CHO + OH → 0.546 CHOCH(OH)CH <sub>2</sub> CH(OH)(OO·) + 0.048 CH <sub>2</sub> (OH)CH(OO·)CH(OH)CHO + 0.091 CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH)(OO·)CHO + 0.315 CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CO(OO·) + H <sub>2</sub> O – O <sub>2</sub>	3.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 01100	*		CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CHO + NO <sub>3</sub> → 0.546 CHOCH(OH)CH <sub>2</sub> CH(OH)(OO·) + 0.048 CH <sub>2</sub> (OH)CH(OO·)CH(OH)CHO + 0.091 CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH)(OO·)CHO + 0.315 CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CO(OO·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – O <sub>2</sub>	3.8 · 10 <sup>+07</sup>		
R <sub>o</sub> 01101	*	*	CHOCH(OH)CH <sub>2</sub> CH(OH)(OO·) → CHOCH <sub>2</sub> CH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01102	*	*	CH <sub>2</sub> (OH)CH(OO·)CH(OH)CHO $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(O·)CH(OH)CHO + 0.550 CH <sub>2</sub> (OH)COCH(OH)CHO + 0.250 CH <sub>2</sub> (OH)CH(OH)CH(OH)CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01103	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH)(OO·)CHO → CH <sub>2</sub> (OH)CH <sub>2</sub> COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01104	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CO(OO·) → CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CO(OH) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01105	*	*	CH <sub>2</sub> (OH)CH(O·)CH(OH)CHO $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01106	*	*	CH <sub>2</sub> (OH)CH(O·)CH(OH)CHO → 0.500 CH <sub>2</sub> (OH)· + 0.500 CHOCH(OH)CHO + 0.500 CH <sub>2</sub> (OH)CHO + 0.500 CHOCH(OH)(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00133	*	*	CH <sub>3</sub> CH <sub>2</sub> CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH(OH) <sub>2</sub>	7.4 · 10 <sup>+00</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01107	*	*	CH <sub>3</sub> CH <sub>2</sub> CH(OH)CHO + OH → 0.201 CHOCH(OH)CH <sub>2</sub> CH <sub>2</sub> (OO·) + 0.172 CH <sub>3</sub> CH(OO·)CH(OH)CHO + 0.139 CH <sub>3</sub> CH <sub>2</sub> C(OH)(OO·)CHO + 0.453 CH <sub>3</sub> CH <sub>2</sub> CH(OH)CO(OO·) + 0.034 CH <sub>3</sub> CH <sub>2</sub> CH(O·)CHO + H <sub>2</sub> O – 0.966 O <sub>2</sub>	2.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 01108	*		CH <sub>3</sub> CH <sub>2</sub> CH(OH)CHO + NO <sub>3</sub> → 0.201 CHOCH(OH)CH <sub>2</sub> CH <sub>2</sub> (OO·) + 0.172 CH <sub>3</sub> CH(OO·)CH(OH)CHO + 0.139 CH <sub>3</sub> CH <sub>2</sub> C(OH)(OO·)CHO + 0.453 CH <sub>3</sub> CH <sub>2</sub> CH(OH)CO(OO·) + 0.034 CH <sub>3</sub> CH <sub>2</sub> CH(O·)CHO + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.966 O <sub>2</sub>	4.1 · 10 <sup>+07</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01109	*	*	$\text{CHOCH(OH)CH}_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{RO_2}$ 0.200 $\text{CHOCH(OH)CH}_2\text{CH}_2(\text{O}\cdot) + 0.550 \text{CHOCH}_2\text{CH(OH)CHO} +$ 0.250 $\text{CH}_2(\text{OH})\text{CH}_2\text{CH(OH)CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01110	*	*	$\text{CH}_3\text{CH(OO}\cdot\text{)CH(OH)CHO} \xrightarrow{RO_2}$ 0.200 $\text{CH}_3\text{CH(O}\cdot\text{)CH(OH)CHO} + 0.550 \text{CH}_3\text{COCH(OH)CHO} +$ 0.250 $\text{CH}_3\text{CH(OH)CH(OH)CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01111	*	*	$\text{CH}_3\text{CH}_2\text{C(OH)(OO}\cdot\text{)CHO} \rightarrow \text{CH}_3\text{CH}_2\text{COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01112	*	*	$\text{CH}_3\text{CH}_2\text{CH(OH)CO(OO}\cdot\text{)} \rightarrow \text{CH}_3\text{CH}_2\text{CH(OH)CO(OH)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01113	*	*	$\text{CH}_3\text{CH}_2\text{CH(O}\cdot\text{)CHO} \xrightarrow{O_2} \text{CH}_3\text{CH}_2\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01114	*	*	$\text{CH}_3\text{CH}_2\text{CH(O}\cdot\text{)CHO} \rightarrow 0.500 \text{CH}_3\text{CH}_2(\text{OO}\cdot) + 0.500 \text{CHOCHO} +$ 0.500 $\text{CH}_3\text{CH}_2\text{CHO} + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{O}_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01115	*	*	$\text{CHOCH(OH)CH}_2\text{CH}_2(\text{O}\cdot) \xrightarrow{O_2} \text{CHOCH}_2\text{CH(OH)CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01116	*	*	$\text{CHOCH(OH)CH}_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CHOCH(OH)CH}_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01117	*	*	$\text{CH}_3\text{CH(O}\cdot\text{)CH(OH)CHO} \xrightarrow{O_2} \text{CH}_3\text{COCH(OH)CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01118	*	*	$\text{CH}_3\text{CH(O}\cdot\text{)CH(OH)CHO} \rightarrow 0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CHOCH(OH)CHO} +$ 0.500 $\text{CH}_3\text{CHO} + 0.500 \text{CHOCH(OH)(OO}\cdot\text{)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00134	*	*	$\text{CH}_2(\text{OH})\text{CH(OH)CH}_2\text{CHO} \xrightleftharpoons{H_2O} \text{CH}_2(\text{OH})\text{CH(OH)CH}_2\text{CH(OH)}_2$	$3.3 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01119	*	*	$\text{CH}_2(\text{OH})\text{CH(OH)CH}_2\text{CHO} + \text{OH} \rightarrow$ 0.200 $\text{CHOCH}_2\text{CH(OH)CH(OH)(OO}\cdot\text{)} +$ 0.156 $\text{CH}_2(\text{OH})\text{C(OH)(OO}\cdot\text{)CH}_2\text{CHO} +$ 0.644 $\text{CH}_2(\text{OH})\text{CH(OH)CH}_2\text{CO(OO}\cdot\text{)} + \text{H}_2\text{O} - \text{O}_2$	$3.7 \cdot 10^{+09}$		
R <sub>o</sub> 01120	*		$\text{CH}_2(\text{OH})\text{CH(OH)CH}_2\text{CHO} + \text{NO}_3 \rightarrow$ 0.200 $\text{CHOCH}_2\text{CH(OH)CH(OH)(OO}\cdot\text{)} +$ 0.156 $\text{CH}_2(\text{OH})\text{C(OH)(OO}\cdot\text{)CH}_2\text{CHO} +$ 0.644 $\text{CH}_2(\text{OH})\text{CH(OH)CH}_2\text{CO(OO}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$3.7 \cdot 10^{+07}$		
R <sub>o</sub> 01121	*	*	$\text{CHOCH}_2\text{CH(OH)CH(OH)(OO}\cdot\text{)} \rightarrow \text{CHOCH}_2\text{CH(OH)CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01122	*	*	$\text{CH}_2(\text{OH})\text{C(OH)(OO}\cdot\text{)CH}_2\text{CHO} \rightarrow \text{CH}_2(\text{OH})\text{COCH}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01123	*	*	$\text{CH}_2(\text{OH})\text{CH(OH)CH}_2\text{CO(OO}\cdot\text{)} \rightarrow$ $\text{CH}_2(\text{OH})\text{CH(OH)CH}_2\text{CO(OH)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
E <sub>o</sub> 00135	*	*	$\text{CH}_3\text{COCH}_2\text{CHO} \xrightleftharpoons{H_2O} \text{CH}_3\text{COCH}_2\text{CH(OH)}_2$	$9.0 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01124	*	*	CH <sub>3</sub> COCH <sub>2</sub> CHO + OH → 0.040 CHOCH <sub>2</sub> COCH <sub>2</sub> (OO·) + 0.960 CH <sub>3</sub> COCH <sub>2</sub> CO(OO·) + H <sub>2</sub> O – O <sub>2</sub>	2.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 01125	*		CH <sub>3</sub> COCH <sub>2</sub> CHO + NO <sub>3</sub> → 0.040 CHOCH <sub>2</sub> COCH <sub>2</sub> (OO·) + 0.960 CH <sub>3</sub> COCH <sub>2</sub> CO(OO·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – O <sub>2</sub>	1.5 · 10 <sup>+07</sup>		
R <sub>o</sub> 01126	*	*	CHOCH <sub>2</sub> COCH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CHOCH <sub>2</sub> COCH <sub>2</sub> (O·) + 0.550 CHOCH <sub>2</sub> COCHO + 0.250 CH <sub>2</sub> (OH)COCH <sub>2</sub> CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01127	*	*	CH <sub>3</sub> COCH <sub>2</sub> CO(OO·) → CH <sub>3</sub> COCH <sub>2</sub> CO(OH) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01128	*	*	CHOCH <sub>2</sub> COCH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CHOCH <sub>2</sub> COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01129	*	*	CHOCH <sub>2</sub> COCH <sub>2</sub> (O·) → CHOCH <sub>2</sub> CO(OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00136	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> COCHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)CH <sub>2</sub> COCH(OH) <sub>2</sub>	1.3 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00137	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> COCHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	6.4 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01130	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> COCHO + OH → 0.709 CHOCOCH <sub>2</sub> CH(OH)(OO·) + 0.033 CH <sub>2</sub> (OH)CH(OO·)COCHO + 0.215 CH <sub>2</sub> (OH)CH <sub>2</sub> COCO(OO·) + 0.044 CHOCOCH <sub>2</sub> CH <sub>2</sub> (O·) + H <sub>2</sub> O – 0.956 O <sub>2</sub>	2.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 01131	*		CH <sub>2</sub> (OH)CH <sub>2</sub> COCHO + NO <sub>3</sub> → 0.709 CHOCOCH <sub>2</sub> CH(OH)(OO·) + 0.033 CH <sub>2</sub> (OH)CH(OO·)COCHO + 0.215 CH <sub>2</sub> (OH)CH <sub>2</sub> COCO(OO·) + 0.044 CHOCOCH <sub>2</sub> CH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.956 O <sub>2</sub>	1.4 · 10 <sup>+07</sup>		
R <sub>o</sub> 01132	*	*	CHOCOCH <sub>2</sub> CH(OH)(OO·) → CHOCH <sub>2</sub> COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01133	*	*	CH <sub>2</sub> (OH)CH(OO·)COCHO $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(O·)COCHO + 0.550 CH <sub>2</sub> (OH)COCOCHO + 0.250 CH <sub>2</sub> (OH)CH(OH)COCHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01134	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> COCO(OO·) → CH <sub>2</sub> (OH)CH <sub>2</sub> COCO(OH) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01135	*	*	CHOCOCH <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CHOCH <sub>2</sub> COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01136	*	*	CHOCOCH <sub>2</sub> CH <sub>2</sub> (O·) → CHOCOCH <sub>2</sub> (OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01137	*	*	CH <sub>2</sub> (OH)CH(O·)COCHO $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCOCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01138	*	*	CH <sub>2</sub> (OH)CH(O·)COCHO → 0.500 CH <sub>2</sub> (OH)· + 0.500 CHOCOCHO + 0.500 CH <sub>2</sub> (OH)CHO + 0.500 CHOCO(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00138	*	*	CH <sub>3</sub> CH <sub>2</sub> COCHO $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> CH <sub>2</sub> COCH(OH) <sub>2</sub>	1.4 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00139	*	*	$\text{CH}_3\text{CH}_2\text{COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{C}(\text{OH})_2\text{CH}(\text{OH})_2$	$3.3 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01139	*	*	$\text{CH}_3\text{CH}_2\text{COCHO} + \text{OH} \rightarrow 0.380 \text{CHOCOCH}_2\text{CH}_2(\text{OO}\cdot) +$ $0.171 \text{CH}_3\text{CH}(\text{OO}\cdot)\text{COCHO} + 0.449 \text{CH}_3\text{CH}_2\text{COCO}(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$1.0 \cdot 10^{+09}$		
R <sub>o</sub> 01140	*		$\text{CH}_3\text{CH}_2\text{COCHO} + \text{NO}_3 \rightarrow 0.380 \text{CHOCOCH}_2\text{CH}_2(\text{OO}\cdot) +$ $0.171 \text{CH}_3\text{CH}(\text{OO}\cdot)\text{COCHO} + 0.449 \text{CH}_3\text{CH}_2\text{COCO}(\text{OO}\cdot) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$1.5 \cdot 10^{+07}$		
R <sub>o</sub> 01141	*	*	$\text{CHOCOCH}_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2} 0.200 \text{CHOCOCH}_2\text{CH}_2(\text{O}\cdot) + 0.550 \text{CHOCH}_2\text{COCHO} +$ $0.250 \text{CH}_2(\text{OH})\text{CH}_2\text{COCHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01142	*	*	$\text{CH}_3\text{CH}(\text{OO}\cdot)\text{COCHO} \xrightarrow{\text{RO}_2} 0.200 \text{CH}_3\text{CH}(\text{O}\cdot)\text{COCHO} +$ $0.550 \text{CH}_3\text{COCOCHO} + 0.250 \text{CH}_3\text{CH}(\text{OH})\text{COCHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01143	*	*	$\text{CH}_3\text{CH}_2\text{COCO}(\text{OO}\cdot) \rightarrow \text{CH}_3\text{CH}_2\text{COCO}(\text{OH}) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01144	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{COCHO} \xrightarrow{\text{O}_2} \text{CH}_3\text{COCOCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01145	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{COCHO} \rightarrow 0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CHOCOCHO} +$ $0.500 \text{CH}_3\text{CHO} + 0.500 \text{CHOCO}(\text{OO}\cdot) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00140	*	*	$\text{CH}_2(\text{OH})\text{COCH}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{COCH}_2\text{CH}(\text{OH})_2$	$1.2 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00141	*	*	$\text{CH}_2(\text{OH})\text{COCH}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}_2\text{CH}(\text{OH})_2$	$1.5 \cdot 10^{+00}$		
R <sub>o</sub> 01146	*	*	$\text{CH}_2(\text{OH})\text{COCH}_2\text{CHO} + \text{OH} \rightarrow$ $0.136 \text{CHOCH}_2\text{COCH}(\text{OH})(\text{OO}\cdot) + 0.833 \text{CH}_2(\text{OH})\text{COCH}_2\text{CO}(\text{OO}\cdot) +$ $0.031 \text{CHOCH}_2\text{COCH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.969 \text{O}_2$	$2.4 \cdot 10^{+09}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01147	*		$\text{CH}_2(\text{OH})\text{COCH}_2\text{CHO} + \text{NO}_3 \rightarrow$ $0.136 \text{CHOCH}_2\text{COCH}(\text{OH})(\text{OO}\cdot) + 0.833 \text{CH}_2(\text{OH})\text{COCH}_2\text{CO}(\text{OO}\cdot) +$ $0.031 \text{CHOCH}_2\text{COCH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.969 \text{O}_2$	$1.5 \cdot 10^{+07}$		
R <sub>o</sub> 01148	*	*	$\text{CHOCH}_2\text{COCH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CHOCH}_2\text{COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01149	*	*	$\text{CH}_2(\text{OH})\text{COCH}_2\text{CO}(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{COCH}_2\text{CO}(\text{OH}) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
E <sub>o</sub> 00142	*	*	$\text{CHOCH}_2\text{CH}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{CH}_2\text{CH}_2\text{CHO}$	$6.6 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00143	*	*	$\text{CHOCH}_2\text{CH}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{CH}_2\text{CH}_2\text{CH}(\text{OH})_2$	$1.4 \cdot 10^{+01}$		
R <sub>o</sub> 01150	*	*	$\text{CHOCH}_2\text{CH}_2\text{CHO} + \text{OH} \rightarrow$ $0.941 \text{CHOCH}_2\text{CH}_2\text{CO}(\text{OO}\cdot) + 0.059 \text{CHOCH}_2\text{CH}(\text{OO}\cdot)\text{CHO} + \text{H}_2\text{O} - \text{O}_2$	$5.3 \cdot 10^{+09}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01151	*		$\text{CHOCH}_2\text{CH}_2\text{CHO} + \text{NO}_3 \rightarrow 0.941 \text{CHOCH}_2\text{CH}_2\text{CO}(\text{OO}\cdot) +$ $0.059 \text{CHOCH}_2\text{CH}(\text{OO}\cdot)\text{CHO} + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$1.3 \cdot 10^{+07}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01152	*	*	$\text{CHOCH}_2\text{CH}_2\text{CO}(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CHO} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01153	*	*	$\text{CHOCH}_2\text{CH}(\text{OO}\cdot)\text{CHO} \xrightarrow{\text{RO}_2}$ $0.200 \text{ CHOCH}_2\text{CH}(\text{O}\cdot)\text{CHO} + 0.550 \text{ CHOCH}_2\text{COCHO} +$ $0.250 \text{ CHOCH}_2\text{CH}(\text{OH})\text{CHO} + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01154	*	*	$\text{CHOCH}_2\text{CH}(\text{O}\cdot)\text{CHO} \xrightarrow{\text{O}_2} \text{CHOCH}_2\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01155	*	*	$\text{CHOCH}_2\text{CH}(\text{O}\cdot)\text{CHO} \rightarrow 0.500 \text{ CHOCH}_2(\text{OO}\cdot) + 0.500 \text{ CHOCHO} +$ $0.500 \text{ CHOCH}_2\text{CHO} + 0.500 \text{ CH}\cdot(\text{OH})_2 - 0.500 \text{ O}_2 - 0.500 \text{ H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00144	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CO}(\text{OH}) \rightleftharpoons \text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CO}(\text{O}^-) + \text{H}^+$	$2.0 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 01156	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CO}(\text{OH}) + \text{OH} \rightarrow 0.825 \text{ CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.133 \text{ CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{CH}_2\text{CO}(\text{OH}) + 0.042 \text{ CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2(\text{O}\cdot) +$ $\text{H}_2\text{O} - 0.958 \text{ O}_2$	$2.2 \cdot 10^{+09}$		
R <sub>o</sub> 01157	*		$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CO}(\text{OH}) + \text{NO}_3 \rightarrow$ $0.825 \text{ CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.133 \text{ CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{CH}_2\text{CO}(\text{OH}) + 0.042 \text{ CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2(\text{O}\cdot) +$ $\text{NO}_3^- + \text{H}^+ - 0.958 \text{ O}_2$	$3.6 \cdot 10^{+02}$		
R <sub>o</sub> 01158	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01159	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{CH}_2\text{CO}(\text{OH}) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2\text{CO}(\text{OH}) + 0.550 \text{ CH}_2(\text{OH})\text{COCH}_2\text{CO}(\text{OH}) +$ $0.250 \text{ CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CO}(\text{OH}) + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01160	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01161	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}_2\text{CH}_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01162	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2\text{CO}(\text{OH}) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCH}_2\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01163	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2\text{CO}(\text{OH}) \rightarrow$ $0.500 \text{ CH}_2(\text{OH})\cdot + 0.500 \text{ CO}(\text{OH})\text{CH}_2\text{CHO} + 0.500 \text{ CH}_2(\text{OH})\text{CHO} +$ $0.500 \text{ CO}(\text{OH})\text{CH}_2(\text{OO}\cdot) - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01164	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{CH}_2\text{CH}(\text{OH})_2 + \text{OH} \rightarrow$ $0.597 \text{ CH}(\text{OH})_2\text{CH}_2\text{CH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.124 \text{ CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{OO}\cdot)\text{CH}(\text{OH})_2 +$ $0.279 \text{ CH}(\text{OH})_2\text{CH}_2\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.721 \text{ O}_2$	$2.9 \cdot 10^{+09}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01165	*		CH(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.597 CH(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.124 CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OO·)CH(OH) <sub>2</sub> + 0.279 CH(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.721 O <sub>2</sub>	1.2 · 10 <sup>+07</sup>		
R <sub>o</sub> 01166	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CH(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01167	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OO·)CH(OH) <sub>2</sub> $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH <sub>2</sub> CH(O·)CH(OH) <sub>2</sub> + 0.550 CH(OH) <sub>2</sub> CH <sub>2</sub> COCH(OH) <sub>2</sub> + 0.250 CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01168	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01169	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OH)(O·) → CH(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> (OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01170	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH(O·)CH(OH) <sub>2</sub> $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH <sub>2</sub> COCH(OH) <sub>2</sub> + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01171	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH(O·)CH(OH) <sub>2</sub> → 0.500 CH(OH) <sub>2</sub> CH <sub>2</sub> (OO·) + 0.500 CH(OH) <sub>2</sub> CHO + 0.500 CH(OH) <sub>2</sub> CH <sub>2</sub> CHO + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01172	*	*	CH <sub>3</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + OH → 0.287 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> (OO·) + 0.119 CH <sub>3</sub> CH(OO·)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + 0.093 CH <sub>3</sub> CH <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.256 CH <sub>3</sub> CH <sub>2</sub> C(OH)(O·)CH(OH) <sub>2</sub> + 0.246 CH <sub>3</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) + H <sub>2</sub> O - 0.498 O <sub>2</sub>	1.5 · 10 <sup>+09</sup>		
R <sub>o</sub> 01173	*		CH <sub>3</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.287 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> (OO·) + 0.119 CH <sub>3</sub> CH(OO·)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + 0.093 CH <sub>3</sub> CH <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.256 CH <sub>3</sub> CH <sub>2</sub> C(OH)(O·)CH(OH) <sub>2</sub> + 0.246 CH <sub>3</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.498 O <sub>2</sub>	1.1 · 10 <sup>+07</sup>		
R <sub>o</sub> 01174	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> (O·) + 0.550 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CHO + 0.250 CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01175	*	*	CH <sub>3</sub> CH(OO·)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> $\xrightarrow{RO_2}$ 0.200 CH <sub>3</sub> CH(O·)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + 0.550 CH <sub>3</sub> COC(OH) <sub>2</sub> CH(OH) <sub>2</sub> + 0.250 CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01176	*	*	CH <sub>3</sub> CH <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CH <sub>3</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01177	*	*	CH <sub>3</sub> CH <sub>2</sub> C(OH)(O·)CH(OH) <sub>2</sub> → 0.500 CH <sub>3</sub> CH <sub>2</sub> (OO·) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CH <sub>3</sub> CH <sub>2</sub> CO(OH) + 0.500 CH·(OH) <sub>2</sub> – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01178	*	*	CH <sub>3</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>3</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01179	*	*	CH <sub>3</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) → CH <sub>3</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01180	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01181	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> (O·) → CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01182	*	*	CH <sub>3</sub> CH(O·)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> $\xrightarrow{O_2}$ CH <sub>3</sub> COC(OH) <sub>2</sub> CH(OH) <sub>2</sub> + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01183	*	*	CH <sub>3</sub> CH(O·)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> → 0.500 CH <sub>3</sub> (OO·) + 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + 0.500 CH <sub>3</sub> CHO + 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01184	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH <sub>2</sub> CH(OH) <sub>2</sub> + OH → 0.149 CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) + 0.399 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.043 CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.203 CH <sub>2</sub> (OH)C(OH)(O·)CH <sub>2</sub> CH(OH) <sub>2</sub> + 0.205 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)(O·) + H <sub>2</sub> O – 0.548 O <sub>2</sub>	1.9 · 10 <sup>+09</sup>		
R <sub>o</sub> 01185	*		CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH <sub>2</sub> CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.149 CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) + 0.399 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.043 CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.203 CH <sub>2</sub> (OH)C(OH)(O·)CH <sub>2</sub> CH(OH) <sub>2</sub> + 0.205 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.548 O <sub>2</sub>	1.2 · 10 <sup>+07</sup>		
R <sub>o</sub> 01186	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) → CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01187	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH <sub>2</sub> CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01188	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01189	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) → CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01190	*	*	CH <sub>2</sub> (OH)C(OH)(O·)CH <sub>2</sub> CH(OH) <sub>2</sub> → 0.500 CH <sub>2</sub> (OH)· + 0.500 CH(OH) <sub>2</sub> CH <sub>2</sub> CO(OH) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CH(OH) <sub>2</sub> CH <sub>2</sub> (OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01191	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}_2\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01192	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01193	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) + 0.550 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01194	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})_2\text{CH}(\text{OH})_2 + \text{OH} \rightarrow$ $0.630 \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.052 \text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.035 \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2\text{CH}_2(\text{O}\cdot) +$ $0.144 \text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})_2 +$ $0.139 \text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.682 \text{O}_2$	$2.6 \cdot 10^{+09}$		
R <sub>o</sub> 01195	*		$\text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})_2\text{CH}(\text{OH})_2 + \text{NO}_3 \rightarrow$ $0.630 \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.052 \text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.035 \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2\text{CH}_2(\text{O}\cdot) +$ $0.144 \text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})_2 +$ $0.139 \text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.682 \text{O}_2$	$1.1 \cdot 10^{+07}$		
R <sub>o</sub> 01196	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01197	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01198	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})_2 \rightarrow$ $0.500 \text{CH}_2(\text{OH})\text{CH}_2(\text{OO}\cdot) + 0.500 \text{CH}(\text{OH})_2\text{CO}(\text{OH}) +$ $0.500 \text{CH}_2(\text{OH})\text{CH}_2\text{CO}(\text{OH}) + 0.500 \text{CH} \cdot (\text{OH})_2 - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01199	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01200	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01201	*	*	CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH(OH) <sub>2</sub> + OH → 0.222 CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> (OO·) + 0.221 CH <sub>3</sub> CH(OO·)CH(OH)CH(OH) <sub>2</sub> + 0.150 CH <sub>3</sub> CH <sub>2</sub> C(OH)(OO·)CH(OH) <sub>2</sub> + 0.172 CH <sub>3</sub> CH <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO·) + 0.044 CH <sub>3</sub> CH <sub>2</sub> CH(O·)CH(OH) <sub>2</sub> + 0.190 CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH(OH)(O·) + H <sub>2</sub> O – 0.765 O <sub>2</sub>	2.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 01202	*		CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.222 CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> (OO·) + 0.221 CH <sub>3</sub> CH(OO·)CH(OH)CH(OH) <sub>2</sub> + 0.150 CH <sub>3</sub> CH <sub>2</sub> C(OH)(OO·)CH(OH) <sub>2</sub> + 0.172 CH <sub>3</sub> CH <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO·) + 0.044 CH <sub>3</sub> CH <sub>2</sub> CH(O·)CH(OH) <sub>2</sub> + 0.190 CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.765 O <sub>2</sub>	1.4 · 10 <sup>+07</sup>		
R <sub>o</sub> 01203	*	*	CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> (O·) + 0.550 CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CHO + 0.250 CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01204	*	*	CH <sub>3</sub> CH(OO·)CH(OH)CH(OH) <sub>2</sub> $\xrightarrow{RO_2}$ 0.200 CH <sub>3</sub> CH(O·)CH(OH)CH(OH) <sub>2</sub> + 0.550 CH <sub>3</sub> COCH(OH)CH(OH) <sub>2</sub> + 0.250 CH <sub>3</sub> CH(OH)CH(OH)CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01205	*	*	CH <sub>3</sub> CH <sub>2</sub> C(OH)(OO·)CH(OH) <sub>2</sub> → CH <sub>3</sub> CH <sub>2</sub> COCH(OH) <sub>2</sub> + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01206	*	*	CH <sub>3</sub> CH <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO·) → CH <sub>3</sub> CH <sub>2</sub> CH(OH)CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01207	*	*	CH <sub>3</sub> CH <sub>2</sub> CH(O·)CH(OH) <sub>2</sub> $\xrightarrow{O_2}$ CH <sub>3</sub> CH <sub>2</sub> COCH(OH) <sub>2</sub> + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01208	*	*	CH <sub>3</sub> CH <sub>2</sub> CH(O·)CH(OH) <sub>2</sub> → 0.500 CH <sub>3</sub> CH <sub>2</sub> (OO·) + 0.500 CH(OH) <sub>2</sub> CHO + 0.500 CH <sub>3</sub> CH <sub>2</sub> CHO + 0.500 CH·(OH) <sub>2</sub> – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01209	*	*	CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>3</sub> CH <sub>2</sub> CH(OH)CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01210	*	*	CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH(OH)(O·) → CH <sub>3</sub> CH <sub>2</sub> CH(OH)(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01211	*	*	CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01212	*	*	CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> (O·) → CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01213	*	*	CH <sub>3</sub> CH(O·)CH(OH)CH(OH) <sub>2</sub> $\xrightarrow{O_2}$ CH <sub>3</sub> COCH(OH)CH(OH) <sub>2</sub> + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01214	*	*	CH <sub>3</sub> CH(O $\cdot$ )CH(OH)CH(OH) <sub>2</sub> $\rightarrow$ 0.500 CH <sub>3</sub> (OO $\cdot$ ) + 0.500 CH(OH) <sub>2</sub> CH(OH)CHO + 0.500 CH <sub>3</sub> CHO + 0.500 CH(OH) <sub>2</sub> CH(OH)(OO $\cdot$ ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01215	*	*	CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH(OH) <sub>2</sub> + OH $\rightarrow$ 0.059 CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CH <sub>2</sub> (OO $\cdot$ ) + 0.526 CH <sub>3</sub> C(OH)(OO $\cdot$ )CH <sub>2</sub> CH(OH) <sub>2</sub> + 0.257 CH <sub>3</sub> CH(OH)CH <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.031 CH <sub>3</sub> CH(O $\cdot$ )CH <sub>2</sub> CH(OH) <sub>2</sub> + 0.126 CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH(OH)(O $\cdot$ ) + H <sub>2</sub> O - 0.843 O <sub>2</sub>	3.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 01216	*		CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH(OH) <sub>2</sub> + NO <sub>3</sub> $\rightarrow$ 0.059 CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CH <sub>2</sub> (OO $\cdot$ ) + 0.526 CH <sub>3</sub> C(OH)(OO $\cdot$ )CH <sub>2</sub> CH(OH) <sub>2</sub> + 0.257 CH <sub>3</sub> CH(OH)CH <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.031 CH <sub>3</sub> CH(O $\cdot$ )CH <sub>2</sub> CH(OH) <sub>2</sub> + 0.126 CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH(OH)(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.843 O <sub>2</sub>	1.3 · 10 <sup>+07</sup>		
R <sub>o</sub> 01217	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CH <sub>2</sub> (OO $\cdot$ ) $\xrightarrow{RO_2^{\cdot}}$ 0.200 CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CH <sub>2</sub> (O $\cdot$ ) + 0.550 CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CHO + 0.250 CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01218	*	*	CH <sub>3</sub> C(OH)(OO $\cdot$ )CH <sub>2</sub> CH(OH) <sub>2</sub> $\rightarrow$ CH <sub>3</sub> COCH <sub>2</sub> CH(OH) <sub>2</sub> + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01219	*	*	CH <sub>3</sub> CH(OH)CH <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CH <sub>3</sub> CH(OH)CH <sub>2</sub> CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01220	*	*	CH <sub>3</sub> CH(O $\cdot$ )CH <sub>2</sub> CH(OH) <sub>2</sub> $\xrightarrow{O_2}$ CH <sub>3</sub> COCH <sub>2</sub> CH(OH) <sub>2</sub> + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01221	*	*	CH <sub>3</sub> CH(O $\cdot$ )CH <sub>2</sub> CH(OH) <sub>2</sub> $\rightarrow$ 0.500 CH <sub>3</sub> (OO $\cdot$ ) + 0.500 CH(OH) <sub>2</sub> CH <sub>2</sub> CHO + 0.500 CH <sub>3</sub> CHO + 0.500 CH(OH) <sub>2</sub> CH <sub>2</sub> (OO $\cdot$ ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01222	*	*	CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CH <sub>3</sub> CH(OH)CH <sub>2</sub> CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01223	*	*	CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH(OH)(O $\cdot$ ) $\rightarrow$ CH <sub>3</sub> CH(OH)CH <sub>2</sub> (OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01224	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CH <sub>2</sub> (O $\cdot$ ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01225	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CH <sub>2</sub> (O $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)(OO $\cdot$ ) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01226	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (OH) + OH → 0.059 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (OO·) + 0.228 CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) + 0.330 CH <sub>3</sub> C(OH)(O·)C(OH) <sub>2</sub> CH <sub>2</sub> (OH) + 0.311 CH <sub>3</sub> C(OH) <sub>2</sub> C(OH)(O·)CH <sub>2</sub> (OH) + 0.072 CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + H <sub>2</sub> O – 0.287 O <sub>2</sub>	1.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 01227	*		CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (OH) + NO <sub>3</sub> → 0.059 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (OO·) + 0.228 CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) + 0.330 CH <sub>3</sub> C(OH)(O·)C(OH) <sub>2</sub> CH <sub>2</sub> (OH) + 0.311 CH <sub>3</sub> C(OH) <sub>2</sub> C(OH)(O·)CH <sub>2</sub> (OH) + 0.072 CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.287 O <sub>2</sub>	9.8 · 10 <sup>+06</sup>		
R <sub>o</sub> 01228	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.550 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + 0.250 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01229	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) → CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01230	*	*	CH <sub>3</sub> C(OH)(O·)C(OH) <sub>2</sub> CH <sub>2</sub> (OH) → 0.500 CH <sub>3</sub> (OO·) + 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CO(OH) + 0.500 CH <sub>3</sub> CO(OH) + 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO·) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01231	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> C(OH)(O·)CH <sub>2</sub> (OH) → 0.500 CH <sub>3</sub> C(OH) <sub>2</sub> (OO·) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CH <sub>3</sub> C(OH) <sub>2</sub> CO(OH) + 0.500 CH <sub>2</sub> (OH)· – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01232	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01233	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) → CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01234	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01235	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01236	*	*	CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (OH) + OH → 0.134 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (OO·) + 0.219 CH <sub>3</sub> C(OH)(OO·)C(OH) <sub>2</sub> CH <sub>2</sub> (OH) + 0.217 CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CH(OH)(OO·) + 0.070 CH <sub>3</sub> CH(O·)C(OH) <sub>2</sub> CH <sub>2</sub> (OH) + 0.295 CH <sub>3</sub> CH(OH)C(OH)(O·)CH <sub>2</sub> (OH) + 0.065 CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + H <sub>2</sub> O – 0.569 O <sub>2</sub>	1.3 · 10 <sup>+09</sup>		
R <sub>o</sub> 01237	*		CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (OH) + NO <sub>3</sub> → 0.134 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (OO·) + 0.219 CH <sub>3</sub> C(OH)(OO·)C(OH) <sub>2</sub> CH <sub>2</sub> (OH) + 0.217 CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CH(OH)(OO·) + 0.070 CH <sub>3</sub> CH(O·)C(OH) <sub>2</sub> CH <sub>2</sub> (OH) + 0.295 CH <sub>3</sub> CH(OH)C(OH)(O·)CH <sub>2</sub> (OH) + 0.065 CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.569 O <sub>2</sub>	1.3 · 10 <sup>+07</sup>		
R <sub>o</sub> 01238	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) + 0.550 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CHO + 0.250 CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01239	*	*	CH <sub>3</sub> C(OH)(OO·)C(OH) <sub>2</sub> CH <sub>2</sub> (OH) → CH <sub>3</sub> COC(OH) <sub>2</sub> CH <sub>2</sub> (OH) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01240	*	*	CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CH(OH)(OO·) → CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01241	*	*	CH <sub>3</sub> CH(O·)C(OH) <sub>2</sub> CH <sub>2</sub> (OH) $\xrightarrow{O_2}$ CH <sub>3</sub> COC(OH) <sub>2</sub> CH <sub>2</sub> (OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01242	*	*	CH <sub>3</sub> CH(O·)C(OH) <sub>2</sub> CH <sub>2</sub> (OH) → 0.500 CH <sub>3</sub> (OO·) + 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CHO + 0.500 CH <sub>3</sub> CHO + 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO·) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01243	*	*	CH <sub>3</sub> CH(OH)C(OH)(O·)CH <sub>2</sub> (OH) → 0.500 CH <sub>3</sub> CH(OH)(OO·) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CH <sub>3</sub> CH(OH)CO(OH) + 0.500 CH <sub>2</sub> (OH)· – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01244	*	*	CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01245	*	*	CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) → CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> (OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01246	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01247	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)(OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01248	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OH)CH <sub>2</sub> (OH) + OH → 0.604 CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(OH)(OO·) + 0.244 CH <sub>2</sub> (OH)CH(OH)C(OH)(OO·)CH <sub>2</sub> (OH) + 0.076 CH <sub>2</sub> (OH)CH(OH)CH(OH)CH <sub>2</sub> (O·) + 0.076 CH <sub>2</sub> (OH)CH(OH)CH(O·)CH <sub>2</sub> (OH) + H <sub>2</sub> O – 0.848 O <sub>2</sub>	1.9 · 10 <sup>+09</sup>	–1948.0	Hoffmann et al. (2009)
R <sub>o</sub> 01249	*		CH <sub>2</sub> (OH)CH(OH)CH(OH)CH <sub>2</sub> (OH) + NO <sub>3</sub> → 0.604 CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(OH)(OO·) + 0.244 CH <sub>2</sub> (OH)CH(OH)C(OH)(OO·)CH <sub>2</sub> (OH) + 0.076 CH <sub>2</sub> (OH)CH(OH)CH(OH)CH <sub>2</sub> (O·) + 0.076 CH <sub>2</sub> (OH)CH(OH)CH(O·)CH <sub>2</sub> (OH) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.848 O <sub>2</sub>	1.4 · 10 <sup>+07</sup>	–2321.0	Hoffmann et al. (2009)
R <sub>o</sub> 01250	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(OH)(OO·) → CH <sub>2</sub> (OH)CH(OH)CH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01251	*	*	CH <sub>2</sub> (OH)CH(OH)C(OH)(OO·)CH <sub>2</sub> (OH) → CH <sub>2</sub> (OH)CH(OH)COCH <sub>2</sub> (OH) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01252	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CH(OH) <sub>2</sub> + OH → 0.594 CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CH(OH)(OO·) + 0.061 CH <sub>2</sub> (OH)CH(OO·)CH(OH)CH(OH) <sub>2</sub> + 0.097 CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH)(OO·)CH(OH) <sub>2</sub> + 0.118 CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO·) + 0.131 CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CH(OH)(O·) + H <sub>2</sub> O – 0.869 O <sub>2</sub>	2.9 · 10 <sup>+09</sup>		
R <sub>o</sub> 01253	*		CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.594 CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CH(OH)(OO·) + 0.061 CH <sub>2</sub> (OH)CH(OO·)CH(OH)CH(OH) <sub>2</sub> + 0.097 CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH)(OO·)CH(OH) <sub>2</sub> + 0.118 CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO·) + 0.131 CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.869 O <sub>2</sub>	1.5 · 10 <sup>+07</sup>		
R <sub>o</sub> 01254	*	*	CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CH(OH)(OO·) → CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01255	*	*	CH <sub>2</sub> (OH)CH(OO·)CH(OH)CH(OH) <sub>2</sub> $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(O·)CH(OH)CH(OH) <sub>2</sub> + 0.550 CH <sub>2</sub> (OH)COCH(OH)CH(OH) <sub>2</sub> + 0.250 CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01256	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH)(OO·)CH(OH) <sub>2</sub> → CH <sub>2</sub> (OH)CH <sub>2</sub> COCH(OH) <sub>2</sub> + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01257	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01258	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01259	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CH(OH)(O·) → CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01260	*	*	CH <sub>2</sub> (OH)CH(O·)CH(OH)CH(OH) <sub>2</sub> $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCH(OH)CH(OH) <sub>2</sub> + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01261	*	*	CH <sub>2</sub> (OH)CH(O·)CH(OH)CH(OH) <sub>2</sub> → 0.500 CH <sub>2</sub> (OH)· + 0.500 CH(OH) <sub>2</sub> CH(OH)CHO + 0.500 CH <sub>2</sub> (OH)CHO + 0.500 CH(OH) <sub>2</sub> CH(OH)(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01262	*	*	CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> CH(OH) <sub>2</sub> + OH → 0.262 CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CH(OH)(OO·) + 0.239 CH <sub>2</sub> (OH)C(OH)(OO·)CH <sub>2</sub> CH(OH) <sub>2</sub> + 0.292 CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.031 CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) + 0.033 CH <sub>2</sub> (OH)CH(O·)CH <sub>2</sub> CH(OH) <sub>2</sub> + 0.143 CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> CH(OH)(O·) + H <sub>2</sub> O – 0.793 O <sub>2</sub>	2.8 · 10 <sup>+09</sup>		
R <sub>o</sub> 01263	*		CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.262 CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CH(OH)(OO·) + 0.239 CH <sub>2</sub> (OH)C(OH)(OO·)CH <sub>2</sub> CH(OH) <sub>2</sub> + 0.292 CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.031 CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) + 0.033 CH <sub>2</sub> (OH)CH(O·)CH <sub>2</sub> CH(OH) <sub>2</sub> + 0.143 CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> CH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.793 O <sub>2</sub>	1.5 · 10 <sup>+07</sup>		
R <sub>o</sub> 01264	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CH(OH)(OO·) → CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01265	*	*	CH <sub>2</sub> (OH)C(OH)(OO·)CH <sub>2</sub> CH(OH) <sub>2</sub> → CH <sub>2</sub> (OH)COCH <sub>2</sub> CH(OH) <sub>2</sub> + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01266	*	*	CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01267	*	*	CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01268	*	*	CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> CH(OH)(O·) → CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> (OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01269	*	*	CH <sub>3</sub> CH <sub>2</sub> COCH(OH) <sub>2</sub> + OH → 0.359 CH(OH) <sub>2</sub> COCH <sub>2</sub> CH <sub>2</sub> (OO·) + 0.188 CH <sub>3</sub> CH(OO·)COCH(OH) <sub>2</sub> + 0.146 CH <sub>3</sub> CH <sub>2</sub> COC(OH) <sub>2</sub> (OO·) + 0.307 CH <sub>3</sub> CH <sub>2</sub> COCH(OH)(O·) + H <sub>2</sub> O – 0.693 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 01270	*		CH <sub>3</sub> CH <sub>2</sub> COCH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.359 CH(OH) <sub>2</sub> COCH <sub>2</sub> CH <sub>2</sub> (OO·) + 0.188 CH <sub>3</sub> CH(OO·)COCH(OH) <sub>2</sub> + 0.146 CH <sub>3</sub> CH <sub>2</sub> COC(OH) <sub>2</sub> (OO·) + 0.307 CH <sub>3</sub> CH <sub>2</sub> COCH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.693 O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 01271	*	*	CH(OH) <sub>2</sub> COCH <sub>2</sub> CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> COCH <sub>2</sub> CH <sub>2</sub> (O·) + 0.550 CH(OH) <sub>2</sub> COCH <sub>2</sub> CHO + 0.250 CH <sub>2</sub> (OH)CH <sub>2</sub> COCH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01272	*	*	CH <sub>3</sub> CH(OO·)COCH(OH) <sub>2</sub> $\xrightarrow{RO_2}$ 0.200 CH <sub>3</sub> CH(O·)COCH(OH) <sub>2</sub> + 0.550 CH <sub>3</sub> COCOCH(OH) <sub>2</sub> + 0.250 CH <sub>3</sub> CH(OH)COCH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01273	*	*	CH <sub>3</sub> CH <sub>2</sub> COC(OH) <sub>2</sub> (OO·) → CH <sub>3</sub> CH <sub>2</sub> COCO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01274	*	*	CH <sub>3</sub> CH <sub>2</sub> COCH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>3</sub> CH <sub>2</sub> COCO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01275	*	*	CH <sub>3</sub> CH <sub>2</sub> COCH(OH)(O·) → CH <sub>3</sub> CH <sub>2</sub> CO(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01276	*	*	CH(OH) <sub>2</sub> COCH <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCH <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01277	*	*	CH(OH) <sub>2</sub> COCH <sub>2</sub> CH <sub>2</sub> (O·) → CH(OH) <sub>2</sub> COCH <sub>2</sub> (OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01278	*	*	CH <sub>3</sub> CH(O·)COCH(OH) <sub>2</sub> $\xrightarrow{O_2}$ CH <sub>3</sub> COCOCH(OH) <sub>2</sub> + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01279	*	*	CH <sub>3</sub> CH(O·)COCH(OH) <sub>2</sub> → 0.500 CH <sub>3</sub> (OO·) + 0.500 CH(OH) <sub>2</sub> COCHO + 0.500 CH <sub>3</sub> CHO + 0.500 CH(OH) <sub>2</sub> CO(OO·) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01280	*	*	CH <sub>3</sub> COCH <sub>2</sub> CH(OH) <sub>2</sub> + OH → 0.072 CH(OH) <sub>2</sub> CH <sub>2</sub> COCH <sub>2</sub> (OO·) + 0.591 CH <sub>3</sub> COCH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.338 CH <sub>3</sub> COCH <sub>2</sub> CH(OH)(O·) + H <sub>2</sub> O – 0.662 O <sub>2</sub>	1.2 · 10 <sup>+09</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01281	*		CH <sub>3</sub> COCH <sub>2</sub> CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.072 CH(OH) <sub>2</sub> CH <sub>2</sub> COCH <sub>2</sub> (OO·) + 0.591 CH <sub>3</sub> COCH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.338 CH <sub>3</sub> COCH <sub>2</sub> CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.662 O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 01282	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> COCH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH <sub>2</sub> COCH <sub>2</sub> (O·) + 0.550 CH(OH) <sub>2</sub> CH <sub>2</sub> COCHO + 0.250 CH <sub>2</sub> (OH)COCH <sub>2</sub> CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01283	*	*	CH <sub>3</sub> COCH <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CH <sub>3</sub> COCH <sub>2</sub> CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01284	*	*	CH <sub>3</sub> COCH <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>3</sub> COCH <sub>2</sub> CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01285	*	*	CH <sub>3</sub> COCH <sub>2</sub> CH(OH)(O·) → CH <sub>3</sub> COCH <sub>2</sub> (OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01286	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> COCH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH <sub>2</sub> COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01287	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> COCH <sub>2</sub> (O·) → CH(OH) <sub>2</sub> CH <sub>2</sub> CO(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01288	*	*	CH <sub>3</sub> COC(OH) <sub>2</sub> CH <sub>2</sub> (OH) + OH → 0.107 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (OO·) + 0.329 CH <sub>3</sub> COC(OH) <sub>2</sub> CH(OH)(OO·) + 0.448 CH <sub>3</sub> COC(OH)(O·)CH <sub>2</sub> (OH) + 0.116 CH <sub>3</sub> COC(OH) <sub>2</sub> CH <sub>2</sub> (O·) + H <sub>2</sub> O - 0.436 O <sub>2</sub>	7.2 · 10 <sup>+08</sup>		
R <sub>o</sub> 01289	*		CH <sub>3</sub> COC(OH) <sub>2</sub> CH <sub>2</sub> (OH) + NO <sub>3</sub> → 0.107 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (OO·) + 0.329 CH <sub>3</sub> COC(OH) <sub>2</sub> CH(OH)(OO·) + 0.448 CH <sub>3</sub> COC(OH)(O·)CH <sub>2</sub> (OH) + 0.116 CH <sub>3</sub> COC(OH) <sub>2</sub> CH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.436 O <sub>2</sub>	9.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 01290	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (O·) + 0.550 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCHO + 0.250 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01291	*	*	CH <sub>3</sub> COC(OH) <sub>2</sub> CH(OH)(OO·) → CH <sub>3</sub> COC(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01292	*	*	CH <sub>3</sub> COC(OH)(O·)CH <sub>2</sub> (OH) → 0.500 CH <sub>3</sub> CO(OO·) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CH <sub>3</sub> COCO(OH) + 0.500 CH <sub>2</sub> (OH)· - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01293	*	*	CH <sub>3</sub> COC(OH) <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>3</sub> COC(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01294	*	*	CH <sub>3</sub> COC(OH) <sub>2</sub> CH <sub>2</sub> (O·) → CH <sub>3</sub> COC(OH) <sub>2</sub> (OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01295	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01296	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (O·) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CO(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01297	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> COCH <sub>2</sub> (OH) + OH → 0.078 CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH <sub>2</sub> (OO·) + 0.385 CH <sub>3</sub> C(OH) <sub>2</sub> COCH(OH)(OO·) + 0.441 CH <sub>3</sub> C(OH)(O·)COCH <sub>2</sub> (OH) + 0.096 CH <sub>3</sub> C(OH) <sub>2</sub> COCH <sub>2</sub> (O·) + H <sub>2</sub> O - 0.463 O <sub>2</sub>	7.8 · 10 <sup>+08</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01298	*		$\text{CH}_3\text{C}(\text{OH})_2\text{COCH}_2(\text{OH}) + \text{NO}_3 \rightarrow 0.078 \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) +$ $0.385 \text{CH}_3\text{C}(\text{OH})_2\text{COCH}(\text{OH})(\text{OO}\cdot) + 0.441 \text{CH}_3\text{C}(\text{OH})(\text{O}\cdot)\text{COCH}_2(\text{OH}) +$ $0.096 \text{CH}_3\text{C}(\text{OH})_2\text{COCH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.463 \text{O}_2$	$9.7 \cdot 10^{+06}$		
R <sub>o</sub> 01299	*	*	$\text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CH}_2(\text{O}\cdot) + 0.550 \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}_2(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01300	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{COCH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_3\text{C}(\text{OH})_2\text{COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01301	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{O}\cdot)\text{COCH}_2(\text{OH}) \rightarrow$ $0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CH}_2(\text{OH})\text{COCO}(\text{OH}) + 0.500 \text{CH}_3\text{CO}(\text{OH}) +$ $0.500 \text{CH}_2(\text{OH})\text{CO}(\text{OO}\cdot) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01302	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{COCH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_3\text{C}(\text{OH})_2\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01303	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{COCH}_2(\text{O}\cdot) \rightarrow \text{CH}_3\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01304	*	*	$\text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01305	*	*	$\text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01306	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) \rightarrow \text{CH}_3\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
E <sub>o</sub> 00145	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCH}_2(\text{OH}) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{OH})$	$2.9 \cdot 10^{-01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01307	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCH}_2(\text{OH}) + \text{OH} \rightarrow$ $0.468 \text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.099 \text{CH}_2(\text{OH})\text{COC}(\text{OH})(\text{OO}\cdot)\text{CH}_2(\text{OH}) +$ $0.246 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCH}(\text{OH})(\text{OO}\cdot) +$ $0.068 \text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{CH}_2(\text{O}\cdot) + 0.059 \text{CH}_2(\text{OH})\text{COCH}(\text{O}\cdot)\text{CH}_2(\text{OH}) +$ $0.059 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.814 \text{O}_2$	$1.3 \cdot 10^{+09}$		
R <sub>o</sub> 01308	*		$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCH}_2(\text{OH}) + \text{NO}_3 \rightarrow$ $0.468 \text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.099 \text{CH}_2(\text{OH})\text{COC}(\text{OH})(\text{OO}\cdot)\text{CH}_2(\text{OH}) +$ $0.246 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCH}(\text{OH})(\text{OO}\cdot) +$ $0.068 \text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{CH}_2(\text{O}\cdot) + 0.059 \text{CH}_2(\text{OH})\text{COCH}(\text{O}\cdot)\text{CH}_2(\text{OH}) +$ $0.059 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.814 \text{O}_2$	$1.8 \cdot 10^{+06}$		
R <sub>o</sub> 01309	*	*	$\text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01310	*	*	$\text{CH}_2(\text{OH})\text{COC}(\text{OH})(\text{OO}\cdot)\text{CH}_2(\text{OH}) \rightarrow \text{CH}_2(\text{OH})\text{COCOCH}_2(\text{OH}) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A/R^b$	Reference/comment
R <sub>o</sub> 01311	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01312	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{COCH}(\text{OH})_2 + \text{OH} \rightarrow 0.695 \text{CH}(\text{OH})_2\text{COCH}_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.037 \text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{COCH}(\text{OH})_2 +$ $0.073 \text{CH}_2(\text{OH})\text{CH}_2\text{COC}(\text{OH})_2(\text{OO}\cdot) + 0.043 \text{CH}(\text{OH})_2\text{COCH}_2\text{CH}_2(\text{O}\cdot) +$ $0.153 \text{CH}_2(\text{OH})\text{CH}_2\text{COCH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.804 \text{O}_2$	$2.1 \cdot 10^{+09}$		
R <sub>o</sub> 01313	*		$\text{CH}_2(\text{OH})\text{CH}_2\text{COCH}(\text{OH})_2 + \text{NO}_3 \rightarrow$ $0.695 \text{CH}(\text{OH})_2\text{COCH}_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.037 \text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{COCH}(\text{OH})_2 +$ $0.073 \text{CH}_2(\text{OH})\text{CH}_2\text{COC}(\text{OH})_2(\text{OO}\cdot) + 0.043 \text{CH}(\text{OH})_2\text{COCH}_2\text{CH}_2(\text{O}\cdot) +$ $0.153 \text{CH}_2(\text{OH})\text{CH}_2\text{COCH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.804 \text{O}_2$	$1.1 \cdot 10^{+07}$		
R <sub>o</sub> 01314	*	*	$\text{CH}(\text{OH})_2\text{COCH}_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{COCH}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01315	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{COCH}(\text{OH})_2 \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{COCH}(\text{OH})_2 + 0.550 \text{CH}_2(\text{OH})\text{COCOCH}(\text{OH})_2 +$ $0.250 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCH}(\text{OH})_2 + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01316	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{COC}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}_2\text{COCO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01317	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{COCH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{CH}_2\text{COCO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01318	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{COCH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}_2\text{CO}(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01319	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{COCH}(\text{OH})_2 \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCOCH}(\text{OH})_2 + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01320	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{COCH}(\text{OH})_2 \rightarrow$ $0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CH}(\text{OH})_2\text{COCHO} + 0.500 \text{CH}_2(\text{OH})\text{CHO} +$ $0.500 \text{CH}(\text{OH})_2\text{CO}(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01321	*	*	$\text{CH}_2(\text{OH})\text{COCH}_2\text{CH}(\text{OH})_2 + \text{OH} \rightarrow 0.220 \text{CH}(\text{OH})_2\text{CH}_2\text{COCH}(\text{OH})(\text{OO}\cdot) +$ $0.465 \text{CH}_2(\text{OH})\text{COCH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.050 \text{CH}(\text{OH})_2\text{CH}_2\text{COCH}_2(\text{O}\cdot) +$ $0.266 \text{CH}_2(\text{OH})\text{COCH}_2\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.684 \text{O}_2$	$1.5 \cdot 10^{+09}$		
R <sub>o</sub> 01322	*		$\text{CH}_2(\text{OH})\text{COCH}_2\text{CH}(\text{OH})_2 + \text{NO}_3 \rightarrow$ $0.220 \text{CH}(\text{OH})_2\text{CH}_2\text{COCH}(\text{OH})(\text{OO}\cdot) +$ $0.465 \text{CH}_2(\text{OH})\text{COCH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.050 \text{CH}(\text{OH})_2\text{CH}_2\text{COCH}_2(\text{O}\cdot) +$ $0.266 \text{CH}_2(\text{OH})\text{COCH}_2\text{CH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.684 \text{O}_2$	$1.1 \cdot 10^{+07}$		
R <sub>o</sub> 01323	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{COCH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CH}_2\text{COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01324	*	*	$\text{CH}_2(\text{OH})\text{COCH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{COCH}_2\text{CO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01325	*	*	$\text{CH}_2(\text{OH})\text{COCH}_2\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCH}_2\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01326	*	*	$\text{CH}_2(\text{OH})\text{COCH}_2\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{COCH}_2(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00146	*	*	$\text{CH}_2(\text{OH})\text{COCOCH}_2(\text{OH}) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}_2(\text{OH})$	$1.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00147	*	*	$\text{CH}_2(\text{OH})\text{COCOCH}_2(\text{OH}) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{OH})$	$3.3 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01327	*	*	$\text{CH}_2(\text{OH})\text{COCOCH}_2(\text{OH}) + \text{OH} \rightarrow 0.782 \text{ CH}_2(\text{OH})\text{COCOCH}(\text{OH})(\text{OO}\cdot) + 0.218 \text{ CH}_2(\text{OH})\text{COCOCH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.782 \text{ O}_2$	$6.9 \cdot 10^{+08}$		
R <sub>o</sub> 01328	*		$\text{CH}_2(\text{OH})\text{COCOCH}_2(\text{OH}) + \text{NO}_3 \rightarrow 0.782 \text{ CH}_2(\text{OH})\text{COCOCH}(\text{OH})(\text{OO}\cdot) + 0.218 \text{ CH}_2(\text{OH})\text{COCOCH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.782 \text{ O}_2$	$1.4 \cdot 10^{+06}$		
R <sub>o</sub> 01329	*	*	$\text{CH}_2(\text{OH})\text{COCOCH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{COCOCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01330	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{CH}_2\text{CHO} + \text{OH} \rightarrow 0.210 \text{ CHOCH}_2\text{CH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.037 \text{ CH}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CH}_2\text{CHO} + 0.045 \text{ CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{OO}\cdot)\text{CHO} + 0.609 \text{ CH}(\text{OH})_2\text{CH}_2\text{CH}_2\text{CO}(\text{OO}\cdot) + 0.098 \text{ CHOCH}_2\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.902 \text{ O}_2$	$4.1 \cdot 10^{+09}$		
R <sub>o</sub> 01331	*		$\text{CH}(\text{OH})_2\text{CH}_2\text{CH}_2\text{CHO} + \text{NO}_3 \rightarrow 0.210 \text{ CHOCH}_2\text{CH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.037 \text{ CH}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CH}_2\text{CHO} + 0.045 \text{ CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{OO}\cdot)\text{CHO} + 0.609 \text{ CH}(\text{OH})_2\text{CH}_2\text{CH}_2\text{CO}(\text{OO}\cdot) + 0.098 \text{ CHOCH}_2\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.902 \text{ O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 01332	*	*	$\text{CHOCH}_2\text{CH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CHO} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01333	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CH}_2\text{CHO} \xrightarrow{\text{RO}_2} 0.200 \text{ CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CH}_2\text{CHO} + 0.550 \text{ CH}(\text{OH})_2\text{COCH}_2\text{CHO} + 0.250 \text{ CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2\text{CHO} + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01334	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{OO}\cdot)\text{CHO} \xrightarrow{\text{RO}_2} 0.200 \text{ CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{O}\cdot)\text{CHO} + 0.550 \text{ CH}(\text{OH})_2\text{CH}_2\text{COCHO} + 0.250 \text{ CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{OH})\text{CHO} + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01335	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{CH}_2\text{CO}(\text{OO}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CH}_2\text{CH}_2\text{CO}(\text{OH}) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01336	*	*	$\text{CHOCH}_2\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01337	*	*	$\text{CHOCH}_2\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CHOCH}_2\text{CH}_2(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01338	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CH}_2\text{CHO} \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{COCH}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01339	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CH}_2\text{CHO} \rightarrow 0.500 \text{ CH}\cdot(\text{OH})_2 + 0.500 \text{ CHOCH}_2\text{CHO} + 0.500 \text{ CH}(\text{OH})_2\text{CHO} + 0.500 \text{ CHOCH}_2(\text{OO}\cdot) - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01340	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{O}\cdot)\text{CHO} \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{CH}_2\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01341	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH(O $\cdot$ )CHO $\rightarrow$ 0.500 CH(OH) <sub>2</sub> CH <sub>2</sub> (OO $\cdot$ ) + 0.500 CHOCHO + 0.500 CH(OH) <sub>2</sub> CH <sub>2</sub> CHO + 0.500 CH $\cdot$ (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00148	*	*	CH <sub>3</sub> CH(OH)CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> CH(OH)CH(OH)CH(OH) <sub>2</sub>	$1.5 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01342	*	*	CH <sub>3</sub> CH(OH)CH(OH)CHO + OH $\rightarrow$ 0.090 CHOCH(OH)CH(OH)CH <sub>2</sub> (OO $\cdot$ ) + 0.288 CH <sub>3</sub> C(OH)(OO $\cdot$ )CH(OH)CHO + 0.062 CH <sub>3</sub> CH(OH)C(OH)(OO $\cdot$ )CHO + 0.477 CH <sub>3</sub> CH(OH)CH(OH)CO(OO $\cdot$ ) + 0.047 CH <sub>3</sub> CH(O $\cdot$ )CH(OH)CHO + 0.036 CH <sub>3</sub> CH(OH)CH(O $\cdot$ )CHO + H <sub>2</sub> O - 0.917 O <sub>2</sub>	$2.0 \cdot 10^{+09}$		
R <sub>o</sub> 01343	*		CH <sub>3</sub> CH(OH)CH(OH)CHO + NO <sub>3</sub> $\rightarrow$ 0.090 CHOCH(OH)CH(OH)CH <sub>2</sub> (OO $\cdot$ ) + 0.288 CH <sub>3</sub> C(OH)(OO $\cdot$ )CH(OH)CHO + 0.062 CH <sub>3</sub> CH(OH)C(OH)(OO $\cdot$ )CHO + 0.477 CH <sub>3</sub> CH(OH)CH(OH)CO(OO $\cdot$ ) + 0.047 CH <sub>3</sub> CH(O $\cdot$ )CH(OH)CHO + 0.036 CH <sub>3</sub> CH(OH)CH(O $\cdot$ )CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.917 O <sub>2</sub>	$3.9 \cdot 10^{+07}$		
R <sub>o</sub> 01344	*	*	CHOCH(OH)CH(OH)CH <sub>2</sub> (OO $\cdot$ ) $\xrightarrow{RO_2}$ 0.200 CHOCH(OH)CH(OH)CH <sub>2</sub> (O $\cdot$ ) + 0.550 CHOCH(OH)CH(OH)CHO + 0.250 CH <sub>2</sub> (OH)CH(OH)CH(OH)CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01345	*	*	CH <sub>3</sub> C(OH)(OO $\cdot$ )CH(OH)CHO $\rightarrow$ CH <sub>3</sub> COCH(OH)CHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01346	*	*	CH <sub>3</sub> CH(OH)C(OH)(OO $\cdot$ )CHO $\rightarrow$ CH <sub>3</sub> CH(OH)COCHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01347	*	*	CH <sub>3</sub> CH(OH)CH(OH)CO(OO $\cdot$ ) $\rightarrow$ CH <sub>3</sub> CH(OH)CH(OH)CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01348	*	*	CH <sub>3</sub> CH(OH)CH(O $\cdot$ )CHO $\xrightarrow{O_2}$ CH <sub>3</sub> CH(OH)COCHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01349	*	*	CH <sub>3</sub> CH(OH)CH(O $\cdot$ )CHO $\rightarrow$ 0.500 CH <sub>3</sub> CH(OH)(OO $\cdot$ ) + 0.500 CHOCHO + 0.500 CH <sub>3</sub> CH(OH)CHO + 0.500 CH $\cdot$ (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01350	*	*	CHOCH(OH)CH(OH)CH <sub>2</sub> (O $\cdot$ ) $\xrightarrow{O_2}$ CHOCH(OH)CH(OH)CHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01351	*	*	CHOCH(OH)CH(OH)CH <sub>2</sub> (O $\cdot$ ) $\rightarrow$ CHOCH(OH)CH(OH)(OO $\cdot$ ) + CH <sub>2</sub> O - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00149	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(OH) <sub>2</sub>	$2.0 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01352	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OH)CHO + OH → 0.311 CHOCH(OH)CH(OH)CH(OH)(OO·) + 0.103 CH <sub>2</sub> (OH)C(OH)(OO·)CH(OH)CHO + 0.052 CH <sub>2</sub> (OH)CH(OH)C(OH)(OO·)CHO + 0.424 CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(OO·) + 0.039 CHOCH(OH)CH(OH)CH <sub>2</sub> (O·) + 0.039 CH <sub>2</sub> (OH)CH(O·)CH(OH)CHO + 0.032 CH <sub>2</sub> (OH)CH(OH)CH(O·)CHO + H <sub>2</sub> O - 0.890 O <sub>2</sub>	2.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 01353	*		CH <sub>2</sub> (OH)CH(OH)CH(OH)CHO + NO <sub>3</sub> → 0.311 CHOCH(OH)CH(OH)CH(OH)(OO·) + 0.103 CH <sub>2</sub> (OH)C(OH)(OO·)CH(OH)CHO + 0.052 CH <sub>2</sub> (OH)CH(OH)C(OH)(OO·)CHO + 0.424 CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(OO·) + 0.039 CHOCH(OH)CH(OH)CH <sub>2</sub> (O·) + 0.039 CH <sub>2</sub> (OH)CH(O·)CH(OH)CHO + 0.032 CH <sub>2</sub> (OH)CH(OH)CH(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.890 O <sub>2</sub>	3.8 · 10 <sup>+07</sup>		
R <sub>o</sub> 01354	*	*	CHOCH(OH)CH(OH)CH(OH)(OO·) → CHOCH(OH)CH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01355	*	*	CH <sub>2</sub> (OH)C(OH)(OO·)CH(OH)CHO → CH <sub>2</sub> (OH)COCH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01356	*	*	CH <sub>2</sub> (OH)CH(OH)C(OH)(OO·)CHO → CH <sub>2</sub> (OH)CH(OH)COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01357	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(OO·) → CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01358	*	*	CH <sub>2</sub> (OH)CH(OH)CH(O·)CHO $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(OH)COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01359	*	*	CH <sub>2</sub> (OH)CH(OH)CH(O·)CHO → 0.500 CH <sub>2</sub> (OH)CH(OH)(OO·) + 0.500 CHOCHO + 0.500 CH <sub>2</sub> (OH)CH(OH)CHO + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00150	*	*	CH <sub>3</sub> COCOCHO $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> COC(OH) <sub>2</sub> CH(OH) <sub>2</sub>	2.6 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00151	*	*	CH <sub>3</sub> COCOCHO $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	1.9 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01360	*	*	CH <sub>3</sub> COCOCHO → 0.250 CH <sub>3</sub> CO(OO·) + 0.250 CHOCO(OO·) + 0.250 CH <sub>3</sub> COCO(OO·) + 0.250 CHO(OO·)	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 01361	*	*	CH <sub>3</sub> COCOCHO + OH → 0.158 CHOCOCOCH <sub>2</sub> (OO·) + 0.842 CH <sub>3</sub> COCOCO(OO·) + H <sub>2</sub> O - O <sub>2</sub>	4.4 · 10 <sup>+08</sup>		
R <sub>o</sub> 01362	*		CH <sub>3</sub> COCOCHO + NO <sub>3</sub> → 0.158 CHOCOCOCH <sub>2</sub> (OO·) + 0.842 CH <sub>3</sub> COCOCO(OO·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	5.8 · 10 <sup>+06</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01363	*	*	CHOCOCOCH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CHOCOCOCH <sub>2</sub> (O·) + 0.550 CHOCOCOCHO + 0.250 CH <sub>2</sub> (OH)COCOCHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01364	*	*	CH <sub>3</sub> COCOCO(OO·) $\rightarrow$ CH <sub>3</sub> COCOCO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01365	*	*	CHOCOCOCH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CHOCOCOCHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01366	*	*	CHOCOCOCH <sub>2</sub> (O·) $\rightarrow$ CHOCOCO(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00152	*	*	CH <sub>2</sub> (OH)COCOCHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH(OH) <sub>2</sub>	$1.1 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00153	*	*	CH <sub>2</sub> (OH)COCOCHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	$4.5 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01367	*	*	CH <sub>2</sub> (OH)COCOCHO $\rightarrow$ 0.250 CH <sub>2</sub> (OH)CO(OO·) + 0.250 CHOCO(OO·) + 0.250 CH <sub>2</sub> (OH)COCO(OO·) + 0.250 CHO(OO·)	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 01368	*	*	CH <sub>2</sub> (OH)COCOCHO + OH $\rightarrow$ 0.379 CHOCOCOCH(OH)(OO·) + 0.516 CH <sub>2</sub> (OH)COCOCO(OO·) + 0.105 CHOCOCOCH <sub>2</sub> (O·) + H <sub>2</sub> O - 0.895 O <sub>2</sub>	$7.1 \cdot 10^{+08}$		
R <sub>o</sub> 01369	*		CH <sub>2</sub> (OH)COCOCHO + NO <sub>3</sub> $\rightarrow$ 0.379 CHOCOCOCH(OH)(OO·) + 0.516 CH <sub>2</sub> (OH)COCOCO(OO·) + 0.105 CHOCOCOCH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.895 O <sub>2</sub>	$5.6 \cdot 10^{+06}$		
R <sub>o</sub> 01370	*	*	CHOCOCOCH(OH)(OO·) $\rightarrow$ CHOCOCOCHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01371	*	*	CH <sub>2</sub> (OH)COCOCO(OO·) $\rightarrow$ CH <sub>2</sub> (OH)COCOCO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
E <sub>o</sub> 00154	*	*	CH <sub>3</sub> COCH(OH)CHO $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> COCH(OH)CH(OH) <sub>2</sub>	$5.6 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00155	*	*	CH <sub>3</sub> COCH(OH)CHO $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH)CH(OH) <sub>2</sub>	$6.7 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01372	*	*	CH <sub>3</sub> COCH(OH)CHO + OH $\rightarrow$ 0.080 CHOCH(OH)COCH <sub>2</sub> (OO·) + 0.055 CH <sub>3</sub> COC(OH)(OO·)CHO + 0.804 CH <sub>3</sub> COCH(OH)CO(OO·) + 0.061 CH <sub>3</sub> COCH(O·)CHO + H <sub>2</sub> O - 0.939 O <sub>2</sub>	$1.0 \cdot 10^{+09}$		
R <sub>o</sub> 01373	*		CH <sub>3</sub> COCH(OH)CHO + NO <sub>3</sub> $\rightarrow$ 0.080 CHOCH(OH)COCH <sub>2</sub> (OO·) + 0.055 CH <sub>3</sub> COC(OH)(OO·)CHO + 0.804 CH <sub>3</sub> COCH(OH)CO(OO·) + 0.061 CH <sub>3</sub> COCH(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.939 O <sub>2</sub>	$1.6 \cdot 10^{+07}$		
R <sub>o</sub> 01374	*	*	CHOCH(OH)COCH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CHOCH(OH)COCH <sub>2</sub> (O·) + 0.550 CHOCH(OH)COCHO + 0.250 CH <sub>2</sub> (OH)COCH(OH)CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01375	*	*	CH <sub>3</sub> COC(OH)(OO·)CHO $\rightarrow$ CH <sub>3</sub> COCOCHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01376	*	*	CH <sub>3</sub> COCH(OH)CO(OO·) $\rightarrow$ CH <sub>3</sub> COCH(OH)CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01377	*	*	$\text{CH}_3\text{COCH}(\text{O}\cdot)\text{CHO} \xrightarrow{\text{O}_2} \text{CH}_3\text{COCOCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01378	*	*	$\text{CH}_3\text{COCH}(\text{O}\cdot)\text{CHO} \rightarrow 0.500 \text{CH}_3\text{CO}(\text{OO}\cdot) + 0.500 \text{CHOCHO} +$ $0.500 \text{CH}_3\text{COCHO} + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{O}_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01379	*	*	$\text{CHOCH}(\text{OH})\text{COCH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CHOCH}(\text{OH})\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01380	*	*	$\text{CHOCH}(\text{OH})\text{COCH}_2(\text{O}\cdot) \rightarrow \text{CHOCH}(\text{OH})\text{CO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00156	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCH}(\text{OH})_2$	$7.0 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00157	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})_2$	$2.0 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01381	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCHO} + \text{OH} \rightarrow 0.463 \text{CHOCOCH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.080 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{COCHO} +$ $0.331 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{OO}\cdot) + 0.068 \text{CHOCOCH}(\text{OH})\text{CH}_2(\text{O}\cdot) +$ $0.058 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{COCHO} + \text{H}_2\text{O} - 0.874 \text{O}_2$	$1.3 \cdot 10^{+09}$		
R <sub>o</sub> 01382	*		$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCHO} + \text{NO}_3 \rightarrow$ $0.463 \text{CHOCOCH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.080 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{COCHO} +$ $0.331 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{OO}\cdot) + 0.068 \text{CHOCOCH}(\text{OH})\text{CH}_2(\text{O}\cdot) +$ $0.058 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{COCHO} + \text{NO}_3^- + \text{H}^+ - 0.874 \text{O}_2$	$1.5 \cdot 10^{+07}$		
R <sub>o</sub> 01383	*	*	$\text{CHOCOCH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CHOCH}(\text{OH})\text{COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01384	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{COCHO} \rightarrow \text{CH}_2(\text{OH})\text{COCOCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01385	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{OO}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{OH}) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01386	*	*	$\text{CHOCOCH}(\text{OH})\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CHOCH}(\text{OH})\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01387	*	*	$\text{CHOCOCH}(\text{OH})\text{CH}_2(\text{O}\cdot) \rightarrow \text{CHOCOCH}(\text{OH})(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00158	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{CH}(\text{OH})\text{COCH}(\text{OH})_2$	$9.7 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00159	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})_2$	$1.4 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01388	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{COCHO} + \text{OH} \rightarrow$ $0.166 \text{CHOCOCH}(\text{OH})\text{CH}_2(\text{OO}\cdot) + 0.281 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{COCHO} +$ $0.465 \text{CH}_3\text{CH}(\text{OH})\text{COCO}(\text{OO}\cdot) + 0.087 \text{CH}_3\text{CH}(\text{O}\cdot)\text{COCHO} + \text{H}_2\text{O} - 0.913 \text{O}_2$	$9.2 \cdot 10^{+08}$		
R <sub>o</sub> 01389	*		$\text{CH}_3\text{CH}(\text{OH})\text{COCHO} + \text{NO}_3 \rightarrow 0.166 \text{CHOCOCH}(\text{OH})\text{CH}_2(\text{OO}\cdot) +$ $0.281 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{COCHO} + 0.465 \text{CH}_3\text{CH}(\text{OH})\text{COCO}(\text{OO}\cdot) +$ $0.087 \text{CH}_3\text{CH}(\text{O}\cdot)\text{COCHO} + \text{NO}_3^- + \text{H}^+ - 0.913 \text{O}_2$	$1.5 \cdot 10^{+07}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01390	*	*	CHOCOCH(OH)CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CHOCOCH(OH)CH <sub>2</sub> (O·) + 0.550 CHOCH(OH)COCHO + 0.250 CH <sub>2</sub> (OH)CH(OH)COCHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01391	*	*	CH <sub>3</sub> C(OH)(OO·)COCHO $\rightarrow$ CH <sub>3</sub> COCOCHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01392	*	*	CH <sub>3</sub> CH(OH)COCO(OO·) $\rightarrow$ CH <sub>3</sub> CH(OH)COCO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
E <sub>o</sub> 00160	*	*	CH <sub>2</sub> (OH)COCH(OH)CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)COCH(OH)CH(OH) <sub>2</sub>	$5.2 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00161	*	*	CH <sub>2</sub> (OH)COCH(OH)CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH(OH) <sub>2</sub>	$3.8 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01393	*	*	CH <sub>2</sub> (OH)COCH(OH)CHO + OH $\rightarrow$ 0.238 CHOCH(OH)COCH(OH)(OO·) + 0.040 CH <sub>2</sub> (OH)COC(OH)(OO·)CHO + 0.618 CH <sub>2</sub> (OH)COCH(OH)CO(OO·) + 0.057 CHOCH(OH)COCH <sub>2</sub> (O·) + 0.047 CH <sub>2</sub> (OH)COCH(O·)CHO + H <sub>2</sub> O - 0.896 O <sub>2</sub>	$1.3 \cdot 10^{+09}$		
R <sub>o</sub> 01394	*		CH <sub>2</sub> (OH)COCH(OH)CHO + NO <sub>3</sub> $\rightarrow$ 0.238 CHOCH(OH)COCH(OH)(OO·) + 0.040 CH <sub>2</sub> (OH)COC(OH)(OO·)CHO + 0.618 CH <sub>2</sub> (OH)COCH(OH)CO(OO·) + 0.057 CHOCH(OH)COCH <sub>2</sub> (O·) + 0.047 CH <sub>2</sub> (OH)COCH(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.896 O <sub>2</sub>	$1.5 \cdot 10^{+07}$		
R <sub>o</sub> 01395	*	*	CHOCH(OH)COCH(OH)(OO·) $\rightarrow$ CHOCH(OH)COCHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01396	*	*	CH <sub>2</sub> (OH)COC(OH)(OO·)CHO $\rightarrow$ CH <sub>2</sub> (OH)COCOCHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01397	*	*	CH <sub>2</sub> (OH)COCH(OH)CO(OO·) $\rightarrow$ CH <sub>2</sub> (OH)COCH(OH)CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01398	*	*	CH <sub>2</sub> (OH)COCH(O·)CHO $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCOCHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01399	*	*	CH <sub>2</sub> (OH)COCH(O·)CHO $\rightarrow$ 0.500 CH <sub>2</sub> (OH)CO(OO·) + 0.500 CHOCHO + 0.500 CH <sub>2</sub> (OH)COCHO + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00162	*	*	CHOCH <sub>2</sub> COCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH <sub>2</sub> COCH(OH) <sub>2</sub>	$4.8 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00163	*	*	CHOCH <sub>2</sub> COCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CHO	$8.4 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00164	*	*	CHOCH <sub>2</sub> COCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	$5.7 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01400	*	*	CHOCH <sub>2</sub> COCHO $\rightarrow$ 0.500 + 0.500	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 01401	*	*	CHOCH <sub>2</sub> COCHO + OH $\rightarrow$ 0.818 CHOCOCH <sub>2</sub> CO(OO·) + 0.182 CHOCH <sub>2</sub> COCO(OO·) + H <sub>2</sub> O - O <sub>2</sub>	$2.5 \cdot 10^{+09}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01402	*		CHOCH <sub>2</sub> COCHO + NO <sub>3</sub> → 0.818 CHOCOCH <sub>2</sub> CO(OO·) + 0.182 CHOCH <sub>2</sub> COCO(OO·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	5.3 · 10 <sup>+06</sup>		
R <sub>o</sub> 01403	*	*	CHOCOCH <sub>2</sub> CO(OO·) → CO(OH)CH <sub>2</sub> COCHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01404	*	*	CHOCH <sub>2</sub> COCO(OO·) → CO(OH)COCH <sub>2</sub> CHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
E <sub>o</sub> 00165	*	*	CHOCH <sub>2</sub> CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CHO	6.8 · 10 <sup>+00</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00166	*	*	CHOCH <sub>2</sub> CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CHO	2.0 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00167	*	*	CHOCH <sub>2</sub> CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CH(OH) <sub>2</sub>	8.9 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01405	*	*	CHOCH <sub>2</sub> CH(OH)CHO + OH → 0.657 CHOCH(OH)CH <sub>2</sub> CO(OO·) + 0.066 CHOCH <sub>2</sub> C(OH)(OO·)CHO + 0.278 CHOCH <sub>2</sub> CH(OH)CO(OO·) + H <sub>2</sub> O - O <sub>2</sub>	3.6 · 10 <sup>+09</sup>		
R <sub>o</sub> 01406	*		CHOCH <sub>2</sub> CH(OH)CHO + NO <sub>3</sub> → 0.657 CHOCH(OH)CH <sub>2</sub> CO(OO·) + 0.066 CHOCH <sub>2</sub> C(OH)(OO·)CHO + 0.278 CHOCH <sub>2</sub> CH(OH)CO(OO·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	1.4 · 10 <sup>+07</sup>		
R <sub>o</sub> 01407	*	*	CHOCH(OH)CH <sub>2</sub> CO(OO·) → CO(OH)CH <sub>2</sub> CH(OH)CHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01408	*	*	CHOCH <sub>2</sub> C(OH)(OO·)CHO → CHOCH <sub>2</sub> COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01409	*	*	CHOCH <sub>2</sub> CH(OH)CO(OO·) → CO(OH)CH(OH)CH <sub>2</sub> CHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01410	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH <sub>2</sub> CO(O <sup>-</sup> ) + OH → 0.690 CO(O <sup>-</sup> )CH <sub>2</sub> CH <sub>2</sub> CH(OH)(OO·) + 0.196 CH <sub>2</sub> (OH)CH(OO·)CH <sub>2</sub> CO(O <sup>-</sup> ) + 0.079 CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OO·)CO(O <sup>-</sup> ) + 0.035 CO(O <sup>-</sup> )CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> (O·) + H <sub>2</sub> O - 0.965 O <sub>2</sub>	2.6 · 10 <sup>+09</sup>		
R <sub>o</sub> 01411	*		CH <sub>2</sub> (OH)CH <sub>2</sub> CH <sub>2</sub> CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>2</sub> (OH)CH <sub>2</sub> CH <sub>2</sub> CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 01412	*	*	CO(O <sup>-</sup> )CH <sub>2</sub> CH <sub>2</sub> CH(OH)(OO·) → CO(O <sup>-</sup> )CH <sub>2</sub> CH <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01413	*	*	CH <sub>2</sub> (OH)CH(OO·)CH <sub>2</sub> CO(O <sup>-</sup> ) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(O·)CH <sub>2</sub> CO(O <sup>-</sup> ) + 0.550 CH <sub>2</sub> (OH)COCH <sub>2</sub> CO(O <sup>-</sup> ) + 0.250 CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> CO(O <sup>-</sup> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01414	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OO·)CO(O <sup>-</sup> ) + CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OO·)CO(O <sup>-</sup> ) → 2.000 CH <sub>2</sub> (OH)CH <sub>2</sub> CHO + 2.000 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2.000 OH <sup>-</sup> - 2.000 H <sub>2</sub> O	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 01415	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OO·)CO(O <sup>-</sup> ) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH <sub>2</sub> CH(O·)CO(O <sup>-</sup> ) + 0.550 CH <sub>2</sub> (OH)CH <sub>2</sub> COCO(O <sup>-</sup> ) + 0.250 CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CO(O <sup>-</sup> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01416	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01417	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01418	*		$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}_2\text{CH}_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01419	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2\text{CO}(\text{O}^-) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCH}_2\text{CO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01420	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CO}(\text{O}^-)\text{CH}_2\text{CHO} + 0.500 \text{CH}_2(\text{OH})\text{CHO} +$ $0.500 \text{CO}(\text{O}^-)\text{CH}_2(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01421	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{CH}_2\text{COCO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01422	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) \rightarrow 0.500 \text{CH}_2(\text{OH})\text{CH}_2(\text{OO}\cdot) +$ $0.500 \text{CO}(\text{O}^-)\text{CHO} + 0.500 \text{CH}_2(\text{OH})\text{CH}_2\text{CHO} + 0.500 \cdot \text{CO}(\text{O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00168	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CO}(\text{OH}) \rightleftharpoons \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CO}(\text{O}^-) + \text{H}^+$	$3.0 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 01423	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CO}(\text{OH}) + \text{OH} \rightarrow$ $0.540 \text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.328 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2\text{CO}(\text{OH}) +$ $0.065 \text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) + 0.068 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2\text{CO}(\text{OH}) +$ $\text{H}_2\text{O} - 0.867 \text{O}_2$	$1.4 \cdot 10^{+09}$		
R <sub>o</sub> 01424	*		$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CO}(\text{OH}) + \text{NO}_3 \rightarrow$ $0.540 \text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.328 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2\text{CO}(\text{OH}) +$ $0.065 \text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) + 0.068 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2\text{CO}(\text{OH}) +$ $\text{NO}_3^- + \text{H}^+ - 0.867 \text{O}_2$	$4.0 \cdot 10^{+02}$		
R <sub>o</sub> 01425	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01426	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2\text{CO}(\text{OH}) \rightarrow \text{CH}_2(\text{OH})\text{COCH}_2\text{CO}(\text{OH}) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01427	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01428	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00169	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CO}(\text{OH}) \rightleftharpoons \text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{H}^+$	$4.7 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 01429	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CO}(\text{OH}) + \text{OH} \rightarrow$ $0.852 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.058 \text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{CH}(\text{OH})\text{CO}(\text{OH}) +$ $0.045 \text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{OH}) +$ $0.045 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.955 \text{O}_2$	$2.0 \cdot 10^{+09}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01430	*		CH <sub>2</sub> (OH)CH <sub>2</sub> CH(OH)CO(OH) + NO <sub>3</sub> → 0.852 CO(OH)CH(OH)CH <sub>2</sub> CH(OH)(OO·) + 0.058 CH <sub>2</sub> (OH)CH(OO·)CH(OH)CO(OH) + 0.045 CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH)(OO·)CO(OH) + 0.045 CO(OH)CH(OH)CH <sub>2</sub> CH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.955 O <sub>2</sub>	3.5 · 10 <sup>+02</sup>		
R <sub>o</sub> 01431	*	*	CO(OH)CH(OH)CH <sub>2</sub> CH(OH)(OO·) → CO(OH)CH(OH)CH <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01432	*	*	CH <sub>2</sub> (OH)CH(OO·)CH(OH)CO(OH) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(O·)CH(OH)CO(OH) + 0.550 CH <sub>2</sub> (OH)COCH(OH)CO(OH) + 0.250 CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01433	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH)(OO·)CO(OH) → CH <sub>2</sub> (OH)CH <sub>2</sub> COCO(OH) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01434	*	*	CO(OH)CH(OH)CH <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(OH)CH(OH)CH <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01435	*	*	CO(OH)CH(OH)CH <sub>2</sub> CH <sub>2</sub> (O·) → CO(OH)CH(OH)CH <sub>2</sub> (OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01436	*	*	CH <sub>2</sub> (OH)CH(O·)CH(OH)CO(OH) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCH(OH)CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01437	*	*	CH <sub>2</sub> (OH)CH(O·)CH(OH)CO(OH) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)CH(OH)CHO + 0.500 CH <sub>2</sub> (OH)CHO + 0.500 CO(OH)CH(OH)(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00170	*	*	CH <sub>3</sub> CH(OH)CH <sub>2</sub> CO(OH) ⇌ CH <sub>3</sub> CH(OH)CH <sub>2</sub> CO(O <sup>-</sup> ) + H <sup>+</sup>	2.5 · 10 <sup>-05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 01438	*	*	CH <sub>3</sub> CH(OH)CH <sub>2</sub> CO(OH) + OH → 0.134 CO(OH)CH <sub>2</sub> CH(OH)CH <sub>2</sub> (OO·) + 0.795 CH <sub>3</sub> C(OH)(OO·)CH <sub>2</sub> CO(OH) + 0.070 CH <sub>3</sub> CH(O·)CH <sub>2</sub> CO(OH) + H <sub>2</sub> O - 0.930 O <sub>2</sub>	1.4 · 10 <sup>+09</sup>		
R <sub>o</sub> 01439	*		CH <sub>3</sub> CH(OH)CH <sub>2</sub> CO(OH) + NO <sub>3</sub> → 0.134 CO(OH)CH <sub>2</sub> CH(OH)CH <sub>2</sub> (OO·) + 0.795 CH <sub>3</sub> C(OH)(OO·)CH <sub>2</sub> CO(OH) + 0.070 CH <sub>3</sub> CH(O·)CH <sub>2</sub> CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.930 O <sub>2</sub>	3.5 · 10 <sup>+02</sup>		
R <sub>o</sub> 01440	*	*	CO(OH)CH <sub>2</sub> CH(OH)CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CO(OH)CH <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) + 0.550 CO(OH)CH <sub>2</sub> CH(OH)CHO + 0.250 CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01441	*	*	CH <sub>3</sub> C(OH)(OO·)CH <sub>2</sub> CO(OH) → CH <sub>3</sub> COCH <sub>2</sub> CO(OH) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01442	*	*	CH <sub>3</sub> CH(O·)CH <sub>2</sub> CO(OH) $\xrightarrow{O_2}$ CH <sub>3</sub> COCH <sub>2</sub> CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01443	*	*	CH <sub>3</sub> CH(O·)CH <sub>2</sub> CO(OH) → 0.500 CH <sub>3</sub> (OO·) + 0.500 CO(OH)CH <sub>2</sub> CHO + 0.500 CH <sub>3</sub> CHO + 0.500 CO(OH)CH <sub>2</sub> (OO·) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00171	*	*	$\text{CH}_2(\text{OH})\text{COCH}_2\text{CO}(\text{OH}) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}_2\text{CO}(\text{OH})$	$2.6 \cdot 10^{-01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00172	*	*	$\text{CH}_2(\text{OH})\text{COCH}_2\text{CO}(\text{OH}) \rightleftharpoons \text{CH}_2(\text{OH})\text{COCH}_2\text{CO}(\text{O}^-) + \text{H}^+$	$6.2 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 01444	*	*	$\text{CH}_2(\text{OH})\text{COCH}_2\text{CO}(\text{OH}) + \text{OH} \rightarrow 0.815 \text{ CO}(\text{OH})\text{CH}_2\text{COCH}(\text{OH})(\text{OO}\cdot) + 0.185 \text{ CO}(\text{OH})\text{CH}_2\text{COCH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.815 \text{ O}_2$	$4.1 \cdot 10^{+08}$		
R <sub>o</sub> 01445	*		$\text{CH}_2(\text{OH})\text{COCH}_2\text{CO}(\text{OH}) + \text{NO}_3 \rightarrow 0.815 \text{ CO}(\text{OH})\text{CH}_2\text{COCH}(\text{OH})(\text{OO}\cdot) + 0.185 \text{ CO}(\text{OH})\text{CH}_2\text{COCH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.815 \text{ O}_2$	$7.5 \cdot 10^{+03}$		
R <sub>o</sub> 01446	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{COCH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}_2\text{COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01447	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{COCH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{CH}_2\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01448	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{COCH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}_2\text{CO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00173	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{COCO}(\text{OH}) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})_2\text{CO}(\text{OH})$	$3.4 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00174	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{COCO}(\text{OH}) \rightleftharpoons \text{CH}_2(\text{OH})\text{CH}_2\text{COCO}(\text{O}^-) + \text{H}^+$	$2.7 \cdot 10^{-02}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 01449	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{COCO}(\text{OH}) + \text{OH} \rightarrow 0.911 \text{ CO}(\text{OH})\text{COCH}_2\text{CH}(\text{OH})(\text{OO}\cdot) + 0.033 \text{ CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{COCO}(\text{OH}) + 0.056 \text{ CO}(\text{OH})\text{COCH}_2\text{CH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.944 \text{ O}_2$	$1.6 \cdot 10^{+09}$		
R <sub>o</sub> 01450	*		$\text{CH}_2(\text{OH})\text{CH}_2\text{COCO}(\text{OH}) + \text{NO}_3 \rightarrow 0.911 \text{ CO}(\text{OH})\text{COCH}_2\text{CH}(\text{OH})(\text{OO}\cdot) + 0.033 \text{ CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{COCO}(\text{OH}) + 0.056 \text{ CO}(\text{OH})\text{COCH}_2\text{CH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.944 \text{ O}_2$	$9.6 \cdot 10^{+03}$		
R <sub>o</sub> 01451	*	*	$\text{CO}(\text{OH})\text{COCH}_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{COCH}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01452	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{COCO}(\text{OH}) \xrightarrow{\text{RO}_2} 0.200 \text{ CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{COCO}(\text{OH}) + 0.550 \text{ CH}_2(\text{OH})\text{COCOCO}(\text{OH}) + 0.250 \text{ CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{OH}) + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01453	*	*	$\text{CO}(\text{OH})\text{COCH}_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{COCH}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01454	*	*	$\text{CO}(\text{OH})\text{COCH}_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{OH})\text{COCH}_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01455	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{COCO}(\text{OH}) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCOCO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01456	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{COCO}(\text{OH}) \rightarrow 0.500 \text{ CH}_2(\text{OH})\cdot + 0.500 \text{ CO}(\text{OH})\text{COCHO} + 0.500 \text{ CH}_2(\text{OH})\text{CHO} + 0.500 \text{ CO}(\text{OH})\text{CO}(\text{OO}\cdot) - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00175	*	*	$\text{CH}_3\text{COCH}_2\text{CO}(\text{OH}) \rightleftharpoons \text{CH}_3\text{COCH}_2\text{CO}(\text{O}^-) + \text{H}^+$	$5.3 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 01457	*	*	$\text{CH}_3\text{COCH}_2\text{CO}(\text{OH}) + \text{OH} \rightarrow 0.879 \text{ CO}(\text{OH})\text{CH}_2\text{COCH}_2(\text{OO}\cdot) + 0.121 \text{ CH}_3\text{COCH}(\text{OO}\cdot)\text{CO}(\text{OH}) + \text{H}_2\text{O} - \text{O}_2$	$9.6 \cdot 10^{+07}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01458	*		$\text{CH}_3\text{COCH}_2\text{CO}(\text{OH}) + \text{NO}_3 \rightarrow 0.879 \text{CO}(\text{OH})\text{CH}_2\text{COCH}_2(\text{OO}\cdot) + 0.121 \text{CH}_3\text{COCH}(\text{OO}\cdot)\text{CO}(\text{OH}) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$6.6 \cdot 10^{+03}$		
R <sub>o</sub> 01459	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{COCH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CO}(\text{OH})\text{CH}_2\text{COCH}_2(\text{O}\cdot) + 0.550 \text{CO}(\text{OH})\text{CH}_2\text{COCHO} + 0.250 \text{CH}_2(\text{OH})\text{COCH}_2\text{CO}(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01460	*	*	$\text{CH}_3\text{COCH}(\text{OO}\cdot)\text{CO}(\text{OH}) + \text{CH}_3\text{COCH}(\text{OO}\cdot)\text{CO}(\text{OH}) \rightarrow 2.000 \text{CH}_3\text{COCHO} + 2.000 \text{CO}_2 + -\text{O}_2 -$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 01461	*	*	$\text{CH}_3\text{COCH}(\text{OO}\cdot)\text{CO}(\text{OH}) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_3\text{COCH}(\text{O}\cdot)\text{CO}(\text{OH}) + 0.550 \text{CH}_3\text{COCOCO}(\text{OH}) + 0.250 \text{CH}_3\text{COCH}(\text{OH})\text{CO}(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01462	*	*	$\text{CH}_3\text{COCH}(\text{O}\cdot)\text{CO}(\text{OH}) \xrightarrow{\text{O}_2} \text{CH}_3\text{COCOCO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01463	*	*	$\text{CH}_3\text{COCH}(\text{O}\cdot)\text{CO}(\text{OH}) \rightarrow 0.500 \text{CH}_3\text{CO}(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CHO} + 0.500 \text{CH}_3\text{COCHO} + 0.500 \cdot \text{CO}(\text{OH}) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00176	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{CH}_2\text{CH}_2\text{CO}(\text{OH})$	$3.2 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{s}^{-1}$ estimated
E <sub>o</sub> 00177	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CHO} \rightleftharpoons \text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2\text{CHO} + \text{H}^+$	$3.0 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 01464	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CHO} + \text{OH} \rightarrow 0.047 \text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OO}\cdot)\text{CHO} + 0.953 \text{CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CO}(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$2.6 \cdot 10^{+09}$		
R <sub>o</sub> 01465	*		$\text{CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CHO} + \text{NO}_3 \rightarrow 0.047 \text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OO}\cdot)\text{CHO} + 0.953 \text{CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CO}(\text{OO}\cdot) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$1.5 \cdot 10^{+07}$		
R <sub>o</sub> 01466	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OO}\cdot)\text{CHO} \xrightarrow{\text{RO}_2}$ $0.200 \text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{O}\cdot)\text{CHO} + 0.550 \text{CO}(\text{OH})\text{CH}_2\text{COCHO} + 0.250 \text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01467	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CO}(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CO}(\text{OH}) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01468	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{O}\cdot)\text{CHO} \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{CH}_2\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01469	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{O}\cdot)\text{CHO} \rightarrow 0.500 \text{CO}(\text{OH})\text{CH}_2(\text{OO}\cdot) + 0.500 \text{CHOCHO} + 0.500 \text{CO}(\text{OH})\text{CH}_2\text{CHO} + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{O}_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01470	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{C}(\text{OH})_2\text{CH}(\text{OH})_2 \rightarrow 0.500 + 0.500 + 0.500$	$1.0 \cdot 10^{-01}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01471	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + OH $\rightarrow$ 0.378 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.067 CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.195 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)(O $\cdot$ ) + 0.184 CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH)(O $\cdot$ )CH(OH) <sub>2</sub> + 0.177 CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O $\cdot$ ) + H <sub>2</sub> O - 0.445 O <sub>2</sub>	2.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 01472	*		CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + NO <sub>3</sub> $\rightarrow$ 0.378 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.067 CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.195 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)(O $\cdot$ ) + 0.184 CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH)(O $\cdot$ )CH(OH) <sub>2</sub> + 0.177 CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.445 O <sub>2</sub>	1.1 · 10 <sup>+07</sup>		
R <sub>o</sub> 01473	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01474	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01475	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01476	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)(O $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01477	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH)(O $\cdot$ )CH(OH) <sub>2</sub> $\rightarrow$ 0.500 CH(OH) <sub>2</sub> CH <sub>2</sub> (OO $\cdot$ ) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CH(OH) <sub>2</sub> CH <sub>2</sub> CO(OH) + 0.500 CH $\cdot$ (OH) <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01478	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01479	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01480	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub> $\rightarrow$ 0.250 CH <sub>3</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.250 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.250 CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.250 CHO(OH) + 0.250 HO <sub>2</sub>	1.0 · 10 <sup>-01</sup>		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01481	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + OH → 0.053 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (OO·) + 0.097 CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.299 CH <sub>3</sub> C(OH)(O·)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + 0.268 CH <sub>3</sub> C(OH) <sub>2</sub> C(OH)(O·)CH(OH) <sub>2</sub> + 0.283 CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) + H <sub>2</sub> O – 0.150 O <sub>2</sub>	1.3 · 10 <sup>+09</sup>		
R <sub>o</sub> 01482	*		CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.053 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (OO·) + 0.097 CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.299 CH <sub>3</sub> C(OH)(O·)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + 0.268 CH <sub>3</sub> C(OH) <sub>2</sub> C(OH)(O·)CH(OH) <sub>2</sub> + 0.283 CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.150 O <sub>2</sub>	8.9 · 10 <sup>+06</sup>		
R <sub>o</sub> 01483	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.550 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + 0.250 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01484	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01485	*	*	CH <sub>3</sub> C(OH)(O·)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> → 0.500 CH <sub>3</sub> (OO·) + 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + 0.500 CH <sub>3</sub> CO(OH) + 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01486	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> C(OH)(O·)CH(OH) <sub>2</sub> → 0.500 CH <sub>3</sub> C(OH) <sub>2</sub> (OO·) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CH <sub>3</sub> C(OH) <sub>2</sub> CO(OH) + 0.500 CH·(OH) <sub>2</sub> – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01487	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01488	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) → CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01489	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01490	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) → CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01491	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH)CH(OH) <sub>2</sub> + OH → 0.055 CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (OO·) + 0.037 CH <sub>3</sub> C(OH) <sub>2</sub> C(OH)(OO·)CH(OH) <sub>2</sub> + 0.242 CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO·) + 0.310 CH <sub>3</sub> C(OH)(O·)CH(OH)CH(OH) <sub>2</sub> + 0.062 CH <sub>3</sub> C(OH) <sub>2</sub> CH(O·)CH(OH) <sub>2</sub> + 0.294 CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH)CH(OH)(O·) + H <sub>2</sub> O – 0.334 O <sub>2</sub>	1.3 · 10 <sup>+09</sup>		
R <sub>o</sub> 01492	*		CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH)CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.055 CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (OO·) + 0.037 CH <sub>3</sub> C(OH) <sub>2</sub> C(OH)(OO·)CH(OH) <sub>2</sub> + 0.242 CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO·) + 0.310 CH <sub>3</sub> C(OH)(O·)CH(OH)CH(OH) <sub>2</sub> + 0.062 CH <sub>3</sub> C(OH) <sub>2</sub> CH(O·)CH(OH) <sub>2</sub> + 0.294 CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH)CH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.334 O <sub>2</sub>	1.2 · 10 <sup>+07</sup>		
R <sub>o</sub> 01493	*	*	CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.550 CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CHO + 0.250 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01494	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> C(OH)(OO·)CH(OH) <sub>2</sub> → CH <sub>3</sub> C(OH) <sub>2</sub> COCH(OH) <sub>2</sub> + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01495	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO·) → CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH)CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01496	*	*	CH <sub>3</sub> C(OH)(O·)CH(OH)CH(OH) <sub>2</sub> → 0.500 CH <sub>3</sub> (OO·) + 0.500 CH(OH) <sub>2</sub> CH(OH)CO(OH) + 0.500 CH <sub>3</sub> CO(OH) + 0.500 CH(OH) <sub>2</sub> CH(OH)(OO·) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01497	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> CH(O·)CH(OH) <sub>2</sub> $\xrightarrow{O_2}$ CH <sub>3</sub> C(OH) <sub>2</sub> COCH(OH) <sub>2</sub> + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01498	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> CH(O·)CH(OH) <sub>2</sub> → 0.500 CH <sub>3</sub> C(OH) <sub>2</sub> (OO·) + 0.500 CH(OH) <sub>2</sub> CHO + 0.500 CH <sub>3</sub> C(OH) <sub>2</sub> CHO + 0.500 CH·(OH) <sub>2</sub> – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01499	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH)CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH)CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01500	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH)CH(OH)(O·) → CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH)(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01501	*	*	CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01502	*	*	CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) → CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01503	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH)(OO·) → CH <sub>3</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01504	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub> → 0.250 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO·) + 0.250 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.250 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.250 CHO(OH) + 0.250 HO <sub>2</sub>	1.0 · 10 <sup>–01</sup>		
R <sub>o</sub> 01505	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + OH → 0.172 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) + 0.081 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.054 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.234 CH <sub>2</sub> (OH)C(OH)(O·)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + 0.223 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(O·)CH(OH) <sub>2</sub> + 0.236 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) + H <sub>2</sub> O – 0.253 O <sub>2</sub>	1.5 · 10 <sup>+09</sup>		
R <sub>o</sub> 01506	*		CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.172 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) + 0.081 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.054 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.234 CH <sub>2</sub> (OH)C(OH)(O·)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + 0.223 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(O·)CH(OH) <sub>2</sub> + 0.236 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.253 O <sub>2</sub>	9.7 · 10 <sup>+06</sup>		
R <sub>o</sub> 01507	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) → CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01508	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01509	*	*	CH <sub>2</sub> (OH)C(OH)(O·)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> → 0.500 CH <sub>2</sub> (OH)· + 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01510	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(O·)CH(OH) <sub>2</sub> → 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO·) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CO(OH) + 0.500 CH·(OH) <sub>2</sub> – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01511	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01512	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01513	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})_2 + \text{OH} \rightarrow$ $0.124 \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) +$ $0.193 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CH}(\text{OH})_2 +$ $0.094 \text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.065 \text{CH}_3\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CH}(\text{OH})_2 +$ $0.261 \text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})_2 +$ $0.263 \text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.411 \text{O}_2$	$1.4 \cdot 10^{+09}$		
R <sub>o</sub> 01514	*		$\text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})_2 + \text{NO}_3 \rightarrow$ $0.124 \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) +$ $0.193 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CH}(\text{OH})_2 +$ $0.094 \text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.065 \text{CH}_3\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CH}(\text{OH})_2 +$ $0.261 \text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})_2 +$ $0.263 \text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.411 \text{O}_2$	$1.2 \cdot 10^{+07}$		
R <sub>o</sub> 01515	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) +$ $0.550 \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})_2 + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01516	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CH}(\text{OH})_2 \rightarrow \text{CH}_3\text{COC}(\text{OH})_2\text{CH}(\text{OH})_2 + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01517	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01518	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})_2 \rightarrow$ $0.500 \text{CH}_3\text{CH}(\text{OH})(\text{OO}\cdot) + 0.500 \text{CH}(\text{OH})_2\text{CO}(\text{OH}) +$ $0.500 \text{CH}_3\text{CH}(\text{OH})\text{CO}(\text{OH}) + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01519	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01520	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow$ $\text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01521	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01522	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)CH}_2(\text{O}\cdot) \rightarrow$ $\text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)(OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01523	*	*	$\text{CH(OH)}_2\text{CH}_2\text{CH(OH)CH(OH)}_2 + \text{OH} \rightarrow$ $0.344 \text{ CH(OH)}_2\text{CH(OH)CH}_2\text{C(OH)}_2(\text{OO}\cdot) +$ $0.030 \text{ CH(OH)}_2\text{CH(OH)CH(OO}\cdot)\text{CH(OH)}_2 +$ $0.114 \text{ CH(OH)}_2\text{CH}_2\text{C(OH)(OO}\cdot)\text{CH(OH)}_2 +$ $0.145 \text{ CH(OH)}_2\text{CH}_2\text{CH(OH)C(OH)}_2(\text{OO}\cdot) +$ $0.169 \text{ CH(OH)}_2\text{CH(OH)CH}_2\text{CH(OH)(O}\cdot) +$ $0.037 \text{ CH(OH)}_2\text{CH}_2\text{CH(O}\cdot)\text{CH(OH)}_2 +$ $0.161 \text{ CH(OH)}_2\text{CH}_2\text{CH(OH)CH(OH)(O}\cdot) + \text{H}_2\text{O} - 0.633 \text{ O}_2$	$2.4 \cdot 10^{+09}$		
R <sub>o</sub> 01524	*		$\text{CH(OH)}_2\text{CH}_2\text{CH(OH)CH(OH)}_2 + \text{NO}_3 \rightarrow$ $0.344 \text{ CH(OH)}_2\text{CH(OH)CH}_2\text{C(OH)}_2(\text{OO}\cdot) +$ $0.030 \text{ CH(OH)}_2\text{CH(OH)CH(OO}\cdot)\text{CH(OH)}_2 +$ $0.114 \text{ CH(OH)}_2\text{CH}_2\text{C(OH)(OO}\cdot)\text{CH(OH)}_2 +$ $0.145 \text{ CH(OH)}_2\text{CH}_2\text{CH(OH)C(OH)}_2(\text{OO}\cdot) +$ $0.169 \text{ CH(OH)}_2\text{CH(OH)CH}_2\text{CH(OH)(O}\cdot) +$ $0.037 \text{ CH(OH)}_2\text{CH}_2\text{CH(O}\cdot)\text{CH(OH)}_2 +$ $0.161 \text{ CH(OH)}_2\text{CH}_2\text{CH(OH)CH(OH)(O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.633 \text{ O}_2$	$1.3 \cdot 10^{+07}$		
R <sub>o</sub> 01525	*	*	$\text{CH(OH)}_2\text{CH(OH)CH}_2\text{C(OH)}_2(\text{OO}\cdot) \rightarrow$ $\text{CH(OH)}_2\text{CH(OH)CH}_2\text{CO(OH)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01526	*	*	$\text{CH(OH)}_2\text{CH(OH)CH(OO}\cdot)\text{CH(OH)}_2 \xrightarrow{\text{RO}_2}$ $0.200 \text{ CH(OH)}_2\text{CH(OH)CH(O}\cdot)\text{CH(OH)}_2 +$ $0.550 \text{ CH(OH)}_2\text{CH(OH)COCH(OH)}_2 +$ $0.250 \text{ CH(OH)}_2\text{CH(OH)CH(OH)CH(OH)}_2 + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01527	*	*	$\text{CH(OH)}_2\text{CH}_2\text{C(OH)(OO}\cdot)\text{CH(OH)}_2 \rightarrow \text{CH(OH)}_2\text{CH}_2\text{COCH(OH)}_2 + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01528	*	*	$\text{CH(OH)}_2\text{CH}_2\text{CH(OH)C(OH)}_2(\text{OO}\cdot) \rightarrow$ $\text{CH(OH)}_2\text{CH}_2\text{CH(OH)CO(OH)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01529	*	*	$\text{CH(OH)}_2\text{CH(OH)CH}_2\text{CH(OH)(O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CH(OH)}_2\text{CH(OH)CH}_2\text{CO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01530	*	*	$\text{CH(OH)}_2\text{CH(OH)CH}_2\text{CH(OH)(O}\cdot\text{)} \rightarrow$ $\text{CH(OH)}_2\text{CH(OH)CH}_2(\text{OO}\cdot) + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01531	*	*	$\text{CH(OH)}_2\text{CH}_2\text{CH(OH)CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2}$ $\text{CH(OH)}_2\text{CH}_2\text{CH(OH)CO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01532	*	*	$\text{CH(OH)}_2\text{CH}_2\text{CH(OH)CH(OH)(O}\cdot\text{)} \rightarrow$ $\text{CH(OH)}_2\text{CH}_2\text{CH(OH)(OO}\cdot\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01533	*	*	$\text{CH(OH)}_2\text{CH(OH)CH(O}\cdot\text{)CH(OH)}_2 \xrightarrow{\text{O}_2}$ $\text{CH(OH)}_2\text{CH(OH)COCH(OH)}_2 + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01534	*	*	$\text{CH(OH)}_2\text{CH(OH)CH(O}\cdot\text{)CH(OH)}_2 \rightarrow$ $0.500 \text{CH(OH)}_2\text{CH(OH)(OO}\cdot\text{)} + 0.500 \text{CH(OH)}_2\text{CHO} +$ $0.500 \text{CH(OH)}_2\text{CH(OH)CHO} + 0.500 \text{CH}\cdot\text{(OH)}_2 - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01535	*	*	$\text{CH}_2(\text{OH})\text{C(OH)}_2\text{CH(OH)CH(OH)}_2 + \text{OH} \rightarrow$ $0.183 \text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CH(OH)(OO}\cdot\text{)} +$ $0.207 \text{CH}_2(\text{OH})\text{C(OH)}_2\text{CH(OH)C(OH)}_2(\text{OO}\cdot) +$ $0.055 \text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CH}_2(\text{O}\cdot) +$ $0.250 \text{CH}_2(\text{OH})\text{C(OH)}(\text{O}\cdot)\text{CH(OH)CH(OH)}_2 +$ $0.053 \text{CH}_2(\text{OH})\text{C(OH)}_2\text{CH(O}\cdot\text{)CH(OH)}_2 +$ $0.252 \text{CH}_2(\text{OH})\text{C(OH)}_2\text{CH(OH)CH(OH)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.390 \text{O}_2$	$1.5 \cdot 10^{+09}$		
R <sub>o</sub> 01536	*		$\text{CH}_2(\text{OH})\text{C(OH)}_2\text{CH(OH)CH(OH)}_2 + \text{NO}_3 \rightarrow$ $0.183 \text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CH(OH)(OO}\cdot\text{)} +$ $0.207 \text{CH}_2(\text{OH})\text{C(OH)}_2\text{CH(OH)C(OH)}_2(\text{OO}\cdot) +$ $0.055 \text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CH}_2(\text{O}\cdot) +$ $0.250 \text{CH}_2(\text{OH})\text{C(OH)}(\text{O}\cdot)\text{CH(OH)CH(OH)}_2 +$ $0.053 \text{CH}_2(\text{OH})\text{C(OH)}_2\text{CH(O}\cdot\text{)CH(OH)}_2 +$ $0.252 \text{CH}_2(\text{OH})\text{C(OH)}_2\text{CH(OH)CH(OH)(O}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - 0.390 \text{O}_2$	$1.3 \cdot 10^{+07}$		
R <sub>o</sub> 01537	*	*	$\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CH(OH)(OO}\cdot\text{)} \rightarrow$ $\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01538	*	*	$\text{CH}_2(\text{OH})\text{C(OH)}_2\text{CH(OH)C(OH)}_2(\text{OO}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{C(OH)}_2\text{CH(OH)CO(OH)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01539	*	*	CH <sub>2</sub> (OH)C(OH)(O·)CH(OH)CH(OH) <sub>2</sub> → 0.500 CH <sub>2</sub> (OH)· + 0.500 CH(OH) <sub>2</sub> CH(OH)CO(OH) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CH(OH) <sub>2</sub> CH(OH)(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01540	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O·)CH(OH) <sub>2</sub> $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH(OH) <sub>2</sub> + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01541	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O·)CH(OH) <sub>2</sub> → 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO·) + 0.500 CH(OH) <sub>2</sub> CHO + 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CHO + 0.500 CH·(OH) <sub>2</sub> – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01542	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01543	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH(OH)(O·) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01544	*	*	CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + OH → 0.370 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CH(OH)(OO·) + 0.059 CH <sub>2</sub> (OH)C(OH)(OO·)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + 0.072 CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.049 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) + 0.047 CH <sub>2</sub> (OH)CH(O·)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + 0.200 CH <sub>2</sub> (OH)CH(OH)C(OH)(O·)CH(OH) <sub>2</sub> + 0.202 CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CH(OH)(O·) + H <sub>2</sub> O – 0.502 O <sub>2</sub>	1.8 · 10 <sup>+09</sup>		
R <sub>o</sub> 01545	*		CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.370 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CH(OH)(OO·) + 0.059 CH <sub>2</sub> (OH)C(OH)(OO·)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + 0.072 CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.049 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) + 0.047 CH <sub>2</sub> (OH)CH(O·)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + 0.200 CH <sub>2</sub> (OH)CH(OH)C(OH)(O·)CH(OH) <sub>2</sub> + 0.202 CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.502 O <sub>2</sub>	1.3 · 10 <sup>+07</sup>		
R <sub>o</sub> 01546	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CH(OH)(OO·) → CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01547	*	*	CH <sub>2</sub> (OH)C(OH)(OO·)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> → CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH(OH) <sub>2</sub> + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01548	*	*	CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01549	*	*	CH <sub>2</sub> (OH)CH(O·)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH(OH) <sub>2</sub> + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01550	*	*	CH <sub>2</sub> (OH)CH(O·)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> → 0.500 CH <sub>2</sub> (OH)· + 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + 0.500 CH <sub>2</sub> (OH)CHO + 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01551	*	*	CH <sub>2</sub> (OH)CH(OH)C(OH)(O·)CH(OH) <sub>2</sub> → 0.500 CH <sub>2</sub> (OH)CH(OH)(OO·) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CH <sub>2</sub> (OH)CH(OH)CO(OH) + 0.500 CH·(OH) <sub>2</sub> – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01552	*	*	CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01553	*	*	CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CH(OH)(O·) → CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> (OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01554	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(OH) <sub>2</sub> + OH → 0.341 CH(OH) <sub>2</sub> CH(OH)CH(OH)CH(OH)(OO·) + 0.131 CH <sub>2</sub> (OH)C(OH)(OO·)CH(OH)CH(OH) <sub>2</sub> + 0.055 CH <sub>2</sub> (OH)CH(OH)C(OH)(OO·)CH(OH) <sub>2</sub> + 0.160 CH <sub>2</sub> (OH)CH(OH)CH(OH)C(OH) <sub>2</sub> (OO·) + 0.043 CH(OH) <sub>2</sub> CH(OH)CH(OH)CH <sub>2</sub> (O·) + 0.043 CH <sub>2</sub> (OH)CH(O·)CH(OH)CH(OH) <sub>2</sub> + 0.041 CH <sub>2</sub> (OH)CH(OH)CH(O·)CH(OH) <sub>2</sub> + 0.186 CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(OH)(O·) + H <sub>2</sub> O – 0.688 O <sub>2</sub>	2.1 · 10 <sup>+09</sup>		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01555	*		CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.341 CH(OH) <sub>2</sub> CH(OH)CH(OH)CH(OH)(OO·) + 0.131 CH <sub>2</sub> (OH)C(OH)(OO·)CH(OH)CH(OH) <sub>2</sub> + 0.055 CH <sub>2</sub> (OH)CH(OH)C(OH)(OO·)CH(OH) <sub>2</sub> + 0.160 CH <sub>2</sub> (OH)CH(OH)CH(OH)C(OH) <sub>2</sub> (OO·) + 0.043 CH(OH) <sub>2</sub> CH(OH)CH(OH)CH <sub>2</sub> (O·) + 0.043 CH <sub>2</sub> (OH)CH(O·)CH(OH)CH(OH) <sub>2</sub> + 0.041 CH <sub>2</sub> (OH)CH(OH)CH(O·)CH(OH) <sub>2</sub> + 0.186 CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.688 O <sub>2</sub>	1.6 · 10 <sup>+07</sup>		
R <sub>o</sub> 01556	*	*	CH(OH) <sub>2</sub> CH(OH)CH(OH)CH(OH)(OO·) → CH(OH) <sub>2</sub> CH(OH)CH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01557	*	*	CH <sub>2</sub> (OH)C(OH)(OO·)CH(OH)CH(OH) <sub>2</sub> → CH <sub>2</sub> (OH)COCH(OH)CH(OH) <sub>2</sub> + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01558	*	*	CH <sub>2</sub> (OH)CH(OH)C(OH)(OO·)CH(OH) <sub>2</sub> → CH <sub>2</sub> (OH)CH(OH)COCH(OH) <sub>2</sub> + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01559	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OH)C(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01560	*	*	CH(OH) <sub>2</sub> CH(OH)CH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(OH)CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01561	*	*	CH(OH) <sub>2</sub> CH(OH)CH(OH)CH <sub>2</sub> (O·) → CH(OH) <sub>2</sub> CH(OH)CH(OH)(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01562	*	*	CH <sub>2</sub> (OH)CH(OH)CH(O·)CH(OH) <sub>2</sub> $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(OH)COCH(OH) <sub>2</sub> + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01563	*	*	CH <sub>2</sub> (OH)CH(OH)CH(O·)CH(OH) <sub>2</sub> → 0.500 CH <sub>2</sub> (OH)CH(OH)(OO·) + 0.500 CH(OH) <sub>2</sub> CHO + 0.500 CH <sub>2</sub> (OH)CH(OH)CHO + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01564	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01565	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(OH)(O·) → CH <sub>2</sub> (OH)CH(OH)CH(OH)(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01566	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{OH}) + \text{OH} \rightarrow$ $0.395 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.066 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2(\text{OH}) +$ $0.164 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.052 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) +$ $0.050 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) +$ $0.224 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CH}_2(\text{OH}) +$ $0.049 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.625 \text{O}_2$	$1.7 \cdot 10^{+09}$		
R <sub>o</sub> 01567	*		$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{OH}) + \text{NO}_3 \rightarrow$ $0.395 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.066 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2(\text{OH}) +$ $0.164 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.052 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) +$ $0.050 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) +$ $0.224 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CH}_2(\text{OH}) +$ $0.049 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.625 \text{O}_2$	$1.4 \cdot 10^{+07}$		
R <sub>o</sub> 01568	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01569	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2(\text{OH}) \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}_2(\text{OH}) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01570	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01571	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) \xrightarrow{\text{O}_2}$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}_2(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01572	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CH}_2(\text{OH}) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.500 \text{CH}_2(\text{OH})\text{CHO} +$ $0.500 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CHO} + 0.500 \text{CH}_2(\text{OH})\cdot - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01573	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CH}_2(\text{OH}) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) + 0.500 \text{CH}_2(\text{OH})\text{CO}(\text{OH}) +$ $0.500 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{OH}) + 0.500 \text{CH}_2(\text{OH})\cdot - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01574	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01575	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01576	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{OH}) + \text{OH} \rightarrow$ $0.374 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.118 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) +$ $0.508 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CH}_2(\text{OH}) + \text{H}_2\text{O} - 0.374 \text{O}_2$	$1.4 \cdot 10^{+09}$		
R <sub>o</sub> 01577	*		$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{OH}) + \text{NO}_3 \rightarrow$ $0.374 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.118 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) +$ $0.508 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CH}_2(\text{OH}) + \text{NO}_3^- + \text{H}^+ - 0.374 \text{O}_2$	$1.1 \cdot 10^{+07}$		
R <sub>o</sub> 01578	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01579	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CH}_2(\text{OH}) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.500 \text{CH}_2(\text{OH})\text{CO}(\text{OH}) +$ $0.500 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OH}) + 0.500 \text{CH}_2(\text{OH})\cdot - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01580	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})_2 + \text{OH} \rightarrow$ $0.096 \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) +$ $0.361 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})\text{CH}(\text{OH})_2 +$ $0.065 \text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})_2 +$ $0.177 \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.051 \text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CH}(\text{OH})_2 + 0.045 \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})_2 +$ $0.205 \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.699 \text{O}_2$	$1.9 \cdot 10^{+09}$		
R <sub>o</sub> 01581	*		$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})_2 + \text{NO}_3 \rightarrow$ $0.096 \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) +$ $0.361 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})\text{CH}(\text{OH})_2 +$ $0.065 \text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})_2 +$ $0.177 \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.051 \text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CH}(\text{OH})_2 + 0.045 \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})_2 +$ $0.205 \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.699 \text{O}_2$	$1.5 \cdot 10^{+07}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01582	*	*	CH(OH) <sub>2</sub> CH(OH)CH(OH)CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH(OH)CH(OH)CH <sub>2</sub> (O·) + 0.550 CH(OH) <sub>2</sub> CH(OH)CH(OH)CHO + 0.250 CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01583	*	*	CH <sub>3</sub> C(OH)(OO·)CH(OH)CH(OH) <sub>2</sub> → CH <sub>3</sub> COCH(OH)CH(OH) <sub>2</sub> + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01584	*	*	CH <sub>3</sub> CH(OH)C(OH)(OO·)CH(OH) <sub>2</sub> → CH <sub>3</sub> CH(OH)COCH(OH) <sub>2</sub> + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01585	*	*	CH <sub>3</sub> CH(OH)CH(OH)C(OH) <sub>2</sub> (OO·) → CH <sub>3</sub> CH(OH)CH(OH)CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01586	*	*	CH <sub>3</sub> CH(OH)CH(O·)CH(OH) <sub>2</sub> $\xrightarrow{O_2}$ CH <sub>3</sub> CH(OH)COCH(OH) <sub>2</sub> + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01587	*	*	CH <sub>3</sub> CH(OH)CH(O·)CH(OH) <sub>2</sub> → 0.500 CH <sub>3</sub> CH(OH)(OO·) + 0.500 CH(OH) <sub>2</sub> CHO + 0.500 CH <sub>3</sub> CH(OH)CHO + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01588	*	*	CH <sub>3</sub> CH(OH)CH(OH)CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>3</sub> CH(OH)CH(OH)CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01589	*	*	CH <sub>3</sub> CH(OH)CH(OH)CH(OH)(O·) → CH <sub>3</sub> CH(OH)CH(OH)(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01590	*	*	CH <sub>3</sub> COC(OH) <sub>2</sub> CH(OH) <sub>2</sub> → 0.250 CH <sub>3</sub> CO(OO·) + 0.250 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.250 CH <sub>3</sub> COC(OH) <sub>2</sub> (OO·) + 0.250 CHO(OH) + 0.250 HO <sub>2</sub>	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 01591	*	*	CH <sub>3</sub> COC(OH) <sub>2</sub> CH(OH) <sub>2</sub> + OH → 0.089 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH <sub>2</sub> (OO·) + 0.130 CH <sub>3</sub> COC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.359 CH <sub>3</sub> COC(OH)(O·)CH(OH) <sub>2</sub> + 0.422 CH <sub>3</sub> COC(OH) <sub>2</sub> CH(OH)(O·) + H <sub>2</sub> O - 0.219 O <sub>2</sub>	8.6 · 10 <sup>+08</sup>		
R <sub>o</sub> 01592	*		CH <sub>3</sub> COC(OH) <sub>2</sub> CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.089 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH <sub>2</sub> (OO·) + 0.130 CH <sub>3</sub> COC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.359 CH <sub>3</sub> COC(OH)(O·)CH(OH) <sub>2</sub> + 0.422 CH <sub>3</sub> COC(OH) <sub>2</sub> CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.219 O <sub>2</sub>	8.8 · 10 <sup>+06</sup>		
R <sub>o</sub> 01593	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH <sub>2</sub> (O·) + 0.550 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCHO + 0.250 CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01594	*	*	CH <sub>3</sub> COC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CH <sub>3</sub> COC(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01595	*	*	CH <sub>3</sub> COC(OH)(O·)CH(OH) <sub>2</sub> → 0.500 CH <sub>3</sub> CO(OO·) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CH <sub>3</sub> COCO(OH) + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01596	*	*	CH <sub>3</sub> COC(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>3</sub> COC(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01597	*	*	CH <sub>3</sub> COC(OH) <sub>2</sub> CH(OH)(O·) → CH <sub>3</sub> COC(OH) <sub>2</sub> (OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01598	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{COCH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH(OH)}_2\text{C(OH)}_2\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01599	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{COCH}_2(\text{O}\cdot) \rightarrow \text{CH(OH)}_2\text{C(OH)}_2\text{CO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01600	*	*	$\text{CH(OH)}_2\text{CH}_2\text{COCH(OH)}_2 \rightarrow 0.500 + 0.500 + 0.500$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 01601	*	*	$\text{CH(OH)}_2\text{CH}_2\text{COCH(OH)}_2 + \text{OH} \rightarrow 0.442 \text{CH(OH)}_2\text{COCH}_2\text{C(OH)}_2(\text{OO}\cdot) + 0.098 \text{CH(OH)}_2\text{CH}_2\text{COC(OH)}_2(\text{OO}\cdot) + 0.253 \text{CH(OH)}_2\text{COCH}_2\text{CH(OH)}(\text{O}\cdot) + 0.207 \text{CH(OH)}_2\text{CH}_2\text{COCH(OH)}(\text{O}\cdot) + \text{H}_2\text{O} - 0.540 \text{O}_2$	$1.6 \cdot 10^{+09}$		
R <sub>o</sub> 01602	*		$\text{CH(OH)}_2\text{CH}_2\text{COCH(OH)}_2 + \text{NO}_3 \rightarrow 0.442 \text{CH(OH)}_2\text{COCH}_2\text{C(OH)}_2(\text{OO}\cdot) + 0.098 \text{CH(OH)}_2\text{CH}_2\text{COC(OH)}_2(\text{OO}\cdot) + 0.253 \text{CH(OH)}_2\text{COCH}_2\text{CH(OH)}(\text{O}\cdot) + 0.207 \text{CH(OH)}_2\text{CH}_2\text{COCH(OH)}(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.540 \text{O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 01603	*	*	$\text{CH(OH)}_2\text{COCH}_2\text{C(OH)}_2(\text{OO}\cdot) \rightarrow \text{CH(OH)}_2\text{COCH}_2\text{CO(OH)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01604	*	*	$\text{CH(OH)}_2\text{CH}_2\text{COC(OH)}_2(\text{OO}\cdot) \rightarrow \text{CH(OH)}_2\text{CH}_2\text{COCO(OH)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01605	*	*	$\text{CH(OH)}_2\text{COCH}_2\text{CH(OH)}(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH(OH)}_2\text{COCH}_2\text{CO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01606	*	*	$\text{CH(OH)}_2\text{COCH}_2\text{CH(OH)}(\text{O}\cdot) \rightarrow \text{CH(OH)}_2\text{COCH}_2(\text{OO}\cdot) + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01607	*	*	$\text{CH(OH)}_2\text{CH}_2\text{COCH(OH)}(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH(OH)}_2\text{CH}_2\text{COCO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01608	*	*	$\text{CH(OH)}_2\text{CH}_2\text{COCH(OH)}(\text{O}\cdot) \rightarrow \text{CH(OH)}_2\text{CH}_2\text{CO}(\text{OO}\cdot) + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01609	*	*	$\text{CH}_2(\text{OH})\text{COC(OH)}_2\text{CH(OH)}_2 \rightarrow 0.250 \text{CH}_2(\text{OH})\text{CO}(\text{OO}\cdot) + 0.250 \text{CH(OH)}_2\text{C(OH)}_2(\text{OO}\cdot) + 0.250 \text{CH}_2(\text{OH})\text{COC(OH)}_2(\text{OO}\cdot) + 0.250 \text{CHO(OH)} + 0.250 \text{HO}_2$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 01610	*	*	$\text{CH}_2(\text{OH})\text{COC(OH)}_2\text{CH(OH)}_2 + \text{OH} \rightarrow 0.259 \text{CH(OH)}_2\text{C(OH)}_2\text{COCH(OH)}(\text{OO}\cdot) + 0.096 \text{CH}_2(\text{OH})\text{COC(OH)}_2\text{C(OH)}_2(\text{OO}\cdot) + 0.065 \text{CH(OH)}_2\text{C(OH)}_2\text{COCH}_2(\text{O}\cdot) + 0.267 \text{CH}_2(\text{OH})\text{COC(OH)}(\text{O}\cdot)\text{CH(OH)}_2 + 0.313 \text{CH}_2(\text{OH})\text{COC(OH)}_2\text{CH(OH)}(\text{O}\cdot) + \text{H}_2\text{O} - 0.355 \text{O}_2$	$1.2 \cdot 10^{+09}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01611	*		CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.259 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH(OH)(OO·) + 0.096 CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.065 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH <sub>2</sub> (O·) + 0.267 CH <sub>2</sub> (OH)COC(OH)(O·)CH(OH) <sub>2</sub> + 0.313 CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.355 O <sub>2</sub>	9.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 01612	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH(OH)(OO·) → CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01613	*	*	CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01614	*	*	CH <sub>2</sub> (OH)COC(OH)(O·)CH(OH) <sub>2</sub> → 0.500 CH <sub>2</sub> (OH)CO(OO·) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CH <sub>2</sub> (OH)COCO(OH) + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01615	*	*	CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01616	*	*	CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH(OH)(O·) → CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> (OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01617	*	*	CH <sub>2</sub> (OH)CH(OH)COCH(OH) <sub>2</sub> + OH → 0.441 CH(OH) <sub>2</sub> COCH(OH)CH(OH)(OO·) + 0.089 CH <sub>2</sub> (OH)C(OH)(OO·)COCH(OH) <sub>2</sub> + 0.109 CH <sub>2</sub> (OH)CH(OH)COC(OH) <sub>2</sub> (OO·) + 0.064 CH(OH) <sub>2</sub> COCH(OH)CH <sub>2</sub> (O·) + 0.056 CH <sub>2</sub> (OH)CH(O·)COCH(OH) <sub>2</sub> + 0.240 CH <sub>2</sub> (OH)CH(OH)COCH(OH)(O·) + H <sub>2</sub> O - 0.639 O <sub>2</sub>	1.4 · 10 <sup>+09</sup>		
R <sub>o</sub> 01618	*		CH <sub>2</sub> (OH)CH(OH)COCH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.441 CH(OH) <sub>2</sub> COCH(OH)CH(OH)(OO·) + 0.089 CH <sub>2</sub> (OH)C(OH)(OO·)COCH(OH) <sub>2</sub> + 0.109 CH <sub>2</sub> (OH)CH(OH)COC(OH) <sub>2</sub> (OO·) + 0.064 CH(OH) <sub>2</sub> COCH(OH)CH <sub>2</sub> (O·) + 0.056 CH <sub>2</sub> (OH)CH(O·)COCH(OH) <sub>2</sub> + 0.240 CH <sub>2</sub> (OH)CH(OH)COCH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.639 O <sub>2</sub>	1.2 · 10 <sup>+07</sup>		
R <sub>o</sub> 01619	*	*	CH(OH) <sub>2</sub> COCH(OH)CH(OH)(OO·) → CH(OH) <sub>2</sub> COCH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01620	*	*	CH <sub>2</sub> (OH)C(OH)(OO·)COCH(OH) <sub>2</sub> → CH <sub>2</sub> (OH)COCOCH(OH) <sub>2</sub> + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01621	*	*	CH <sub>2</sub> (OH)CH(OH)COC(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)CH(OH)COCO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01622	*	*	CH(OH) <sub>2</sub> COCH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01623	*	*	CH(OH) <sub>2</sub> COCH(OH)CH <sub>2</sub> (O·) → CH(OH) <sub>2</sub> COCH(OH)(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01624	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01625	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCH}(\text{OH})(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01626	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}_2(\text{OH}) + \text{OH} \rightarrow$ $0.233 \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.294 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}(\text{OH})(\text{OO}\cdot) +$ $0.082 \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CH}_2(\text{O}\cdot) +$ $0.317 \text{CH}_2(\text{OH})\text{COC}(\text{OH})(\text{O}\cdot)\text{CH}_2(\text{OH}) +$ $0.074 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.527 \text{O}_2$	$1.0 \cdot 10^{+09}$		
R <sub>o</sub> 01627	*		$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}_2(\text{OH}) + \text{NO}_3 \rightarrow$ $0.233 \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.294 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}(\text{OH})(\text{OO}\cdot) +$ $0.082 \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CH}_2(\text{O}\cdot) +$ $0.317 \text{CH}_2(\text{OH})\text{COC}(\text{OH})(\text{O}\cdot)\text{CH}_2(\text{OH}) +$ $0.074 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.527 \text{O}_2$	$1.1 \cdot 10^{+07}$		
R <sub>o</sub> 01628	*	*	$\text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01629	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01630	*	*	$\text{CH}_2(\text{OH})\text{COC}(\text{OH})(\text{O}\cdot)\text{CH}_2(\text{OH}) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\text{CO}(\text{OO}\cdot) + 0.500 \text{CH}_2(\text{OH})\text{CO}(\text{OH}) +$ $0.500 \text{CH}_2(\text{OH})\text{COCO}(\text{OH}) + 0.500 \text{CH}_2(\text{OH})\cdot - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01631	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{COCH}(\text{OH})_2 + \text{OH} \rightarrow$ $0.152 \text{CH}(\text{OH})_2\text{COCH}(\text{OH})\text{CH}_2(\text{OO}\cdot) + 0.299 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{COCH}(\text{OH})_2 +$ $0.146 \text{CH}_3\text{CH}(\text{OH})\text{COC}(\text{OH})_2(\text{OO}\cdot) + 0.080 \text{CH}_3\text{CH}(\text{O}\cdot)\text{COCH}(\text{OH})_2 +$ $0.323 \text{CH}_3\text{CH}(\text{OH})\text{COCH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.598 \text{O}_2$	$1.0 \cdot 10^{+09}$		
R <sub>o</sub> 01632	*		$\text{CH}_3\text{CH}(\text{OH})\text{COCH}(\text{OH})_2 + \text{NO}_3 \rightarrow$ $0.152 \text{CH}(\text{OH})_2\text{COCH}(\text{OH})\text{CH}_2(\text{OO}\cdot) + 0.299 \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{COCH}(\text{OH})_2 +$ $0.146 \text{CH}_3\text{CH}(\text{OH})\text{COC}(\text{OH})_2(\text{OO}\cdot) + 0.080 \text{CH}_3\text{CH}(\text{O}\cdot)\text{COCH}(\text{OH})_2 +$ $0.323 \text{CH}_3\text{CH}(\text{OH})\text{COCH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.598 \text{O}_2$	$1.1 \cdot 10^{+07}$		
R <sub>o</sub> 01633	*	*	$\text{CH}(\text{OH})_2\text{COCH}(\text{OH})\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}(\text{OH})_2\text{COCH}(\text{OH})\text{CH}_2(\text{O}\cdot) + 0.550 \text{CH}(\text{OH})_2\text{COCH}(\text{OH})\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCH}(\text{OH})_2 + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01634	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{COCH}(\text{OH})_2 \rightarrow \text{CH}_3\text{COCOCH}(\text{OH})_2 + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01635	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{COC}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{COCO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01636	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{COCH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_3\text{CH}(\text{OH})\text{COCO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01637	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{COCH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01638	*	*	$\text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{CH}(\text{OH})_2 + \text{OH} \rightarrow$ $0.268 \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{COCH}(\text{OH})(\text{OO}\cdot) +$ $0.044 \text{CH}_2(\text{OH})\text{COC}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})_2 +$ $0.240 \text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.064 \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{COCH}_2(\text{O}\cdot) + 0.061 \text{CH}_2(\text{OH})\text{COCH}(\text{O}\cdot)\text{CH}(\text{OH})_2 +$ $0.324 \text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.551 \text{O}_2$	$1.2 \cdot 10^{+09}$		
R <sub>o</sub> 01639	*		$\text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{CH}(\text{OH})_2 + \text{NO}_3 \rightarrow$ $0.268 \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{COCH}(\text{OH})(\text{OO}\cdot) +$ $0.044 \text{CH}_2(\text{OH})\text{COC}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})_2 +$ $0.240 \text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.064 \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{COCH}_2(\text{O}\cdot) + 0.061 \text{CH}_2(\text{OH})\text{COCH}(\text{O}\cdot)\text{CH}(\text{OH})_2 +$ $0.324 \text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.551 \text{O}_2$	$1.2 \cdot 10^{+07}$		
R <sub>o</sub> 01640	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{COCH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01641	*	*	$\text{CH}_2(\text{OH})\text{COC}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})_2 \rightarrow \text{CH}_2(\text{OH})\text{COCOCH}(\text{OH})_2 + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01642	*	*	$\text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{CO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01643	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{COCH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01644	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{COCH}_2(\text{O}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01645	*	*	$\text{CH}_2(\text{OH})\text{COCH}(\text{O}\cdot)\text{CH}(\text{OH})_2 \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCOCH}(\text{OH})_2 + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01646	*	*	$\text{CH}_2(\text{OH})\text{COCH}(\text{O}\cdot)\text{CH}(\text{OH})_2 \rightarrow 0.500 \text{CH}_2(\text{OH})\text{CO}(\text{OO}\cdot) +$ $0.500 \text{CH}(\text{OH})_2\text{CHO} + 0.500 \text{CH}_2(\text{OH})\text{COCHO} + 0.500 \text{CH} \cdot (\text{OH})_2 - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01647	*	*	$\text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01648	*	*	$\text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{COCH}(\text{OH})(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01649	*	*	$\text{CH}_3\text{COCH}(\text{OH})\text{CH}(\text{OH})_2 + \text{OH} \rightarrow$ $0.093 \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{COCH}_2(\text{OO}\cdot) + 0.063 \text{CH}_3\text{COC}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})_2 +$ $0.324 \text{CH}_3\text{COCH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.083 \text{CH}_3\text{COCH}(\text{O}\cdot)\text{CH}(\text{OH})_2 +$ $0.438 \text{CH}_3\text{COCH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.479 \text{O}_2$	$8.7 \cdot 10^{+08}$		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01650	*		CH <sub>3</sub> COCH(OH)CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.093 CH(OH) <sub>2</sub> CH(OH)COCH <sub>2</sub> (OO·) + 0.063 CH <sub>3</sub> COC(OH)(OO·)CH(OH) <sub>2</sub> + 0.324 CH <sub>3</sub> COCH(OH)C(OH) <sub>2</sub> (OO·) + 0.083 CH <sub>3</sub> COCH(O·)CH(OH) <sub>2</sub> + 0.438 CH <sub>3</sub> COCH(OH)CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.479 O <sub>2</sub>	1.1 · 10 <sup>+07</sup>		
R <sub>o</sub> 01651	*	*	CH(OH) <sub>2</sub> CH(OH)COCH <sub>2</sub> (OO·) $\xrightarrow{RO_2^-}$ 0.200 CH(OH) <sub>2</sub> CH(OH)COCH <sub>2</sub> (O·) + 0.550 CH(OH) <sub>2</sub> CH(OH)COCHO + 0.250 CH <sub>2</sub> (OH)COCH(OH)CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01652	*	*	CH <sub>3</sub> COC(OH)(OO·)CH(OH) <sub>2</sub> → CH <sub>3</sub> COCOCH(OH) <sub>2</sub> + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01653	*	*	CH <sub>3</sub> COCH(OH)C(OH) <sub>2</sub> (OO·) → CH <sub>3</sub> COCH(OH)CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01654	*	*	CH <sub>3</sub> COCH(O·)CH(OH) <sub>2</sub> $\xrightarrow{O_2}$ CH <sub>3</sub> COCOCH(OH) <sub>2</sub> + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01655	*	*	CH <sub>3</sub> COCH(O·)CH(OH) <sub>2</sub> → 0.500 CH <sub>3</sub> CO(OO·) + 0.500 CH(OH) <sub>2</sub> CHO + 0.500 CH <sub>3</sub> COCHO + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01656	*	*	CH <sub>3</sub> COCH(OH)CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>3</sub> COCH(OH)CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01657	*	*	CH <sub>3</sub> COCH(OH)CH(OH)(O·) → CH <sub>3</sub> COCH(OH)(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00178	*	*	CH <sub>2</sub> (OH)COCOCH(OH) <sub>2</sub> $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH(OH) <sub>2</sub>	1.1 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00179	*	*	CH <sub>2</sub> (OH)COCOCH(OH) <sub>2</sub> $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	4.5 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01658	*	*	CH <sub>2</sub> (OH)COCOCH(OH) <sub>2</sub> → 0.250 CH <sub>2</sub> (OH)CO(OO·) + 0.250 CH(OH) <sub>2</sub> CO(OO·) + 0.250 CH <sub>2</sub> (OH)COCO(OO·) + 0.250 CHO(OH) + 0.250 HO <sub>2</sub>	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 01659	*	*	CH <sub>2</sub> (OH)COCOCH(OH) <sub>2</sub> + OH → 0.338 CH(OH) <sub>2</sub> COCOCH(OH)(OO·) + 0.159 CH <sub>2</sub> (OH)COCOC(OH) <sub>2</sub> (OO·) + 0.094 CH(OH) <sub>2</sub> COCOCH <sub>2</sub> (O·) + 0.409 CH <sub>2</sub> (OH)COCOCH(OH)(O·) + H <sub>2</sub> O - 0.497 O <sub>2</sub>	8.0 · 10 <sup>+08</sup>		
R <sub>o</sub> 01660	*		CH <sub>2</sub> (OH)COCOCH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.338 CH(OH) <sub>2</sub> COCOCH(OH)(OO·) + 0.159 CH <sub>2</sub> (OH)COCOC(OH) <sub>2</sub> (OO·) + 0.094 CH(OH) <sub>2</sub> COCOCH <sub>2</sub> (O·) + 0.409 CH <sub>2</sub> (OH)COCOCH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.497 O <sub>2</sub>	9.5 · 10 <sup>+06</sup>		
R <sub>o</sub> 01661	*	*	CH(OH) <sub>2</sub> COCOCH(OH)(OO·) → CH(OH) <sub>2</sub> COCOCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01662	*	*	CH <sub>2</sub> (OH)COCOC(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)COCOCO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01663	*	*	CH(OH) <sub>2</sub> COCOCH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCOCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01664	*	*	CH(OH) <sub>2</sub> COCOCH <sub>2</sub> (O·) → CH(OH) <sub>2</sub> COCO(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01665	*	*	CH <sub>2</sub> (OH)COCOCH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCOCO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01666	*	*	$\text{CH}_2(\text{OH})\text{COCOCH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{COCO}(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00180	*	*	$\text{CH}_3\text{COCOCH}(\text{OH})_2 \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{COC}(\text{OH})_2\text{CH}(\text{OH})_2$	$2.6 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00181	*	*	$\text{CH}_3\text{COCOCH}(\text{OH})_2 \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})_2$	$1.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01667	*	*	$\text{CH}_3\text{COCOCH}(\text{OH})_2 \rightarrow 0.250 \text{ CH}_3\text{CO}(\text{OO}\cdot) + 0.250 \text{ CH}(\text{OH})_2\text{CO}(\text{OO}\cdot) + 0.250 \text{ CH}_3\text{COCO}(\text{OO}\cdot) + 0.250 \text{ CHO}(\text{OH}) + 0.250 \text{ HO}_2$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 01668	*	*	$\text{CH}_3\text{COCOCH}(\text{OH})_2 + \text{OH} \rightarrow 0.132 \text{ CH}(\text{OH})_2\text{COCOCH}_2(\text{OO}\cdot) + 0.243 \text{ CH}_3\text{COCOC}(\text{OH})_2(\text{OO}\cdot) + 0.625 \text{ CH}_3\text{COCOCH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.375 \text{ O}_2$	$5.2 \cdot 10^{+08}$		
R <sub>o</sub> 01669	*		$\text{CH}_3\text{COCOCH}(\text{OH})_2 + \text{NO}_3 \rightarrow 0.132 \text{ CH}(\text{OH})_2\text{COCOCH}_2(\text{OO}\cdot) + 0.243 \text{ CH}_3\text{COCOC}(\text{OH})_2(\text{OO}\cdot) + 0.625 \text{ CH}_3\text{COCOCH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.375 \text{ O}_2$	$8.7 \cdot 10^{+06}$		
R <sub>o</sub> 01670	*	*	$\text{CH}(\text{OH})_2\text{COCOCH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_3} 0.200 \text{ CH}(\text{OH})_2\text{COCOCH}_2(\text{O}\cdot) + 0.550 \text{ CH}(\text{OH})_2\text{COCOCHO} + 0.250 \text{ CH}_2(\text{OH})\text{COCOCH}(\text{OH})_2 + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01671	*	*	$\text{CH}_3\text{COCOC}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CH}_3\text{COCOCO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01672	*	*	$\text{CH}_3\text{COCOCH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_3\text{COCOCO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01673	*	*	$\text{CH}_3\text{COCOCH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CH}_3\text{COCO}(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00182	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{COC}(\text{OH})_2\text{CH}(\text{OH})_2$	$2.6 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00183	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})_2$	$1.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01674	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CHO} \rightarrow 0.250 \text{ CH}_3\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.250 \text{ CHOC}(\text{OH})_2(\text{OO}\cdot) + 0.250 \text{ CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.250 \text{ CHO}(\text{OO}\cdot)$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 01675	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CHO} + \text{OH} \rightarrow 0.061 \text{ CHOC}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) + 0.326 \text{ CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) + 0.346 \text{ CH}_3\text{C}(\text{OH})(\text{O}\cdot)\text{C}(\text{OH})_2\text{CHO} + 0.266 \text{ CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CHO} + \text{H}_2\text{O} - 0.387 \text{ O}_2$	$1.1 \cdot 10^{+09}$		
R <sub>o</sub> 01676	*		$\text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CHO} + \text{NO}_3 \rightarrow 0.061 \text{ CHOC}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) + 0.326 \text{ CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) + 0.346 \text{ CH}_3\text{C}(\text{OH})(\text{O}\cdot)\text{C}(\text{OH})_2\text{CHO} + 0.266 \text{ CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CHO} + \text{NO}_3^- + \text{H}^+ - 0.387 \text{ O}_2$	$7.3 \cdot 10^{+06}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01677	*	*	CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.550 CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + 0.250 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01678	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OO·) → CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01679	*	*	CH <sub>3</sub> C(OH)(O·)C(OH) <sub>2</sub> CHO → 0.500 CH <sub>3</sub> (OO·) + 0.500 CO(OH)C(OH) <sub>2</sub> CHO + 0.500 CH <sub>3</sub> CO(OH) + 0.500 CHOC(OH) <sub>2</sub> (OO·) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01680	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> C(OH)(O·)CHO → 0.500 CH <sub>3</sub> C(OH) <sub>2</sub> (OO·) + 0.500 CO(OH)CHO + 0.500 CH <sub>3</sub> C(OH) <sub>2</sub> CO(OH) + 0.500 CH·(OH) <sub>2</sub> – 0.500 O <sub>2</sub> – 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01681	*	*	CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01682	*	*	CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) → CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00184	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH <sub>2</sub> COCH(OH) <sub>2</sub>	4.8 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00185	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CHO	8.4 · 10 <sup>+00</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00186	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	5.7 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01683	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CHO → 0.500 + 0.500	1.0 · 10 <sup>–01</sup>		
R <sub>o</sub> 01684	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CHO + OH → 0.410 CHOC(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.209 CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CO(OO·) + 0.211 CHOC(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)(O·) + 0.171 CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH)(O·)CHO + H <sub>2</sub> O – 0.619 O <sub>2</sub>	1.9 · 10 <sup>+09</sup>		
R <sub>o</sub> 01685	*		CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CHO + NO <sub>3</sub> → 0.410 CHOC(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.209 CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CO(OO·) + 0.211 CHOC(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)(O·) + 0.171 CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH)(O·)CHO + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.619 O <sub>2</sub>	8.7 · 10 <sup>+06</sup>		
R <sub>o</sub> 01686	*	*	CHOC(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01687	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CO(OO·) → CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01688	*	*	CHOC(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01689	*	*	CHOC(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)(O·) → CHOC(OH) <sub>2</sub> CH <sub>2</sub> (OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01690	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH)(O·)CHO $\rightarrow$ 0.500 CH(OH) <sub>2</sub> CH <sub>2</sub> (OO·) + 0.500 CO(OH)CHO + 0.500 CH(OH) <sub>2</sub> CH <sub>2</sub> CO(OH) + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01691	*	*	CHOC(OH) <sub>2</sub> CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CHOC(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.550 CHOC(OH) <sub>2</sub> CHO + 0.250 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01692	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CHO $\rightarrow$ 0.500 + 0.500 + 0.500	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 01693	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CHO + OH $\rightarrow$ 0.044 CHOCH <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.719 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CO(OO·) + 0.116 CHOCH <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) + 0.121 CH(OH) <sub>2</sub> C(OH)(O·)CH <sub>2</sub> CHO + H <sub>2</sub> O - 0.763 O <sub>2</sub>	$3.1 \cdot 10^{+09}$		
R <sub>o</sub> 01694	*		CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CHO + NO <sub>3</sub> $\rightarrow$ 0.044 CHOCH <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.719 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CO(OO·) + 0.116 CHOCH <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) + 0.121 CH(OH) <sub>2</sub> C(OH)(O·)CH <sub>2</sub> CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.763 O <sub>2</sub>	$8.7 \cdot 10^{+06}$		
R <sub>o</sub> 01695	*	*	CHOCH <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) $\rightarrow$ CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> CHO + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01696	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CO(OO·) $\rightarrow$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01697	*	*	CHOCH <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> CHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01698	*	*	CHOCH <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) $\rightarrow$ CHOCH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01699	*	*	CH(OH) <sub>2</sub> C(OH)(O·)CH <sub>2</sub> CHO $\rightarrow$ 0.500 CH·(OH) <sub>2</sub> + 0.500 CO(OH)CH <sub>2</sub> CHO + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CHOCH <sub>2</sub> (OO·) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00187	*	*	CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> CH(OH)COCH(OH) <sub>2</sub>	$9.7 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00188	*	*	CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	$1.4 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01700	*	*	CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CHO + OH $\rightarrow$ 0.145 CHOC(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (OO·) + 0.194 CH <sub>3</sub> C(OH)(OO·)C(OH) <sub>2</sub> CHO + 0.321 CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CO(OO·) + 0.076 CH <sub>3</sub> CH(O·)C(OH) <sub>2</sub> CHO + 0.263 CH <sub>3</sub> CH(OH)C(OH)(O·)CHO + H <sub>2</sub> O - 0.661 O <sub>2</sub>	$1.2 \cdot 10^{+09}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01701	*		CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CHO + NO <sub>3</sub> → 0.145 CHOC(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (OO·) + 0.194 CH <sub>3</sub> C(OH)(OO·)C(OH) <sub>2</sub> CHO + 0.321 CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CO(OO·) + 0.076 CH <sub>3</sub> CH(O·)C(OH) <sub>2</sub> CHO + 0.263 CH <sub>3</sub> CH(OH)C(OH)(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.661 O <sub>2</sub>	9.5 · 10 <sup>+06</sup>		
R <sub>o</sub> 01702	*	*	CHOC(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (OO·) $\xrightarrow{RO_2^{\cdot}}$ 0.200 CHOC(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) + 0.550 CHOCH(OH)C(OH) <sub>2</sub> CHO + 0.250 CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01703	*	*	CH <sub>3</sub> C(OH)(OO·)C(OH) <sub>2</sub> CHO → CH <sub>3</sub> COC(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01704	*	*	CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CO(OO·) → CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01705	*	*	CH <sub>3</sub> CH(O·)C(OH) <sub>2</sub> CHO $\xrightarrow{O_2}$ CH <sub>3</sub> COC(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01706	*	*	CH <sub>3</sub> CH(O·)C(OH) <sub>2</sub> CHO → 0.500 CH <sub>3</sub> (OO·) + 0.500 CHOC(OH) <sub>2</sub> CHO + 0.500 CH <sub>3</sub> CHO + 0.500 CHOC(OH) <sub>2</sub> (OO·) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01707	*	*	CH <sub>3</sub> CH(OH)C(OH)(O·)CHO → 0.500 CH <sub>3</sub> CH(OH)(OO·) + 0.500 CO(OH)CHO + 0.500 CH <sub>3</sub> CH(OH)CO(OH) + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01708	*	*	CHOC(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CHOCH(OH)C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01709	*	*	CHOC(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) → CHOC(OH) <sub>2</sub> CH(OH)(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00189	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)COCH(OH)CH(OH) <sub>2</sub>	5.2 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00190	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH(OH) <sub>2</sub>	3.8 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01710	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CHO + OH → 0.162 CHOCH(OH)C(OH) <sub>2</sub> CH(OH)(OO·) + 0.529 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CO(OO·) + 0.049 CHOCH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.220 CH <sub>2</sub> (OH)C(OH)(O·)CH(OH)CHO + 0.040 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O·)CHO + H <sub>2</sub> O - 0.691 O <sub>2</sub>	1.7 · 10 <sup>+09</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01711	*		CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CHO + NO <sub>3</sub> → 0.162 CHOCH(OH)C(OH) <sub>2</sub> CH(OH)(OO·) + 0.529 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CO(OO·) + 0.049 CHOCH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.220 CH <sub>2</sub> (OH)C(OH)(O·)CH(OH)CHO + 0.040 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.691 O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 01712	*	*	CHOCH(OH)C(OH) <sub>2</sub> CH(OH)(OO·) → CHOCH(OH)C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01713	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CO(OO·) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01714	*	*	CHOCH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CHOCH(OH)C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01715	*	*	CHOCH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) → CHOCH(OH)C(OH) <sub>2</sub> (OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01716	*	*	CH <sub>2</sub> (OH)C(OH)(O·)CH(OH)CHO → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)CH(OH)CHO + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CHOCH(OH)(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01717	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O·)CHO $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01718	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O·)CHO → 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO·) + 0.500 CHOCHO + 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CHO + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00191	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH(OH) <sub>2</sub>	1.1 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00192	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	4.5 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01719	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO → 0.250 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO·) + 0.250 CHOC(OH) <sub>2</sub> (OO·) + 0.250 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.250 CHO(OO·)	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 01720	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + OH → 0.194 CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) + 0.264 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OO·) + 0.061 CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.264 CH <sub>2</sub> (OH)C(OH)(O·)C(OH) <sub>2</sub> CHO + 0.216 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(O·)CHO + H <sub>2</sub> O - 0.458 O <sub>2</sub>	1.4 · 10 <sup>+09</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01721	*		CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + NO <sub>3</sub> → 0.194 CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) + 0.264 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OO·) + 0.061 CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.264 CH <sub>2</sub> (OH)C(OH)(O·)C(OH) <sub>2</sub> CHO + 0.216 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.458 O <sub>2</sub>	8.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01722	*	*	CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) → CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01723	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OO·) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01724	*	*	CH <sub>2</sub> (OH)C(OH)(O·)C(OH) <sub>2</sub> CHO → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)C(OH) <sub>2</sub> CHO + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CHOC(OH) <sub>2</sub> (OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01725	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(O·)CHO → 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO·) + 0.500 CO(OH)CHO + 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CO(OH) + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01726	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CHO + OH → 0.327 CHOCH(OH)CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.111 CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH)(OO·)CHO + 0.401 CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CO(OO·) + 0.160 CHOCH(OH)CH <sub>2</sub> CH(OH)(O·) + H <sub>2</sub> O - 0.840 O <sub>2</sub>	2.5 · 10 <sup>+09</sup>		
R <sub>o</sub> 01727	*		CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CHO + NO <sub>3</sub> → 0.327 CHOCH(OH)CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.111 CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH)(OO·)CHO + 0.401 CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CO(OO·) + 0.160 CHOCH(OH)CH <sub>2</sub> CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.840 O <sub>2</sub>	1.1 · 10 <sup>+07</sup>		
R <sub>o</sub> 01728	*	*	CHOCH(OH)CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CO(OH)CH <sub>2</sub> CH(OH)CHO + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01729	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH)(OO·)CHO → CH(OH) <sub>2</sub> CH <sub>2</sub> COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01730	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CO(OO·) → CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01731	*	*	CHOCH(OH)CH <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH <sub>2</sub> CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01732	*	*	CHOCH(OH)CH <sub>2</sub> CH(OH)(O·) → CHOCH(OH)CH <sub>2</sub> (OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01733	*	*	CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CHO + OH $\rightarrow$ 0.104 CHOCH <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.070 CH(OH) <sub>2</sub> C(OH)(OO $\cdot$ )CH <sub>2</sub> CHO + 0.712 CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CO(OO $\cdot$ ) + 0.115 CHOCH <sub>2</sub> CH(OH)CH(OH)(O $\cdot$ ) + H <sub>2</sub> O - 0.885 O <sub>2</sub>	$3.3 \cdot 10^{+09}$		
R <sub>o</sub> 01734	*		CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CHO + NO <sub>3</sub> $\rightarrow$ 0.104 CHOCH <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.070 CH(OH) <sub>2</sub> C(OH)(OO $\cdot$ )CH <sub>2</sub> CHO + 0.712 CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CO(OO $\cdot$ ) + 0.115 CHOCH <sub>2</sub> CH(OH)CH(OH)(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.885 O <sub>2</sub>	$1.1 \cdot 10^{+07}$		
R <sub>o</sub> 01735	*	*	CHOCH <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)CH(OH)CH <sub>2</sub> CHO + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01736	*	*	CH(OH) <sub>2</sub> C(OH)(OO $\cdot$ )CH <sub>2</sub> CHO $\rightarrow$ CH(OH) <sub>2</sub> COCH <sub>2</sub> CHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01737	*	*	CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CO(OO $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01738	*	*	CHOCH <sub>2</sub> CH(OH)CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)CH(OH)CH <sub>2</sub> CHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01739	*	*	CHOCH <sub>2</sub> CH(OH)CH(OH)(O $\cdot$ ) $\rightarrow$ CHOCH <sub>2</sub> CH(OH)(OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00193	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> COCHO $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> COC(OH) <sub>2</sub> CH(OH) <sub>2</sub>	$2.6 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00194	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> COCHO $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	$1.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01740	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> COCHO $\rightarrow$ 0.250 CH <sub>3</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.250 CHOCO(OO $\cdot$ ) + 0.250 CH <sub>3</sub> C(OH) <sub>2</sub> CO(OO $\cdot$ ) + 0.250 CHO(OO $\cdot$ )	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 01741	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> COCHO + OH $\rightarrow$ 0.075 CHOCOC(OH) <sub>2</sub> CH <sub>2</sub> (OO $\cdot$ ) + 0.502 CH <sub>3</sub> C(OH) <sub>2</sub> COCO(OO $\cdot$ ) + 0.423 CH <sub>3</sub> C(OH)(O $\cdot$ )COCHO + H <sub>2</sub> O - 0.577 O <sub>2</sub>	$8.1 \cdot 10^{+08}$		
R <sub>o</sub> 01742	*		CH <sub>3</sub> C(OH) <sub>2</sub> COCHO + NO <sub>3</sub> $\rightarrow$ 0.075 CHOCOC(OH) <sub>2</sub> CH <sub>2</sub> (OO $\cdot$ ) + 0.502 CH <sub>3</sub> C(OH) <sub>2</sub> COCO(OO $\cdot$ ) + 0.423 CH <sub>3</sub> C(OH)(O $\cdot$ )COCHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.577 O <sub>2</sub>	$7.4 \cdot 10^{+06}$		
R <sub>o</sub> 01743	*	*	CHOCOC(OH) <sub>2</sub> CH <sub>2</sub> (OO $\cdot$ ) $\xrightarrow{RO_2}$ 0.200 CHOCOC(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) + 0.550 CHOC(OH) <sub>2</sub> COCHO + 0.250 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01744	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> COCO(OO $\cdot$ ) $\rightarrow$ CH <sub>3</sub> C(OH) <sub>2</sub> COCO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01745	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{O}\cdot)\text{COCHO} \rightarrow 0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{COCHO} + 0.500 \text{CH}_3\text{CO}(\text{OH}) + 0.500 \text{CHOCO}(\text{OO}\cdot) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01746	*	*	$\text{CHOCOC}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CHOC}(\text{OH})_2\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01747	*	*	$\text{CHOCOC}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CHOCOC}(\text{OH})_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00195	*	*	$\text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CH}(\text{OH})_2$	$1.1 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00196	*	*	$\text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})_2$	$4.5 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01748	*	*	$\text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CHO} \rightarrow 0.250 \text{CH}_2(\text{OH})\text{CO}(\text{OO}\cdot) + 0.250 \text{CHOC}(\text{OH})_2(\text{OO}\cdot) + 0.250 \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2(\text{OO}\cdot) + 0.250 \text{CHO}(\text{OO}\cdot)$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 01749	*	*	$\text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CHO} + \text{OH} \rightarrow 0.311 \text{CHOC}(\text{OH})_2\text{COCH}(\text{OH})(\text{OO}\cdot) + 0.336 \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CO}(\text{OO}\cdot) + 0.078 \text{CHOC}(\text{OH})_2\text{COCH}_2(\text{O}\cdot) + 0.275 \text{CH}_2(\text{OH})\text{COC}(\text{OH})(\text{O}\cdot)\text{CHO} + \text{H}_2\text{O} - 0.647 \text{O}_2$	$9.6 \cdot 10^{+08}$		
R <sub>o</sub> 01750	*		$\text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CHO} + \text{NO}_3 \rightarrow 0.311 \text{CHOC}(\text{OH})_2\text{COCH}(\text{OH})(\text{OO}\cdot) + 0.336 \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CO}(\text{OO}\cdot) + 0.078 \text{CHOC}(\text{OH})_2\text{COCH}_2(\text{O}\cdot) + 0.275 \text{CH}_2(\text{OH})\text{COC}(\text{OH})(\text{O}\cdot)\text{CHO} + \text{NO}_3^- + \text{H}^+ - 0.647 \text{O}_2$	$8.0 \cdot 10^{+06}$		
R <sub>o</sub> 01751	*	*	$\text{CHOC}(\text{OH})_2\text{COCH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CHOC}(\text{OH})_2\text{COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01752	*	*	$\text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CO}(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CO}(\text{OH}) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01753	*	*	$\text{CHOC}(\text{OH})_2\text{COCH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CHOC}(\text{OH})_2\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01754	*	*	$\text{CHOC}(\text{OH})_2\text{COCH}_2(\text{O}\cdot) \rightarrow \text{CHOC}(\text{OH})_2\text{CO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01755	*	*	$\text{CH}_2(\text{OH})\text{COC}(\text{OH})(\text{O}\cdot)\text{CHO} \rightarrow 0.500 \text{CH}_2(\text{OH})\text{CO}(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CHO} + 0.500 \text{CH}_2(\text{OH})\text{COCO}(\text{OH}) + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{O}_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00197	*	*	$\text{CH}_3\text{COC}(\text{OH})_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{COC}(\text{OH})_2\text{CH}(\text{OH})_2$	$2.6 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00198	*	*	$\text{CH}_3\text{COC}(\text{OH})_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})_2$	$1.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01756	*	*	$\text{CH}_3\text{COC}(\text{OH})_2\text{CHO} \rightarrow 0.250 \text{CH}_3\text{CO}(\text{OO}\cdot) + 0.250 \text{CHOC}(\text{OH})_2(\text{OO}\cdot) + 0.250 \text{CH}_3\text{COC}(\text{OH})_2(\text{OO}\cdot) + 0.250 \text{CHO}(\text{OO}\cdot)$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 01757	*	*	$\text{CH}_3\text{COC}(\text{OH})_2\text{CHO} + \text{OH} \rightarrow 0.116 \text{CHOC}(\text{OH})_2\text{COCH}_2(\text{OO}\cdot) + 0.487 \text{CH}_3\text{COC}(\text{OH})_2\text{CO}(\text{OO}\cdot) + 0.398 \text{CH}_3\text{COC}(\text{OH})(\text{O}\cdot)\text{CHO} + \text{H}_2\text{O} - 0.602 \text{O}_2$	$6.7 \cdot 10^{+08}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01758	*		CH <sub>3</sub> COC(OH) <sub>2</sub> CHO + NO <sub>3</sub> → 0.116 CHOC(OH) <sub>2</sub> COCH <sub>2</sub> (OO·) + 0.487 CH <sub>3</sub> COC(OH) <sub>2</sub> CO(OO·) + 0.398 CH <sub>3</sub> COC(OH)(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.602 O <sub>2</sub>	7.3 · 10 <sup>+06</sup>		
R <sub>o</sub> 01759	*	*	CHOC(OH) <sub>2</sub> COCH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CHOC(OH) <sub>2</sub> COCH <sub>2</sub> (O·) + 0.550 CHOC(OH) <sub>2</sub> COCHO + 0.250 CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01760	*	*	CH <sub>3</sub> COC(OH) <sub>2</sub> CO(OO·) → CH <sub>3</sub> COC(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01761	*	*	CH <sub>3</sub> COC(OH)(O·)CHO → 0.500 CH <sub>3</sub> CO(OO·) + 0.500 CO(OH)CHO + 0.500 CH <sub>3</sub> COCO(OH) + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00199	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH(OH) <sub>2</sub>	1.1 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00200	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	4.5 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01762	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCHO → 0.250 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO·) + 0.250 CHOCO(OO·) + 0.250 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CO(OO·) + 0.250 CHO(OO·)	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 01763	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCHO + OH → 0.226 CHOCOC(OH) <sub>2</sub> CH(OH)(OO·) + 0.388 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCO(OO·) + 0.079 CHOCOC(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.307 CH <sub>2</sub> (OH)C(OH)(O·)COCHO + H <sub>2</sub> O - 0.614 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 01764	*		CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCHO + NO <sub>3</sub> → 0.226 CHOCOC(OH) <sub>2</sub> CH(OH)(OO·) + 0.388 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCO(OO·) + 0.079 CHOCOC(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.307 CH <sub>2</sub> (OH)C(OH)(O·)COCHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.614 O <sub>2</sub>	8.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01765	*	*	CHOCOC(OH) <sub>2</sub> CH(OH)(OO·) → CHOC(OH) <sub>2</sub> COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01766	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCO(OO·) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01767	*	*	CH <sub>2</sub> (OH)C(OH)(O·)COCHO → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)COCHO + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CHOCO(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00201	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> COCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH <sub>2</sub> COCH(OH) <sub>2</sub>	4.8 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00202	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> COCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CHO	8.4 · 10 <sup>+00</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00203	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> COCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	5.7 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01768	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> COCHO → 0.500 + 0.500	1.0 · 10 <sup>-01</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01769	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> COCHO + OH $\rightarrow$ 0.451 CHOCOCH <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.291 CH(OH) <sub>2</sub> CH <sub>2</sub> COCO(OO $\cdot$ ) + 0.258 CHOCOCH <sub>2</sub> CH(OH)(O $\cdot$ ) + H <sub>2</sub> O - 0.742 O <sub>2</sub>	$1.5 \cdot 10^{+09}$		
R <sub>o</sub> 01770	*		CH(OH) <sub>2</sub> CH <sub>2</sub> COCHO + NO <sub>3</sub> $\rightarrow$ 0.451 CHOCOCH <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.291 CH(OH) <sub>2</sub> CH <sub>2</sub> COCO(OO $\cdot$ ) + 0.258 CHOCOCH <sub>2</sub> CH(OH)(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.742 O <sub>2</sub>	$8.5 \cdot 10^{+06}$		
R <sub>o</sub> 01771	*	*	CHOCOCH <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)CH <sub>2</sub> COCHO + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01772	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> COCO(OO $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> CH <sub>2</sub> COCO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01773	*	*	CHOCOCH <sub>2</sub> CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)CH <sub>2</sub> COCHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01774	*	*	CHOCOCH <sub>2</sub> CH(OH)(O $\cdot$ ) $\rightarrow$ CHOCOCH <sub>2</sub> (OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00204	*	*	CH(OH) <sub>2</sub> COCH <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH <sub>2</sub> COCH(OH) <sub>2</sub>	$4.8 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00205	*	*	CH(OH) <sub>2</sub> COCH <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CHO	$8.4 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00206	*	*	CH(OH) <sub>2</sub> COCH <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	$5.7 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01775	*	*	CH(OH) <sub>2</sub> COCH <sub>2</sub> CHO $\rightarrow$ 0.500 + 0.500 + 0.500	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 01776	*	*	CH(OH) <sub>2</sub> COCH <sub>2</sub> CHO + OH $\rightarrow$ 0.062 CHOCH <sub>2</sub> COC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.808 CH(OH) <sub>2</sub> COCH <sub>2</sub> CO(OO $\cdot$ ) + 0.130 CHOCH <sub>2</sub> COCH(OH)(O $\cdot$ ) + H <sub>2</sub> O - 0.870 O <sub>2</sub>	$2.5 \cdot 10^{+09}$		
R <sub>o</sub> 01777	*		CH(OH) <sub>2</sub> COCH <sub>2</sub> CHO + NO <sub>3</sub> $\rightarrow$ 0.062 CHOCH <sub>2</sub> COC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.808 CH(OH) <sub>2</sub> COCH <sub>2</sub> CO(OO $\cdot$ ) + 0.130 CHOCH <sub>2</sub> COCH(OH)(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.870 O <sub>2</sub>	$8.6 \cdot 10^{+06}$		
R <sub>o</sub> 01778	*	*	CHOCH <sub>2</sub> COC(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)COCH <sub>2</sub> CHO + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01779	*	*	CH(OH) <sub>2</sub> COCH <sub>2</sub> CO(OO $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> COCH <sub>2</sub> CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01780	*	*	CHOCH <sub>2</sub> COCH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)COCH <sub>2</sub> CHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01781	*	*	CHOCH <sub>2</sub> COCH(OH)(O $\cdot$ ) $\rightarrow$ CHOCH <sub>2</sub> CO(OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00207	*	*	CHOCH(OH)COCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)COCH(OH) <sub>2</sub>	$1.3 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00208	*	*	CHOCH(OH)COCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	$9.1 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01782	*	*	CHOCH(OH)COCHO $\rightarrow$ 0.500 + 0.500	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 01783	*	*	CHOCH(OH)COCHO + OH $\rightarrow$ 0.605 CHOCOCH(OH)CO(OO $\cdot$ ) + 0.032 CHOCOC(OH)(OO $\cdot$ )CHO + 0.318 CHOCH(OH)COCO(OO $\cdot$ ) + 0.046 CHOCOCH(O $\cdot$ )CHO + H <sub>2</sub> O - 0.954 O <sub>2</sub>	$1.4 \cdot 10^{+09}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01784	*		CHOCH(OH)COCHO + NO <sub>3</sub> → 0.605 CHOCOCH(OH)CO(OO·) + 0.032 CHOCOC(OH)(OO·)CHO + 0.318 CHOCH(OH)COCO(OO·) + 0.046 CHOCOCH(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.954 O <sub>2</sub>	5.5 · 10 <sup>+06</sup>		
R <sub>o</sub> 01785	*	*	CHOCOC(OH)(OO·)CHO → CHOCOCOCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01786	*	*	CHOCH(OH)COCO(OO·) → CO(OH)COCH(OH)CHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 01787	*	*	CHOCOCH(O·)CHO $\xrightarrow{O_2}$ CHOCOCOCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01788	*	*	CHOCOCH(O·)CHO → 0.500 CHOCO(OO·) + 0.500 CHOCHO + 0.500 CHOCOCHO + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00209	*	*	CHOCOCOCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	7.1 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01789	*	*	CHOCOCOCHO → 0.250 CHO(OO·) + 0.250 CHOCOCO(OO·) + 0.500 CHOCO(OO·)	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 01790	*	*	CHOCOCOCHO + OH → CHOCOCOCO(OO·) + H <sub>2</sub> O - O <sub>2</sub>	7.4 · 10 <sup>+08</sup>		
R <sub>o</sub> 01791	*		CHOCOCOCHO + NO <sub>3</sub> → CHOCOCOCO(OO·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	2.1 · 10 <sup>+06</sup>		
R <sub>o</sub> 01792	*	*	CHOCOCOCO(OO·) → CO(OH)COCOCHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
E <sub>o</sub> 00210	*	*	CHOCH(OH)CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)CH(OH)CH(OH) <sub>2</sub>	5.4 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01793	*	*	CHOCH(OH)CH(OH)CHO + OH → 0.850 CHOCH(OH)CH(OH)CO(OO·) + 0.085 CHOCH(OH)C(OH)(OO·)CHO + 0.065 CHOCH(OH)CH(O·)CHO + H <sub>2</sub> O - 0.935 O <sub>2</sub>	2.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 01794	*		CHOCH(OH)CH(OH)CHO + NO <sub>3</sub> → 0.850 CHOCH(OH)CH(OH)CO(OO·) + 0.085 CHOCH(OH)C(OH)(OO·)CHO + 0.065 CHOCH(OH)CH(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.935 O <sub>2</sub>	1.4 · 10 <sup>+07</sup>		
R <sub>o</sub> 01795	*	*	CHOCH(OH)C(OH)(OO·)CHO → CHOCH(OH)COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01796	*	*	CHOCH(OH)CH(O·)CHO $\xrightarrow{O_2}$ CHOCH(OH)COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01797	*	*	CHOCH(OH)CH(O·)CHO → 0.500 CHOCH(OH)(OO·) + 0.500 CHOCHO + 0.500 CHOCH(OH)CHO + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01798	*	*	CH <sub>3</sub> CH(OH)CH <sub>2</sub> CO(O <sup>-</sup> ) + OH → 0.081 CO(O <sup>-</sup> )CH <sub>2</sub> CH(OH)CH <sub>2</sub> (OO·) + 0.839 CH <sub>3</sub> C(OH)(OO·)CH <sub>2</sub> CO(O <sup>-</sup> ) + 0.038 CH <sub>3</sub> CH(OH)CH(OO·)CO(O <sup>-</sup> ) + 0.042 CH <sub>3</sub> CH(O·)CH <sub>2</sub> CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.958 O <sub>2</sub>	2.3 · 10 <sup>+09</sup>		
R <sub>o</sub> 01799	*		CH <sub>3</sub> CH(OH)CH <sub>2</sub> CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>3</sub> CH(OH)CH <sub>2</sub> CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01800	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) \xrightarrow{RO_2}$ 0.200 $\text{CO}(\text{O}^-)\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) + 0.550 \text{CO}(\text{O}^-)\text{CH}_2\text{CH}(\text{OH})\text{CHO} +$ 0.250 $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01801	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2\text{CO}(\text{O}^-) \rightarrow \text{CH}_3\text{COCH}_2\text{CO}(\text{O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01802	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) \rightarrow$ 2.000 $\text{CH}_3\text{CH}(\text{OH})\text{CHO} + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 01803	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) \xrightarrow{RO_2}$ 0.200 $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) + 0.550 \text{CH}_3\text{CH}(\text{OH})\text{COCO}(\text{O}^-) +$ 0.250 $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01804	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}_2\text{CO}(\text{O}^-) \xrightarrow{O_2} \text{CH}_3\text{COCH}_2\text{CO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01805	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}_2\text{CO}(\text{O}^-) \rightarrow 0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CO}(\text{O}^-)\text{CH}_2\text{CHO} +$ 0.500 $\text{CH}_3\text{CHO} + 0.500 \text{CO}(\text{O}^-)\text{CH}_2(\text{OO}\cdot) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01806	*		$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01807	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \xrightarrow{O_2} \text{CO}(\text{O}^-)\text{CH}_2\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01808	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01809	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) \xrightarrow{O_2} \text{CH}_3\text{CH}(\text{OH})\text{COCO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01810	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) \rightarrow 0.500 \text{CH}_3\text{CH}(\text{OH})(\text{OO}\cdot) +$ 0.500 $\text{CO}(\text{O}^-)\text{CHO} + 0.500 \text{CH}_3\text{CH}(\text{OH})\text{CHO} + 0.500 \cdot \text{CO}(\text{O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01811	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{OH} \rightarrow$ 0.707 $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ 0.085 $\text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) +$ 0.129 $\text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{O}^-) +$ 0.037 $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}_2\text{CH}_2(\text{O}\cdot) + 0.042 \text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) +$ $\text{H}_2\text{O} - 0.920 \text{O}_2$	$2.5 \cdot 10^{+09}$		
R <sub>o</sub> 01812	*		$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 01813	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01814	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) \xrightarrow{RO_2}$ 0.200 $\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) +$ 0.550 $\text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{CO}(\text{O}^-) +$ 0.250 $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01815	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{O}^-) \rightarrow \text{CH}_2(\text{OH})\text{CH}_2\text{COCO}(\text{O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01816	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01817	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01818	*		$\text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01819	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{CO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01820	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CHO} + 0.500 \text{CH}_2(\text{OH})\text{CHO} +$ $0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01821	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CO}(\text{O}^-) + \text{OH} \rightarrow$ $0.412 \text{CO}(\text{O}^-)\text{CH}_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.439 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2\text{CO}(\text{O}^-) +$ $0.047 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) +$ $0.049 \text{CO}(\text{O}^-)\text{CH}_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) + 0.052 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2\text{CO}(\text{O}^-) +$ $\text{H}_2\text{O} - 0.899 \text{O}_2$	$1.8 \cdot 10^{+09}$		
R <sub>o</sub> 01822	*		$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 01823	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{CH}_2\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01824	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2\text{CO}(\text{O}^-) \rightarrow \text{CH}_2(\text{OH})\text{COCH}_2\text{CO}(\text{O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01825	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) +$ $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) \rightarrow$ $2.000 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CHO} + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 01826	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) +$ $0.550 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{O}^-) +$ $0.250 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01827	*		$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01828	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01829	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) + 0.500 \text{CO}(\text{O}^-)\text{CHO} +$ $0.500 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CHO} + 0.500 \cdot \text{CO}(\text{O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01830	*	*	$\text{CH}_3\text{COCH}_2\text{CO}(\text{O}^-) + \text{OH} \rightarrow 0.678 \text{CO}(\text{O}^-)\text{CH}_2\text{COCH}_2(\text{OO}\cdot) + 0.322 \text{CH}_3\text{COCH}(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{H}_2\text{O} - \text{O}_2$	$1.2 \cdot 10^{+08}$		
R <sub>o</sub> 01831	*		$\text{CH}_3\text{COCH}_2\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow \text{CH}_3\text{COCH}_2\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 01832	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{COCH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CO}(\text{O}^-)\text{CH}_2\text{COCH}_2(\text{O}\cdot) + 0.550 \text{CO}(\text{O}^-)\text{CH}_2\text{COCHO} + 0.250 \text{CH}_2(\text{OH})\text{COCH}_2\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01833	*	*	$\text{CH}_3\text{COCH}(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CH}_3\text{COCH}(\text{OO}\cdot)\text{CO}(\text{O}^-) \rightarrow 2.000 \text{CH}_3\text{COCHO} + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 01834	*	*	$\text{CH}_3\text{COCH}(\text{OO}\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_3\text{COCH}(\text{O}\cdot)\text{CO}(\text{O}^-) + 0.550 \text{CH}_3\text{COCOCO}(\text{O}^-) + 0.250 \text{CH}_3\text{COCH}(\text{OH})\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01835	*		$\text{CH}_3\text{COCH}_2\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_3\text{COCH}_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01836	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{COCH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{CH}_2\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01837	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{COCH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{CH}_2\text{CO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01838	*	*	$\text{CH}_3\text{COCH}(\text{O}\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{O}_2} \text{CH}_3\text{COCOCO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01839	*	*	$\text{CH}_3\text{COCH}(\text{O}\cdot)\text{CO}(\text{O}^-) \rightarrow 0.500 \text{CH}_3\text{CO}(\text{OO}\cdot) + 0.500 \text{CO}(\text{O}^-)\text{CHO} + 0.500 \text{CH}_3\text{COCHO} + 0.500 \cdot \text{CO}(\text{O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01840	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CO}(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}_2\text{CO}(\text{O}^-) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01841	*	*	$\text{CH}_2(\text{OH})\text{CH}_2\text{COCO}(\text{O}^-) + \text{OH} \rightarrow 0.889 \text{CO}(\text{O}^-)\text{COCH}_2\text{CH}(\text{OH})(\text{OO}\cdot) + 0.056 \text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{COCO}(\text{O}^-) + 0.055 \text{CO}(\text{O}^-)\text{COCH}_2\text{CH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.945 \text{O}_2$	$1.7 \cdot 10^{+09}$		
R <sub>o</sub> 01842	*		$\text{CH}_2(\text{OH})\text{CH}_2\text{COCO}(\text{O}^-) + \text{NO}_3 \rightarrow \text{CH}_2(\text{OH})\text{CH}_2\text{COCO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 01843	*	*	$\text{CO}(\text{O}^-)\text{COCH}_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{COCH}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01844	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{COCO}(\text{O}^-) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{COCO}(\text{O}^-) + 0.550 \text{CH}_2(\text{OH})\text{COCOCO}(\text{O}^-) + 0.250 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01845	*	*	$\text{CO}(\text{O}^-)\text{COCH}_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{COCH}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01846	*	*	$\text{CO}(\text{O}^-)\text{COCH}_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{COCH}_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01847	*		$\text{CH}_2(\text{OH})\text{CH}_2\text{COCO}(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}_2\text{CO}(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01848	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{COCO}(\text{O}^-) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCOCO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01849	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{COCO}(\text{O}^-) \rightarrow 0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CO}(\text{O}^-)\text{COCHO} + 0.500 \text{CH}_2(\text{OH})\text{CHO} + 0.500 \text{CO}(\text{O}^-)\text{CO}(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01850	*	*	$\text{CH}_2(\text{OH})\text{COCH}_2\text{CO}(\text{O}^-) + \text{OH} \rightarrow 0.745 \text{CO}(\text{O}^-)\text{CH}_2\text{COCH}(\text{OH})(\text{OO}\cdot) + 0.085 \text{CH}_2(\text{OH})\text{COCH}(\text{OO}\cdot)\text{CO}(\text{O}^-) + 0.170 \text{CO}(\text{O}^-)\text{CH}_2\text{COCH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.830 \text{O}_2$	$4.4 \cdot 10^{+08}$		
R <sub>o</sub> 01851	*		$\text{CH}_2(\text{OH})\text{COCH}_2\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow \text{CH}_2(\text{OH})\text{COCH}_2\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 01852	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{COCH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{CH}_2\text{COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01853	*	*	$\text{CH}_2(\text{OH})\text{COCH}(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CH}_2(\text{OH})\text{COCH}(\text{OO}\cdot)\text{CO}(\text{O}^-) \rightarrow 2.000 \text{CH}_2(\text{OH})\text{COCHO} + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 01854	*	*	$\text{CH}_2(\text{OH})\text{COCH}(\text{OO}\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{RO}_2} 0.200 \text{CH}_2(\text{OH})\text{COCH}(\text{O}\cdot)\text{CO}(\text{O}^-) + 0.550 \text{CH}_2(\text{OH})\text{COCOCO}(\text{O}^-) + 0.250 \text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01855	*		$\text{CH}_2(\text{OH})\text{COCH}_2\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{COCH}_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01856	*	*	$\text{CH}_2(\text{OH})\text{COCH}(\text{O}\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCOCO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01857	*	*	$\text{CH}_2(\text{OH})\text{COCH}(\text{O}\cdot)\text{CO}(\text{O}^-) \rightarrow 0.500 \text{CH}_2(\text{OH})\text{CO}(\text{OO}\cdot) + 0.500 \text{CO}(\text{O}^-)\text{CHO} + 0.500 \text{CH}_2(\text{OH})\text{COCHO} + 0.500 \cdot \text{CO}(\text{O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00211	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{CH}_2\text{CH}_2\text{CO}(\text{O}^-)$	$1.2 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01858	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2\text{CHO} + \text{OH} \rightarrow 0.059 \text{CO}(\text{O}^-)\text{CH}(\text{OO}\cdot)\text{CH}_2\text{CHO} + 0.074 \text{CO}(\text{O}^-)\text{CH}_2\text{CH}(\text{OO}\cdot)\text{CHO} + 0.866 \text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2\text{CO}(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$2.9 \cdot 10^{+09}$		
R <sub>o</sub> 01859	*		$\text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2\text{CHO} + \text{NO}_3 \rightarrow \text{CHOCH}_2\text{CH}_2\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 01860	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OO}\cdot)\text{CH}_2\text{CHO} + \text{CO}(\text{O}^-)\text{CH}(\text{OO}\cdot)\text{CH}_2\text{CHO} \rightarrow 2.000 \text{CHOCH}_2\text{CHO} + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 01861	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OO}\cdot)\text{CH}_2\text{CHO} \xrightarrow{\text{RO}_2} 0.200 \text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{CH}_2\text{CHO} + 0.550 \text{CO}(\text{O}^-)\text{COCH}_2\text{CHO} + 0.250 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}_2\text{CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01862	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CH}(\text{OO}\cdot)\text{CHO} \xrightarrow{\text{RO}_2} 0.200 \text{CO}(\text{O}^-)\text{CH}_2\text{CH}(\text{O}\cdot)\text{CHO} + 0.550 \text{CO}(\text{O}^-)\text{CH}_2\text{COCHO} + 0.250 \text{CO}(\text{O}^-)\text{CH}_2\text{CH}(\text{OH})\text{CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01863	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2\text{CO}(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CO}(\text{O}^-) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01864	*		$\text{CHOCH}_2\text{CH}_2\text{CO}(\text{O}\cdot) \rightarrow \text{CHOCH}_2\text{CH}_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01865	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{CH}_2\text{CHO} \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{COCH}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01866	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{CH}_2\text{CHO} \rightarrow 0.500 \cdot \text{CO}(\text{O}^-) + 0.500 \text{CHOCH}_2\text{CHO} +$ $0.500 \text{CO}(\text{O}^-)\text{CHO} + 0.500 \text{CHOCH}_2(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01867	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CH}(\text{O}\cdot)\text{CHO} \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{CH}_2\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01868	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CH}(\text{O}\cdot)\text{CHO} \rightarrow 0.500 \text{CO}(\text{O}^-)\text{CH}_2(\text{OO}\cdot) + 0.500 \text{CHOCHO} +$ $0.500 \text{CO}(\text{O}^-)\text{CH}_2\text{CHO} + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{O}_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00212	*	*	$\text{CH}_3\text{CH}_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) \rightleftharpoons \text{CH}_3\text{CH}_2\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{H}^+$	$8.0 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 01869	*	*	$\text{CH}_3\text{CH}_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{OH} \rightarrow$ $0.534 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2\text{CH}_2(\text{OO}\cdot) + 0.148 \text{CH}_3\text{CH}(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{OH}) +$ $0.318 \text{CH}_3\text{CH}_2\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) + \text{H}_2\text{O} - 0.682 \text{O}_2$	$7.9 \cdot 10^{+08}$		
R <sub>o</sub> 01870	*		$\text{CH}_3\text{CH}_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{NO}_3 \rightarrow$ $0.534 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2\text{CH}_2(\text{OO}\cdot) + 0.148 \text{CH}_3\text{CH}(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{OH}) +$ $0.318 \text{CH}_3\text{CH}_2\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) + \text{NO}_3^- + \text{H}^+ - 0.682 \text{O}_2$	$8.9 \cdot 10^{+06}$		
R <sub>o</sub> 01871	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2\text{CH}_2(\text{O}\cdot) + 0.550 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01872	*	*	$\text{CH}_3\text{CH}(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{OH}) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_3\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{OH}) + 0.550 \text{CH}_3\text{COC}(\text{OH})_2\text{CO}(\text{OH}) +$ $0.250 \text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01873	*	*	$\text{CH}_3\text{CH}_2\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) \rightarrow 0.500 \text{CH}_3\text{CH}_2(\text{OO}\cdot) +$ $0.500 \text{CO}(\text{OH})\text{CO}(\text{OH}) + 0.500 \text{CH}_3\text{CH}_2\text{CO}(\text{OH}) + 0.500 \cdot \text{CO}(\text{OH}) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01874	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01875	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01876	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{OH}) \xrightarrow{\text{O}_2} \text{CH}_3\text{COC}(\text{OH})_2\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01877	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{OH}) \rightarrow$ $0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CHO} + 0.500 \text{CH}_3\text{CHO} +$ $0.500 \text{CO}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00213	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{CH}_2\text{CO}(\text{OH}) \rightleftharpoons \text{CH}(\text{OH})_2\text{CH}_2\text{CH}_2\text{CO}(\text{O}^-) + \text{H}^+$	$2.4 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01878	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CO(OH) + OH $\rightarrow$ 0.597 CO(OH)CH <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.083 CH(OH) <sub>2</sub> CH(OO $\cdot$ )CH <sub>2</sub> CO(OH) + 0.040 CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OO $\cdot$ )CO(OH) + 0.279 CO(OH)CH <sub>2</sub> CH <sub>2</sub> CH(OH)(O $\cdot$ ) + H <sub>2</sub> O - 0.721 O <sub>2</sub>	$1.4 \cdot 10^{+09}$		
R <sub>o</sub> 01879	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CO(OH) + NO <sub>3</sub> $\rightarrow$ 0.597 CO(OH)CH <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.083 CH(OH) <sub>2</sub> CH(OO $\cdot$ )CH <sub>2</sub> CO(OH) + 0.040 CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OO $\cdot$ )CO(OH) + 0.279 CO(OH)CH <sub>2</sub> CH <sub>2</sub> CH(OH)(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.721 O <sub>2</sub>	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 01880	*	*	CO(OH)CH <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)CH <sub>2</sub> CH <sub>2</sub> CO(OH) + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01881	*	*	CH(OH) <sub>2</sub> CH(OO $\cdot$ )CH <sub>2</sub> CO(OH) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH(O $\cdot$ )CH <sub>2</sub> CO(OH) + 0.550 CH(OH) <sub>2</sub> COCH <sub>2</sub> CO(OH) + 0.250 CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01882	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OO $\cdot$ )CO(OH) + CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OO $\cdot$ )CO(OH) $\rightarrow$ 2.000 CH(OH) <sub>2</sub> CH <sub>2</sub> CHO + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 01883	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OO $\cdot$ )CO(OH) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH <sub>2</sub> CH(O $\cdot$ )CO(OH) + 0.550 CH(OH) <sub>2</sub> CH <sub>2</sub> COCO(OH) + 0.250 CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01884	*	*	CO(OH)CH <sub>2</sub> CH <sub>2</sub> CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)CH <sub>2</sub> CH <sub>2</sub> CO(OH) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01885	*	*	CO(OH)CH <sub>2</sub> CH <sub>2</sub> CH(OH)(O $\cdot$ ) $\rightarrow$ CO(OH)CH <sub>2</sub> CH <sub>2</sub> (OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01886	*	*	CH(OH) <sub>2</sub> CH(O $\cdot$ )CH <sub>2</sub> CO(OH) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCH <sub>2</sub> CO(OH) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01887	*	*	CH(OH) <sub>2</sub> CH(O $\cdot$ )CH <sub>2</sub> CO(OH) $\rightarrow$ 0.500 CH $\cdot$ (OH) <sub>2</sub> + 0.500 CO(OH)CH <sub>2</sub> CHO + 0.500 CH(OH) <sub>2</sub> CHO + 0.500 CO(OH)CH <sub>2</sub> (OO $\cdot$ ) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01888	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH(O $\cdot$ )CO(OH) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH <sub>2</sub> COCO(OH) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01889	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH(O $\cdot$ )CO(OH) $\rightarrow$ 0.500 CH(OH) <sub>2</sub> CH <sub>2</sub> (OO $\cdot$ ) + 0.500 CO(OH)CHO + 0.500 CH(OH) <sub>2</sub> CH <sub>2</sub> CHO + 0.500 $\cdot$ CO(OH) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00214	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(OH) $\rightleftharpoons$ CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(O $^-$ ) + H <sup>+</sup>	$6.9 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01890	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(OH) + OH → 0.609 CO(OH)CH(OH)CH(OH)CH(OH)(OO·) + 0.156 CH <sub>2</sub> (OH)C(OH)(OO·)CH(OH)CO(OH) + 0.032 CH <sub>2</sub> (OH)CH(OH)C(OH)(OO·)CO(OH) + 0.076 CO(OH)CH(OH)CH(OH)CH <sub>2</sub> (O·) + 0.077 CH <sub>2</sub> (OH)CH(O·)CH(OH)CO(OH) + 0.049 CH <sub>2</sub> (OH)CH(OH)CH(O·)CO(OH) + H <sub>2</sub> O – 0.798 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 01891	*		CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(OH) + NO <sub>3</sub> → 0.609 CO(OH)CH(OH)CH(OH)CH(OH)(OO·) + 0.156 CH <sub>2</sub> (OH)C(OH)(OO·)CH(OH)CO(OH) + 0.032 CH <sub>2</sub> (OH)CH(OH)C(OH)(OO·)CO(OH) + 0.076 CO(OH)CH(OH)CH(OH)CH <sub>2</sub> (O·) + 0.077 CH <sub>2</sub> (OH)CH(O·)CH(OH)CO(OH) + 0.049 CH <sub>2</sub> (OH)CH(OH)CH(O·)CO(OH) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.798 O <sub>2</sub>	3.7 · 10 <sup>+02</sup>		
R <sub>o</sub> 01892	*	*	CO(OH)CH(OH)CH(OH)CH(OH)(OO·) → CO(OH)CH(OH)CH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01893	*	*	CH <sub>2</sub> (OH)C(OH)(OO·)CH(OH)CO(OH) → CH <sub>2</sub> (OH)COCH(OH)CO(OH) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01894	*	*	CH <sub>2</sub> (OH)CH(OH)C(OH)(OO·)CO(OH) → CH <sub>2</sub> (OH)CH(OH)COCO(OH) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01895	*	*	CO(OH)CH(OH)CH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(OH)CH(OH)CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01896	*	*	CO(OH)CH(OH)CH(OH)CH <sub>2</sub> (O·) → CO(OH)CH(OH)CH(OH)(OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01897	*	*	CH <sub>2</sub> (OH)CH(OH)CH(O·)CO(OH) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(OH)COCO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01898	*	*	CH <sub>2</sub> (OH)CH(OH)CH(O·)CO(OH) → 0.500 CH <sub>2</sub> (OH)CH(OH)(OO·) + 0.500 CO(OH)CHO + 0.500 CH <sub>2</sub> (OH)CH(OH)CHO + 0.500 · CO(OH) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00215	*	*	CH <sub>3</sub> CH(OH)CH(OH)CO(OH) ⇌ CH <sub>3</sub> CH(OH)CH(OH)CO(O <sup>–</sup> ) + H <sup>+</sup>	5.9 · 10 <sup>–05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01899	*	*	CH <sub>3</sub> CH(OH)CH(OH)CO(OH) + OH → 0.219 CO(OH)CH(OH)CH(OH)CH <sub>2</sub> (OO·) + 0.549 CH <sub>3</sub> C(OH)(OO·)CH(OH)CO(OH) + 0.048 CH <sub>3</sub> CH(OH)C(OH)(OO·)CO(OH) + 0.115 CH <sub>3</sub> CH(O·)CH(OH)CO(OH) + 0.069 CH <sub>3</sub> CH(OH)CH(O·)CO(OH) + H <sub>2</sub> O – 0.816 O <sub>2</sub>	8.2 · 10 <sup>+08</sup>		
R <sub>o</sub> 01900	*		CH <sub>3</sub> CH(OH)CH(OH)CO(OH) + NO <sub>3</sub> → 0.219 CO(OH)CH(OH)CH(OH)CH <sub>2</sub> (OO·) + 0.549 CH <sub>3</sub> C(OH)(OO·)CH(OH)CO(OH) + 0.048 CH <sub>3</sub> CH(OH)C(OH)(OO·)CO(OH) + 0.115 CH <sub>3</sub> CH(O·)CH(OH)CO(OH) + 0.069 CH <sub>3</sub> CH(OH)CH(O·)CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> – 0.816 O <sub>2</sub>	3.2 · 10 <sup>+02</sup>		
R <sub>o</sub> 01901	*	*	CO(OH)CH(OH)CH(OH)CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CO(OH)CH(OH)CH(OH)CH <sub>2</sub> (O·) + 0.550 CO(OH)CH(OH)CH(OH)CHO + 0.250 CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01902	*	*	CH <sub>3</sub> C(OH)(OO·)CH(OH)CO(OH) → CH <sub>3</sub> COCH(OH)CO(OH) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01903	*	*	CH <sub>3</sub> CH(OH)C(OH)(OO·)CO(OH) → CH <sub>3</sub> CH(OH)COCO(OH) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01904	*	*	CH <sub>3</sub> CH(O·)CH(OH)CO(OH) $\xrightarrow{O_2}$ CH <sub>3</sub> COCH(OH)CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01905	*	*	CH <sub>3</sub> CH(O·)CH(OH)CO(OH) → 0.500 CH <sub>3</sub> (OO·) + 0.500 CO(OH)CH(OH)CHO + 0.500 CH <sub>3</sub> CHO + 0.500 CO(OH)CH(OH)(OO·) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01906	*	*	CH <sub>3</sub> CH(OH)CH(O·)CO(OH) $\xrightarrow{O_2}$ CH <sub>3</sub> CH(OH)COCO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01907	*	*	CH <sub>3</sub> CH(OH)CH(O·)CO(OH) → 0.500 CH <sub>3</sub> CH(OH)(OO·) + 0.500 CO(OH)CHO + 0.500 CH <sub>3</sub> CH(OH)CHO + 0.500 · CO(OH) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00216	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH) <sub>2</sub> CO(OH) ⇌ CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + H <sup>+</sup>	9.7 · 10 <sup>-05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 01908	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + OH → 0.828 CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)(OO·) + 0.046 CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> (O·) + 0.126 CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH)(O·)CO(OH) + H <sub>2</sub> O – 0.828 O <sub>2</sub>	2.0 · 10 <sup>+09</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01909	*		CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + NO <sub>3</sub> → 0.828 CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)(OO·) + 0.046 CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> (O·) + 0.126 CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH)(O·)CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.828 O <sub>2</sub>	9.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 01910	*	*	CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)(OO·) → CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01911	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH)(O·)CO(OH) → 0.500 CH <sub>2</sub> (OH)CH <sub>2</sub> (OO·) + 0.500 CO(OH)CO(OH) + 0.500 CH <sub>2</sub> (OH)CH <sub>2</sub> CO(OH) + 0.500 · CO(OH) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00217	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH <sub>2</sub> CO(OH) ⇌ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH <sub>2</sub> CO(O <sup>-</sup> ) + H <sup>+</sup>	4.4 · 10 <sup>-05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 01912	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH <sub>2</sub> CO(OH) + OH → 0.378 CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) + 0.108 CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.514 CH <sub>2</sub> (OH)C(OH)(O·)CH <sub>2</sub> CO(OH) + H <sub>2</sub> O - 0.378 O <sub>2</sub>	7.7 · 10 <sup>+08</sup>		
R <sub>o</sub> 01913	*		CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH <sub>2</sub> CO(OH) + NO <sub>3</sub> → 0.378 CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) + 0.108 CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.514 CH <sub>2</sub> (OH)C(OH)(O·)CH <sub>2</sub> CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.378 O <sub>2</sub>	9.7 · 10 <sup>+06</sup>		
R <sub>o</sub> 01914	*	*	CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) → CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01915	*	*	CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01916	*	*	CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) → CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01917	*	*	CH <sub>2</sub> (OH)C(OH)(O·)CH <sub>2</sub> CO(OH) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)CH <sub>2</sub> CO(OH) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CO(OH)CH <sub>2</sub> (OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00218	*	*	CH <sub>2</sub> (OH)COCH(OH)CO(OH) $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CO(OH)	1.6 · 10 <sup>+00</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00219	*	*	CH <sub>2</sub> (OH)COCH(OH)CO(OH) ⇌ CH <sub>2</sub> (OH)COCH(OH)CO(O <sup>-</sup> ) + H <sup>+</sup>	1.4 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 01918	*	*	CH <sub>2</sub> (OH)COCH(OH)CO(OH) + OH → 0.692 CO(OH)CH(OH)COCH(OH)(OO·) + 0.037 CH <sub>2</sub> (OH)COC(OH)(OO·)CO(OH) + 0.165 CO(OH)CH(OH)COCH <sub>2</sub> (O·) + 0.106 CH <sub>2</sub> (OH)COCH(O·)CO(OH) + H <sub>2</sub> O - 0.729 O <sub>2</sub>	4.6 · 10 <sup>+08</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01919	*		CH <sub>2</sub> (OH)COCH(OH)CO(OH) + NO <sub>3</sub> → 0.692 CO(OH)CH(OH)COCH(OH)(OO·) + 0.037 CH <sub>2</sub> (OH)COC(OH)(OO·)CO(OH) + 0.165 CO(OH)CH(OH)COCH <sub>2</sub> (O·) + 0.106 CH <sub>2</sub> (OH)COCH(O·)CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.729 O <sub>2</sub>	7.2 · 10 <sup>+03</sup>		
R <sub>o</sub> 01920	*	*	CO(OH)CH(OH)COCH(OH)(OO·) → CO(OH)CH(OH)COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01921	*	*	CH <sub>2</sub> (OH)COC(OH)(OO·)CO(OH) → CH <sub>2</sub> (OH)COCOCO(OH) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01922	*	*	CO(OH)CH(OH)COCH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(OH)CH(OH)COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01923	*	*	CO(OH)CH(OH)COCH <sub>2</sub> (O·) → CO(OH)CH(OH)CO(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01924	*	*	CH <sub>2</sub> (OH)COCH(O·)CO(OH) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCOCO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01925	*	*	CH <sub>2</sub> (OH)COCH(O·)CO(OH) → 0.500 CH <sub>2</sub> (OH)CO(OO·) + 0.500 CO(OH)CHO + 0.500 CH <sub>2</sub> (OH)COCHO + 0.500 · CO(OH) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00220	*	*	CH <sub>3</sub> CH(OH)COCO(OH) $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CO(OH)	9.9 · 10 <sup>+00</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00221	*	*	CH <sub>3</sub> CH(OH)COCO(OH) $\rightleftharpoons$ CH <sub>3</sub> CH(OH)COCO(O <sup>-</sup> ) + H <sup>+</sup>	4.7 · 10 <sup>-02</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 01926	*	*	CH <sub>3</sub> CH(OH)COCO(OH) + OH → 0.352 CO(OH)COCH(OH)CH <sub>2</sub> (OO·) + 0.463 CH <sub>3</sub> C(OH)(OO·)COCO(OH) + 0.185 CH <sub>3</sub> CH(O·)COCO(OH) + H <sub>2</sub> O - 0.815 O <sub>2</sub>	4.4 · 10 <sup>+08</sup>		
R <sub>o</sub> 01927	*		CH <sub>3</sub> CH(OH)COCO(OH) + NO <sub>3</sub> → 0.352 CO(OH)COCH(OH)CH <sub>2</sub> (OO·) + 0.463 CH <sub>3</sub> C(OH)(OO·)COCO(OH) + 0.185 CH <sub>3</sub> CH(O·)COCO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.815 O <sub>2</sub>	7.4 · 10 <sup>+03</sup>		
R <sub>o</sub> 01928	*	*	CO(OH)COCH(OH)CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CO(OH)COCH(OH)CH <sub>2</sub> (O·) + 0.550 CO(OH)COCH(OH)CHO + 0.250 CH <sub>2</sub> (OH)CH(OH)COCO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 01929	*	*	CH <sub>3</sub> C(OH)(OO·)COCO(OH) → CH <sub>3</sub> COCOCO(OH) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01930	*	*	CH <sub>3</sub> CH(O·)COCO(OH) $\xrightarrow{O_2}$ CH <sub>3</sub> COCOCO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01931	*	*	CH <sub>3</sub> CH(O·)COCO(OH) → 0.500 CH <sub>3</sub> (OO·) + 0.500 CO(OH)COCHO + 0.500 CH <sub>3</sub> CHO + 0.500 CO(OH)CO(OO·) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 01932	*	*	CO(OH)COCH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(OH)COCH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 01933	*	*	CO(OH)COCH(OH)CH <sub>2</sub> (O·) → CO(OH)COCH(OH)(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00222	*	*	CH <sub>2</sub> (OH)CH(OH)COCO(OH) $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CO(OH)	2.0 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00223	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{OH}) \rightleftharpoons \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{O}^-) + \text{H}^+$	$6.8 \cdot 10^{-02}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 01934	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{OH}) + \text{OH} \rightarrow$ $0.711 \text{ CO}(\text{OH})\text{COCH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.096 \text{ CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{COCO}(\text{OH}) +$ $0.104 \text{ CO}(\text{OH})\text{COCH}(\text{OH})\text{CH}_2(\text{O}\cdot) + 0.090 \text{ CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{COCO}(\text{OH}) +$ $\text{H}_2\text{O} - 0.806 \text{ O}_2$	$8.4 \cdot 10^{+08}$		
R <sub>o</sub> 01935	*		$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{OH}) + \text{NO}_3 \rightarrow$ $0.711 \text{ CO}(\text{OH})\text{COCH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.096 \text{ CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{COCO}(\text{OH}) +$ $0.104 \text{ CO}(\text{OH})\text{COCH}(\text{OH})\text{CH}_2(\text{O}\cdot) + 0.090 \text{ CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{COCO}(\text{OH}) +$ $\text{NO}_3^- + \text{H}^+ - 0.806 \text{ O}_2$	$8.6 \cdot 10^{+03}$		
R <sub>o</sub> 01936	*	*	$\text{CO}(\text{OH})\text{COCH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{COCH}(\text{OH})\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01937	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{COCO}(\text{OH}) \rightarrow \text{CH}_2(\text{OH})\text{COCOCO}(\text{OH}) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
E <sub>o</sub> 00224	*	*	$\text{CH}_3\text{COCH}(\text{OH})\text{CO}(\text{OH}) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{OH})$	$2.6 \cdot 10^{-01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00225	*	*	$\text{CH}_3\text{COCH}(\text{OH})\text{CO}(\text{OH}) \rightleftharpoons \text{CH}_3\text{COCH}(\text{OH})\text{CO}(\text{O}^-) + \text{H}^+$	$1.2 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 01938	*	*	$\text{CH}_3\text{COCH}(\text{OH})\text{CO}(\text{OH}) + \text{OH} \rightarrow$ $0.550 \text{ CO}(\text{OH})\text{CH}(\text{OH})\text{COCH}_2(\text{OO}\cdot) + 0.121 \text{ CH}_3\text{COC}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{OH}) +$ $0.328 \text{ CH}_3\text{COCH}(\text{O}\cdot)\text{CO}(\text{OH}) + \text{H}_2\text{O} - 0.672 \text{ O}_2$	$1.5 \cdot 10^{+08}$		
R <sub>o</sub> 01939	*		$\text{CH}_3\text{COCH}(\text{OH})\text{CO}(\text{OH}) + \text{NO}_3 \rightarrow$ $0.550 \text{ CO}(\text{OH})\text{CH}(\text{OH})\text{COCH}_2(\text{OO}\cdot) + 0.121 \text{ CH}_3\text{COC}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{OH}) +$ $0.328 \text{ CH}_3\text{COCH}(\text{O}\cdot)\text{CO}(\text{OH}) + \text{NO}_3^- + \text{H}^+ - 0.672 \text{ O}_2$	$6.3 \cdot 10^{+03}$		
R <sub>o</sub> 01940	*	*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{COCH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CO}(\text{OH})\text{CH}(\text{OH})\text{COCH}_2(\text{O}\cdot) + 0.550 \text{ CO}(\text{OH})\text{CH}(\text{OH})\text{COCHO} +$ $0.250 \text{ CH}_2(\text{OH})\text{COCH}(\text{OH})\text{CO}(\text{OH}) + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01941	*	*	$\text{CH}_3\text{COC}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{OH}) \rightarrow \text{CH}_3\text{COCOCO}(\text{OH}) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
E <sub>o</sub> 00226	*	*	$\text{CH}_2(\text{OH})\text{COCOCO}(\text{OH}) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CO}(\text{OH})$	$3.7 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00227	*	*	$\text{CH}_2(\text{OH})\text{COCOCO}(\text{OH}) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OH})$	$3.5 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00228	*	*	$\text{CH}_2(\text{OH})\text{COCOCO}(\text{OH}) \rightleftharpoons \text{CH}_2(\text{OH})\text{COCOCO}(\text{O}^-) + \text{H}^+$	$4.0 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 01942	*	*	$\text{CH}_2(\text{OH})\text{COCOCO}(\text{OH}) + \text{OH} \rightarrow 0.782 \text{ CO}(\text{OH})\text{COCOCH}(\text{OH})(\text{OO}\cdot) +$ $0.218 \text{ CO}(\text{OH})\text{COCOCH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.782 \text{ O}_2$	$3.5 \cdot 10^{+08}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A/R^b$	Reference/comment
R <sub>o</sub> 01943	*		$\text{CH}_2(\text{OH})\text{COCOCO}(\text{OH}) + \text{NO}_3 \rightarrow 0.782 \text{CO}(\text{OH})\text{COCOCH}(\text{OH})(\text{OO}\cdot) + 0.218 \text{CO}(\text{OH})\text{COCOCH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.782 \text{O}_2$	$1.9 \cdot 10^{+05}$		
R <sub>o</sub> 01944	*	*	$\text{CO}(\text{OH})\text{COCOCH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{COCOCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01945	*	*	$\text{CO}(\text{OH})\text{COCOCH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{COCOCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01946	*	*	$\text{CO}(\text{OH})\text{COCOCH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{OH})\text{COCO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00229	*	*	$\text{CH}_3\text{COCOCO}(\text{OH}) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{COC}(\text{OH})_2\text{CO}(\text{OH})$	$8.5 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00230	*	*	$\text{CH}_3\text{COCOCO}(\text{OH}) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OH})$	$1.3 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00231	*	*	$\text{CH}_3\text{COCOCO}(\text{OH}) \rightleftharpoons \text{CH}_3\text{COCOCO}(\text{O}^-) + \text{H}^+$	$2.8 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 01947	*	*	$\text{CH}_3\text{COCOCO}(\text{OH}) + \text{OH} \rightarrow \text{CO}(\text{OH})\text{COCOCH}_2(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$6.9 \cdot 10^{+07}$		
R <sub>o</sub> 01948	*		$\text{CH}_3\text{COCOCO}(\text{OH}) + \text{NO}_3 \rightarrow \text{CO}(\text{OH})\text{COCOCH}_2(\text{OO}\cdot) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$1.7 \cdot 10^{+05}$		
R <sub>o</sub> 01949	*	*	$\text{CO}(\text{OH})\text{COCOCH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2} 0.200 \text{CO}(\text{OH})\text{COCOCH}_2(\text{O}\cdot) + 0.550 \text{CO}(\text{OH})\text{COCOCHO} + 0.250 \text{CH}_2(\text{OH})\text{COCOCO}(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
E <sub>o</sub> 00232	*	*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{OH})\text{CO}(\text{OH})$	$6.6 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00233	*	*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CHO} \rightleftharpoons \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}_2\text{CHO} + \text{H}^+$	$6.9 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 01950	*	*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CHO} + \text{OH} \rightarrow \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CO}(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$2.4 \cdot 10^{+09}$		
R <sub>o</sub> 01951	*		$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CHO} + \text{NO}_3 \rightarrow \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CO}(\text{OO}\cdot) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$1.5 \cdot 10^{+07}$		
R <sub>o</sub> 01952	*	*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{CO}(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CO}(\text{OH}) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
E <sub>o</sub> 00234	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2\text{CO}(\text{OH})$	$1.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00235	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CHO} \rightleftharpoons \text{CO}(\text{O}^-)\text{CH}_2\text{CH}(\text{OH})\text{CHO} + \text{H}^+$	$4.3 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 01953	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CHO} + \text{OH} \rightarrow 0.146 \text{CO}(\text{OH})\text{CH}_2\text{C}(\text{OH})(\text{OO}\cdot)\text{CHO} + 0.794 \text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) + 0.060 \text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{O}\cdot)\text{CHO} + \text{H}_2\text{O} - 0.940 \text{O}_2$	$1.3 \cdot 10^{+09}$		
R <sub>o</sub> 01954	*		$\text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CHO} + \text{NO}_3 \rightarrow 0.146 \text{CO}(\text{OH})\text{CH}_2\text{C}(\text{OH})(\text{OO}\cdot)\text{CHO} + 0.794 \text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) + 0.060 \text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{O}\cdot)\text{CHO} + \text{NO}_3^- + \text{H}^+ - 0.940 \text{O}_2$	$1.5 \cdot 10^{+07}$		
R <sub>o</sub> 01955	*	*	$\text{CO}(\text{OH})\text{CH}_2\text{C}(\text{OH})(\text{OO}\cdot)\text{CHO} \rightarrow \text{CO}(\text{OH})\text{CH}_2\text{COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01956	*	*	CO(OH)CH <sub>2</sub> CH(OH)CO(OO·) → CO(OH)CH <sub>2</sub> CH(OH)CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
E <sub>o</sub> 00236	*	*	CO(OH)COCH <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH <sub>2</sub> COCO(OH)	$2.6 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00237	*	*	CO(OH)COCH <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> CHO	$2.0 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00238	*	*	CO(OH)COCH <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CO(OH)	$2.2 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00239	*	*	CO(OH)COCH <sub>2</sub> CHO $\rightleftharpoons$ CO(O <sup>-</sup> )COCH <sub>2</sub> CHO + H <sup>+</sup>	$6.8 \cdot 10^{-02}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 01957	*	*	CO(OH)COCH <sub>2</sub> CHO + OH → CO(OH)COCH <sub>2</sub> CO(OO·) + H <sub>2</sub> O - O <sub>2</sub>	$2.0 \cdot 10^{+09}$		
R <sub>o</sub> 01958	*		CO(OH)COCH <sub>2</sub> CHO + NO <sub>3</sub> → CO(OH)COCH <sub>2</sub> CO(OO·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	$5.7 \cdot 10^{+06}$		
R <sub>o</sub> 01959	*	*	CO(OH)COCH <sub>2</sub> CO(OO·) → CO(OH)CH <sub>2</sub> COCO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
E <sub>o</sub> 00240	*	*	CO(OH)CH <sub>2</sub> COCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> COCH <sub>2</sub> CO(OH)	$7.4 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00241	*	*	CO(OH)CH <sub>2</sub> COCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CO(OH)	$1.9 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00242	*	*	CO(OH)CH <sub>2</sub> COCHO $\rightleftharpoons$ CO(O <sup>-</sup> )CH <sub>2</sub> COCHO + H <sup>+</sup>	$9.0 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 01960	*	*	CO(OH)CH <sub>2</sub> COCHO + OH → CO(OH)CH <sub>2</sub> COCO(OO·) + H <sub>2</sub> O - O <sub>2</sub>	$4.5 \cdot 10^{+08}$		
R <sub>o</sub> 01961	*		CO(OH)CH <sub>2</sub> COCHO + NO <sub>3</sub> → CO(OH)CH <sub>2</sub> COCO(OO·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	$5.9 \cdot 10^{+06}$		
R <sub>o</sub> 01962	*	*	CO(OH)CH <sub>2</sub> COCO(OO·) → CO(OH)CH <sub>2</sub> COCO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01963	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub> → 0.250 CHO(OH) + 0.250 HO <sub>2</sub> + 0.250 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·)	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 01964	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + OH → 0.150 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.437 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) + 0.413 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(O·)CH(OH) <sub>2</sub> + H <sub>2</sub> O - 0.150 O <sub>2</sub>	$1.7 \cdot 10^{+09}$		
R <sub>o</sub> 01965	*		CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.150 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.437 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) + 0.413 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(O·)CH(OH) <sub>2</sub> + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.150 O <sub>2</sub>	$8.8 \cdot 10^{+06}$		
R <sub>o</sub> 01966	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01967	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{C(OH)}_2\text{CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2}$ $\text{CH(OH)}_2\text{C(OH)}_2\text{C(OH)}_2\text{CO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01968	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{C(OH)}_2\text{CH(OH)(O}\cdot\text{)} \rightarrow$ $\text{CH(OH)}_2\text{C(OH)}_2\text{C(OH)}_2(\text{OO}\cdot) + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01969	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{C(OH)(O}\cdot\text{)CH(OH)}_2 \rightarrow$ $0.500 \text{CH(OH)}_2\text{C(OH)}_2(\text{OO}\cdot) + 0.500 \text{CH(OH)}_2\text{CO(OH)} +$ $0.500 \text{CH(OH)}_2\text{C(OH)}_2\text{CO(OH)} + 0.500 \text{CH}\cdot\text{(OH)}_2 - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01970	*	*	$\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CH(OH)}_2 \rightarrow 0.500 + 0.500 + 0.500$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 01971	*	*	$\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CH(OH)}_2 + \text{OH} \rightarrow$ $0.192 \text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)C(OH)}_2(\text{OO}\cdot) +$ $0.080 \text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{C(OH)}_2(\text{OO}\cdot) +$ $0.234 \text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)CH(OH)(O}\cdot\text{)} +$ $0.049 \text{CH(OH)}_2\text{C(OH)}_2\text{CH(O}\cdot\text{)CH(OH)}_2 +$ $0.221 \text{CH(OH)}_2\text{CH(OH)C(OH)(O}\cdot\text{)CH(OH)}_2 +$ $0.223 \text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CH(OH)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.272 \text{O}_2$	$1.6 \cdot 10^{+09}$		
R <sub>o</sub> 01972	*		$\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CH(OH)}_2 + \text{NO}_3 \rightarrow$ $0.192 \text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)C(OH)}_2(\text{OO}\cdot) +$ $0.080 \text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{C(OH)}_2(\text{OO}\cdot) +$ $0.234 \text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)CH(OH)(O}\cdot\text{)} +$ $0.049 \text{CH(OH)}_2\text{C(OH)}_2\text{CH(O}\cdot\text{)CH(OH)}_2 +$ $0.221 \text{CH(OH)}_2\text{CH(OH)C(OH)(O}\cdot\text{)CH(OH)}_2 +$ $0.223 \text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CH(OH)(O}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - 0.272 \text{O}_2$	$1.2 \cdot 10^{+07}$		
R <sub>o</sub> 01973	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)C(OH)}_2(\text{OO}\cdot) \rightarrow$ $\text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)CO(OH)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01974	*	*	$\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{C(OH)}_2(\text{OO}\cdot) \rightarrow$ $\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CO(OH)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01975	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2}$ $\text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)CO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01976	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)CH(OH)(O}\cdot\text{)} \rightarrow$ $\text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)(OO}\cdot\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01977	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(O}\cdot\text{)CH(OH)}_2 \xrightarrow{\text{O}_2}$ $\text{CH(OH)}_2\text{C(OH)}_2\text{COCH(OH)}_2 + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01978	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(O}\cdot\text{)CH(OH)}_2 \rightarrow$ $0.500 \text{CH(OH)}_2\text{C(OH)}_2(\text{OO}\cdot) + 0.500 \text{CH(OH)}_2\text{CHO} +$ $0.500 \text{CH(OH)}_2\text{C(OH)}_2\text{CHO} + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01979	*	*	$\text{CH(OH)}_2\text{CH(OH)C(OH)(O}\cdot\text{)CH(OH)}_2 \rightarrow$ $0.500 \text{CH(OH)}_2\text{CH(OH)(OO}\cdot\text{)} + 0.500 \text{CH(OH)}_2\text{CO(OH)} +$ $0.500 \text{CH(OH)}_2\text{CH(OH)CO(OH)} + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01980	*	*	$\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2}$ $\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01981	*	*	$\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CH(OH)(O}\cdot\text{)} \rightarrow$ $\text{CH(OH)}_2\text{CH(OH)C(OH)}_2(\text{OO}\cdot) + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01982	*	*	$\text{CH(OH)}_2\text{CH(OH)CH(OH)CH(OH)}_2 + \text{OH} \rightarrow$ $0.364 \text{CH(OH)}_2\text{CH(OH)CH(OH)C(OH)}_2(\text{OO}\cdot) +$ $0.120 \text{CH(OH)}_2\text{CH(OH)C(OH)(OO}\cdot\text{)CH(OH)}_2 +$ $0.422 \text{CH(OH)}_2\text{CH(OH)CH(OH)CH(OH)(O}\cdot\text{)} +$ $0.093 \text{CH(OH)}_2\text{CH(OH)CH(O}\cdot\text{)CH(OH)}_2 + \text{H}_2\text{O} - 0.485 \text{O}_2$	$1.8 \cdot 10^{+09}$		
R <sub>o</sub> 01983	*		$\text{CH(OH)}_2\text{CH(OH)CH(OH)CH(OH)}_2 + \text{NO}_3 \rightarrow$ $0.364 \text{CH(OH)}_2\text{CH(OH)CH(OH)C(OH)}_2(\text{OO}\cdot) +$ $0.120 \text{CH(OH)}_2\text{CH(OH)C(OH)(OO}\cdot\text{)CH(OH)}_2 +$ $0.422 \text{CH(OH)}_2\text{CH(OH)CH(OH)CH(OH)(O}\cdot\text{)} +$ $0.093 \text{CH(OH)}_2\text{CH(OH)CH(O}\cdot\text{)CH(OH)}_2 + \text{NO}_3^- + \text{H}^+ - 0.485 \text{O}_2$	$1.5 \cdot 10^{+07}$		
R <sub>o</sub> 01984	*	*	$\text{CH(OH)}_2\text{CH(OH)CH(OH)C(OH)}_2(\text{OO}\cdot) \rightarrow$ $\text{CH(OH)}_2\text{CH(OH)CH(OH)CO(OH)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01985	*	*	$\text{CH(OH)}_2\text{CH(OH)C(OH)(OO}\cdot\text{)CH(OH)}_2 \rightarrow$ $\text{CH(OH)}_2\text{CH(OH)COCH(OH)}_2 + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 01986	*	*	$\text{CH(OH)}_2\text{CH(OH)CH(OH)CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2}$ $\text{CH(OH)}_2\text{CH(OH)CH(OH)CO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01987	*	*	$\text{CH(OH)}_2\text{CH(OH)CH(OH)CH(OH)(O}\cdot\text{)} \rightarrow$ $\text{CH(OH)}_2\text{CH(OH)CH(OH)(OO}\cdot\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00243	*	*	$\text{CH}_3\text{C(OH)}_2\text{COCH(OH)}_2 \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{COC(OH)}_2\text{CH(OH)}_2$	$2.6 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00244	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{COCH}(\text{OH})_2 \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})_2$	$1.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01988	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{COCH}(\text{OH})_2 \rightarrow$ $0.250 \text{ CH}_3\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.250 \text{ CH}(\text{OH})_2\text{CO}(\text{OO}\cdot) +$ $0.250 \text{ CH}_3\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) + 0.250 \text{ CHO}(\text{OH}) + 0.250 \text{ HO}_2$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 01989	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{COCH}(\text{OH})_2 + \text{OH} \rightarrow 0.070 \text{ CH}(\text{OH})_2\text{COC}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) +$ $0.162 \text{ CH}_3\text{C}(\text{OH})_2\text{COC}(\text{OH})_2(\text{OO}\cdot) + 0.394 \text{ CH}_3\text{C}(\text{OH})(\text{O}\cdot)\text{COCH}(\text{OH})_2 +$ $0.374 \text{ CH}_3\text{C}(\text{OH})_2\text{COCH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.231 \text{ O}_2$	$8.7 \cdot 10^{+08}$		
R <sub>o</sub> 01990	*		$\text{CH}_3\text{C}(\text{OH})_2\text{COCH}(\text{OH})_2 + \text{NO}_3 \rightarrow 0.070 \text{ CH}(\text{OH})_2\text{COC}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) +$ $0.162 \text{ CH}_3\text{C}(\text{OH})_2\text{COC}(\text{OH})_2(\text{OO}\cdot) + 0.394 \text{ CH}_3\text{C}(\text{OH})(\text{O}\cdot)\text{COCH}(\text{OH})_2 +$ $0.374 \text{ CH}_3\text{C}(\text{OH})_2\text{COCH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.231 \text{ O}_2$	$8.9 \cdot 10^{+06}$		
R <sub>o</sub> 01991	*	*	$\text{CH}(\text{OH})_2\text{COC}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CH}(\text{OH})_2\text{COC}(\text{OH})_2\text{CH}_2(\text{O}\cdot) + 0.550 \text{ CH}(\text{OH})_2\text{COC}(\text{OH})_2\text{CHO} +$ $0.250 \text{ CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}(\text{OH})_2 + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 01992	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{COC}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CH}_3\text{C}(\text{OH})_2\text{COCO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 01993	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{O}\cdot)\text{COCH}(\text{OH})_2 \rightarrow$ $0.500 \text{ CH}_3(\text{OO}\cdot) + 0.500 \text{ CH}(\text{OH})_2\text{COCO}(\text{OH}) + 0.500 \text{ CH}_3\text{CO}(\text{OH}) +$ $0.500 \text{ CH}(\text{OH})_2\text{CO}(\text{OO}\cdot) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01994	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{COCH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_3\text{C}(\text{OH})_2\text{COCO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01995	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{COCH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CH}_3\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 01996	*	*	$\text{CH}(\text{OH})_2\text{COC}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{COC}(\text{OH})_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 01997	*	*	$\text{CH}(\text{OH})_2\text{COC}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{COC}(\text{OH})_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00245	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}(\text{OH})_2 \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CH}(\text{OH})_2$	$1.1 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00246	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}(\text{OH})_2 \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})_2$	$4.5 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 01998	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}(\text{OH})_2 \rightarrow$ $0.250 \text{ CH}_2(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.250 \text{ CH}(\text{OH})_2\text{CO}(\text{OO}\cdot) +$ $0.250 \text{ CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) + 0.250 \text{ CHO}(\text{OH}) + 0.250 \text{ HO}_2$	$1.0 \cdot 10^{-01}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 01999	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH(OH) <sub>2</sub> + OH → 0.214 CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH(OH)(OO·) + 0.127 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COC(OH) <sub>2</sub> (OO·) + 0.075 CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.291 CH <sub>2</sub> (OH)C(OH)(O·)COCH(OH) <sub>2</sub> + 0.294 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH(OH)(O·) + H <sub>2</sub> O – 0.341 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 02000	*		CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.214 CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH(OH)(OO·) + 0.127 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COC(OH) <sub>2</sub> (OO·) + 0.075 CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.291 CH <sub>2</sub> (OH)C(OH)(O·)COCH(OH) <sub>2</sub> + 0.294 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.341 O <sub>2</sub>	9.7 · 10 <sup>+06</sup>		
R <sub>o</sub> 02001	*	*	CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH(OH)(OO·) → CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02002	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COC(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02003	*	*	CH <sub>2</sub> (OH)C(OH)(O·)COCH(OH) <sub>2</sub> → 0.500 CH <sub>2</sub> (OH)· + 0.500 CH(OH) <sub>2</sub> COCO(OH) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CH(OH) <sub>2</sub> CO(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02004	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02005	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH(OH)(O·) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CO(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02006	*	*	CH(OH) <sub>2</sub> CH(OH)COCH(OH) <sub>2</sub> → 0.500 + 0.500 + 0.500	1.0 · 10 <sup>–01</sup>		
R <sub>o</sub> 02007	*	*	CH(OH) <sub>2</sub> CH(OH)COCH(OH) <sub>2</sub> + OH → 0.224 CH(OH) <sub>2</sub> COCH(OH)C(OH) <sub>2</sub> (OO·) + 0.039 CH(OH) <sub>2</sub> COC(OH)(OO·)CH(OH) <sub>2</sub> + 0.118 CH(OH) <sub>2</sub> CH(OH)COC(OH) <sub>2</sub> (OO·) + 0.303 CH(OH) <sub>2</sub> COCH(OH)CH(OH)(O·) + 0.057 CH(OH) <sub>2</sub> COCH(O·)CH(OH) <sub>2</sub> + 0.259 CH(OH) <sub>2</sub> CH(OH)COCH(OH)(O·) + H <sub>2</sub> O – 0.380 O <sub>2</sub>	1.3 · 10 <sup>+09</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02008	*		CH(OH) <sub>2</sub> CH(OH)COCH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.224 CH(OH) <sub>2</sub> COCH(OH)C(OH) <sub>2</sub> (OO·) + 0.039 CH(OH) <sub>2</sub> COC(OH)(OO·)CH(OH) <sub>2</sub> + 0.118 CH(OH) <sub>2</sub> CH(OH)COC(OH) <sub>2</sub> (OO·) + 0.303 CH(OH) <sub>2</sub> COCH(OH)CH(OH)(O·) + 0.057 CH(OH) <sub>2</sub> COCH(O·)CH(OH) <sub>2</sub> + 0.259 CH(OH) <sub>2</sub> CH(OH)COCH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.380 O <sub>2</sub>	1.1 · 10 <sup>+07</sup>		
R <sub>o</sub> 02009	*	*	CH(OH) <sub>2</sub> COCH(OH)C(OH) <sub>2</sub> (OO·) → CH(OH) <sub>2</sub> COCH(OH)CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02010	*	*	CH(OH) <sub>2</sub> COC(OH)(OO·)CH(OH) <sub>2</sub> → CH(OH) <sub>2</sub> COCOCH(OH) <sub>2</sub> + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02011	*	*	CH(OH) <sub>2</sub> CH(OH)COC(OH) <sub>2</sub> (OO·) → CH(OH) <sub>2</sub> CH(OH)COCO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02012	*	*	CH(OH) <sub>2</sub> COCH(OH)CH(OH)(O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCH(OH)CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02013	*	*	CH(OH) <sub>2</sub> COCH(OH)CH(OH)(O·) → CH(OH) <sub>2</sub> COCH(OH)(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02014	*	*	CH(OH) <sub>2</sub> COCH(O·)CH(OH) <sub>2</sub> $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCOCH(OH) <sub>2</sub> + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02015	*	*	CH(OH) <sub>2</sub> COCH(O·)CH(OH) <sub>2</sub> → 0.500 CH(OH) <sub>2</sub> CO(OO·) + 0.500 CH(OH) <sub>2</sub> CHO + 0.500 CH(OH) <sub>2</sub> COCHO + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02016	*	*	CH(OH) <sub>2</sub> CH(OH)COCH(OH)(O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(OH)COCO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02017	*	*	CH(OH) <sub>2</sub> CH(OH)COCH(OH)(O·) → CH(OH) <sub>2</sub> CH(OH)CO(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00247	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	7.1 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02018	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO → 0.250 CHO(OH) + 0.250 HO <sub>2</sub> + 0.250 CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.250 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.250 CHOC(OH) <sub>2</sub> (OO·)	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 02019	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + OH → 0.084 CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.242 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OO·) + 0.244 CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) + 0.231 CH(OH) <sub>2</sub> C(OH)(O·)C(OH) <sub>2</sub> CHO + 0.198 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(O·)CHO + H <sub>2</sub> O - 0.326 O <sub>2</sub>	1.5 · 10 <sup>+09</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02020	*		CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + NO <sub>3</sub> → 0.084 CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.242 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OO·) + 0.244 CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) + 0.231 CH(OH) <sub>2</sub> C(OH)(O·)C(OH) <sub>2</sub> CHO + 0.198 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.326 O <sub>2</sub>	7.3 · 10 <sup>+06</sup>		
R <sub>o</sub> 02021	*	*	CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02022	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OO·) → CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02023	*	*	CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02024	*	*	CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) → CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02025	*	*	CH(OH) <sub>2</sub> C(OH)(O·)C(OH) <sub>2</sub> CHO → 0.500 CH · (OH) <sub>2</sub> + 0.500 CO(OH)C(OH) <sub>2</sub> CHO + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CHOC(OH) <sub>2</sub> (OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02026	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(O·)CHO → 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.500 CO(OH)CHO + 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + 0.500 CH · (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00248	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> COCH(OH) <sub>2</sub>	1.4 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00249	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	3.3 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02027	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> CHO + OH → 0.074 CHOC(OH) <sub>2</sub> CH <sub>2</sub> (OO·) + 0.510 CH <sub>3</sub> C(OH) <sub>2</sub> CO(OO·) + 0.417 CH <sub>3</sub> C(OH)(O·)CHO + H <sub>2</sub> O - 0.583 O <sub>2</sub>	8.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02028	*		CH <sub>3</sub> C(OH) <sub>2</sub> CHO + NO <sub>3</sub> → 0.074 CHOC(OH) <sub>2</sub> CH <sub>2</sub> (OO·) + 0.510 CH <sub>3</sub> C(OH) <sub>2</sub> CO(OO·) + 0.417 CH <sub>3</sub> C(OH)(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.583 O <sub>2</sub>	7.4 · 10 <sup>+06</sup>		
R <sub>o</sub> 02029	*	*	CH <sub>3</sub> C(OH)(O·)CHO → 0.500 CH <sub>3</sub> (OO·) + 0.500 CO(OH)CHO + 0.500 CH <sub>3</sub> CO(OH) + 0.500 CH · (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00250	*	*	CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)CH(OH)COCH(OH) <sub>2</sub>	7.0 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00251	*	*	CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	2.0 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02030	*	*	CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CHO + OH → 0.412 CHOC(OH) <sub>2</sub> CH(OH)CH(OH)(OO·) + 0.057 CH <sub>2</sub> (OH)C(OH)(OO·)C(OH) <sub>2</sub> CHO + 0.234 CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CO(OO·) + 0.054 CHOC(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) + 0.052 CH <sub>2</sub> (OH)CH(O·)C(OH) <sub>2</sub> CHO + 0.191 CH <sub>2</sub> (OH)CH(OH)C(OH)(O·)CHO + H <sub>2</sub> O – 0.703 O <sub>2</sub>	1.6 · 10 <sup>+09</sup>		
R <sub>o</sub> 02031	*		CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CHO + NO <sub>3</sub> → 0.412 CHOC(OH) <sub>2</sub> CH(OH)CH(OH)(OO·) + 0.057 CH <sub>2</sub> (OH)C(OH)(OO·)C(OH) <sub>2</sub> CHO + 0.234 CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CO(OO·) + 0.054 CHOC(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) + 0.052 CH <sub>2</sub> (OH)CH(O·)C(OH) <sub>2</sub> CHO + 0.191 CH <sub>2</sub> (OH)CH(OH)C(OH)(O·)CHO + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.703 O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 02032	*	*	CHOC(OH) <sub>2</sub> CH(OH)CH(OH)(OO·) → CHOCH(OH)C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02033	*	*	CH <sub>2</sub> (OH)C(OH)(OO·)C(OH) <sub>2</sub> CHO → CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02034	*	*	CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CO(OO·) → CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02035	*	*	CH <sub>2</sub> (OH)CH(O·)C(OH) <sub>2</sub> CHO $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02036	*	*	CH <sub>2</sub> (OH)CH(O·)C(OH) <sub>2</sub> CHO → 0.500 CH <sub>2</sub> (OH)· + 0.500 CHOC(OH) <sub>2</sub> CHO + 0.500 CH <sub>2</sub> (OH)CHO + 0.500 CHOC(OH) <sub>2</sub> (OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02037	*	*	CH <sub>2</sub> (OH)CH(OH)C(OH)(O·)CHO → 0.500 CH <sub>2</sub> (OH)CH(OH)(OO·) + 0.500 CO(OH)CHO + 0.500 CH <sub>2</sub> (OH)CH(OH)CO(OH) + 0.500 CH·(OH) <sub>2</sub> – 0.500 O <sub>2</sub> – 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00252	*	*	CH(OH) <sub>2</sub> CH(OH)CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)CH(OH)CH(OH) <sub>2</sub>	5.4 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02038	*	*	CH(OH) <sub>2</sub> CH(OH)CH(OH)CHO + OH → 0.162 CHOCH(OH)CH(OH)C(OH) <sub>2</sub> (OO·) + 0.046 CH(OH) <sub>2</sub> C(OH)(OO·)CH(OH)CHO + 0.055 CH(OH) <sub>2</sub> CH(OH)C(OH)(OO·)CHO + 0.471 CH(OH) <sub>2</sub> CH(OH)CH(OH)CO(OO·) + 0.188 CHOCH(OH)CH(OH)CH(OH)(O·) + 0.042 CH(OH) <sub>2</sub> CH(O·)CH(OH)CHO + 0.036 CH(OH) <sub>2</sub> CH(OH)CH(O·)CHO + H <sub>2</sub> O – 0.734 O <sub>2</sub>	2.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 02039	*		CH(OH) <sub>2</sub> CH(OH)CH(OH)CHO + NO <sub>3</sub> → 0.162 CHOCH(OH)CH(OH)C(OH) <sub>2</sub> (OO·) + 0.046 CH(OH) <sub>2</sub> C(OH)(OO·)CH(OH)CHO + 0.055 CH(OH) <sub>2</sub> CH(OH)C(OH)(OO·)CHO + 0.471 CH(OH) <sub>2</sub> CH(OH)CH(OH)CO(OO·) + 0.188 CHOCH(OH)CH(OH)CH(OH)(O·) + 0.042 CH(OH) <sub>2</sub> CH(O·)CH(OH)CHO + 0.036 CH(OH) <sub>2</sub> CH(OH)CH(O·)CHO + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.734 O <sub>2</sub>	1.2 · 10 <sup>+07</sup>		
R <sub>o</sub> 02040	*	*	CHOCH(OH)CH(OH)C(OH) <sub>2</sub> (OO·) → CO(OH)CH(OH)CH(OH)CHO + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02041	*	*	CH(OH) <sub>2</sub> C(OH)(OO·)CH(OH)CHO → CH(OH) <sub>2</sub> COCH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02042	*	*	CH(OH) <sub>2</sub> CH(OH)C(OH)(OO·)CHO → CH(OH) <sub>2</sub> CH(OH)COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02043	*	*	CH(OH) <sub>2</sub> CH(OH)CH(OH)CO(OO·) → CH(OH) <sub>2</sub> CH(OH)CH(OH)CO(OH) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02044	*	*	CHOCH(OH)CH(OH)CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH(OH)CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02045	*	*	CHOCH(OH)CH(OH)CH(OH)(O·) → CHOCH(OH)CH(OH)(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02046	*	*	CH(OH) <sub>2</sub> CH(O·)CH(OH)CHO $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02047	*	*	CH(OH) <sub>2</sub> CH(O·)CH(OH)CHO → 0.500 CH · (OH) <sub>2</sub> + 0.500 CHOCH(OH)CHO + 0.500 CH(OH) <sub>2</sub> CHO + 0.500 CHOCH(OH)(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02048	*	*	CH(OH) <sub>2</sub> CH(OH)CH(O·)CHO $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(OH)COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A/R^b$	Reference/comment
R <sub>o</sub> 02049	*	*	CH(OH) <sub>2</sub> CH(OH)CH(O $\cdot$ )CHO $\rightarrow$ 0.500 CH(OH) <sub>2</sub> CH(OH)(OO $\cdot$ ) + 0.500 CHOCHO + 0.500 CH(OH) <sub>2</sub> CH(OH)CHO + 0.500 CH $\cdot$ (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 $\cdot$ 10 <sup>+02</sup>		
E <sub>o</sub> 00253	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)COCH(OH) <sub>2</sub>	1.3 $\cdot$ 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00254	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	9.1 $\cdot$ 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02050	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CHO $\rightarrow$ 0.500 + 0.500 + 0.500	1.0 $\cdot$ 10 <sup>-01</sup>		
R <sub>o</sub> 02051	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CHO + OH $\rightarrow$ 0.071 CHOCH(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.496 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CO(OO $\cdot$ ) + 0.198 CHOCH(OH)C(OH) <sub>2</sub> CH(OH)(O $\cdot$ ) + 0.197 CH(OH) <sub>2</sub> C(OH)(O $\cdot$ )CH(OH)CHO + 0.038 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(O $\cdot$ )CHO + H <sub>2</sub> O - 0.567 O <sub>2</sub>	1.8 $\cdot$ 10 <sup>+09</sup>		
R <sub>o</sub> 02052	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CHO + NO <sub>3</sub> $\rightarrow$ 0.071 CHOCH(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.496 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CO(OO $\cdot$ ) + 0.198 CHOCH(OH)C(OH) <sub>2</sub> CH(OH)(O $\cdot$ ) + 0.197 CH(OH) <sub>2</sub> C(OH)(O $\cdot$ )CH(OH)CHO + 0.038 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(O $\cdot$ )CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.567 O <sub>2</sub>	9.5 $\cdot$ 10 <sup>+06</sup>		
R <sub>o</sub> 02053	*	*	CHOCH(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)C(OH) <sub>2</sub> CH(OH)CHO + HO <sub>2</sub>	1.0 $\cdot$ 10 <sup>+03</sup>		
R <sub>o</sub> 02054	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CO(OO $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 $\cdot$ 10 <sup>+03</sup>		
R <sub>o</sub> 02055	*	*	CHOCH(OH)C(OH) <sub>2</sub> CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> CH(OH)CHO + HO <sub>2</sub>	5.0 $\cdot$ 10 <sup>+06</sup>		
R <sub>o</sub> 02056	*	*	CHOCH(OH)C(OH) <sub>2</sub> CH(OH)(O $\cdot$ ) $\rightarrow$ CHOCH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	5.0 $\cdot$ 10 <sup>+02</sup>		
R <sub>o</sub> 02057	*	*	CH(OH) <sub>2</sub> C(OH)(O $\cdot$ )CH(OH)CHO $\rightarrow$ 0.500 CH $\cdot$ (OH) <sub>2</sub> + 0.500 CO(OH)CH(OH)CHO + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CHOCH(OH)(OO $\cdot$ ) - 0.500 O <sub>2</sub>	5.0 $\cdot$ 10 <sup>+02</sup>		
R <sub>o</sub> 02058	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(O $\cdot$ )CHO $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCHO + HO <sub>2</sub>	5.0 $\cdot$ 10 <sup>+06</sup>		
R <sub>o</sub> 02059	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(O $\cdot$ )CHO $\rightarrow$ 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.500 CHOCHO + 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + 0.500 CH $\cdot$ (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 $\cdot$ 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00255	*	*	$\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{CH(OH)COCH(OH)}_2$	$1.3 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00256	*	*	$\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CH(OH)}_2$	$9.1 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02060	*	*	$\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CHO} \rightarrow 0.500 + 0.500$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 02061	*	*	$\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CHO} + \text{OH} \rightarrow$ $0.214 \text{ CHOC(OH)}_2\text{CH(OH)C(OH)}_2(\text{OO}\cdot) +$ $0.259 \text{ CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CO(OO}\cdot) +$ $0.261 \text{ CHOC(OH)}_2\text{CH(OH)CH(OH)(O}\cdot) +$ $0.055 \text{ CH(OH)}_2\text{CH(O}\cdot\text{)C(OH)}_2\text{CHO} +$ $0.211 \text{ CH(OH)}_2\text{CH(OH)C(OH)(O}\cdot\text{)CHO} + \text{H}_2\text{O} - 0.473 \text{ O}_2$	$1.5 \cdot 10^{+09}$		
R <sub>o</sub> 02062	*		$\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CHO} + \text{NO}_3 \rightarrow$ $0.214 \text{ CHOC(OH)}_2\text{CH(OH)C(OH)}_2(\text{OO}\cdot) +$ $0.259 \text{ CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CO(OO}\cdot) +$ $0.261 \text{ CHOC(OH)}_2\text{CH(OH)CH(OH)(O}\cdot) +$ $0.055 \text{ CH(OH)}_2\text{CH(O}\cdot\text{)C(OH)}_2\text{CHO} +$ $0.211 \text{ CH(OH)}_2\text{CH(OH)C(OH)(O}\cdot\text{)CHO} + \text{NO}_3^- + \text{H}^+ - 0.473 \text{ O}_2$	$9.5 \cdot 10^{+06}$		
R <sub>o</sub> 02063	*	*	$\text{CHOC(OH)}_2\text{CH(OH)C(OH)}_2(\text{OO}\cdot) \rightarrow \text{CO(OH)CH(OH)C(OH)}_2\text{CHO} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02064	*	*	$\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CO(OO}\cdot) \rightarrow$ $\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CO(OH)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02065	*	*	$\text{CHOC(OH)}_2\text{CH(OH)CH(OH)(O}\cdot) \xrightarrow{\text{O}_2} \text{CO(OH)CH(OH)C(OH)}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02066	*	*	$\text{CHOC(OH)}_2\text{CH(OH)CH(OH)(O}\cdot) \rightarrow$ $\text{CHOC(OH)}_2\text{CH(OH)(OO}\cdot) + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02067	*	*	$\text{CH(OH)}_2\text{CH(O}\cdot\text{)C(OH)}_2\text{CHO} \xrightarrow{\text{O}_2} \text{CH(OH)}_2\text{COC(OH)}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02068	*	*	$\text{CH(OH)}_2\text{CH(O}\cdot\text{)C(OH)}_2\text{CHO} \rightarrow$ $0.500 \text{ CH} \cdot (\text{OH})_2 + 0.500 \text{ CHOC(OH)}_2\text{CHO} + 0.500 \text{ CH(OH)}_2\text{CHO} +$ $0.500 \text{ CHOC(OH)}_2(\text{OO}\cdot) - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02069	*	*	$\text{CH(OH)}_2\text{CH(OH)C(OH)(O}\cdot\text{)CHO} \rightarrow$ $0.500 \text{ CH(OH)}_2\text{CH(OH)(OO}\cdot) + 0.500 \text{ CO(OH)CHO} +$ $0.500 \text{ CH(OH)}_2\text{CH(OH)CO(OH)} + 0.500 \text{ CH} \cdot (\text{OH})_2 - 0.500 \text{ O}_2 - 0.500 \text{ H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00257	*	*	$\text{CH(OH)}_2\text{COCOCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)}_2\text{C(OH)}_2\text{CH(OH)}_2$	$7.1 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02070	*	*	CH(OH) <sub>2</sub> COCOCHO $\rightarrow$ 0.250 CHO(OH) + 0.250 HO <sub>2</sub> + 0.250 CHOCOCO(OO $\cdot$ ) + 0.250 CH(OH) <sub>2</sub> CO(OO $\cdot$ ) + 0.250 CHOCO(OO $\cdot$ )	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 02071	*	*	CH(OH) <sub>2</sub> COCOCHO + OH $\rightarrow$ 0.155 CHOCOCOC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.448 CH(OH) <sub>2</sub> COCOCO(OO $\cdot$ ) + 0.397 CHOCOCOCH(OH)(O $\cdot$ ) + H <sub>2</sub> O - 0.603 O <sub>2</sub>	$8.2 \cdot 10^{+08}$		
R <sub>o</sub> 02072	*		CH(OH) <sub>2</sub> COCOCHO + NO <sub>3</sub> $\rightarrow$ 0.155 CHOCOCOC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.448 CH(OH) <sub>2</sub> COCOCO(OO $\cdot$ ) + 0.397 CHOCOCOCH(OH)(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.603 O <sub>2</sub>	$7.2 \cdot 10^{+06}$		
R <sub>o</sub> 02073	*	*	CHOCOCOC(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)COCOCHO + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02074	*	*	CH(OH) <sub>2</sub> COCOCO(OO $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> COCOCO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02075	*	*	CHOCOCOCH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)COCOCHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02076	*	*	CHOCOCOCH(OH)(O $\cdot$ ) $\rightarrow$ CHOCOCO(OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00258	*	*	CH(OH) <sub>2</sub> CH(OH)COCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)COCH(OH) <sub>2</sub>	$1.3 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00259	*	*	CH(OH) <sub>2</sub> CH(OH)COCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	$9.1 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02077	*	*	CH(OH) <sub>2</sub> CH(OH)COCHO $\rightarrow$ 0.500 + 0.500	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 02078	*	*	CH(OH) <sub>2</sub> CH(OH)COCHO + OH $\rightarrow$ 0.234 CHOCOCH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.035 CH(OH) <sub>2</sub> C(OH)(OO $\cdot$ )COCHO + 0.356 CH(OH) <sub>2</sub> CH(OH)COCO(OO $\cdot$ ) + 0.316 CHOCOCH(OH)CH(OH)(O $\cdot$ ) + 0.060 CH(OH) <sub>2</sub> CH(O $\cdot$ )COCHO + H <sub>2</sub> O - 0.624 O <sub>2</sub>	$1.2 \cdot 10^{+09}$		
R <sub>o</sub> 02079	*		CH(OH) <sub>2</sub> CH(OH)COCHO + NO <sub>3</sub> $\rightarrow$ 0.234 CHOCOCH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.035 CH(OH) <sub>2</sub> C(OH)(OO $\cdot$ )COCHO + 0.356 CH(OH) <sub>2</sub> CH(OH)COCO(OO $\cdot$ ) + 0.316 CHOCOCH(OH)CH(OH)(O $\cdot$ ) + 0.060 CH(OH) <sub>2</sub> CH(O $\cdot$ )COCHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.624 O <sub>2</sub>	$9.4 \cdot 10^{+06}$		
R <sub>o</sub> 02080	*	*	CHOCOCH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)CH(OH)COCHO + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02081	*	*	CH(OH) <sub>2</sub> C(OH)(OO $\cdot$ )COCHO $\rightarrow$ CH(OH) <sub>2</sub> COCOCHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02082	*	*	CH(OH) <sub>2</sub> CH(OH)COCO(OO $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> CH(OH)COCO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02083	*	*	CHOCOCH(OH)CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)CH(OH)COCHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02084	*	*	CHOCOCH(OH)CH(OH)(O $\cdot$ ) $\rightarrow$ CHOCOCH(OH)(OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02085	*	*	CH(OH) <sub>2</sub> CH(O $\cdot$ )COCHO $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCOCHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02086	*	*	$\text{CH(OH)}_2\text{CH(O}\cdot\text{)COCHO} \rightarrow 0.500 \text{ CH}\cdot(\text{OH})_2 + 0.500 \text{ CHOCOCHO} + 0.500 \text{ CH(OH)}_2\text{CHO} + 0.500 \text{ CHOCO(OO}\cdot\text{)} - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00260	*	*	$\text{CH(OH)}_2\text{COCH(OH)CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{CH(OH)COCH(OH)}_2$	$1.3 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00261	*	*	$\text{CH(OH)}_2\text{COCH(OH)CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CH(OH)}_2$	$9.1 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02087	*	*	$\text{CH(OH)}_2\text{COCH(OH)CHO} \rightarrow 0.500 + 0.500 + 0.500$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 02088	*	*	$\text{CH(OH)}_2\text{COCH(OH)CHO} + \text{OH} \rightarrow 0.106 \text{ CHOCH(OH)COC(OH)}_2(\text{OO}\cdot) + 0.036 \text{ CH(OH)}_2\text{COC(OH)(OO}\cdot\text{)CHO} + 0.582 \text{ CH(OH)}_2\text{COCH(OH)CO(OO}\cdot\text{)} + 0.233 \text{ CHOCH(OH)COCH(OH)(O}\cdot\text{)} + 0.044 \text{ CH(OH)}_2\text{COCH(O}\cdot\text{)CHO} + \text{H}_2\text{O} - 0.723 \text{ O}_2$	$1.4 \cdot 10^{+09}$		
R <sub>o</sub> 02089	*		$\text{CH(OH)}_2\text{COCH(OH)CHO} + \text{NO}_3 \rightarrow 0.106 \text{ CHOCH(OH)COC(OH)}_2(\text{OO}\cdot) + 0.036 \text{ CH(OH)}_2\text{COC(OH)(OO}\cdot\text{)CHO} + 0.582 \text{ CH(OH)}_2\text{COCH(OH)CO(OO}\cdot\text{)} + 0.233 \text{ CHOCH(OH)COCH(OH)(O}\cdot\text{)} + 0.044 \text{ CH(OH)}_2\text{COCH(O}\cdot\text{)CHO} + \text{NO}_3^- + \text{H}^+ - 0.723 \text{ O}_2$	$9.5 \cdot 10^{+06}$		
R <sub>o</sub> 02090	*	*	$\text{CHOCH(OH)COC(OH)}_2(\text{OO}\cdot) \rightarrow \text{CO(OH)COCH(OH)CHO} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02091	*	*	$\text{CH(OH)}_2\text{COC(OH)(OO}\cdot\text{)CHO} \rightarrow \text{CH(OH)}_2\text{COCOCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02092	*	*	$\text{CH(OH)}_2\text{COCH(OH)CO(OO}\cdot\text{)} \rightarrow \text{CH(OH)}_2\text{COCH(OH)CO(OH)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02093	*	*	$\text{CHOCH(OH)COCH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CO(OH)COCH(OH)CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02094	*	*	$\text{CHOCH(OH)COCH(OH)(O}\cdot\text{)} \rightarrow \text{CHOCH(OH)CO(OO}\cdot\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02095	*	*	$\text{CH(OH)}_2\text{COCH(O}\cdot\text{)CHO} \xrightarrow{\text{O}_2} \text{CH(OH)}_2\text{COCOCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02096	*	*	$\text{CH(OH)}_2\text{COCH(O}\cdot\text{)CHO} \rightarrow 0.500 \text{ CH(OH)}_2\text{CO(OO}\cdot\text{)} + 0.500 \text{ CHOCHO} + 0.500 \text{ CH(OH)}_2\text{COCHO} + 0.500 \text{ CH}\cdot(\text{OH})_2 - 0.500 \text{ O}_2 - 0.500 \text{ H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00262	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)}_2\text{C(OH)}_2\text{CH(OH)}_2$	$7.1 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02097	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{COCHO} \rightarrow 0.250 \text{ CHO(OH)} + 0.250 \text{ HO}_2 + 0.250 \text{ CHOCOC(OH)}_2(\text{OO}\cdot) + 0.250 \text{ CH(OH)}_2\text{C(OH)}_2(\text{OO}\cdot) + 0.250 \text{ CHOCO(OO}\cdot\text{)}$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 02098	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{COCHO} + \text{OH} \rightarrow 0.094 \text{ CHOCOC(OH)}_2\text{C(OH)}_2(\text{OO}\cdot) + 0.343 \text{ CH(OH)}_2\text{C(OH)}_2\text{COCO(OO}\cdot\text{)} + 0.304 \text{ CHOCOC(OH)}_2\text{CH(OH)(O}\cdot\text{)} + 0.259 \text{ CH(OH)}_2\text{C(OH)(O}\cdot\text{)COCHO} + \text{H}_2\text{O} - 0.437 \text{ O}_2$	$1.2 \cdot 10^{+09}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02099	*		CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCHO + NO <sub>3</sub> → 0.094 CHOCOC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.343 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCO(OO·) + 0.304 CHOCOC(OH) <sub>2</sub> CH(OH)(O·) + 0.259 CH(OH) <sub>2</sub> C(OH)(O·)COCHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.437 O <sub>2</sub>	7.3 · 10 <sup>+06</sup>		
R <sub>o</sub> 02100	*	*	CHOCOC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CO(OH)C(OH) <sub>2</sub> COCHO + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02101	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCO(OO·) → CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02102	*	*	CHOCOC(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02103	*	*	CHOCOC(OH) <sub>2</sub> CH(OH)(O·) → CHOCOC(OH) <sub>2</sub> (OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02104	*	*	CH(OH) <sub>2</sub> C(OH)(O·)COCHO → 0.500 CH·(OH) <sub>2</sub> + 0.500 CO(OH)COCHO + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CHOCO(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00263	*	*	CHOC(OH) <sub>2</sub> COCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	7.1 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02105	*	*	CHOC(OH) <sub>2</sub> COCHO → 0.250 CHO(OO·) + 0.250 CHOCOC(OH) <sub>2</sub> (OO·) + 0.250 CHOC(OH) <sub>2</sub> (OO·) + 0.250 CHOCO(OO·)	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 02106	*	*	CHOC(OH) <sub>2</sub> COCHO + OH → 0.325 CHOCOC(OH) <sub>2</sub> CO(OO·) + 0.410 CHOC(OH) <sub>2</sub> COCO(OO·) + 0.265 CHOCOC(OH)(O·)CHO + H <sub>2</sub> O - 0.735 O <sub>2</sub>	1.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 02107	*		CHOC(OH) <sub>2</sub> COCHO + NO <sub>3</sub> → 0.325 CHOCOC(OH) <sub>2</sub> CO(OO·) + 0.410 CHOC(OH) <sub>2</sub> COCO(OO·) + 0.265 CHOCOC(OH)(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.735 O <sub>2</sub>	6.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02108	*	*	CHOCOC(OH) <sub>2</sub> CO(OO·) → CO(OH)C(OH) <sub>2</sub> COCHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02109	*	*	CHOC(OH) <sub>2</sub> COCO(OO·) → CO(OH)COC(OH) <sub>2</sub> CHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02110	*	*	CHOCOC(OH)(O·)CHO → 0.500 CHOCO(OO·) + 0.500 CO(OH)CHO + 0.500 CO(OH)COCHO + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00264	*	*	CHOCH(OH)C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)COCH(OH) <sub>2</sub>	1.3 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00265	*	*	CHOCH(OH)C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	9.1 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02111	*	*	CHOCH(OH)C(OH) <sub>2</sub> CHO → 0.500 + 0.500	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 02112	*	*	CHOCH(OH)C(OH) <sub>2</sub> CHO + OH → 0.546 CHOC(OH) <sub>2</sub> CH(OH)CO(OO·) + 0.227 CHOCH(OH)C(OH) <sub>2</sub> CO(OO·) + 0.041 CHOC(OH) <sub>2</sub> CH(O·)CHO + 0.186 CHOCH(OH)C(OH)(O·)CHO + H <sub>2</sub> O - 0.773 O <sub>2</sub>	1.7 · 10 <sup>+09</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02113	*		CHOCH(OH)C(OH) <sub>2</sub> CHO + NO <sub>3</sub> → 0.546 CHOC(OH) <sub>2</sub> CH(OH)CO(OO·) + 0.227 CHOCH(OH)C(OH) <sub>2</sub> CO(OO·) + 0.041 CHOC(OH) <sub>2</sub> CH(O·)CHO + 0.186 CHOCH(OH)C(OH)(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.773 O <sub>2</sub>	7.8 · 10 <sup>+06</sup>		
R <sub>o</sub> 02114	*	*	CHOC(OH) <sub>2</sub> CH(OH)CO(OO·) → CO(OH)CH(OH)C(OH) <sub>2</sub> CHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02115	*	*	CHOCH(OH)C(OH) <sub>2</sub> CO(OO·) → CO(OH)C(OH) <sub>2</sub> CH(OH)CHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02116	*	*	CHOC(OH) <sub>2</sub> CH(O·)CHO $\xrightarrow{O_2}$ CHOC(OH) <sub>2</sub> COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02117	*	*	CHOC(OH) <sub>2</sub> CH(O·)CHO → 0.500 CHOC(OH) <sub>2</sub> (OO·) + 0.500 CHOCHO + 0.500 CHOC(OH) <sub>2</sub> CHO + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02118	*	*	CHOCH(OH)C(OH)(O·)CHO → 0.500 CHOCH(OH)(OO·) + 0.500 CO(OH)CHO + 0.500 CO(OH)CH(OH)CHO + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00266	*	*	CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	7.1 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02119	*	*	CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO → 0.250 CHO(OO·) + 0.250 CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.500 CHOC(OH) <sub>2</sub> (OO·)	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 02120	*	*	CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + OH → 0.550 CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OO·) + 0.450 CHOC(OH) <sub>2</sub> C(OH)(O·)CHO + H <sub>2</sub> O - 0.550 O <sub>2</sub>	1.3 · 10 <sup>+09</sup>		
R <sub>o</sub> 02121	*		CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + NO <sub>3</sub> → 0.550 CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OO·) + 0.450 CHOC(OH) <sub>2</sub> C(OH)(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.550 O <sub>2</sub>	6.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02122	*	*	CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OO·) → CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02123	*	*	CHOC(OH) <sub>2</sub> C(OH)(O·)CHO → 0.500 CHOC(OH) <sub>2</sub> (OO·) + 0.500 CO(OH)CHO + 0.500 CO(OH)C(OH) <sub>2</sub> CHO + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02124	*	*	CH <sub>3</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + OH → 0.395 CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> (OO·) + 0.192 CH <sub>3</sub> CH(OO·)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + 0.413 CH <sub>3</sub> CH <sub>2</sub> C(OH)(O·)CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.587 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 02125	*		CH <sub>3</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>3</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02126	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ 0.200 $\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}_2\text{CH}_2(\text{O}\cdot) + 0.550 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}_2\text{CHO} +$ 0.250 $\text{CH}_2(\text{OH})\text{CH}_2\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02127	*	*	$\text{CH}_3\text{CH}(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{O}^-) \xrightarrow{\text{RO}_2}$ 0.200 $\text{CH}_3\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + 0.550 \text{CH}_3\text{COC}(\text{OH})_2\text{CO}(\text{O}^-) +$ 0.250 $\text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02128	*	*	$\text{CH}_3\text{CH}_2\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{O}^-) \rightarrow 0.500 \text{CH}_3\text{CH}_2(\text{OO}\cdot) +$ 0.500 $\text{CO}(\text{OH})\text{CO}(\text{O}^-) + 0.500 \text{CH}_3\text{CH}_2\text{CO}(\text{OH}) + 0.500 \cdot \text{CO}(\text{O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02129	*	*	$\text{CH}_3\text{CH}_2\text{C}(\text{OH})_2\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_3\text{CH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02130	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02131	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02132	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{O}^-) \xrightarrow{\text{O}_2} \text{CH}_3\text{COC}(\text{OH})_2\text{CO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02133	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{O}^-) \rightarrow$ 0.500 $\text{CH}_3(\text{OO}\cdot) + 0.500 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CHO} + 0.500 \text{CH}_3\text{CHO} +$ 0.500 $\text{CO}(\text{O}^-)\text{C}(\text{OH})_2(\text{OO}\cdot) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02134	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{CH}_2\text{CO}(\text{O}^-) + \text{OH} \rightarrow 0.515 \text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) +$ 0.125 $\text{CH}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CH}_2\text{CO}(\text{O}^-) +$ 0.119 $\text{CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) +$ 0.241 $\text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.759 \text{O}_2$	$1.7 \cdot 10^{+09}$		
R <sub>o</sub> 02135	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{CH}_2\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow \text{CH}(\text{OH})_2\text{CH}_2\text{CH}_2\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02136	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CO}(\text{O}^-) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02137	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CH}_2\text{CO}(\text{O}^-) \xrightarrow{\text{RO}_2}$ 0.200 $\text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CH}_2\text{CO}(\text{O}^-) + 0.550 \text{CH}(\text{OH})_2\text{COCH}_2\text{CO}(\text{O}^-) +$ 0.250 $\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02138	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) \rightarrow$ 2.000 $\text{CH}(\text{OH})_2\text{CH}_2\text{CHO} + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 02139	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{RO}_2}$ 0.200 $\text{CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) + 0.550 \text{CH}(\text{OH})_2\text{CH}_2\text{COCO}(\text{O}^-) +$ 0.250 $\text{CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{OH})\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02140	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{CH}_2\text{CH}_2\text{CO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02141	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{CH}_2\text{CH}_2(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02142	*		$\text{CH}(\text{OH})_2\text{CH}_2\text{CH}_2\text{CO}(\text{O}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CH}_2\text{CH}_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02143	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CH}_2\text{CO}(\text{O}^-) \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{COCH}_2\text{CO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02144	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CH}_2\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CH}\cdot(\text{OH})_2 + 0.500 \text{CO}(\text{O}^-)\text{CH}_2\text{CHO} + 0.500 \text{CH}(\text{OH})_2\text{CHO} +$ $0.500 \text{CO}(\text{O}^-)\text{CH}_2(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02145	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{CH}_2\text{COCO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02146	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) \rightarrow 0.500 \text{CH}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) +$ $0.500 \text{CO}(\text{O}^-)\text{CHO} + 0.500 \text{CH}(\text{OH})_2\text{CH}_2\text{CHO} + 0.500 \cdot \text{CO}(\text{O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02147	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}_2\text{CO}(\text{O}^-) + \text{OH} \rightarrow$ $0.362 \text{CO}(\text{O}^-)\text{CH}_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.041 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) +$ $0.104 \text{CO}(\text{O}^-)\text{CH}_2\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) +$ $0.493 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CH}_2\text{CO}(\text{O}^-) + \text{H}_2\text{O} - 0.403 \text{O}_2$	$8.0 \cdot 10^{+08}$		
R <sub>o</sub> 02148	*		$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}_2\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}_2\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02149	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{CH}_2\text{C}(\text{OH})_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02150	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) \rightarrow$ $2.000 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CHO} + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 02151	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) +$ $0.550 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCO}(\text{O}^-) +$ $0.250 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02152	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{CH}_2\text{C}(\text{OH})_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02153	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{CH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02154	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CH}_2\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CO}(\text{OH})\text{CH}_2\text{CO}(\text{O}^-) + 0.500 \text{CH}_2(\text{OH})\text{CO}(\text{OH}) +$ $0.500 \text{CO}(\text{O}^-)\text{CH}_2(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02155	*		$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}_2\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02156	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02157	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O $\cdot$ )CO(O $^-$ ) $\rightarrow$ 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.500 CO(O $^-$ )CHO + 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CHO + 0.500 $\cdot$ CO(O $^-$ ) - 0.500 O <sub>2</sub>	5.0 $\cdot$ 10 <sup>+02</sup>		
R <sub>o</sub> 02158	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH) <sub>2</sub> CO(O $^-$ ) + OH $\rightarrow$ 0.728 CO(O $^-$ )C(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)(OO $\cdot$ ) + 0.036 CH <sub>2</sub> (OH)CH(OO $\cdot$ )C(OH) <sub>2</sub> CO(O $^-$ ) + 0.040 CO(O $^-$ )C(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) + 0.195 CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH)(O $\cdot$ )CO(O $^-$ ) + H <sub>2</sub> O - 0.764 O <sub>2</sub>	2.3 $\cdot$ 10 <sup>+09</sup>		
R <sub>o</sub> 02159	*		CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH) <sub>2</sub> CO(O $^-$ ) + NO <sub>3</sub> $\rightarrow$ CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH) <sub>2</sub> CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	2.0 $\cdot$ 10 <sup>+07</sup>		
R <sub>o</sub> 02160	*	*	CO(O $^-$ )C(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)(OO $\cdot$ ) $\rightarrow$ CO(O $^-$ )C(OH) <sub>2</sub> CH <sub>2</sub> CHO + HO <sub>2</sub>	2.0 $\cdot$ 10 <sup>+02</sup>		
R <sub>o</sub> 02161	*	*	CH <sub>2</sub> (OH)CH(OO $\cdot$ )C(OH) <sub>2</sub> CO(O $^-$ ) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(O $\cdot$ )C(OH) <sub>2</sub> CO(O $^-$ ) + 0.550 CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CO(O $^-$ ) + 0.250 CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CO(O $^-$ ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 $\cdot$ 10 <sup>+08</sup>		
R <sub>o</sub> 02162	*	*	CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH)(O $\cdot$ )CO(O $^-$ ) $\rightarrow$ 0.500 CH <sub>2</sub> (OH)CH <sub>2</sub> (OO $\cdot$ ) + 0.500 CO(OH)CO(O $^-$ ) + 0.500 CH <sub>2</sub> (OH)CH <sub>2</sub> CO(OH) + 0.500 $\cdot$ CO(O $^-$ ) - 0.500 O <sub>2</sub>	5.0 $\cdot$ 10 <sup>+02</sup>		
R <sub>o</sub> 02163	*		CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH) <sub>2</sub> CO(O $\cdot$ ) $\rightarrow$ CH <sub>2</sub> (OH)CH <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 $\cdot$ 10 <sup>+02</sup>		
R <sub>o</sub> 02164	*	*	CH <sub>2</sub> (OH)CH(O $\cdot$ )C(OH) <sub>2</sub> CO(O $^-$ ) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CO(O $^-$ ) + HO <sub>2</sub>	5.0 $\cdot$ 10 <sup>+06</sup>		
R <sub>o</sub> 02165	*	*	CH <sub>2</sub> (OH)CH(O $\cdot$ )C(OH) <sub>2</sub> CO(O $^-$ ) $\rightarrow$ 0.500 CH <sub>2</sub> (OH) $\cdot$ + 0.500 CO(O $^-$ )C(OH) <sub>2</sub> CHO + 0.500 CH <sub>2</sub> (OH)CHO + 0.500 CO(O $^-$ )C(OH) <sub>2</sub> (OO $\cdot$ ) - 0.500 O <sub>2</sub>	5.0 $\cdot$ 10 <sup>+02</sup>		
R <sub>o</sub> 02166	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(O $^-$ ) + OH $\rightarrow$ 0.494 CO(O $^-$ )CH(OH)CH(OH)CH(OH)(OO $\cdot$ ) + 0.223 CH <sub>2</sub> (OH)C(OH)(OO $\cdot$ )CH(OH)CO(O $^-$ ) + 0.090 CH <sub>2</sub> (OH)CH(OH)C(OH)(OO $\cdot$ )CO(O $^-$ ) + 0.062 CO(O $^-$ )CH(OH)CH(OH)CH <sub>2</sub> (O $\cdot$ ) + 0.062 CH <sub>2</sub> (OH)CH(O $\cdot$ )CH(OH)CO(O $^-$ ) + 0.070 CH <sub>2</sub> (OH)CH(OH)CH(O $\cdot$ )CO(O $^-$ ) + H <sub>2</sub> O - 0.806 O <sub>2</sub>	1.4 $\cdot$ 10 <sup>+09</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02167	*		CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(O <sup>·</sup> ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 02168	*	*	CO(O <sup>-</sup> )CH(OH)CH(OH)CH(OH)(OO <sup>·</sup> ) → CO(O <sup>-</sup> )CH(OH)CH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02169	*	*	CH <sub>2</sub> (OH)C(OH)(OO <sup>·</sup> )CH(OH)CO(O <sup>-</sup> ) → CH <sub>2</sub> (OH)COCH(OH)CO(O <sup>-</sup> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02170	*	*	CH <sub>2</sub> (OH)CH(OH)C(OH)(OO <sup>·</sup> )CO(O <sup>-</sup> ) → CH <sub>2</sub> (OH)CH(OH)COCO(O <sup>-</sup> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02171	*	*	CO(O <sup>-</sup> )CH(OH)CH(OH)CH <sub>2</sub> (O <sup>·</sup> ) $\xrightarrow{O_2}$ CO(O <sup>-</sup> )CH(OH)CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02172	*	*	CO(O <sup>-</sup> )CH(OH)CH(OH)CH <sub>2</sub> (O <sup>·</sup> ) → CO(O <sup>-</sup> )CH(OH)CH(OH)(OO <sup>·</sup> ) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02173	*		CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(O <sup>·</sup> ) → CH <sub>2</sub> (OH)CH(OH)CH(OH)(OO <sup>·</sup> ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02174	*	*	CH <sub>3</sub> CH(OH)CH(OH)CO(O <sup>-</sup> ) + OH → 0.138 CO(O <sup>-</sup> )CH(OH)CH(OH)CH <sub>2</sub> (OO <sup>·</sup> ) + 0.608 CH <sub>3</sub> C(OH)(OO <sup>·</sup> )CH(OH)CO(O <sup>-</sup> ) + 0.104 CH <sub>3</sub> CH(OH)C(OH)(OO <sup>·</sup> )CO(O <sup>-</sup> ) + 0.073 CH <sub>3</sub> CH(O <sup>·</sup> )CH(OH)CO(O <sup>-</sup> ) + 0.076 CH <sub>3</sub> CH(OH)CH(O <sup>·</sup> )CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.851 O <sub>2</sub>	1.3 · 10 <sup>+09</sup>		
R <sub>o</sub> 02175	*		CH <sub>3</sub> CH(OH)CH(OH)CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>3</sub> CH(OH)CH(OH)CO(O <sup>·</sup> ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 02176	*	*	CO(O <sup>-</sup> )CH(OH)CH(OH)CH <sub>2</sub> (OO <sup>·</sup> ) $\xrightarrow{RO_2}$ 0.200 CO(O <sup>-</sup> )CH(OH)CH(OH)CH <sub>2</sub> (O <sup>·</sup> ) + 0.550 CO(O <sup>-</sup> )CH(OH)CH(OH)CHO + 0.250 CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(O <sup>-</sup> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02177	*	*	CH <sub>3</sub> C(OH)(OO <sup>·</sup> )CH(OH)CO(O <sup>-</sup> ) → CH <sub>3</sub> COCH(OH)CO(O <sup>-</sup> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02178	*	*	CH <sub>3</sub> CH(OH)C(OH)(OO <sup>·</sup> )CO(O <sup>-</sup> ) → CH <sub>3</sub> CH(OH)COCO(O <sup>-</sup> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02179	*	*	CH <sub>3</sub> CH(O <sup>·</sup> )CH(OH)CO(O <sup>-</sup> ) $\xrightarrow{O_2}$ CH <sub>3</sub> COCH(OH)CO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A/R^b$	Reference/comment
R <sub>o</sub> 02180	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CHO} + 0.500 \text{CH}_3\text{CHO} +$ $0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})(\text{OO}\cdot) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02181	*		$\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00267	*	*	$\text{CH}_2(\text{OH})\text{COCOCO}(\text{O}^-) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCO}(\text{O}^-)$	$4.5 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00268	*	*	$\text{CH}_2(\text{OH})\text{COCOCO}(\text{O}^-) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CO}(\text{O}^-)$	$1.5 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00269	*	*	$\text{CH}_2(\text{OH})\text{COCOCO}(\text{O}^-) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}^-)$	$1.3 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02182	*	*	$\text{CH}_2(\text{OH})\text{COCOCO}(\text{O}^-) + \text{OH} \rightarrow 0.782 \text{CO}(\text{O}^-)\text{COCOCH}(\text{OH})(\text{OO}\cdot) +$ $0.218 \text{CO}(\text{O}^-)\text{COCOCH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.782 \text{O}_2$	$3.5 \cdot 10^{+08}$		
R <sub>o</sub> 02183	*		$\text{CH}_2(\text{OH})\text{COCOCO}(\text{O}^-) + \text{NO}_3 \rightarrow \text{CH}_2(\text{OH})\text{COCOCO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02184	*	*	$\text{CO}(\text{O}^-)\text{COCOCH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{COCOCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02185	*	*	$\text{CO}(\text{O}^-)\text{COCOCH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{COCOCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02186	*	*	$\text{CO}(\text{O}^-)\text{COCOCH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{COCO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02187	*		$\text{CH}_2(\text{OH})\text{COCOCO}(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{COCO}(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02188	*	*	$\text{CH}_3\text{COCH}(\text{OH})\text{CO}(\text{O}^-) + \text{OH} \rightarrow$ $0.357 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCH}_2(\text{OO}\cdot) + 0.269 \text{CH}_3\text{COC}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{O}^-) +$ $0.374 \text{CH}_3\text{COCH}(\text{O}\cdot)\text{CO}(\text{O}^-) + \text{H}_2\text{O} - 0.626 \text{O}_2$	$2.3 \cdot 10^{+08}$		
R <sub>o</sub> 02189	*		$\text{CH}_3\text{COCH}(\text{OH})\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow \text{CH}_3\text{COCH}(\text{OH})\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02190	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCH}_2(\text{O}\cdot) + 0.550 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCHO} +$ $0.250 \text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02191	*	*	$\text{CH}_3\text{COC}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{O}^-) \rightarrow \text{CH}_3\text{COCOCO}(\text{O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02192	*		$\text{CH}_3\text{COCH}(\text{OH})\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_3\text{COCH}(\text{OH})(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02193	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02194	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00270	*	*	$\text{CH}_3\text{COCOCO}(\text{O}^-) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C}(\text{OH})_2\text{COCO}(\text{O}^-)$	$7.5 \cdot 10^{-01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00271	*	*	$\text{CH}_3\text{COCOCO}(\text{O}^-) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{COC}(\text{OH})_2\text{CO}(\text{O}^-)$	$7.5 \cdot 10^{-01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02195	*	*	$\text{CH}_3\text{COCOCO}(\text{O}^-) + \text{OH} \rightarrow \text{CO}(\text{O}^-)\text{COCOCH}_2(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$6.9 \cdot 10^{+07}$		
R <sub>o</sub> 02196	*		$\text{CH}_3\text{COCOCO}(\text{O}^-) + \text{NO}_3 \rightarrow \text{CH}_3\text{COCOCO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02197	*	*	$\text{CO(O}^-\text{)COCOCH}_2\text{(OO}\cdot\text{)} \xrightarrow{\text{RO}_2}$ 0.200 $\text{CO(O}^-\text{)COCOCH}_2\text{(O}\cdot\text{)} + 0.550 \text{CO(O}^-\text{)COCOCHO} +$ 0.250 $\text{CH}_2\text{(OH)COCOCO(O}^-\text{)} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02198	*		$\text{CH}_3\text{COCOCO(O}\cdot\text{)} \rightarrow \text{CH}_3\text{COCO(OO}\cdot\text{)} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02199	*	*	$\text{CH}_2\text{(OH)CH(OH)COCO(O}^-\text{)} + \text{OH} \rightarrow$ 0.662 $\text{CO(O}^-\text{)COCH(OH)CH(OH)(OO}\cdot\text{)} +$ 0.157 $\text{CH}_2\text{(OH)C(OH)(OO}\cdot\text{)COCO(O}^-\text{)} +$ 0.097 $\text{CO(O}^-\text{)COCH(OH)CH}_2\text{(O}\cdot\text{)} + 0.084 \text{CH}_2\text{(OH)CH(O}\cdot\text{)COCO(O}^-\text{)} +$ $\text{H}_2\text{O} - 0.819 \text{O}_2$	$9.1 \cdot 10^{+08}$		
R <sub>o</sub> 02200	*		$\text{CH}_2\text{(OH)CH(OH)COCO(O}^-\text{)} + \text{NO}_3 \rightarrow$ $\text{CH}_2\text{(OH)CH(OH)COCO(O}\cdot\text{)} + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02201	*	*	$\text{CO(O}^-\text{)COCH(OH)CH(OH)(OO}\cdot\text{)} \rightarrow \text{CO(O}^-\text{)COCH(OH)CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02202	*	*	$\text{CH}_2\text{(OH)C(OH)(OO}\cdot\text{)COCO(O}^-\text{)} \rightarrow \text{CH}_2\text{(OH)COCOCO(O}^-\text{)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02203	*	*	$\text{CO(O}^-\text{)COCH(OH)CH}_2\text{(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CO(O}^-\text{)COCH(OH)CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02204	*	*	$\text{CO(O}^-\text{)COCH(OH)CH}_2\text{(O}\cdot\text{)} \rightarrow \text{CO(O}^-\text{)COCH(OH)(OO}\cdot\text{)} + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02205	*		$\text{CH}_2\text{(OH)CH(OH)COCO(O}\cdot\text{)} \rightarrow \text{CH}_2\text{(OH)CH(OH)CO(OO}\cdot\text{)} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00272	*	*	$\text{CH}_2\text{(OH)COCH(OH)CO(O}^-\text{)} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2\text{(OH)C(OH)}_2\text{CH(OH)CO(O}^-\text{)}$	$1.4 \cdot 10^{-01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02206	*	*	$\text{CH}_2\text{(OH)COCH(OH)CO(O}^-\text{)} + \text{OH} \rightarrow$ 0.592 $\text{CO(O}^-\text{)CH(OH)COCH(OH)(OO}\cdot\text{)} +$ 0.108 $\text{CH}_2\text{(OH)COC(OH)(OO}\cdot\text{)CO(O}^-\text{)} +$ 0.141 $\text{CO(O}^-\text{)CH(OH)COCH}_2\text{(O}\cdot\text{)} + 0.159 \text{CH}_2\text{(OH)COCH(O}\cdot\text{)CO(O}^-\text{)} +$ $\text{H}_2\text{O} - 0.700 \text{O}_2$	$5.3 \cdot 10^{+08}$		
R <sub>o</sub> 02207	*		$\text{CH}_2\text{(OH)COCH(OH)CO(O}^-\text{)} + \text{NO}_3 \rightarrow$ $\text{CH}_2\text{(OH)COCH(OH)CO(O}\cdot\text{)} + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02208	*	*	$\text{CO(O}^-\text{)CH(OH)COCH(OH)(OO}\cdot\text{)} \rightarrow \text{CO(O}^-\text{)CH(OH)COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02209	*	*	$\text{CH}_2\text{(OH)COC(OH)(OO}\cdot\text{)CO(O}^-\text{)} \rightarrow \text{CH}_2\text{(OH)COCOCO(O}^-\text{)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02210	*		$\text{CH}_2\text{(OH)COCH(OH)CO(O}\cdot\text{)} \rightarrow \text{CH}_2\text{(OH)COCH(OH)(OO}\cdot\text{)} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02211	*	*	$\text{CH}_3\text{CH(OH)COCO(O}^-\text{)} + \text{OH} \rightarrow$ 0.261 $\text{CO(O}^-\text{)COCH(OH)CH}_2\text{(OO}\cdot\text{)} + 0.602 \text{CH}_3\text{C(OH)(OO}\cdot\text{)COCO(O}^-\text{)} +$ 0.137 $\text{CH}_3\text{CH(O}\cdot\text{)COCO(O}^-\text{)} + \text{H}_2\text{O} - 0.863 \text{O}_2$	$5.9 \cdot 10^{+08}$		
R <sub>o</sub> 02212	*		$\text{CH}_3\text{CH(OH)COCO(O}^-\text{)} + \text{NO}_3 \rightarrow \text{CH}_3\text{CH(OH)COCO(O}\cdot\text{)} + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02213	*	*	$\text{CO}(\text{O}^-)\text{COCH}(\text{OH})\text{CH}_2(\text{OO}\cdot) \xrightarrow{RO_2}$ 0.200 $\text{CO}(\text{O}^-)\text{COCH}(\text{OH})\text{CH}_2(\text{O}\cdot) + 0.550 \text{CO}(\text{O}^-)\text{COCH}(\text{OH})\text{CHO} +$ 0.250 $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02214	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{COCO}(\text{O}^-) \rightarrow \text{CH}_3\text{COCOCO}(\text{O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02215	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{COCO}(\text{O}^-) \xrightarrow{O_2} \text{CH}_3\text{COCOCO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02216	*	*	$\text{CH}_3\text{CH}(\text{O}\cdot)\text{COCO}(\text{O}^-) \rightarrow 0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CO}(\text{O}^-)\text{COCHO} +$ 0.500 $\text{CH}_3\text{CHO} + 0.500 \text{CO}(\text{O}^-)\text{CO}(\text{OO}\cdot) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02217	*		$\text{CH}_3\text{CH}(\text{OH})\text{COCO}(\text{O}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00273	*	*	$\text{CO}(\text{O}^-)\text{COCH}_2\text{CHO} \xrightleftharpoons{H_2O} \text{CH}(\text{OH})_2\text{CH}_2\text{COCO}(\text{O}^-)$	$9.0 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02218	*	*	$\text{CO}(\text{O}^-)\text{COCH}_2\text{CHO} + \text{OH} \rightarrow \text{CO}(\text{O}^-)\text{COCH}_2\text{CO}(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$2.0 \cdot 10^{+09}$		
R <sub>o</sub> 02219	*		$\text{CO}(\text{O}^-)\text{COCH}_2\text{CHO} + \text{NO}_3 \rightarrow \text{CHOCH}_2\text{COCO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02220	*	*	$\text{CO}(\text{O}^-)\text{COCH}_2\text{CO}(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}_2\text{COCO}(\text{O}^-) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02221	*		$\text{CHOCH}_2\text{COCO}(\text{O}\cdot) \rightarrow \text{CHOCH}_2\text{CO}(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00274	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{COCHO} \xrightleftharpoons{H_2O} \text{CH}(\text{OH})_2\text{COCH}_2\text{CO}(\text{O}^-)$	$1.4 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00275	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{COCHO} \xrightleftharpoons{H_2O} \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2\text{CO}(\text{O}^-)$	$3.3 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02222	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{COCHO} + \text{OH} \rightarrow 0.064 \text{CO}(\text{O}^-)\text{CH}(\text{OO}\cdot)\text{COCHO} +$ 0.936 $\text{CO}(\text{O}^-)\text{CH}_2\text{COCO}(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$4.8 \cdot 10^{+08}$		
R <sub>o</sub> 02223	*		$\text{CO}(\text{O}^-)\text{CH}_2\text{COCHO} + \text{NO}_3 \rightarrow \text{CHOCOCH}_2\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02224	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OO}\cdot)\text{COCHO} + \text{CO}(\text{O}^-)\text{CH}(\text{OO}\cdot)\text{COCHO} \rightarrow$ 2.000 $\text{CHOCOCHO} + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 02225	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OO}\cdot)\text{COCHO} \xrightarrow{RO_2}$ 0.200 $\text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{COCHO} + 0.550 \text{CO}(\text{O}^-)\text{COCOCHO} +$ 0.250 $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02226	*	*	$\text{CO}(\text{O}^-)\text{CH}_2\text{COCO}(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{COCH}_2\text{CO}(\text{O}^-) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02227	*		$\text{CHOCOCH}_2\text{CO}(\text{O}\cdot) \rightarrow \text{CHOCOCH}_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02228	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{COCHO} \xrightarrow{O_2} \text{CO}(\text{O}^-)\text{COCOCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02229	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{COCHO} \rightarrow 0.500 \cdot \text{CO}(\text{O}^-) + 0.500 \text{CHOCOCHO} +$ 0.500 $\text{CO}(\text{O}^-)\text{CHO} + 0.500 \text{CHOCO}(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00276	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}_2\text{CHO} \xrightleftharpoons{H_2O} \text{CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{OH})\text{CO}(\text{O}^-)$	$2.5 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02230	*	*	CO(O <sup>-</sup> )CH(OH)CH <sub>2</sub> CHO + OH → 0.092 CO(O <sup>-</sup> )C(OH)(OO $\cdot$ )CH <sub>2</sub> CHO + 0.031 CO(O <sup>-</sup> )CH(OH)CH(OO $\cdot$ )CHO + 0.841 CO(O <sup>-</sup> )CH(OH)CH <sub>2</sub> CO(OO $\cdot$ ) + 0.037 CO(O <sup>-</sup> )CH(O $\cdot$ )CH <sub>2</sub> CHO + H <sub>2</sub> O - 0.963 O <sub>2</sub>	2.8 · 10 <sup>+09</sup>		
R <sub>o</sub> 02231	*		CO(O <sup>-</sup> )CH(OH)CH <sub>2</sub> CHO + NO <sub>3</sub> → CHOCH <sub>2</sub> CH(OH)CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 02232	*	*	CO(O <sup>-</sup> )C(OH)(OO $\cdot$ )CH <sub>2</sub> CHO → CO(O <sup>-</sup> )COCH <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02233	*	*	CO(O <sup>-</sup> )CH(OH)CH(OO $\cdot$ )CHO $\xrightarrow{RO_2}$ 0.200 CO(O <sup>-</sup> )CH(OH)CH(O $\cdot$ )CHO + 0.550 CO(O <sup>-</sup> )CH(OH)COCHO + 0.250 CO(O <sup>-</sup> )CH(OH)CH(OH)CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02234	*	*	CO(O <sup>-</sup> )CH(OH)CH <sub>2</sub> CO(OO $\cdot$ ) → CO(OH)CH <sub>2</sub> CH(OH)CO(O <sup>-</sup> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02235	*		CHOCH <sub>2</sub> CH(OH)CO(O $\cdot$ ) → CHOCH <sub>2</sub> CH(OH)(OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02236	*	*	CO(O <sup>-</sup> )CH(OH)CH(O $\cdot$ )CHO $\xrightarrow{O_2}$ CO(O <sup>-</sup> )CH(OH)COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02237	*	*	CO(O <sup>-</sup> )CH(OH)CH(O $\cdot$ )CHO → 0.500 CO(O <sup>-</sup> )CH(OH)(OO $\cdot$ ) + 0.500 CHOCHO + 0.500 CO(O <sup>-</sup> )CH(OH)CHO + 0.500 CH $\cdot$ (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00277	*	*	CO(O <sup>-</sup> )CH <sub>2</sub> CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CO(O <sup>-</sup> )	7.4 · 10 <sup>+00</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02238	*	*	CO(O <sup>-</sup> )CH <sub>2</sub> CH(OH)CHO + OH → 0.047 CO(O <sup>-</sup> )CH(OO $\cdot$ )CH(OH)CHO + 0.220 CO(O <sup>-</sup> )CH <sub>2</sub> C(OH)(OO $\cdot$ )CHO + 0.681 CO(O <sup>-</sup> )CH <sub>2</sub> CH(OH)CO(OO $\cdot$ ) + 0.052 CO(O <sup>-</sup> )CH <sub>2</sub> CH(O $\cdot$ )CHO + H <sub>2</sub> O - 0.948 O <sub>2</sub>	1.5 · 10 <sup>+09</sup>		
R <sub>o</sub> 02239	*		CO(O <sup>-</sup> )CH <sub>2</sub> CH(OH)CHO + NO <sub>3</sub> → CHOCH(OH)CH <sub>2</sub> CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 02240	*	*	CO(O <sup>-</sup> )CH(OO $\cdot$ )CH(OH)CHO + CO(O <sup>-</sup> )CH(OO $\cdot$ )CH(OH)CHO → 2.000 CHOCH(OH)CHO + 2.000 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2.000 OH <sup>-</sup> - 2.000 H <sub>2</sub> O	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 02241	*	*	CO(O <sup>-</sup> )CH(OO $\cdot$ )CH(OH)CHO $\xrightarrow{RO_2}$ 0.200 CO(O <sup>-</sup> )CH(O $\cdot$ )CH(OH)CHO + 0.550 CO(O <sup>-</sup> )COCH(OH)CHO + 0.250 CO(O <sup>-</sup> )CH(OH)CH(OH)CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02242	*	*	CO(O <sup>-</sup> )CH <sub>2</sub> C(OH)(OO $\cdot$ )CHO → CO(O <sup>-</sup> )CH <sub>2</sub> COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02243	*	*	CO(O <sup>-</sup> )CH <sub>2</sub> CH(OH)CO(OO $\cdot$ ) → CO(OH)CH(OH)CH <sub>2</sub> CO(O <sup>-</sup> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02244	*		CHOCH(OH)CH <sub>2</sub> CO(O $\cdot$ ) → CHOCH(OH)CH <sub>2</sub> (OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02245	*	*	CO(O <sup>-</sup> )CH(O $\cdot$ )CH(OH)CHO $\xrightarrow{O_2}$ CO(O <sup>-</sup> )COCH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02246	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CHO} \rightarrow 0.500 \cdot \text{CO}(\text{O}^-) + 0.500 \text{CHOCH}(\text{OH})\text{CHO} +$ $0.500 \text{CO}(\text{O}^-)\text{CHO} + 0.500 \text{CHOCH}(\text{OH})(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00278	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) \rightleftharpoons \text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{H}^+$	$2.0 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02247	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{OH} \rightarrow$ $0.100 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) +$ $0.563 \text{CH}_3\text{C}(\text{OH})(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{OH}) +$ $0.337 \text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) + \text{H}_2\text{O} - 0.100 \text{O}_2$	$6.8 \cdot 10^{+08}$		
R <sub>o</sub> 02248	*		$\text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{NO}_3 \rightarrow$ $0.100 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) +$ $0.563 \text{CH}_3\text{C}(\text{OH})(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{OH}) +$ $0.337 \text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) + \text{NO}_3^- + \text{H}^+ - 0.100 \text{O}_2$	$7.5 \cdot 10^{+06}$		
R <sub>o</sub> 02249	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2\cdot}$ $0.200 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) +$ $0.550 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02250	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{OH}) \rightarrow$ $0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OH}) + 0.500 \text{CH}_3\text{CO}(\text{OH}) +$ $0.500 \text{CO}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02251	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) \rightarrow$ $0.500 \text{CH}_3\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CO}(\text{OH}) +$ $0.500 \text{CH}_3\text{C}(\text{OH})_2\text{CO}(\text{OH}) + 0.500 \cdot \text{CO}(\text{OH}) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02252	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02253	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00279	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) \rightleftharpoons \text{CH}(\text{OH})_2\text{CH}_2\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{H}^+$	$1.2 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02254	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{OH} \rightarrow$ $0.544 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.280 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) +$ $0.176 \text{CH}(\text{OH})_2\text{CH}_2\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) + \text{H}_2\text{O} - 0.544 \text{O}_2$	$1.4 \cdot 10^{+09}$		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02255	*		CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + NO <sub>3</sub> → 0.544 CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.280 CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)(O·) + 0.176 CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH)(O·)CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.544 O <sub>2</sub>	8.8 · 10 <sup>+06</sup>		
R <sub>o</sub> 02256	*	*	CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02257	*	*	CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02258	*	*	CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)(O·) → CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02259	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH)(O·)CO(OH) → 0.500 CH(OH) <sub>2</sub> CH <sub>2</sub> (OO·) + 0.500 CO(OH)CO(OH) + 0.500 CH(OH) <sub>2</sub> CH <sub>2</sub> CO(OH) + 0.500 · CO(OH) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00280	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CO(OH) ⇌ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CO(O <sup>-</sup> ) + H <sup>+</sup>	5.1 · 10 <sup>-05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02260	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CO(OH) + OH → 0.156 CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.414 CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) + 0.431 CH(OH) <sub>2</sub> C(OH)(O·)CH <sub>2</sub> CO(OH) + H <sub>2</sub> O - 0.156 O <sub>2</sub>	8.8 · 10 <sup>+08</sup>		
R <sub>o</sub> 02261	*		CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CO(OH) + NO <sub>3</sub> → 0.156 CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.414 CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) + 0.431 CH(OH) <sub>2</sub> C(OH)(O·)CH <sub>2</sub> CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.156 O <sub>2</sub>	8.9 · 10 <sup>+06</sup>		
R <sub>o</sub> 02262	*	*	CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02263	*	*	CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02264	*	*	CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) → CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02265	*	*	CH(OH) <sub>2</sub> C(OH)(O·)CH <sub>2</sub> CO(OH) → 0.500 CH · (OH) <sub>2</sub> + 0.500 CO(OH)CH <sub>2</sub> CO(OH) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CO(OH)CH <sub>2</sub> (OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00281	*	*	CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CO(OH) ⇌ CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + H <sup>+</sup>	1.5 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02266	*	*	CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CO(OH) + OH → 0.580 CO(OH)C(OH) <sub>2</sub> CH(OH)CH(OH)(OO·) + 0.062 CH <sub>2</sub> (OH)C(OH)(OO·)C(OH) <sub>2</sub> CO(OH) + 0.076 CO(OH)C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) + 0.073 CH <sub>2</sub> (OH)CH(O·)C(OH) <sub>2</sub> CO(OH) + 0.209 CH <sub>2</sub> (OH)CH(OH)C(OH)(O·)CO(OH) + H <sub>2</sub> O – 0.642 O <sub>2</sub>	1.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 02267	*		CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CO(OH) + NO <sub>3</sub> → 0.580 CO(OH)C(OH) <sub>2</sub> CH(OH)CH(OH)(OO·) + 0.062 CH <sub>2</sub> (OH)C(OH)(OO·)C(OH) <sub>2</sub> CO(OH) + 0.076 CO(OH)C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) + 0.073 CH <sub>2</sub> (OH)CH(O·)C(OH) <sub>2</sub> CO(OH) + 0.209 CH <sub>2</sub> (OH)CH(OH)C(OH)(O·)CO(OH) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.642 O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 02268	*	*	CO(OH)C(OH) <sub>2</sub> CH(OH)CH(OH)(OO·) → CO(OH)C(OH) <sub>2</sub> CH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02269	*	*	CH <sub>2</sub> (OH)C(OH)(OO·)C(OH) <sub>2</sub> CO(OH) → CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02270	*	*	CO(OH)C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02271	*	*	CO(OH)C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) → CO(OH)C(OH) <sub>2</sub> CH(OH)(OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02272	*	*	CH <sub>2</sub> (OH)CH(O·)C(OH) <sub>2</sub> CO(OH) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02273	*	*	CH <sub>2</sub> (OH)CH(O·)C(OH) <sub>2</sub> CO(OH) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)C(OH) <sub>2</sub> CHO + 0.500 CH <sub>2</sub> (OH)CHO + 0.500 CO(OH)C(OH) <sub>2</sub> (OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02274	*	*	CH <sub>2</sub> (OH)CH(OH)C(OH)(O·)CO(OH) → 0.500 CH <sub>2</sub> (OH)CH(OH)(OO·) + 0.500 CO(OH)CO(OH) + 0.500 CH <sub>2</sub> (OH)CH(OH)CO(OH) + 0.500 · CO(OH) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00282	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CO(OH) ⇌ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CO(O <sup>–</sup> ) + H <sup>+</sup>	1.0 · 10 <sup>–04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02275	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CO(OH) + OH → 0.350 CO(OH)CH(OH)C(OH) <sub>2</sub> CH(OH)(OO·) + 0.105 CO(OH)CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.477 CH <sub>2</sub> (OH)C(OH)(O·)CH(OH)CO(OH) + 0.068 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O·)CO(OH) + H <sub>2</sub> O – 0.350 O <sub>2</sub>	7.9 · 10 <sup>+08</sup>		
R <sub>o</sub> 02276	*		CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CO(OH) + NO <sub>3</sub> → 0.350 CO(OH)CH(OH)C(OH) <sub>2</sub> CH(OH)(OO·) + 0.105 CO(OH)CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.477 CH <sub>2</sub> (OH)C(OH)(O·)CH(OH)CO(OH) + 0.068 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O·)CO(OH) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.350 O <sub>2</sub>	1.1 · 10 <sup>+07</sup>		
R <sub>o</sub> 02277	*	*	CO(OH)CH(OH)C(OH) <sub>2</sub> CH(OH)(OO·) → CO(OH)CH(OH)C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02278	*	*	CO(OH)CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(OH)CH(OH)C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02279	*	*	CO(OH)CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) → CO(OH)CH(OH)C(OH) <sub>2</sub> (OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02280	*	*	CH <sub>2</sub> (OH)C(OH)(O·)CH(OH)CO(OH) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)CH(OH)CO(OH) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CO(OH)CH(OH)(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02281	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O·)CO(OH) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02282	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O·)CO(OH) → 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO·) + 0.500 CO(OH)CHO + 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CHO + 0.500 · CO(OH) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00283	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CO(OH) ⇌ CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CO(O <sup>–</sup> ) + H <sup>+</sup>	5.5 · 10 <sup>–05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02283	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CO(OH) + OH → 0.579 CO(OH)CH(OH)CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.034 CH(OH) <sub>2</sub> CH(OO·)CH(OH)CO(OH) + 0.062 CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH)(OO·)CO(OH) + 0.283 CO(OH)CH(OH)CH <sub>2</sub> CH(OH)(O·) + 0.042 CH(OH) <sub>2</sub> CH <sub>2</sub> CH(O·)CO(OH) + H <sub>2</sub> O – 0.675 O <sub>2</sub>	1.4 · 10 <sup>+09</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02284	*		CH(OH) <sub>2</sub> CH <sub>2</sub> CH(OH)CO(OH) + NO <sub>3</sub> → 0.579 CO(OH)CH(OH)CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.034 CH(OH) <sub>2</sub> CH(OO·)CH(OH)CO(OH) + 0.062 CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH)(OO·)CO(OH) + 0.283 CO(OH)CH(OH)CH <sub>2</sub> CH(OH)(O·) + 0.042 CH(OH) <sub>2</sub> CH <sub>2</sub> CH(O·)CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.675 O <sub>2</sub>	1.1 · 10 <sup>+07</sup>		
R <sub>o</sub> 02285	*	*	CO(OH)CH(OH)CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CO(OH)CH <sub>2</sub> CH(OH)CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02286	*	*	CH(OH) <sub>2</sub> CH(OO·)CH(OH)CO(OH) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH(O·)CH(OH)CO(OH) + 0.550 CH(OH) <sub>2</sub> COCH(OH)CO(OH) + 0.250 CH(OH) <sub>2</sub> CH(OH)CH(OH)CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02287	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> C(OH)(OO·)CO(OH) → CH(OH) <sub>2</sub> CH <sub>2</sub> COCO(OH) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02288	*	*	CO(OH)CH(OH)CH <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH <sub>2</sub> CH(OH)CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02289	*	*	CO(OH)CH(OH)CH <sub>2</sub> CH(OH)(O·) → CO(OH)CH(OH)CH <sub>2</sub> (OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02290	*	*	CH(OH) <sub>2</sub> CH(O·)CH(OH)CO(OH) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCH(OH)CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02291	*	*	CH(OH) <sub>2</sub> CH(O·)CH(OH)CO(OH) → 0.500 CH · (OH) <sub>2</sub> + 0.500 CO(OH)CH(OH)CHO + 0.500 CH(OH) <sub>2</sub> CHO + 0.500 CO(OH)CH(OH)(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00284	*	*	CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CO(OH) ⇌ CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CO(O <sup>-</sup> ) + H <sup>+</sup>	3.5 · 10 <sup>-05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02292	*	*	CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CO(OH) + OH → 0.347 CO(OH)CH <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO·) + 0.181 CH(OH) <sub>2</sub> C(OH)(OO·)CH <sub>2</sub> CO(OH) + 0.384 CO(OH)CH <sub>2</sub> CH(OH)CH(OH)(O·) + 0.089 CH(OH) <sub>2</sub> CH(O·)CH <sub>2</sub> CO(OH) + H <sub>2</sub> O - 0.527 O <sub>2</sub>	9.9 · 10 <sup>+08</sup>		
R <sub>o</sub> 02293	*		CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CO(OH) + NO <sub>3</sub> → 0.347 CO(OH)CH <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO·) + 0.181 CH(OH) <sub>2</sub> C(OH)(OO·)CH <sub>2</sub> CO(OH) + 0.384 CO(OH)CH <sub>2</sub> CH(OH)CH(OH)(O·) + 0.089 CH(OH) <sub>2</sub> CH(O·)CH <sub>2</sub> CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.527 O <sub>2</sub>	1.1 · 10 <sup>+07</sup>		
R <sub>o</sub> 02294	*	*	CO(OH)CH <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO·) → CO(OH)CH <sub>2</sub> CH(OH)CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02295	*	*	$\text{CH(OH)}_2\text{C(OH)(OO}\cdot\text{)CH}_2\text{CO(OH)} \rightarrow \text{CH(OH)}_2\text{COCH}_2\text{CO(OH)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02296	*	*	$\text{CO(OH)CH}_2\text{CH(OH)CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CO(OH)CH}_2\text{CH(OH)CO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02297	*	*	$\text{CO(OH)CH}_2\text{CH(OH)CH(OH)(O}\cdot\text{)} \rightarrow$ $\text{CO(OH)CH}_2\text{CH(OH)(OO}\cdot\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00285	*	*	$\text{CH}_3\text{CH(OH)C(OH)}_2\text{CO(OH)} \rightleftharpoons \text{CH}_3\text{CH(OH)C(OH)}_2\text{CO(O}^-\text{)} + \text{H}^+$	$1.3 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02298	*	*	$\text{CH}_3\text{CH(OH)C(OH)}_2\text{CO(OH)} + \text{OH} \rightarrow$ $0.252 \text{ CO(OH)C(OH)}_2\text{CH(OH)CH}_2\text{(OO}\cdot\text{)} +$ $0.262 \text{ CH}_3\text{C(OH)(OO}\cdot\text{)C(OH)}_2\text{CO(OH)} + 0.132 \text{ CH}_3\text{CH(O}\cdot\text{)C(OH)}_2\text{CO(OH)} +$ $0.354 \text{ CH}_3\text{CH(OH)C(OH)(O}\cdot\text{)CO(OH)} + \text{H}_2\text{O} - 0.514 \text{ O}_2$	$6.8 \cdot 10^{+08}$		
R <sub>o</sub> 02299	*		$\text{CH}_3\text{CH(OH)C(OH)}_2\text{CO(OH)} + \text{NO}_3 \rightarrow$ $0.252 \text{ CO(OH)C(OH)}_2\text{CH(OH)CH}_2\text{(OO}\cdot\text{)} +$ $0.262 \text{ CH}_3\text{C(OH)(OO}\cdot\text{)C(OH)}_2\text{CO(OH)} + 0.132 \text{ CH}_3\text{CH(O}\cdot\text{)C(OH)}_2\text{CO(OH)} +$ $0.354 \text{ CH}_3\text{CH(OH)C(OH)(O}\cdot\text{)CO(OH)} + \text{NO}_3^- + \text{H}^+ - 0.514 \text{ O}_2$	$9.6 \cdot 10^{+06}$		
R <sub>o</sub> 02300	*	*	$\text{CO(OH)C(OH)}_2\text{CH(OH)CH}_2\text{(OO}\cdot\text{)} \xrightarrow{\text{RO}_2}$ $0.200 \text{ CO(OH)C(OH)}_2\text{CH(OH)CH}_2\text{(O}\cdot\text{)} +$ $0.550 \text{ CO(OH)C(OH)}_2\text{CH(OH)CHO} +$ $0.250 \text{ CH}_2\text{(OH)CH(OH)C(OH)}_2\text{CO(OH)} + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02301	*	*	$\text{CH}_3\text{C(OH)(OO}\cdot\text{)C(OH)}_2\text{CO(OH)} \rightarrow \text{CH}_3\text{COC(OH)}_2\text{CO(OH)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02302	*	*	$\text{CH}_3\text{CH(OH)C(OH)(O}\cdot\text{)CO(OH)} \rightarrow$ $0.500 \text{ CH}_3\text{CH(OH)(OO}\cdot\text{)} + 0.500 \text{ CO(OH)CO(OH)} +$ $0.500 \text{ CH}_3\text{CH(OH)CO(OH)} + 0.500 \cdot \text{CO(OH)} - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00286	*	*	$\text{CH}_2\text{(OH)C(OH)}_2\text{C(OH)}_2\text{CO(OH)} \rightleftharpoons$ $\text{CH}_2\text{(OH)C(OH)}_2\text{C(OH)}_2\text{CO(O}^-\text{)} + \text{H}^+$	$2.4 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02303	*	*	$\text{CH}_2\text{(OH)C(OH)}_2\text{C(OH)}_2\text{CO(OH)} + \text{OH} \rightarrow$ $0.282 \text{ CO(OH)C(OH)}_2\text{C(OH)}_2\text{CH(OH)(OO}\cdot\text{)} +$ $0.089 \text{ CO(OH)C(OH)}_2\text{C(OH)}_2\text{CH}_2\text{(O}\cdot\text{)} +$ $0.384 \text{ CH}_2\text{(OH)C(OH)(O}\cdot\text{)C(OH)}_2\text{CO(OH)} +$ $0.244 \text{ CH}_2\text{(OH)C(OH)}_2\text{C(OH)(O}\cdot\text{)CO(OH)} + \text{H}_2\text{O} - 0.282 \text{ O}_2$	$9.4 \cdot 10^{+08}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02304	*		CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + NO <sub>3</sub> → 0.282 CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) + 0.089 CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.384 CH <sub>2</sub> (OH)C(OH)(O·)C(OH) <sub>2</sub> CO(OH) + 0.244 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(O·)CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.282 O <sub>2</sub>	8.1 · 10 <sup>+06</sup>		
R <sub>o</sub> 02305	*	*	CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) → CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02306	*	*	CH <sub>2</sub> (OH)C(OH)(O·)C(OH) <sub>2</sub> CO(OH) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)C(OH) <sub>2</sub> CO(OH) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CO(OH)C(OH) <sub>2</sub> (OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02307	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(O·)CO(OH) → 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO·) + 0.500 CO(OH)CO(OH) + 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CO(OH) + 0.500 ·CO(OH) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00287	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH)CO(OH) ⇌ CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH)CO(O <sup>-</sup> ) + H <sup>+</sup>	8.6 · 10 <sup>-05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02308	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH)CO(OH) + OH → 0.135 CO(OH)CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (OO·) + 0.763 CH <sub>3</sub> C(OH)(O·)CH(OH)CO(OH) + 0.102 CH <sub>3</sub> C(OH) <sub>2</sub> CH(O·)CO(OH) + H <sub>2</sub> O - 0.135 O <sub>2</sub>	5.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02309	*		CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH)CO(OH) + NO <sub>3</sub> → 0.135 CO(OH)CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (OO·) + 0.763 CH <sub>3</sub> C(OH)(O·)CH(OH)CO(OH) + 0.102 CH <sub>3</sub> C(OH) <sub>2</sub> CH(O·)CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.135 O <sub>2</sub>	9.8 · 10 <sup>+06</sup>		
R <sub>o</sub> 02310	*	*	CO(OH)CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CO(OH)CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.550 CO(OH)CH(OH)C(OH) <sub>2</sub> CHO + 0.250 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02311	*	*	CH <sub>3</sub> C(OH)(O·)CH(OH)CO(OH) → 0.500 CH <sub>3</sub> (OO·) + 0.500 CO(OH)CH(OH)CO(OH) + 0.500 CH <sub>3</sub> CO(OH) + 0.500 CO(OH)CH(OH)(OO·) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02312	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> CH(O·)CO(OH) $\xrightarrow{O_2}$ CH <sub>3</sub> C(OH) <sub>2</sub> COCO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02313	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CO}(\text{OH}) \rightarrow 0.500 \text{CH}_3\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CHO} + 0.500 \text{CH}_3\text{C}(\text{OH})_2\text{CHO} + 0.500 \cdot\text{CO}(\text{OH}) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00288	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCO}(\text{OH}) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CO}(\text{OH})$	$3.7 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00289	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCO}(\text{OH}) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OH})$	$3.5 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00290	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCO}(\text{OH}) \rightleftharpoons \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCO}(\text{O}^-) + \text{H}^+$	$1.7 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02314	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCO}(\text{OH}) + \text{OH} \rightarrow 0.369 \text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) + 0.129 \text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CH}_2(\text{O}\cdot) + 0.502 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{COCO}(\text{OH}) + \text{H}_2\text{O} - 0.369 \text{O}_2$	$6.5 \cdot 10^{+08}$		
R <sub>o</sub> 02315	*		$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCO}(\text{OH}) + \text{NO}_3 \rightarrow 0.369 \text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) + 0.129 \text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CH}_2(\text{O}\cdot) + 0.502 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{COCO}(\text{OH}) + \text{NO}_3^- + \text{H}^+ - 0.369 \text{O}_2$	$8.1 \cdot 10^{+06}$		
R <sub>o</sub> 02316	*	*	$\text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02317	*	*	$\text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02318	*	*	$\text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{OH})\text{COC}(\text{OH})_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02319	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{COCO}(\text{OH}) \rightarrow 0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CO}(\text{OH})\text{COCO}(\text{OH}) + 0.500 \text{CH}_2(\text{OH})\text{CO}(\text{OH}) + 0.500 \text{CO}(\text{OH})\text{CO}(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00291	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{COCO}(\text{OH}) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{COC}(\text{OH})_2\text{CO}(\text{OH})$	$8.5 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00292	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{COCO}(\text{OH}) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OH})$	$1.3 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00293	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{COCO}(\text{OH}) \rightleftharpoons \text{CH}_3\text{C}(\text{OH})_2\text{COCO}(\text{O}^-) + \text{H}^+$	$1.2 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02320	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{COCO}(\text{OH}) + \text{OH} \rightarrow 0.150 \text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) + 0.850 \text{CH}_3\text{C}(\text{OH})(\text{O}\cdot)\text{COCO}(\text{OH}) + \text{H}_2\text{O} - 0.150 \text{O}_2$	$4.1 \cdot 10^{+08}$		
R <sub>o</sub> 02321	*		$\text{CH}_3\text{C}(\text{OH})_2\text{COCO}(\text{OH}) + \text{NO}_3 \rightarrow 0.150 \text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) + 0.850 \text{CH}_3\text{C}(\text{OH})(\text{O}\cdot)\text{COCO}(\text{OH}) + \text{NO}_3^- + \text{H}^+ - 0.150 \text{O}_2$	$7.5 \cdot 10^{+06}$		
R <sub>o</sub> 02322	*	*	$\text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2\cdot} 0.200 \text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CH}_2(\text{O}\cdot) + 0.550 \text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CHO} + 0.250 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCO}(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02323	*	*	CH <sub>3</sub> C(OH)(O·)COCO(OH) → 0.500 CH <sub>3</sub> (OO·) + 0.500 CO(OH)COCO(OH) + 0.500 CH <sub>3</sub> CO(OH) + 0.500 CO(OH)CO(OO·) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00294	*	*	CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CO(OH) ⇌ CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CO(O <sup>−</sup> ) + H <sup>+</sup>	3.7 · 10 <sup>−04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02324	*	*	CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CO(OH) + OH → 0.516 CO(OH)C(OH) <sub>2</sub> COCH(OH)(OO·) + 0.129 CO(OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (O·) + 0.354 CH <sub>2</sub> (OH)COC(OH)(O·)CO(OH) + H <sub>2</sub> O – 0.516 O <sub>2</sub>	5.8 · 10 <sup>+08</sup>		
R <sub>o</sub> 02325	*		CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CO(OH) + NO <sub>3</sub> → 0.516 CO(OH)C(OH) <sub>2</sub> COCH(OH)(OO·) + 0.129 CO(OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (O·) + 0.354 CH <sub>2</sub> (OH)COC(OH)(O·)CO(OH) + NO <sub>3</sub> <sup>−</sup> + H <sup>+</sup> – 0.516 O <sub>2</sub>	8.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02326	*	*	CO(OH)C(OH) <sub>2</sub> COCH(OH)(OO·) → CO(OH)C(OH) <sub>2</sub> COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02327	*	*	CO(OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02328	*	*	CO(OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (O·) → CO(OH)C(OH) <sub>2</sub> CO(OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02329	*	*	CH <sub>2</sub> (OH)COC(OH)(O·)CO(OH) → 0.500 CH <sub>2</sub> (OH)CO(OO·) + 0.500 CO(OH)CO(OH) + 0.500 CH <sub>2</sub> (OH)COCO(OH) + 0.500 · CO(OH) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00295	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> COCO(OH) ⇌ CH(OH) <sub>2</sub> CH <sub>2</sub> COCO(O <sup>−</sup> ) + H <sup>+</sup>	3.9 · 10 <sup>−02</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02330	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> COCO(OH) + OH → 0.636 CO(OH)COCH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.364 CO(OH)COCH <sub>2</sub> CH(OH)(O·) + H <sub>2</sub> O – 0.636 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 02331	*		CH(OH) <sub>2</sub> CH <sub>2</sub> COCO(OH) + NO <sub>3</sub> → 0.636 CO(OH)COCH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.364 CO(OH)COCH <sub>2</sub> CH(OH)(O·) + NO <sub>3</sub> <sup>−</sup> + H <sup>+</sup> – 0.636 O <sub>2</sub>	8.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 02332	*	*	CO(OH)COCH <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CO(OH)CH <sub>2</sub> COCO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02333	*	*	CO(OH)COCH <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH <sub>2</sub> COCO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02334	*	*	CO(OH)COCH <sub>2</sub> CH(OH)(O·) → CO(OH)COCH <sub>2</sub> (OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00296	*	*	CH(OH) <sub>2</sub> COCH <sub>2</sub> CO(OH) ⇌ CH(OH) <sub>2</sub> COCH <sub>2</sub> CO(O <sup>−</sup> ) + H <sup>+</sup>	7.2 · 10 <sup>−05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02335	*	*	CH(OH) <sub>2</sub> COCH <sub>2</sub> CO(OH) + OH → 0.322 CO(OH)CH <sub>2</sub> COC(OH) <sub>2</sub> (OO·) + 0.678 CO(OH)CH <sub>2</sub> COCH(OH)(O·) + H <sub>2</sub> O – 0.322 O <sub>2</sub>	4.8 · 10 <sup>+08</sup>		
R <sub>o</sub> 02336	*		CH(OH) <sub>2</sub> COCH <sub>2</sub> CO(OH) + NO <sub>3</sub> → 0.322 CO(OH)CH <sub>2</sub> COC(OH) <sub>2</sub> (OO·) + 0.678 CO(OH)CH <sub>2</sub> COCH(OH)(O·) + NO <sub>3</sub> <sup>−</sup> + H <sup>+</sup> – 0.322 O <sub>2</sub>	8.8 · 10 <sup>+06</sup>		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02337	*	*	$\text{CO(OH)CH}_2\text{COC(OH)}_2(\text{OO}\cdot) \rightarrow \text{CO(OH)CH}_2\text{COCO(OH)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02338	*	*	$\text{CO(OH)CH}_2\text{COCH(OH)(O}\cdot) \xrightarrow{\text{O}_2} \text{CO(OH)CH}_2\text{COCO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02339	*	*	$\text{CO(OH)CH}_2\text{COCH(OH)(O}\cdot) \rightarrow \text{CO(OH)CH}_2\text{CO(OO}\cdot) + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00297	*	*	$\text{CH}_3\text{COC(OH)}_2\text{CO(OH)} \rightleftharpoons \text{CH}_3\text{COC(OH)}_2\text{CO(O}^-) + \text{H}^+$	$3.1 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02340	*	*	$\text{CH}_3\text{COC(OH)}_2\text{CO(OH)} + \text{OH} \rightarrow 0.272 \text{ CO(OH)C(OH)}_2\text{COCH}_2(\text{OO}\cdot) +$ $0.728 \text{ CH}_3\text{COC(OH)(O}\cdot)\text{CO(OH)} + \text{H}_2\text{O} - 0.272 \text{ O}_2$	$2.8 \cdot 10^{+08}$		
R <sub>o</sub> 02341	*		$\text{CH}_3\text{COC(OH)}_2\text{CO(OH)} + \text{NO}_3 \rightarrow 0.272 \text{ CO(OH)C(OH)}_2\text{COCH}_2(\text{OO}\cdot) +$ $0.728 \text{ CH}_3\text{COC(OH)(O}\cdot)\text{CO(OH)} + \text{NO}_3^- + \text{H}^+ - 0.272 \text{ O}_2$	$7.4 \cdot 10^{+06}$		
R <sub>o</sub> 02342	*	*	$\text{CO(OH)C(OH)}_2\text{COCH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CO(OH)C(OH)}_2\text{COCH}_2(\text{O}\cdot) + 0.550 \text{ CO(OH)C(OH)}_2\text{COCHO} +$ $0.250 \text{ CH}_2(\text{OH})\text{COC(OH)}_2\text{CO(OH)} + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02343	*	*	$\text{CH}_3\text{COC(OH)(O}\cdot)\text{CO(OH)} \rightarrow 0.500 \text{ CH}_3\text{CO(OO}\cdot) +$ $0.500 \text{ CO(OH)CO(OH)} + 0.500 \text{ CH}_3\text{COCO(OH)} + 0.500 \cdot \text{CO(OH)} - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00298	*	*	$\text{CO(OH)CH(OH)COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{COCH(OH)CO(OH)}$	$2.8 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00299	*	*	$\text{CO(OH)CH(OH)COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)CO(OH)}$	$4.4 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00300	*	*	$\text{CO(OH)CH(OH)COCHO} \rightleftharpoons \text{CO(O}^-)\text{CH(OH)COCHO} + \text{H}^+$	$2.1 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02344	*	*	$\text{CO(OH)CH(OH)COCHO} + \text{OH} \rightarrow 0.899 \text{ CO(OH)CH(OH)COCO(OO}\cdot) +$ $0.101 \text{ CO(OH)CH(O}\cdot)\text{COCHO} + \text{H}_2\text{O} - 0.899 \text{ O}_2$	$4.8 \cdot 10^{+08}$		
R <sub>o</sub> 02345	*		$\text{CO(OH)CH(OH)COCHO} + \text{NO}_3 \rightarrow 0.899 \text{ CO(OH)CH(OH)COCO(OO}\cdot) +$ $0.101 \text{ CO(OH)CH(O}\cdot)\text{COCHO} + \text{NO}_3^- + \text{H}^+ - 0.899 \text{ O}_2$	$6.0 \cdot 10^{+06}$		
R <sub>o</sub> 02346	*	*	$\text{CO(OH)CH(O}\cdot)\text{COCHO} \xrightarrow{\text{O}_2} \text{CO(OH)COCOCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02347	*	*	$\text{CO(OH)CH(O}\cdot)\text{COCHO} \rightarrow 0.500 \cdot \text{CO(OH)} + 0.500 \text{ CHOCOCHO} +$ $0.500 \text{ CO(OH)CHO} + 0.500 \text{ CHOCO(OO}\cdot) - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00301	*	*	$\text{CO(OH)CH(OH)CH(OH)CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{CH(OH)CH(OH)CO(OH)}$	$4.0 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00302	*	*	$\text{CO(OH)CH(OH)CH(OH)CHO} \rightleftharpoons \text{CO(O}^-)\text{CH(OH)CH(OH)CHO} + \text{H}^+$	$1.0 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02348	*	*	$\text{CO(OH)CH(OH)CH(OH)CHO} + \text{OH} \rightarrow$ $0.064 \text{ CO(OH)CH(OH)C(OH)(OO}\cdot)\text{CHO} +$ $0.825 \text{ CO(OH)CH(OH)CH(OH)CO(OO}\cdot) +$ $0.049 \text{ CO(OH)CH(O}\cdot)\text{CH(OH)CHO} + 0.063 \text{ CO(OH)CH(OH)CH(O}\cdot)\text{CHO} +$ $\text{H}_2\text{O} - 0.889 \text{ O}_2$	$1.2 \cdot 10^{+09}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02349	*		CO(OH)CH(OH)CH(OH)CHO + NO <sub>3</sub> → 0.064 CO(OH)CH(OH)C(OH)(OO·)CHO + 0.825 CO(OH)CH(OH)CH(OH)CO(OO·) + 0.049 CO(OH)CH(O·)CH(OH)CHO + 0.063 CO(OH)CH(OH)CH(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.889 O <sub>2</sub>	1.5 · 10 <sup>+07</sup>		
R <sub>o</sub> 02350	*	*	CO(OH)CH(OH)C(OH)(OO·)CHO → CO(OH)CH(OH)COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02351	*	*	CO(OH)CH(O·)CH(OH)CHO $\xrightarrow{O_2}$ CO(OH)COCH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02352	*	*	CO(OH)CH(O·)CH(OH)CHO → 0.500 · CO(OH) + 0.500 CHOCH(OH)CHO + 0.500 CO(OH)CHO + 0.500 CHOCH(OH)(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02353	*	*	CO(OH)CH(OH)CH(O·)CHO $\xrightarrow{O_2}$ CO(OH)CH(OH)COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02354	*	*	CO(OH)CH(OH)CH(O·)CHO → 0.500 CO(OH)CH(OH)(OO·) + 0.500 CHOCHO + 0.500 CO(OH)CH(OH)CHO + 0.500 CH · (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00303	*	*	CO(OH)COCOCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH)	1.2 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00304	*	*	CO(OH)COCOCHO $\rightleftharpoons$ CO(O <sup>-</sup> )COCOCHO + H <sup>+</sup>	1.0 · 10 <sup>+00</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02355	*	*	CO(OH)COCOCHO → 0.250 CO(OH)CO(OO·) + 0.250 CHOCO(OO·) + 0.250 CO(OH)COCO(OO·) + 0.250 CHO(OO·)	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 02356	*	*	CO(OH)COCOCHO + OH → CO(OH)COCOCO(OO·) + H <sub>2</sub> O - O <sub>2</sub>	3.7 · 10 <sup>+08</sup>		
R <sub>o</sub> 02357	*		CO(OH)COCOCHO + NO <sub>3</sub> → CO(OH)COCOCO(OO·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	2.2 · 10 <sup>+06</sup>		
R <sub>o</sub> 02358	*	*	CO(OH)COCOCO(OO·) → CO(OH)COCOCO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
E <sub>o</sub> 00305	*	*	CO(OH)COCH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CO(OH)	5.9 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00306	*	*	CO(OH)COCH(OH)CHO $\rightleftharpoons$ CO(O <sup>-</sup> )COCH(OH)CHO + H <sup>+</sup>	1.7 · 10 <sup>-01</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02359	*	*	CO(OH)COCH(OH)CHO + OH → 0.037 CO(OH)COC(OH)(OO·)CHO + 0.895 CO(OH)COCH(OH)CO(OO·) + 0.068 CO(OH)COCH(O·)CHO + H <sub>2</sub> O - 0.932 O <sub>2</sub>	9.1 · 10 <sup>+08</sup>		
R <sub>o</sub> 02360	*		CO(OH)COCH(OH)CHO + NO <sub>3</sub> → 0.037 CO(OH)COC(OH)(OO·)CHO + 0.895 CO(OH)COCH(OH)CO(OO·) + 0.068 CO(OH)COCH(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.932 O <sub>2</sub>	6.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02361	*	*	CO(OH)COC(OH)(OO·)CHO → CO(OH)COCOCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02362	*	*	CO(OH)COCH(OH)CO(OO·) → CO(OH)CH(OH)COCO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02363	*	*	$\text{CO(OH)COCH(O}\cdot\text{)CHO} \xrightarrow{\text{O}_2} \text{CO(OH)COCOCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02364	*	*	$\text{CO(OH)COCH(O}\cdot\text{)CHO} \rightarrow 0.500 \text{CO(OH)CO(OO}\cdot\text{)} + 0.500 \text{CHOCHO} +$ $0.500 \text{CO(OH)COCHO} + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{O}_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00307	*	*	$\text{CO(OH)C(OH)}_2\text{CH}_2\text{CHO} \rightleftharpoons \text{CO(O}^-\text{)C(OH)}_2\text{CH}_2\text{CHO} + \text{H}^+$	$1.5 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02365	*	*	$\text{CO(OH)C(OH)}_2\text{CH}_2\text{CHO} + \text{OH} \rightarrow 0.899 \text{CO(OH)C(OH)}_2\text{CH}_2\text{CO(OO}\cdot\text{)} +$ $0.101 \text{CO(OH)C(OH)(O}\cdot\text{)CH}_2\text{CHO} + \text{H}_2\text{O} - 0.899 \text{O}_2$	$2.5 \cdot 10^{+09}$		
R <sub>o</sub> 02366	*		$\text{CO(OH)C(OH)}_2\text{CH}_2\text{CHO} + \text{NO}_3 \rightarrow 0.899 \text{CO(OH)C(OH)}_2\text{CH}_2\text{CO(OO}\cdot\text{)} +$ $0.101 \text{CO(OH)C(OH)(O}\cdot\text{)CH}_2\text{CHO} + \text{NO}_3^- + \text{H}^+ - 0.899 \text{O}_2$	$7.3 \cdot 10^{+06}$		
R <sub>o</sub> 02367	*	*	$\text{CO(OH)C(OH)}_2\text{CH}_2\text{CO(OO}\cdot\text{)} \rightarrow$ $\text{CO(OH)CH}_2\text{C(OH)}_2\text{CO(OH)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02368	*	*	$\text{CO(OH)C(OH)(O}\cdot\text{)CH}_2\text{CHO} \rightarrow 0.500 \cdot \text{CO(OH)} + 0.500 \text{CO(OH)CH}_2\text{CHO} +$ $0.500 \text{CO(OH)CO(OH)} + 0.500 \text{CHOCH}_2(\text{OO}\cdot\text{)} - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00308	*	*	$\text{CO(OH)CH}_2\text{C(OH)}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{COCH}_2\text{CO(OH)}$	$7.4 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00309	*	*	$\text{CO(OH)CH}_2\text{C(OH)}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)}_2\text{CH}_2\text{CO(OH)}$	$1.9 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00310	*	*	$\text{CO(OH)CH}_2\text{C(OH)}_2\text{CHO} \rightleftharpoons \text{CO(O}^-\text{)CH}_2\text{C(OH)}_2\text{CHO} + \text{H}^+$	$6.4 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02369	*	*	$\text{CO(OH)CH}_2\text{C(OH)}_2\text{CHO} + \text{OH} \rightarrow 0.550 \text{CO(OH)CH}_2\text{C(OH)}_2\text{CO(OO}\cdot\text{)} +$ $0.450 \text{CO(OH)CH}_2\text{C(OH)(O}\cdot\text{)CHO} + \text{H}_2\text{O} - 0.550 \text{O}_2$	$7.2 \cdot 10^{+08}$		
R <sub>o</sub> 02370	*		$\text{CO(OH)CH}_2\text{C(OH)}_2\text{CHO} + \text{NO}_3 \rightarrow 0.550 \text{CO(OH)CH}_2\text{C(OH)}_2\text{CO(OO}\cdot\text{)} +$ $0.450 \text{CO(OH)CH}_2\text{C(OH)(O}\cdot\text{)CHO} + \text{NO}_3^- + \text{H}^+ - 0.550 \text{O}_2$	$7.3 \cdot 10^{+06}$		
R <sub>o</sub> 02371	*	*	$\text{CO(OH)CH}_2\text{C(OH)}_2\text{CO(OO}\cdot\text{)} \rightarrow$ $\text{CO(OH)CH}_2\text{C(OH)}_2\text{CO(OH)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02372	*	*	$\text{CO(OH)CH}_2\text{C(OH)(O}\cdot\text{)CHO} \rightarrow$ $0.500 \text{CO(OH)CH}_2(\text{OO}\cdot\text{)} + 0.500 \text{CO(OH)CHO} +$ $0.500 \text{CO(OH)CH}_2\text{CO(OH)} + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{O}_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00311	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{COCH(OH)}_2 \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)}_2\text{C(OH)}_2\text{CH(OH)}_2$	$7.1 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02373	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{COCH(OH)}_2 \rightarrow$ $0.250 \text{CHO(OH)} + 0.250 \text{HO}_2 + 0.250 \text{CH(OH)}_2\text{COC(OH)}_2(\text{OO}\cdot\text{)} +$ $0.250 \text{CH(OH)}_2\text{C(OH)}_2(\text{OO}\cdot\text{)} + 0.250 \text{CH(OH)}_2\text{CO(OO}\cdot\text{)}$	$1.0 \cdot 10^{-01}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02374	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH(OH) <sub>2</sub> + OH $\rightarrow$ 0.089 CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.113 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.290 CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH(OH)(O $\cdot$ ) + 0.247 CH(OH) <sub>2</sub> COC(OH)(O $\cdot$ )CH(OH) <sub>2</sub> + 0.261 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH(OH)(O $\cdot$ ) + H <sub>2</sub> O - 0.202 O <sub>2</sub>	$1.3 \cdot 10^{+09}$		
R <sub>o</sub> 02375	*		CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH(OH) <sub>2</sub> + NO <sub>3</sub> $\rightarrow$ 0.089 CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.113 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.290 CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH(OH)(O $\cdot$ ) + 0.247 CH(OH) <sub>2</sub> COC(OH)(O $\cdot$ )CH(OH) <sub>2</sub> + 0.261 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH(OH)(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.202 O <sub>2</sub>	$8.8 \cdot 10^{+06}$		
R <sub>o</sub> 02376	*	*	CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02377	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COC(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCO(OH) + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02378	*	*	CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02379	*	*	CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH(OH)(O $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> (OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02380	*	*	CH(OH) <sub>2</sub> COC(OH)(O $\cdot$ )CH(OH) <sub>2</sub> $\rightarrow$ 0.500 CH(OH) <sub>2</sub> CO(OO $\cdot$ ) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CH(OH) <sub>2</sub> COCO(OH) + 0.500 CH $\cdot$ (OH) <sub>2</sub> - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02381	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCO(OH) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02382	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH(OH)(O $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00312	*	*	CH(OH) <sub>2</sub> COCOCH(OH) <sub>2</sub> $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	$7.1 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02383	*	*	CH(OH) <sub>2</sub> COCOCH(OH) <sub>2</sub> $\rightarrow$ 0.250 CHO(OH) + 0.250 HO <sub>2</sub> + 0.250 CH(OH) <sub>2</sub> COCO(OO $\cdot$ ) + 0.500 CH(OH) <sub>2</sub> CO(OO $\cdot$ )	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 02384	*	*	CH(OH) <sub>2</sub> COCOCH(OH) <sub>2</sub> + OH $\rightarrow$ 0.280 CH(OH) <sub>2</sub> COCOC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.720 CH(OH) <sub>2</sub> COCOCH(OH)(O $\cdot$ ) + H <sub>2</sub> O - 0.280 O <sub>2</sub>	$9.1 \cdot 10^{+08}$		
R <sub>o</sub> 02385	*		CH(OH) <sub>2</sub> COCOCH(OH) <sub>2</sub> + NO <sub>3</sub> $\rightarrow$ 0.280 CH(OH) <sub>2</sub> COCOC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.720 CH(OH) <sub>2</sub> COCOCH(OH)(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.280 O <sub>2</sub>	$8.8 \cdot 10^{+06}$		
R <sub>o</sub> 02386	*	*	CH(OH) <sub>2</sub> COCOC(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> COCOCO(OH) + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02387	*	*	$\text{CH(OH)}_2\text{COCOCH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CH(OH)}_2\text{COCOCO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02388	*	*	$\text{CH(OH)}_2\text{COCOCH(OH)(O}\cdot\text{)} \rightarrow \text{CH(OH)}_2\text{COCO(OO}\cdot\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00313	*	*	$\text{CH(OH)}_2\text{COC(OH)}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)}_2\text{C(OH)}_2\text{CH(OH)}_2$	$7.1 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02389	*	*	$\text{CH(OH)}_2\text{COC(OH)}_2\text{CHO} \rightarrow$ $0.250 \text{ CHO(OH)} + 0.250 \text{ HO}_2 + 0.250 \text{ CHOC(OH)}_2\text{CO(OO}\cdot\text{)} +$ $0.250 \text{ CH(OH)}_2\text{CO(OO}\cdot\text{)} + 0.250 \text{ CHOC(OH)}_2\text{(OO}\cdot\text{)}$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 02390	*	*	$\text{CH(OH)}_2\text{COC(OH)}_2\text{CHO} + \text{OH} \rightarrow 0.134 \text{ CHOC(OH)}_2\text{COC(OH)}_2\text{(OO}\cdot\text{)} +$ $0.307 \text{ CH(OH)}_2\text{COC(OH)}_2\text{CO(OO}\cdot\text{)} + 0.309 \text{ CHOC(OH)}_2\text{COCH(OH)(O}\cdot\text{)} +$ $0.251 \text{ CH(OH)}_2\text{COC(OH)(O}\cdot\text{)CHO} + \text{H}_2\text{O} - 0.440 \text{ O}_2$	$1.1 \cdot 10^{+09}$		
R <sub>o</sub> 02391	*		$\text{CH(OH)}_2\text{COC(OH)}_2\text{CHO} + \text{NO}_3 \rightarrow 0.134 \text{ CHOC(OH)}_2\text{COC(OH)}_2\text{(OO}\cdot\text{)} +$ $0.307 \text{ CH(OH)}_2\text{COC(OH)}_2\text{CO(OO}\cdot\text{)} + 0.309 \text{ CHOC(OH)}_2\text{COCH(OH)(O}\cdot\text{)} +$ $0.251 \text{ CH(OH)}_2\text{COC(OH)(O}\cdot\text{)CHO} + \text{NO}_3^- + \text{H}^+ - 0.440 \text{ O}_2$	$7.3 \cdot 10^{+06}$		
R <sub>o</sub> 02392	*	*	$\text{CHOC(OH)}_2\text{COC(OH)}_2\text{(OO}\cdot\text{)} \rightarrow \text{CO(OH)COC(OH)}_2\text{CHO} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02393	*	*	$\text{CH(OH)}_2\text{COC(OH)}_2\text{CO(OO}\cdot\text{)} \rightarrow$ $\text{CH(OH)}_2\text{COC(OH)}_2\text{CO(OH)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02394	*	*	$\text{CHOC(OH)}_2\text{COCH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CO(OH)COC(OH)}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02395	*	*	$\text{CHOC(OH)}_2\text{COCH(OH)(O}\cdot\text{)} \rightarrow \text{CHOC(OH)}_2\text{CO(OO}\cdot\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02396	*	*	$\text{CH(OH)}_2\text{COC(OH)(O}\cdot\text{)CHO} \rightarrow$ $0.500 \text{ CH(OH)}_2\text{CO(OO}\cdot\text{)} + 0.500 \text{ CO(OH)CHO} +$ $0.500 \text{ CH(OH)}_2\text{COCO(OH)} + 0.500 \text{ CH}\cdot\text{(OH)}_2 - 0.500 \text{ O}_2 - 0.500 \text{ H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00314	*	*	$\text{CH(OH)}_2\text{CH}_2\text{C(OH)}_2\text{CO(O}^-\text{)} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{CH}_2\text{COCO(O}^-\text{)}$	$9.0 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02397	*	*	$\text{CH(OH)}_2\text{CH}_2\text{C(OH)}_2\text{CO(O}^-\text{)} + \text{OH} \rightarrow$ $0.480 \text{ CO(O}^-\text{)C(OH)}_2\text{CH}_2\text{C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.247 \text{ CO(O}^-\text{)C(OH)}_2\text{CH}_2\text{CH(OH)(O}\cdot\text{)} +$ $0.273 \text{ CH(OH)}_2\text{CH}_2\text{C(OH)(O}\cdot\text{)CO(O}^-\text{)} + \text{H}_2\text{O} - 0.480 \text{ O}_2$	$1.6 \cdot 10^{+09}$		
R <sub>o</sub> 02398	*		$\text{CH(OH)}_2\text{CH}_2\text{C(OH)}_2\text{CO(O}^-\text{)} + \text{NO}_3 \rightarrow$ $\text{CH(OH)}_2\text{CH}_2\text{C(OH)}_2\text{CO(O}\cdot\text{)} + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02399	*	*	$\text{CO(O}^-\text{)C(OH)}_2\text{CH}_2\text{C(OH)}_2\text{(OO}\cdot\text{)} \rightarrow \text{CO(OH)CH}_2\text{C(OH)}_2\text{CO(O}^-\text{)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02400	*	*	$\text{CO(O}^-\text{)C(OH)}_2\text{CH}_2\text{CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CO(OH)CH}_2\text{C(OH)}_2\text{CO(O}^-\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02401	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02402	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CH}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CO}(\text{O}^-) +$ $0.500 \text{CH}(\text{OH})_2\text{CH}_2\text{CO}(\text{OH}) + 0.500 \cdot \text{CO}(\text{O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02403	*		$\text{CH}(\text{OH})_2\text{CH}_2\text{C}(\text{OH})_2\text{CO}(\text{O}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00315	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}^-) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C}(\text{OH})_2\text{COCO}(\text{O}^-)$	$7.5 \cdot 10^{-01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00316	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}^-) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{COC}(\text{OH})_2\text{CO}(\text{O}^-)$	$7.5 \cdot 10^{-01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02404	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{OH} \rightarrow$ $0.079 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) +$ $0.449 \text{CH}_3\text{C}(\text{OH})(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{O}^-) +$ $0.472 \text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{O}^-) + \text{H}_2\text{O} - 0.079 \text{O}_2$	$8.5 \cdot 10^{+08}$		
R <sub>o</sub> 02405	*		$\text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow \text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02406	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) + 0.550 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02407	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + 0.500 \text{CH}_3\text{CO}(\text{OH}) +$ $0.500 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2(\text{OO}\cdot) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02408	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CH}_3\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CO}(\text{O}^-) +$ $0.500 \text{CH}_3\text{C}(\text{OH})_2\text{CO}(\text{OH}) + 0.500 \cdot \text{CO}(\text{O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02409	*		$\text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_3\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02410	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02411	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02412	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2\text{CO}(\text{O}^-) + \text{OH} \rightarrow$ $0.150 \text{CO}(\text{O}^-)\text{CH}_2\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.035 \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) +$ $0.399 \text{CO}(\text{O}^-)\text{CH}_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) +$ $0.416 \text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CH}_2\text{CO}(\text{O}^-) + \text{H}_2\text{O} - 0.185 \text{O}_2$	$9.1 \cdot 10^{+08}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02413	*		$\text{CH(OH)}_2\text{C(OH)}_2\text{CH}_2\text{CO(O}^-) + \text{NO}_3 \rightarrow$ $\text{CH(OH)}_2\text{C(OH)}_2\text{CH}_2\text{CO(O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02414	*	*	$\text{CO(O}^-)\text{CH}_2\text{C(OH)}_2\text{C(OH)}_2(\text{OO}\cdot) \rightarrow \text{CO(OH)C(OH)}_2\text{CH}_2\text{CO(O}^-) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02415	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(OO}\cdot)\text{CO(O}^-) + \text{CH(OH)}_2\text{C(OH)}_2\text{CH(OO}\cdot)\text{CO(O}^-) \rightarrow$ $2.000 \text{ CH(OH)}_2\text{C(OH)}_2\text{CHO} + 2.000 \text{ CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{ OH}^- - 2.000 \text{ H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 02416	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(OO}\cdot)\text{CO(O}^-) \xrightarrow{\text{RO}_2\cdot}$ $0.200 \text{ CH(OH)}_2\text{C(OH)}_2\text{CH(O}\cdot)\text{CO(O}^-) +$ $0.550 \text{ CH(OH)}_2\text{C(OH)}_2\text{COCO(O}^-) +$ $0.250 \text{ CH(OH)}_2\text{C(OH)}_2\text{CH(OH)CO(O}^-) + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02417	*	*	$\text{CO(O}^-)\text{CH}_2\text{C(OH)}_2\text{CH(OH)(O}\cdot) \xrightarrow{\text{O}_2} \text{CO(OH)C(OH)}_2\text{CH}_2\text{CO(O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02418	*	*	$\text{CO(O}^-)\text{CH}_2\text{C(OH)}_2\text{CH(OH)(O}\cdot) \rightarrow$ $\text{CO(O}^-)\text{CH}_2\text{C(OH)}_2(\text{OO}\cdot) + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02419	*	*	$\text{CH(OH)}_2\text{C(OH)(O}\cdot)\text{CH}_2\text{CO(O}^-) \rightarrow$ $0.500 \text{ CH}\cdot(\text{OH})_2 + 0.500 \text{ CO(OH)CH}_2\text{CO(O}^-) + 0.500 \text{ CH(OH)}_2\text{CO(OH)} +$ $0.500 \text{ CO(O}^-)\text{CH}_2(\text{OO}\cdot) - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02420	*		$\text{CH(OH)}_2\text{C(OH)}_2\text{CH}_2\text{CO(O}\cdot) \rightarrow \text{CH(OH)}_2\text{C(OH)}_2\text{CH}_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02421	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(O}\cdot)\text{CO(O}^-) \xrightarrow{\text{O}_2} \text{CH(OH)}_2\text{C(OH)}_2\text{COCO(O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02422	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(O}\cdot)\text{CO(O}^-) \rightarrow$ $0.500 \text{ CH(OH)}_2\text{C(OH)}_2(\text{OO}\cdot) + 0.500 \text{ CO(O}^-)\text{CHO} +$ $0.500 \text{ CH(OH)}_2\text{C(OH)}_2\text{CHO} + 0.500 \cdot \text{CO(O}^-) - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02423	*	*	$\text{CH}_3\text{C(OH)}_2\text{CH(OH)CO(O}^-) + \text{OH} \rightarrow$ $0.115 \text{ CO(O}^-)\text{CH(OH)C(OH)}_2\text{CH}_2(\text{OO}\cdot) +$ $0.086 \text{ CH}_3\text{C(OH)}_2\text{C(OH)(OO}\cdot)\text{CO(O}^-) +$ $0.647 \text{ CH}_3\text{C(OH)(O}\cdot)\text{CH(OH)CO(O}^-) + 0.152 \text{ CH}_3\text{C(OH)}_2\text{CH(O}\cdot)\text{CO(O}^-) +$ $\text{H}_2\text{O} - 0.201 \text{ O}_2$	$6.2 \cdot 10^{+08}$		
R <sub>o</sub> 02424	*		$\text{CH}_3\text{C(OH)}_2\text{CH(OH)CO(O}^-) + \text{NO}_3 \rightarrow \text{CH}_3\text{C(OH)}_2\text{CH(OH)CO(O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02425	*	*	$\text{CO(O}^-)\text{CH(OH)C(OH)}_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2\cdot}$ $0.200 \text{ CO(O}^-)\text{CH(OH)C(OH)}_2\text{CH}_2(\text{O}\cdot) +$ $0.550 \text{ CO(O}^-)\text{CH(OH)C(OH)}_2\text{CHO} +$ $0.250 \text{ CH}_2(\text{OH)C(OH)}_2\text{CH(OH)CO(O}^-) + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02426	*	*	$\text{CH}_3\text{C(OH)}_2\text{C(OH)(OO}\cdot)\text{CO(O}^-) \rightarrow \text{CH}_3\text{C(OH)}_2\text{COCO(O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02427	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^-) + 0.500 \text{CH}_3\text{CO}(\text{OH}) +$ $0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})(\text{OO}\cdot) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02428	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{O}_2} \text{CH}_3\text{C}(\text{OH})_2\text{COCO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02429	*	*	$\text{CH}_3\text{C}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) \rightarrow 0.500 \text{CH}_3\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.500 \text{CO}(\text{O}^-)\text{CHO} + 0.500 \text{CH}_3\text{C}(\text{OH})_2\text{CHO} + 0.500 \cdot \text{CO}(\text{O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02430	*		$\text{CH}_3\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_3\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02431	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02432	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02433	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{OH} \rightarrow$ $0.238 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.075 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) +$ $0.324 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{O}^-) +$ $0.362 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{O}^-) + \text{H}_2\text{O} - 0.238 \text{O}_2$	$1.1 \cdot 10^{+09}$		
R <sub>o</sub> 02434	*		$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02435	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02436	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{O}^-) +$ $0.500 \text{CH}_2(\text{OH})\text{CO}(\text{OH}) + 0.500 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02437	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CO}(\text{O}^-) +$ $0.500 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OH}) + 0.500 \cdot \text{CO}(\text{O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02438	*		$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02439	*	*	CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + OH → 0.481 CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)CH(OH)(OO·) + 0.090 CH <sub>2</sub> (OH)C(OH)(OO·)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + 0.063 CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) + 0.061 CH <sub>2</sub> (OH)CH(O·)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + 0.305 CH <sub>2</sub> (OH)CH(OH)C(OH)(O·)CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.571 O <sub>2</sub>	1.4 · 10 <sup>+09</sup>		
R <sub>o</sub> 02440	*		CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 02441	*	*	CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)CH(OH)(OO·) → CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02442	*	*	CH <sub>2</sub> (OH)C(OH)(OO·)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) → CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CO(O <sup>-</sup> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02443	*	*	CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02444	*	*	CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) → CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02445	*	*	CH <sub>2</sub> (OH)CH(OH)C(OH)(O·)CO(O <sup>-</sup> ) → 0.500 CH <sub>2</sub> (OH)CH(OH)(OO·) + 0.500 CO(OH)CO(O <sup>-</sup> ) + 0.500 CH <sub>2</sub> (OH)CH(OH)CO(OH) + 0.500 · CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02446	*		CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CO(O·) → CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> (OO·) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02447	*	*	CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CO(O <sup>-</sup> ) + OH → 0.314 CO(O <sup>-</sup> )CH(OH)C(OH) <sub>2</sub> CH(OH)(OO·) + 0.057 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(OO·)CO(O <sup>-</sup> ) + 0.095 CO(O <sup>-</sup> )CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.428 CH <sub>2</sub> (OH)C(OH)(O·)CH(OH)CO(O <sup>-</sup> ) + 0.107 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O·)CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.371 O <sub>2</sub>	8.8 · 10 <sup>+08</sup>		
R <sub>o</sub> 02448	*		CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 02449	*	*	CO(O <sup>-</sup> )CH(OH)C(OH) <sub>2</sub> CH(OH)(OO·) → CO(O <sup>-</sup> )CH(OH)C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02450	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{O}^-) \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCO}(\text{O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02451	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^-) +$ $0.500 \text{CH}_2(\text{OH})\text{CO}(\text{OH}) + 0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02452	*		$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02453	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{OH} \rightarrow$ $0.479 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.049 \text{CH}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) +$ $0.177 \text{CH}(\text{OH})_2\text{CH}_2\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{O}^-) +$ $0.235 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) +$ $0.061 \text{CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) + \text{H}_2\text{O} - 0.705 \text{O}_2$	$1.7 \cdot 10^{+09}$		
R <sub>o</sub> 02454	*		$\text{CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $\text{CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02455	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02456	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) \xrightarrow{RO_2}$ $0.200 \text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) +$ $0.550 \text{CH}(\text{OH})_2\text{COCH}(\text{OH})\text{CO}(\text{O}^-) +$ $0.250 \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02457	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{O}^-) \rightarrow \text{CH}(\text{OH})_2\text{CH}_2\text{COCO}(\text{O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02458	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{CH}_2\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02459	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}_2\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}_2(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02460	*		$\text{CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CH}_2\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02461	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{COCH}(\text{OH})\text{CO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02462	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CH}\cdot(\text{OH})_2 + 0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CHO} + 0.500 \text{CH}(\text{OH})_2\text{CHO} +$ $0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02463	*	*	CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CO(O <sup>-</sup> ) + OH → 0.285 CO(O <sup>-</sup> )CH <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO·) + 0.261 CH(OH) <sub>2</sub> C(OH)(OO·)CH <sub>2</sub> CO(O <sup>-</sup> ) + 0.066 CH(OH) <sub>2</sub> CH(OH)CH(OO·)CO(O <sup>-</sup> ) + 0.315 CO(O <sup>-</sup> )CH <sub>2</sub> CH(OH)CH(OH)(O·) + 0.073 CH(OH) <sub>2</sub> CH(O·)CH <sub>2</sub> CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.612 O <sub>2</sub>	1.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 02464	*		CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 02465	*	*	CO(O <sup>-</sup> )CH <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO·) → CO(OH)CH(OH)CH <sub>2</sub> CO(O <sup>-</sup> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02466	*	*	CH(OH) <sub>2</sub> C(OH)(OO·)CH <sub>2</sub> CO(O <sup>-</sup> ) → CH(OH) <sub>2</sub> COCH <sub>2</sub> CO(O <sup>-</sup> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02467	*	*	CH(OH) <sub>2</sub> CH(OH)CH(OO·)CO(O <sup>-</sup> ) + CH(OH) <sub>2</sub> CH(OH)CH(OO·)CO(O <sup>-</sup> ) → 2.000 CH(OH) <sub>2</sub> CH(OH)CHO + 2.000 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2.000 OH <sup>-</sup> - 2.000 H <sub>2</sub> O	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 02468	*	*	CH(OH) <sub>2</sub> CH(OH)CH(OO·)CO(O <sup>-</sup> ) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH(OH)CH(O·)CO(O <sup>-</sup> ) + 0.550 CH(OH) <sub>2</sub> CH(OH)COCO(O <sup>-</sup> ) + 0.250 CH(OH) <sub>2</sub> CH(OH)CH(OH)CO(O <sup>-</sup> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02469	*	*	CO(O <sup>-</sup> )CH <sub>2</sub> CH(OH)CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH(OH)CH <sub>2</sub> CO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02470	*	*	CO(O <sup>-</sup> )CH <sub>2</sub> CH(OH)CH(OH)(O·) → CO(O <sup>-</sup> )CH <sub>2</sub> CH(OH)(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02471	*		CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> CO(O·) → CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (OO·) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02472	*	*	CH(OH) <sub>2</sub> CH(OH)CH(O·)CO(O <sup>-</sup> ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(OH)COCO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02473	*	*	CH(OH) <sub>2</sub> CH(OH)CH(O·)CO(O <sup>-</sup> ) → 0.500 CH(OH) <sub>2</sub> CH(OH)(OO·) + 0.500 CO(O <sup>-</sup> )CHO + 0.500 CH(OH) <sub>2</sub> CH(OH)CHO + 0.500 · CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02474	*	*	CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + OH → 0.172 CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (OO·) + 0.314 CH <sub>3</sub> C(OH)(OO·)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + 0.090 CH <sub>3</sub> CH(O·)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + 0.424 CH <sub>3</sub> CH(OH)C(OH)(O·)CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.486 O <sub>2</sub>	1.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 02475	*		CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02476	*	*	CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (OO $\cdot$ ) $\xrightarrow{RO_2}$ 0.200 CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O $\cdot$ ) + 0.550 CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)CHO + 0.250 CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02477	*	*	CH <sub>3</sub> C(OH)(OO $\cdot$ )C(OH) <sub>2</sub> CO(O <sup>-</sup> ) → CH <sub>3</sub> COC(OH) <sub>2</sub> CO(O <sup>-</sup> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02478	*	*	CH <sub>3</sub> CH(OH)C(OH)(O $\cdot$ )CO(O <sup>-</sup> ) → 0.500 CH <sub>3</sub> CH(OH)(OO $\cdot$ ) + 0.500 CO(OH)CO(O <sup>-</sup> ) + 0.500 CH <sub>3</sub> CH(OH)CO(OH) + 0.500 · CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02479	*		CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> CO(O $\cdot$ ) → CH <sub>3</sub> CH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02480	*	*	CH <sub>3</sub> C(OH) <sub>2</sub> COCO(O <sup>-</sup> ) + OH → 0.150 CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CH <sub>2</sub> (OO $\cdot$ ) + 0.850 CH <sub>3</sub> C(OH)(O $\cdot$ )COCO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.150 O <sub>2</sub>	4.1 · 10 <sup>+08</sup>		
R <sub>o</sub> 02481	*		CH <sub>3</sub> C(OH) <sub>2</sub> COCO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>3</sub> C(OH) <sub>2</sub> COCO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 02482	*	*	CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CH <sub>2</sub> (OO $\cdot$ ) $\xrightarrow{RO_2}$ 0.200 CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) + 0.550 CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CHO + 0.250 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCO(O <sup>-</sup> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02483	*	*	CH <sub>3</sub> C(OH)(O $\cdot$ )COCO(O <sup>-</sup> ) → 0.500 CH <sub>3</sub> (OO $\cdot$ ) + 0.500 CO(OH)COCO(O <sup>-</sup> ) + 0.500 CH <sub>3</sub> CO(OH) + 0.500 CO(O <sup>-</sup> )CO(OO $\cdot$ ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02484	*		CH <sub>3</sub> C(OH) <sub>2</sub> COCO(O $\cdot$ ) → CH <sub>3</sub> C(OH) <sub>2</sub> CO(OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02485	*	*	CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) $\xrightarrow{O_2}$ CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02486	*	*	CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) → CO(O <sup>-</sup> )COC(OH) <sub>2</sub> (OO $\cdot$ ) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02487	*	*	CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CO(O <sup>-</sup> ) + OH → 0.407 CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCH(OH)(OO $\cdot$ ) + 0.102 CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCH <sub>2</sub> (O $\cdot$ ) + 0.491 CH <sub>2</sub> (OH)COC(OH)(O $\cdot$ )CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.407 O <sub>2</sub>	7.4 · 10 <sup>+08</sup>		
R <sub>o</sub> 02488	*		CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 02489	*	*	CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCH(OH)(OO $\cdot$ ) → CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02490	*	*	CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCH <sub>2</sub> (O $\cdot$ ) $\xrightarrow{O_2}$ CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02491	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{COCH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02492	*	*	$\text{CH}_2(\text{OH})\text{COC}(\text{OH})(\text{O}\cdot)\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\text{CO}(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CO}(\text{O}^-) +$ $0.500 \text{CH}_2(\text{OH})\text{COCO}(\text{OH}) + 0.500 \cdot \text{CO}(\text{O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02493	*		$\text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02494	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCO}(\text{O}^-) + \text{OH} \rightarrow$ $0.369 \text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.129 \text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CH}_2(\text{O}\cdot) + 0.502 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{COCO}(\text{O}^-) +$ $\text{H}_2\text{O} - 0.369 \text{O}_2$	$6.5 \cdot 10^{+08}$		
R <sub>o</sub> 02495	*		$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02496	*	*	$\text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02497	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{COCO}(\text{O}^-) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CO}(\text{OH})\text{COCO}(\text{O}^-) + 0.500 \text{CH}_2(\text{OH})\text{CO}(\text{OH}) +$ $0.500 \text{CO}(\text{O}^-)\text{CO}(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02498	*		$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCO}(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02499	*	*	$\text{CH}(\text{OH})_2\text{CH}_2\text{COCO}(\text{O}^-) + \text{OH} \rightarrow$ $0.615 \text{CO}(\text{O}^-)\text{COCH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.033 \text{CH}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{COCO}(\text{O}^-) +$ $0.352 \text{CO}(\text{O}^-)\text{COCH}_2\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.648 \text{O}_2$	$1.1 \cdot 10^{+09}$		
R <sub>o</sub> 02500	*		$\text{CH}(\text{OH})_2\text{CH}_2\text{COCO}(\text{O}^-) + \text{NO}_3 \rightarrow \text{CH}(\text{OH})_2\text{CH}_2\text{COCO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02501	*	*	$\text{CO}(\text{O}^-)\text{COCH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}_2\text{COCO}(\text{O}^-) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02502	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{COCO}(\text{O}^-) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{COCO}(\text{O}^-) + 0.550 \text{CH}(\text{OH})_2\text{COCOCO}(\text{O}^-) +$ $0.250 \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{COCO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02503	*	*	$\text{CO}(\text{O}^-)\text{COCH}_2\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{CH}_2\text{COCO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02504	*	*	$\text{CO}(\text{O}^-)\text{COCH}_2\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{COCH}_2(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02505	*		$\text{CH}(\text{OH})_2\text{CH}_2\text{COCO}(\text{O}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CH}_2\text{CO}(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02506	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{COCO}(\text{O}^-) \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{COCOCO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02507	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{COCO}(\text{O}^-) \rightarrow 0.500 \text{CH}\cdot(\text{OH})_2 + 0.500 \text{CO}(\text{O}^-)\text{COCHO} +$ $0.500 \text{CH}(\text{OH})_2\text{CHO} + 0.500 \text{CO}(\text{O}^-)\text{CO}(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A/R^b$	Reference/comment
R <sub>o</sub> 02508	*	*	CH(OH) <sub>2</sub> COCH <sub>2</sub> CO(O <sup>-</sup> ) + OH → 0.300 CO(O <sup>-</sup> )CH <sub>2</sub> COC(OH) <sub>2</sub> (OO·) + 0.070 CH(OH) <sub>2</sub> COCH(OO·)CO(O <sup>-</sup> ) + 0.631 CO(O <sup>-</sup> )CH <sub>2</sub> COCH(OH)(O·) + H <sub>2</sub> O - 0.369 O <sub>2</sub>	5.2 · 10 <sup>+08</sup>		
R <sub>o</sub> 02509	*	*	CH(OH) <sub>2</sub> COCH <sub>2</sub> CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH(OH) <sub>2</sub> COCH <sub>2</sub> CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 02510	*	*	CO(O <sup>-</sup> )CH <sub>2</sub> COC(OH) <sub>2</sub> (OO·) → CO(OH)COCH <sub>2</sub> CO(O <sup>-</sup> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02511	*	*	CH(OH) <sub>2</sub> COCH(OO·)CO(O <sup>-</sup> ) + CH(OH) <sub>2</sub> COCH(OO·)CO(O <sup>-</sup> ) → 2.000 CH(OH) <sub>2</sub> COCHO + 2.000 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2.000 OH <sup>-</sup> - 2.000 H <sub>2</sub> O	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 02512	*	*	CH(OH) <sub>2</sub> COCH(OO·)CO(O <sup>-</sup> ) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> COCH(O·)CO(O <sup>-</sup> ) + 0.550 CH(OH) <sub>2</sub> COCOCO(O <sup>-</sup> ) + 0.250 CH(OH) <sub>2</sub> COCH(OH)CO(O <sup>-</sup> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02513	*	*	CO(O <sup>-</sup> )CH <sub>2</sub> COCH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)COCH <sub>2</sub> CO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02514	*	*	CO(O <sup>-</sup> )CH <sub>2</sub> COCH(OH)(O·) → CO(O <sup>-</sup> )CH <sub>2</sub> CO(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02515	*	*	CH(OH) <sub>2</sub> COCH <sub>2</sub> CO(O·) → CH(OH) <sub>2</sub> COCH <sub>2</sub> (OO·) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02516	*	*	CH(OH) <sub>2</sub> COCH(O·)CO(O <sup>-</sup> ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCOCO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02517	*	*	CH(OH) <sub>2</sub> COCH(O·)CO(O <sup>-</sup> ) → 0.500 CH(OH) <sub>2</sub> CO(OO·) + 0.500 CO(O <sup>-</sup> )CHO + 0.500 CH(OH) <sub>2</sub> COCHO + 0.500 · CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02518	*	*	CH <sub>3</sub> COC(OH) <sub>2</sub> CO(O <sup>-</sup> ) + OH → 0.175 CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCH <sub>2</sub> (OO·) + 0.825 CH <sub>3</sub> COC(OH)(O·)CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.175 O <sub>2</sub>	4.4 · 10 <sup>+08</sup>		
R <sub>o</sub> 02519	*	*	CH <sub>3</sub> COC(OH) <sub>2</sub> CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>3</sub> COC(OH) <sub>2</sub> CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 02520	*	*	CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCH <sub>2</sub> (O·) + 0.550 CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCHO + 0.250 CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CO(O <sup>-</sup> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02521	*	*	CH <sub>3</sub> COC(OH)(O·)CO(O <sup>-</sup> ) → 0.500 CH <sub>3</sub> CO(OO·) + 0.500 CO(OH)CO(O <sup>-</sup> ) + 0.500 CH <sub>3</sub> COCO(OH) + 0.500 · CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02522	*	*	CH <sub>3</sub> COC(OH) <sub>2</sub> CO(O·) → CH <sub>3</sub> COC(OH) <sub>2</sub> (OO·) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00317	*	*	CO(O <sup>-</sup> )COCH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)COCO(O <sup>-</sup> )	5.6 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00318	*	*	CO(O <sup>-</sup> )COCH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CO(O <sup>-</sup> )	6.7 · 10 <sup>+00</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02523	*	*	CO(O <sup>-</sup> )COCH(OH)CHO + OH → 0.063 CO(O <sup>-</sup> )COC(OH)(OO·)CHO + 0.871 CO(O <sup>-</sup> )COCH(OH)CO(OO·) + 0.066 CO(O <sup>-</sup> )COCH(O·)CHO + H <sub>2</sub> O - 0.934 O <sub>2</sub>	9.4 · 10 <sup>+08</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02524	*		$\text{CO}(\text{O}^-)\text{COCH}(\text{OH})\text{CHO} + \text{NO}_3 \rightarrow \text{CHOCH}(\text{OH})\text{COCO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02525	*	*	$\text{CO}(\text{O}^-)\text{COC}(\text{OH})(\text{OO}\cdot)\text{CHO} \rightarrow \text{CO}(\text{O}^-)\text{COCOCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02526	*	*	$\text{CO}(\text{O}^-)\text{COCH}(\text{OH})\text{CO}(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{O}^-) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02527	*	*	$\text{CO}(\text{O}^-)\text{COCH}(\text{O}\cdot)\text{CHO} \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{COCOCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02528	*	*	$\text{CO}(\text{O}^-)\text{COCH}(\text{O}\cdot)\text{CHO} \rightarrow 0.500 \text{CO}(\text{O}^-)\text{CO}(\text{OO}\cdot) + 0.500 \text{CHOCHO} +$ $0.500 \text{CO}(\text{O}^-)\text{COCHO} + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{O}_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02529	*		$\text{CHOCH}(\text{OH})\text{COCO}(\text{O}\cdot) \rightarrow \text{CHOCH}(\text{OH})\text{CO}(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00319	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{COCH}(\text{OH})\text{CO}(\text{O}^-)$	$9.7 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00320	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}^-)$	$1.4 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02530	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCHO} + \text{OH} \rightarrow$ $0.084 \text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{OO}\cdot)\text{COCHO} + 0.765 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCO}(\text{OO}\cdot) +$ $0.151 \text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{COCHO} + \text{H}_2\text{O} - 0.849 \text{O}_2$	$5.6 \cdot 10^{+08}$		
R <sub>o</sub> 02531	*		$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCHO} + \text{NO}_3 \rightarrow \text{CHOCOCH}(\text{OH})\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02532	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{OO}\cdot)\text{COCHO} \rightarrow \text{CO}(\text{O}^-)\text{COCOCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
E <sub>o</sub> 00321	*	*	$\text{CO}(\text{O}^-)\text{COCOCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{COCO}(\text{O}^-)$	$2.6 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00322	*	*	$\text{CO}(\text{O}^-)\text{COCOCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}^-)$	$1.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02533	*	*	$\text{CO}(\text{O}^-)\text{COCOCHO} \rightarrow 0.250 \text{CO}(\text{O}^-)\text{CO}(\text{OO}\cdot) + 0.250 \text{CHOCO}(\text{OO}\cdot) +$ $0.250 \text{CO}(\text{O}^-)\text{COCO}(\text{OO}\cdot) + 0.250 \text{CHO}(\text{OO}\cdot)$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 02534	*	*	$\text{CO}(\text{O}^-)\text{COCOCHO} + \text{OH} \rightarrow \text{CO}(\text{O}^-)\text{COCOCO}(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$3.7 \cdot 10^{+08}$		
R <sub>o</sub> 02535	*		$\text{CO}(\text{O}^-)\text{COCOCHO} + \text{NO}_3 \rightarrow \text{CHOCOCOCO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02536	*	*	$\text{CO}(\text{O}^-)\text{COCOCO}(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{COCOCO}(\text{O}^-) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02537	*		$\text{CHOCOCOCO}(\text{O}\cdot) \rightarrow \text{CHOCOCO}(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00323	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^-)$	$1.5 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02538	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CHO} + \text{OH} \rightarrow$ $0.077 \text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})\text{CHO} +$ $0.096 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CHO} +$ $0.702 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) +$ $0.073 \text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CHO} + 0.053 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CHO} +$ $\text{H}_2\text{O} - 0.874 \text{O}_2$	$1.4 \cdot 10^{+09}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02539	*		CO(O <sup>-</sup> )CH(OH)CH(OH)CHO + NO <sub>3</sub> → CHOCH(OH)CH(OH)CO(O <sup>·</sup> ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 02540	*	*	CO(O <sup>-</sup> )C(OH)(OO <sup>·</sup> )CH(OH)CHO → CO(O <sup>-</sup> )COCH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02541	*	*	CO(O <sup>-</sup> )CH(OH)C(OH)(OO <sup>·</sup> )CHO → CO(O <sup>-</sup> )CH(OH)COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00324	*	*	CO(O <sup>-</sup> )CH <sub>2</sub> C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> COCH <sub>2</sub> CO(O <sup>-</sup> )	1.4 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00325	*	*	CO(O <sup>-</sup> )CH <sub>2</sub> C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> CO(O <sup>-</sup> )	3.3 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02542	*	*	CO(O <sup>-</sup> )CH <sub>2</sub> C(OH) <sub>2</sub> CHO + OH → 0.036 CO(O <sup>-</sup> )CH(OO <sup>·</sup> )C(OH) <sub>2</sub> CHO + 0.530 CO(O <sup>-</sup> )CH <sub>2</sub> C(OH) <sub>2</sub> CO(OO <sup>·</sup> ) + 0.433 CO(O <sup>-</sup> )CH <sub>2</sub> C(OH)(O <sup>·</sup> )CHO + H <sub>2</sub> O - 0.567 O <sub>2</sub>	7.5 · 10 <sup>+08</sup>		
R <sub>o</sub> 02543	*		CO(O <sup>-</sup> )CH <sub>2</sub> C(OH) <sub>2</sub> CHO + NO <sub>3</sub> → CHOC(OH) <sub>2</sub> CH <sub>2</sub> CO(O <sup>·</sup> ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 02544	*	*	CO(O <sup>-</sup> )CH(OO <sup>·</sup> )C(OH) <sub>2</sub> CHO + CO(O <sup>-</sup> )CH(OO <sup>·</sup> )C(OH) <sub>2</sub> CHO → 2.000 CHOC(OH) <sub>2</sub> CHO + 2.000 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2.000 OH <sup>-</sup> - 2.000 H <sub>2</sub> O	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 02545	*	*	CO(O <sup>-</sup> )CH(OO <sup>·</sup> )C(OH) <sub>2</sub> CHO $\xrightarrow{RO_2}$ 0.200 CO(O <sup>-</sup> )CH(O <sup>·</sup> )C(OH) <sub>2</sub> CHO + 0.550 CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CHO + 0.250 CO(O <sup>-</sup> )CH(OH)C(OH) <sub>2</sub> CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02546	*	*	CO(O <sup>-</sup> )CH <sub>2</sub> C(OH) <sub>2</sub> CO(OO <sup>·</sup> ) → CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> CO(O <sup>-</sup> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02547	*	*	CO(O <sup>-</sup> )CH <sub>2</sub> C(OH)(O <sup>·</sup> )CHO → 0.500 CO(O <sup>-</sup> )CH <sub>2</sub> (OO <sup>·</sup> ) + 0.500 CO(OH)CHO + 0.500 CO(OH)CH <sub>2</sub> CO(O <sup>-</sup> ) + 0.500 CH <sup>·</sup> (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02548	*		CHOC(OH) <sub>2</sub> CH <sub>2</sub> CO(O <sup>·</sup> ) → CHOC(OH) <sub>2</sub> CH <sub>2</sub> (OO <sup>·</sup> ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02549	*	*	CO(O <sup>-</sup> )CH(O <sup>·</sup> )C(OH) <sub>2</sub> CHO $\xrightarrow{O_2}$ CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02550	*	*	CO(O <sup>-</sup> )CH(O <sup>·</sup> )C(OH) <sub>2</sub> CHO → 0.500 · CO(O <sup>-</sup> ) + 0.500 CHOC(OH) <sub>2</sub> CHO + 0.500 CO(O <sup>-</sup> )CHO + 0.500 CHOC(OH) <sub>2</sub> (OO <sup>·</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00326	*	*	CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH <sub>2</sub> COCO(O <sup>-</sup> )	9.0 · 10 <sup>+00</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02551	*	*	CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH <sub>2</sub> CHO + OH → 0.836 CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH <sub>2</sub> CO(OO <sup>·</sup> ) + 0.164 CO(O <sup>-</sup> )C(OH)(O <sup>·</sup> )CH <sub>2</sub> CHO + H <sub>2</sub> O - 0.836 O <sub>2</sub>	2.7 · 10 <sup>+09</sup>		
R <sub>o</sub> 02552	*		CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH <sub>2</sub> CHO + NO <sub>3</sub> → CHOCH <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>·</sup> ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 02553	*	*	CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH <sub>2</sub> CO(OO <sup>·</sup> ) → CO(OH)CH <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02554	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{O}\cdot)\text{CH}_2\text{CHO} \rightarrow 0.500 \cdot \text{CO}(\text{O}^-) + 0.500 \text{CO}(\text{OH})\text{CH}_2\text{CHO} +$ $0.500 \text{CO}(\text{OH})\text{CO}(\text{O}^-) + 0.500 \text{CHOCH}_2(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02555	*		$\text{CHOCH}_2\text{C}(\text{OH})_2\text{CO}(\text{O}\cdot) \rightarrow \text{CHOCH}_2\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00327	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) \rightleftharpoons$ $\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{H}^+$	$2.9 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02556	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) \rightarrow$ $0.250 \text{CHO}(\text{OH}) + 0.250 \text{HO}_2 + 0.250 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.250 \text{CH}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.250 \text{CO}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot)$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 02557	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{OH} \rightarrow$ $0.117 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.343 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) +$ $0.324 \text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{OH}) +$ $0.216 \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) + \text{H}_2\text{O} - 0.117 \text{O}_2$	$1.1 \cdot 10^{+09}$		
R <sub>o</sub> 02558	*		$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{NO}_3 \rightarrow$ $0.117 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.343 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) +$ $0.324 \text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{OH}) +$ $0.216 \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) + \text{NO}_3^- + \text{H}^+ - 0.117 \text{O}_2$	$7.4 \cdot 10^{+06}$		
R <sub>o</sub> 02559	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow$ $\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02560	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02561	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02562	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{OH}) \rightarrow$ $0.500 \text{CH} \cdot (\text{OH})_2 + 0.500 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OH}) +$ $0.500 \text{CH}(\text{OH})_2\text{CO}(\text{OH}) + 0.500 \text{CO}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02563	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) \rightarrow$ $0.500 \text{CH}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CO}(\text{OH}) +$ $0.500 \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OH}) + 0.500 \cdot \text{CO}(\text{OH}) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00328	*	*	$\text{CH(OH)}_2\text{CH(OH)CH(OH)CO(OH)} \rightleftharpoons$ $\text{CH(OH)}_2\text{CH(OH)CH(OH)CO(O}^-) + \text{H}^+$	$8.0 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02564	*	*	$\text{CH(OH)}_2\text{CH(OH)CH(OH)CO(OH)} + \text{OH} \rightarrow$ $0.343 \text{ CO(OH)CH(OH)CH(OH)C(OH)}_2(\text{OO}\cdot) +$ $0.076 \text{ CH(OH)}_2\text{C(OH)(OO}\cdot)\text{CH(OH)CO(OH)} +$ $0.037 \text{ CH(OH)}_2\text{CH(OH)C(OH)(OO}\cdot)\text{CO(OH)} +$ $0.398 \text{ CO(OH)CH(OH)CH(OH)CH(OH)(O}\cdot) +$ $0.088 \text{ CH(OH)}_2\text{CH(O}\cdot)\text{CH(OH)CO(OH)} +$ $0.059 \text{ CH(OH)}_2\text{CH(OH)CH(O}\cdot)\text{CO(OH)} + \text{H}_2\text{O} - 0.456 \text{ O}_2$	$9.6 \cdot 10^{+08}$		
R <sub>o</sub> 02565	*		$\text{CH(OH)}_2\text{CH(OH)CH(OH)CO(OH)} + \text{NO}_3 \rightarrow$ $0.343 \text{ CO(OH)CH(OH)CH(OH)C(OH)}_2(\text{OO}\cdot) +$ $0.076 \text{ CH(OH)}_2\text{C(OH)(OO}\cdot)\text{CH(OH)CO(OH)} +$ $0.037 \text{ CH(OH)}_2\text{CH(OH)C(OH)(OO}\cdot)\text{CO(OH)} +$ $0.398 \text{ CO(OH)CH(OH)CH(OH)CH(OH)(O}\cdot) +$ $0.088 \text{ CH(OH)}_2\text{CH(O}\cdot)\text{CH(OH)CO(OH)} +$ $0.059 \text{ CH(OH)}_2\text{CH(OH)CH(O}\cdot)\text{CO(OH)} + \text{NO}_3^- + \text{H}^+ - 0.456 \text{ O}_2$	$1.2 \cdot 10^{+07}$		
R <sub>o</sub> 02566	*	*	$\text{CO(OH)CH(OH)CH(OH)C(OH)}_2(\text{OO}\cdot) \rightarrow$ $\text{CO(OH)CH(OH)CH(OH)CO(OH)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02567	*	*	$\text{CH(OH)}_2\text{C(OH)(OO}\cdot)\text{CH(OH)CO(OH)} \rightarrow$ $\text{CH(OH)}_2\text{COCH(OH)CO(OH)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02568	*	*	$\text{CH(OH)}_2\text{CH(OH)C(OH)(OO}\cdot)\text{CO(OH)} \rightarrow$ $\text{CH(OH)}_2\text{CH(OH)COCO(OH)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02569	*	*	$\text{CO(OH)CH(OH)CH(OH)CH(OH)(O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CO(OH)CH(OH)CH(OH)CO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02570	*	*	$\text{CO(OH)CH(OH)CH(OH)CH(OH)(O}\cdot) \rightarrow$ $\text{CO(OH)CH(OH)CH(OH)(OO}\cdot) + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02571	*	*	$\text{CH(OH)}_2\text{CH(OH)CH(O}\cdot)\text{CO(OH)} \xrightarrow{\text{O}_2} \text{CH(OH)}_2\text{CH(OH)COCO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02572	*	*	$\text{CH(OH)}_2\text{CH(OH)CH(O}\cdot)\text{CO(OH)} \rightarrow$ $0.500 \text{ CH(OH)}_2\text{CH(OH)(OO}\cdot) + 0.500 \text{ CO(OH)CHO} +$ $0.500 \text{ CH(OH)}_2\text{CH(OH)CHO} + 0.500 \cdot \text{CO(OH)} - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00329	*	*	$\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CO(OH)} \rightleftharpoons$ $\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CO(O}^-) + \text{H}^+$	$1.8 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02573	*	*	$\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CO(OH)} + \text{OH} \rightarrow$ $0.309 \text{ CO(OH)C(OH)}_2\text{CH(OH)C(OH)}_2(\text{OO}\cdot) +$ $0.375 \text{ CO(OH)C(OH)}_2\text{CH(OH)CH(OH)(O}\cdot) +$ $0.079 \text{ CH(OH)}_2\text{CH(O}\cdot)\text{C(OH)}_2\text{CO(OH)} +$ $0.237 \text{ CH(OH)}_2\text{CH(OH)C(OH)(O}\cdot)\text{CO(OH)} + \text{H}_2\text{O} - 0.309 \text{ O}_2$	$1.0 \cdot 10^{+09}$		
R <sub>o</sub> 02574	*		$\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CO(OH)} + \text{NO}_3 \rightarrow$ $0.309 \text{ CO(OH)C(OH)}_2\text{CH(OH)C(OH)}_2(\text{OO}\cdot) +$ $0.375 \text{ CO(OH)C(OH)}_2\text{CH(OH)CH(OH)(O}\cdot) +$ $0.079 \text{ CH(OH)}_2\text{CH(O}\cdot)\text{C(OH)}_2\text{CO(OH)} +$ $0.237 \text{ CH(OH)}_2\text{CH(OH)C(OH)(O}\cdot)\text{CO(OH)} + \text{NO}_3^- + \text{H}^+ - 0.309 \text{ O}_2$	$9.6 \cdot 10^{+06}$		
R <sub>o</sub> 02575	*	*	$\text{CO(OH)C(OH)}_2\text{CH(OH)C(OH)}_2(\text{OO}\cdot) \rightarrow$ $\text{CO(OH)CH(OH)C(OH)}_2\text{CO(OH)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02576	*	*	$\text{CO(OH)C(OH)}_2\text{CH(OH)CH(OH)(O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CO(OH)CH(OH)C(OH)}_2\text{CO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02577	*	*	$\text{CO(OH)C(OH)}_2\text{CH(OH)CH(OH)(O}\cdot) \rightarrow$ $\text{CO(OH)C(OH)}_2\text{CH(OH)(OO}\cdot) + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02578	*	*	$\text{CH(OH)}_2\text{CH(O}\cdot)\text{C(OH)}_2\text{CO(OH)} \xrightarrow{\text{O}_2} \text{CH(OH)}_2\text{COC(OH)}_2\text{CO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02579	*	*	$\text{CH(OH)}_2\text{CH(O}\cdot)\text{C(OH)}_2\text{CO(OH)} \rightarrow$ $0.500 \text{ CH}\cdot(\text{OH})_2 + 0.500 \text{ CO(OH)C(OH)}_2\text{CHO} + 0.500 \text{ CH(OH)}_2\text{CHO} +$ $0.500 \text{ CO(OH)C(OH)}_2(\text{OO}\cdot) - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02580	*	*	$\text{CH(OH)}_2\text{CH(OH)C(OH)(O}\cdot)\text{CO(OH)} \rightarrow$ $0.500 \text{ CH(OH)}_2\text{CH(OH)(OO}\cdot) + 0.500 \text{ CO(OH)CO(OH)} +$ $0.500 \text{ CH(OH)}_2\text{CH(OH)CO(OH)} + 0.500 \cdot \text{CO(OH)} - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00330	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)CO(OH)} \rightleftharpoons$ $\text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)CO(O}^-) + \text{H}^+$	$1.2 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02581	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CO(OH) + OH $\rightarrow$ 0.144 CO(OH)CH(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.400 CO(OH)CH(OH)C(OH) <sub>2</sub> CH(OH)(O $\cdot$ ) + 0.397 CH(OH) <sub>2</sub> C(OH)(O $\cdot$ )CH(OH)CO(OH) + 0.059 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(O $\cdot$ )CO(OH) + H <sub>2</sub> O - 0.144 O <sub>2</sub>	$9.1 \cdot 10^{+08}$		
R <sub>o</sub> 02582	*		CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CO(OH) + NO <sub>3</sub> $\rightarrow$ 0.144 CO(OH)CH(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.400 CO(OH)CH(OH)C(OH) <sub>2</sub> CH(OH)(O $\cdot$ ) + 0.397 CH(OH) <sub>2</sub> C(OH)(O $\cdot$ )CH(OH)CO(OH) + 0.059 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(O $\cdot$ )CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.144 O <sub>2</sub>	$9.7 \cdot 10^{+06}$		
R <sub>o</sub> 02583	*	*	CO(OH)CH(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)CH(OH)C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02584	*	*	CO(OH)CH(OH)C(OH) <sub>2</sub> CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)CH(OH)C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02585	*	*	CO(OH)CH(OH)C(OH) <sub>2</sub> CH(OH)(O $\cdot$ ) $\rightarrow$ CO(OH)CH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02586	*	*	CH(OH) <sub>2</sub> C(OH)(O $\cdot$ )CH(OH)CO(OH) $\rightarrow$ 0.500 CH $\cdot$ (OH) <sub>2</sub> + 0.500 CO(OH)CH(OH)CO(OH) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CO(OH)CH(OH)(OO $\cdot$ ) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02587	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(O $\cdot$ )CO(OH) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCO(OH) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02588	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(O $\cdot$ )CO(OH) $\rightarrow$ 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.500 CO(OH)CHO + 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + 0.500 $\cdot$ CO(OH) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00331	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCO(OH) $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH)	$1.2 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00332	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCO(OH) $\rightleftharpoons$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCO(O <sup>-</sup> ) + H <sup>+</sup>	$2.5 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02589	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCO(OH) $\rightarrow$ 0.250 CHO(OH) + 0.250 HO <sub>2</sub> + 0.250 CO(OH)COC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.250 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.250 CO(OH)CO(OO $\cdot$ )	$1.0 \cdot 10^{-01}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02590	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCO(OH) + OH $\rightarrow$ 0.143 CO(OH)COC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.463 CO(OH)COC(OH) <sub>2</sub> CH(OH)(O $\cdot$ ) + 0.394 CH(OH) <sub>2</sub> C(OH)(O $\cdot$ )COCO(OH) + H <sub>2</sub> O - 0.143 O <sub>2</sub>	$7.8 \cdot 10^{+08}$		
R <sub>o</sub> 02591	*		CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCO(OH) + NO <sub>3</sub> $\rightarrow$ 0.143 CO(OH)COC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.463 CO(OH)COC(OH) <sub>2</sub> CH(OH)(O $\cdot$ ) + 0.394 CH(OH) <sub>2</sub> C(OH)(O $\cdot$ )COCO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.143 O <sub>2</sub>	$7.4 \cdot 10^{+06}$		
R <sub>o</sub> 02592	*	*	CO(OH)COC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)C(OH) <sub>2</sub> COCO(OH) + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02593	*	*	CO(OH)COC(OH) <sub>2</sub> CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> COCO(OH) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02594	*	*	CO(OH)COC(OH) <sub>2</sub> CH(OH)(O $\cdot$ ) $\rightarrow$ CO(OH)COC(OH) <sub>2</sub> (OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02595	*	*	CH(OH) <sub>2</sub> C(OH)(O $\cdot$ )COCO(OH) $\rightarrow$ 0.500 CH $\cdot$ (OH) <sub>2</sub> + 0.500 CO(OH)COCO(OH) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CO(OH)CO(OO $\cdot$ ) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00333	*	*	CH(OH) <sub>2</sub> COCOCO(OH) $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH)	$1.2 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00334	*	*	CH(OH) <sub>2</sub> COCOCO(OH) $\rightleftharpoons$ CH(OH) <sub>2</sub> COCOCO(O <sup>-</sup> ) + H <sup>+</sup>	$5.8 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02596	*	*	CH(OH) <sub>2</sub> COCOCO(OH) $\rightarrow$ 0.250 CHO(OH) + 0.250 HO <sub>2</sub> + 0.250 CO(OH)COCO(OO $\cdot$ ) + 0.250 CH(OH) <sub>2</sub> CO(OO $\cdot$ ) + 0.250 CO(OH)CO(OO $\cdot$ )	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 02597	*	*	CH(OH) <sub>2</sub> COCOCO(OH) + OH $\rightarrow$ 0.280 CO(OH)COCOC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.720 CO(OH)COCOCH(OH)(O $\cdot$ ) + H <sub>2</sub> O - 0.280 O <sub>2</sub>	$4.5 \cdot 10^{+08}$		
R <sub>o</sub> 02598	*		CH(OH) <sub>2</sub> COCOCO(OH) + NO <sub>3</sub> $\rightarrow$ 0.280 CO(OH)COCOC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.720 CO(OH)COCOCH(OH)(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.280 O <sub>2</sub>	$7.3 \cdot 10^{+06}$		
R <sub>o</sub> 02599	*	*	CO(OH)COCOC(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)COCOCO(OH) + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02600	*	*	CO(OH)COCOCH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)COCOCO(OH) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02601	*	*	CO(OH)COCOCH(OH)(O $\cdot$ ) $\rightarrow$ CO(OH)COCO(OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00335	*	*	CH(OH) <sub>2</sub> CH(OH)COCO(OH) $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CO(OH)	$5.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00336	*	*	CH(OH) <sub>2</sub> CH(OH)COCO(OH) $\rightleftharpoons$ CH(OH) <sub>2</sub> CH(OH)COCO(O <sup>-</sup> ) + H <sup>+</sup>	$9.9 \cdot 10^{-02}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02602	*	*	CH(OH) <sub>2</sub> CH(OH)COCO(OH) + OH $\rightarrow$ 0.367 CO(OH)COCH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.043 CH(OH) <sub>2</sub> C(OH)(OO $\cdot$ )COCO(OH) + 0.496 CO(OH)COCH(OH)CH(OH)(O $\cdot$ ) + 0.094 CH(OH) <sub>2</sub> CH(O $\cdot$ )COCO(OH) + H <sub>2</sub> O - 0.410 O <sub>2</sub>	$7.7 \cdot 10^{+08}$		
R <sub>o</sub> 02603	*		CH(OH) <sub>2</sub> CH(OH)COCO(OH) + NO <sub>3</sub> $\rightarrow$ 0.367 CO(OH)COCH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.043 CH(OH) <sub>2</sub> C(OH)(OO $\cdot$ )COCO(OH) + 0.496 CO(OH)COCH(OH)CH(OH)(O $\cdot$ ) + 0.094 CH(OH) <sub>2</sub> CH(O $\cdot$ )COCO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.410 O <sub>2</sub>	$9.5 \cdot 10^{+06}$		
R <sub>o</sub> 02604	*	*	CO(OH)COCH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)CH(OH)COCO(OH) + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02605	*	*	CH(OH) <sub>2</sub> C(OH)(OO $\cdot$ )COCO(OH) $\rightarrow$ CH(OH) <sub>2</sub> COCOCO(OH) + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02606	*	*	CO(OH)COCH(OH)CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)CH(OH)COCO(OH) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02607	*	*	CO(OH)COCH(OH)CH(OH)(O $\cdot$ ) $\rightarrow$ CO(OH)COCH(OH)(OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02608	*	*	CH(OH) <sub>2</sub> CH(O $\cdot$ )COCO(OH) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCOCO(OH) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02609	*	*	CH(OH) <sub>2</sub> CH(O $\cdot$ )COCO(OH) $\rightarrow$ 0.500 CH $\cdot$ (OH) <sub>2</sub> + 0.500 CO(OH)COCHO + 0.500 CH(OH) <sub>2</sub> CHO + 0.500 CO(OH)CO(OO $\cdot$ ) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00337	*	*	CH(OH) <sub>2</sub> COCH(OH)CO(OH) $\rightleftharpoons$ CH(OH) <sub>2</sub> COCH(OH)CO(O <sup>-</sup> ) + H <sup>+</sup>	$1.7 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02610	*	*	CH(OH) <sub>2</sub> COCH(OH)CO(OH) + OH $\rightarrow$ 0.283 CO(OH)CH(OH)COC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.625 CO(OH)CH(OH)COCH(OH)(O $\cdot$ ) + 0.092 CH(OH) <sub>2</sub> COCH(O $\cdot$ )CO(OH) + H <sub>2</sub> O - 0.283 O <sub>2</sub>	$5.2 \cdot 10^{+08}$		
R <sub>o</sub> 02611	*		CH(OH) <sub>2</sub> COCH(OH)CO(OH) + NO <sub>3</sub> $\rightarrow$ 0.283 CO(OH)CH(OH)COC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.625 CO(OH)CH(OH)COCH(OH)(O $\cdot$ ) + 0.092 CH(OH) <sub>2</sub> COCH(O $\cdot$ )CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.283 O <sub>2</sub>	$9.7 \cdot 10^{+06}$		
R <sub>o</sub> 02612	*	*	CO(OH)CH(OH)COC(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)CH(OH)COCO(OH) + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02613	*	*	CO(OH)CH(OH)COCH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)CH(OH)COCO(OH) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02614	*	*	CO(OH)CH(OH)COCH(OH)(O $\cdot$ ) $\rightarrow$ CO(OH)CH(OH)CO(OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02615	*	*	$\text{CH(OH)}_2\text{COCH(O}\cdot\text{)CO(OH)} \xrightarrow{\text{O}_2} \text{CH(OH)}_2\text{COCOCO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02616	*	*	$\text{CH(OH)}_2\text{COCH(O}\cdot\text{)CO(OH)} \rightarrow 0.500 \text{CH(OH)}_2\text{CO(OO}\cdot\text{)} +$ $0.500 \text{CO(OH)CHO} + 0.500 \text{CH(OH)}_2\text{COCHO} + 0.500 \cdot \text{CO(OH)} - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00338	*	*	$\text{CO(OH)COC(OH)}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)}_2\text{C(OH)}_2\text{CO(OH)}$	$1.2 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00339	*	*	$\text{CO(OH)COC(OH)}_2\text{CHO} \rightleftharpoons \text{CO(O}^-\text{)COC(OH)}_2\text{CHO} + \text{H}^+$	$4.3 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02617	*	*	$\text{CO(OH)COC(OH)}_2\text{CHO} \rightarrow 0.250 \text{CO(OH)CO(OO}\cdot\text{)} +$ $0.250 \text{CHOC(OH)}_2\text{(OO}\cdot\text{)} + 0.250 \text{CO(OH)COC(OH)}_2\text{(OO}\cdot\text{)} + 0.250 \text{CHO(OO}\cdot\text{)}$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 02618	*	*	$\text{CO(OH)COC(OH)}_2\text{CHO} + \text{OH} \rightarrow 0.550 \text{CO(OH)COC(OH)}_2\text{CO(OO}\cdot\text{)} +$ $0.450 \text{CO(OH)COC(OH)(O}\cdot\text{)CHO} + \text{H}_2\text{O} - 0.550 \text{O}_2$	$5.9 \cdot 10^{+08}$		
R <sub>o</sub> 02619	*		$\text{CO(OH)COC(OH)}_2\text{CHO} + \text{NO}_3 \rightarrow 0.550 \text{CO(OH)COC(OH)}_2\text{CO(OO}\cdot\text{)} +$ $0.450 \text{CO(OH)COC(OH)(O}\cdot\text{)CHO} + \text{NO}_3^- + \text{H}^+ - 0.550 \text{O}_2$	$6.1 \cdot 10^{+06}$		
R <sub>o</sub> 02620	*	*	$\text{CO(OH)COC(OH)}_2\text{CO(OO}\cdot\text{)} \rightarrow \text{CO(OH)C(OH)}_2\text{COCO(OH)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02621	*	*	$\text{CO(OH)COC(OH)(O}\cdot\text{)CHO} \rightarrow$ $0.500 \text{CO(OH)CO(OO}\cdot\text{)} + 0.500 \text{CO(OH)CHO} +$ $0.500 \text{CO(OH)COCO(OH)} + 0.500 \text{CH} \cdot (\text{OH})_2 - 0.500 \text{O}_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00340	*	*	$\text{CO(OH)C(OH)}_2\text{COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)}_2\text{C(OH)}_2\text{CO(OH)}$	$1.2 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00341	*	*	$\text{CO(OH)C(OH)}_2\text{COCHO} \rightleftharpoons \text{CO(O}^-\text{)C(OH)}_2\text{COCHO} + \text{H}^+$	$5.9 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02622	*	*	$\text{CO(OH)C(OH)}_2\text{COCHO} \rightarrow 0.250 \text{CO(OH)C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.250 \text{CHOCO(OO}\cdot\text{)} + 0.250 \text{CO(OH)C(OH)}_2\text{CO(OO}\cdot\text{)} + 0.250 \text{CHO(OO}\cdot\text{)}$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 02623	*	*	$\text{CO(OH)C(OH)}_2\text{COCHO} + \text{OH} \rightarrow 0.665 \text{CO(OH)C(OH)}_2\text{COCO(OO}\cdot\text{)} +$ $0.335 \text{CO(OH)C(OH)(O}\cdot\text{)COCHO} + \text{H}_2\text{O} - 0.665 \text{O}_2$	$6.2 \cdot 10^{+08}$		
R <sub>o</sub> 02624	*		$\text{CO(OH)C(OH)}_2\text{COCHO} + \text{NO}_3 \rightarrow 0.665 \text{CO(OH)C(OH)}_2\text{COCO(OO}\cdot\text{)} +$ $0.335 \text{CO(OH)C(OH)(O}\cdot\text{)COCHO} + \text{NO}_3^- + \text{H}^+ - 0.665 \text{O}_2$	$6.1 \cdot 10^{+06}$		
R <sub>o</sub> 02625	*	*	$\text{CO(OH)C(OH)}_2\text{COCO(OO}\cdot\text{)} \rightarrow \text{CO(OH)C(OH)}_2\text{COCO(OH)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02626	*	*	$\text{CO(OH)C(OH)(O}\cdot\text{)COCHO} \rightarrow 0.500 \cdot \text{CO(OH)} + 0.500 \text{CO(OH)COCHO} +$ $0.500 \text{CO(OH)CO(OH)} + 0.500 \text{CHOCO(OO}\cdot\text{)} - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00342	*	*	$\text{CO(OH)CH(OH)C(OH)}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{COCH(OH)CO(OH)}$	$2.8 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00343	*	*	$\text{CO(OH)CH(OH)C(OH)}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)CO(OH)}$	$4.4 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00344	*	*	$\text{CO(OH)CH(OH)C(OH)}_2\text{CHO} \rightleftharpoons \text{CO(O}^-\text{)CH(OH)C(OH)}_2\text{CHO} + \text{H}^+$	$1.5 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02627	*	*	CO(OH)CH(OH)C(OH) <sub>2</sub> CHO + OH $\rightarrow$ 0.510 CO(OH)CH(OH)C(OH) <sub>2</sub> CO(OO $\cdot$ ) + 0.072 CO(OH)CH(O $\cdot$ )C(OH) <sub>2</sub> CHO + 0.417 CO(OH)CH(OH)C(OH)(O $\cdot$ )CHO + H <sub>2</sub> O - 0.510 O <sub>2</sub>	$7.4 \cdot 10^{+08}$		
R <sub>o</sub> 02628	*		CO(OH)CH(OH)C(OH) <sub>2</sub> CHO + NO <sub>3</sub> $\rightarrow$ 0.510 CO(OH)CH(OH)C(OH) <sub>2</sub> CO(OO $\cdot$ ) + 0.072 CO(OH)CH(O $\cdot$ )C(OH) <sub>2</sub> CHO + 0.417 CO(OH)CH(OH)C(OH)(O $\cdot$ )CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.510 O <sub>2</sub>	$8.0 \cdot 10^{+06}$		
R <sub>o</sub> 02629	*	*	CO(OH)CH(OH)C(OH) <sub>2</sub> CO(OO $\cdot$ ) $\rightarrow$ CO(OH)CH(OH)C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02630	*	*	CO(OH)CH(O $\cdot$ )C(OH) <sub>2</sub> CHO $\xrightarrow{O_2}$ CO(OH)COC(OH) <sub>2</sub> CHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02631	*	*	CO(OH)CH(O $\cdot$ )C(OH) <sub>2</sub> CHO $\rightarrow$ 0.500 $\cdot$ CO(OH) + 0.500 CHOC(OH) <sub>2</sub> CHO + 0.500 CO(OH)CHO + 0.500 CHOC(OH) <sub>2</sub> (OO $\cdot$ ) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02632	*	*	CO(OH)CH(OH)C(OH)(O $\cdot$ )CHO $\rightarrow$ 0.500 CO(OH)CH(OH)(OO $\cdot$ ) + 0.500 CO(OH)CHO + 0.500 CO(OH)CH(OH)CO(OH) + 0.500 CH $\cdot$ (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00345	*	*	CO(OH)C(OH) <sub>2</sub> CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CO(OH)	$5.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00346	*	*	CO(OH)C(OH) <sub>2</sub> CH(OH)CHO $\rightleftharpoons$ CO(O $\cdot$ )C(OH) <sub>2</sub> CH(OH)CHO + H <sup>+</sup>	$2.4 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02633	*	*	CO(OH)C(OH) <sub>2</sub> CH(OH)CHO + OH $\rightarrow$ 0.746 CO(OH)C(OH) <sub>2</sub> CH(OH)CO(OO $\cdot$ ) + 0.197 CO(OH)C(OH)(O $\cdot$ )CH(OH)CHO + 0.057 CO(OH)C(OH) <sub>2</sub> CH(O $\cdot$ )CHO + H <sub>2</sub> O - 0.746 O <sub>2</sub>	$1.2 \cdot 10^{+09}$		
R <sub>o</sub> 02634	*		CO(OH)C(OH) <sub>2</sub> CH(OH)CHO + NO <sub>3</sub> $\rightarrow$ 0.746 CO(OH)C(OH) <sub>2</sub> CH(OH)CO(OO $\cdot$ ) + 0.197 CO(OH)C(OH)(O $\cdot$ )CH(OH)CHO + 0.057 CO(OH)C(OH) <sub>2</sub> CH(O $\cdot$ )CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.746 O <sub>2</sub>	$8.0 \cdot 10^{+06}$		
R <sub>o</sub> 02635	*	*	CO(OH)C(OH) <sub>2</sub> CH(OH)CO(OO $\cdot$ ) $\rightarrow$ CO(OH)CH(OH)C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02636	*	*	CO(OH)C(OH)(O $\cdot$ )CH(OH)CHO $\rightarrow$ 0.500 $\cdot$ CO(OH) + 0.500 CO(OH)CH(OH)CHO + 0.500 CO(OH)CO(OH) + 0.500 CHOCH(OH)(OO $\cdot$ ) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02637	*	*	$\text{CO(OH)C(OH)}_2\text{CH(O}\cdot\text{)CHO} \xrightarrow{\text{O}_2} \text{CO(OH)C(OH)}_2\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02638	*	*	$\text{CO(OH)C(OH)}_2\text{CH(O}\cdot\text{)CHO} \rightarrow$ $0.500 \text{ CO(OH)C(OH)}_2(\text{OO}\cdot) + 0.500 \text{ CHOCHO} +$ $0.500 \text{ CO(OH)C(OH)}_2\text{CHO} + 0.500 \text{ CH}\cdot(\text{OH})_2 - 0.500 \text{ O}_2 - 0.500 \text{ H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00347	*	*	$\text{CO(OH)C(OH)}_2\text{C(OH)}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)}_2\text{C(OH)}_2\text{CO(OH)}$	$1.2 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00348	*	*	$\text{CO(OH)C(OH)}_2\text{C(OH)}_2\text{CHO} \rightleftharpoons \text{CO(O}^-\text{)C(OH)}_2\text{C(OH)}_2\text{CHO} + \text{H}^+$	$3.8 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02639	*	*	$\text{CO(OH)C(OH)}_2\text{C(OH)}_2\text{CHO} \rightarrow$ $0.250 \text{ CO(OH)C(OH)}_2(\text{OO}\cdot) + 0.250 \text{ CHOC(OH)}_2(\text{OO}\cdot) +$ $0.250 \text{ CO(OH)C(OH)}_2\text{C(OH)}_2(\text{OO}\cdot) + 0.250 \text{ CHO(OO}\cdot\text{)}$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 02640	*	*	$\text{CO(OH)C(OH)}_2\text{C(OH)}_2\text{CHO} + \text{OH} \rightarrow$ $0.408 \text{ CO(OH)C(OH)}_2\text{C(OH)}_2\text{CO(OO}\cdot\text{)} +$ $0.259 \text{ CO(OH)C(OH)(O}\cdot\text{)C(OH)}_2\text{CHO} +$ $0.333 \text{ CO(OH)C(OH)}_2\text{C(OH)(O}\cdot\text{)CHO} + \text{H}_2\text{O} - 0.408 \text{ O}_2$	$8.8 \cdot 10^{+08}$		
R <sub>o</sub> 02641	*		$\text{CO(OH)C(OH)}_2\text{C(OH)}_2\text{CHO} + \text{NO}_3 \rightarrow$ $0.408 \text{ CO(OH)C(OH)}_2\text{C(OH)}_2\text{CO(OO}\cdot\text{)} +$ $0.259 \text{ CO(OH)C(OH)(O}\cdot\text{)C(OH)}_2\text{CHO} +$ $0.333 \text{ CO(OH)C(OH)}_2\text{C(OH)(O}\cdot\text{)CHO} + \text{NO}_3^- + \text{H}^+ - 0.408 \text{ O}_2$	$6.1 \cdot 10^{+06}$		
R <sub>o</sub> 02642	*	*	$\text{CO(OH)C(OH)}_2\text{C(OH)}_2\text{CO(OO}\cdot\text{)} \rightarrow$ $\text{CO(OH)C(OH)}_2\text{C(OH)}_2\text{CO(OH)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02643	*	*	$\text{CO(OH)C(OH)(O}\cdot\text{)C(OH)}_2\text{CHO} \rightarrow$ $0.500 \cdot \text{CO(OH)} + 0.500 \text{ CO(OH)C(OH)}_2\text{CHO} + 0.500 \text{ CO(OH)CO(OH)} +$ $0.500 \text{ CHOC(OH)}_2(\text{OO}\cdot) - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02644	*	*	$\text{CO(OH)C(OH)}_2\text{C(OH)(O}\cdot\text{)CHO} \rightarrow$ $0.500 \text{ CO(OH)C(OH)}_2(\text{OO}\cdot) + 0.500 \text{ CO(OH)CHO} +$ $0.500 \text{ CO(OH)C(OH)}_2\text{CO(OH)} + 0.500 \text{ CH}\cdot(\text{OH})_2 - 0.500 \text{ O}_2 - 0.500 \text{ H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02645	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{C(OH)}_2\text{CO(O}^-\text{)} \rightarrow$ $0.250 \text{ CHO(OH)} + 0.250 \text{ HO}_2 + 0.250 \text{ CO(O}^-\text{)C(OH)}_2\text{C(OH)}_2(\text{OO}\cdot) +$ $0.250 \text{ CH(OH)}_2\text{C(OH)}_2(\text{OO}\cdot) + 0.250 \text{ CO(O}^-\text{)C(OH)}_2(\text{OO}\cdot)$	$1.0 \cdot 10^{-01}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02646	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + OH → 0.101 CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.294 CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) + 0.279 CH(OH) <sub>2</sub> C(OH)(O·)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + 0.326 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(O·)CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.101 O <sub>2</sub>	1.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 02647	*		CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 02648	*	*	CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02649	*	*	CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02650	*	*	CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) → CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02651	*	*	CH(OH) <sub>2</sub> C(OH)(O·)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) → 0.500 CH · (OH) <sub>2</sub> + 0.500 CO(OH)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CO(O <sup>-</sup> )C(OH) <sub>2</sub> (OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02652	*	*	CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(O·)CO(O <sup>-</sup> ) → 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.500 CO(OH)CO(O <sup>-</sup> ) + 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + 0.500 · CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02653	*		CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O·) → CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02654	*	*	CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + OH → 0.251 CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO·) + 0.040 CH(OH) <sub>2</sub> C(OH)(OO·)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + 0.305 CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)CH(OH)(O·) + 0.064 CH(OH) <sub>2</sub> CH(O·)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + 0.339 CH(OH) <sub>2</sub> CH(OH)C(OH)(O·)CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.292 O <sub>2</sub>	1.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 02655	*		CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 02656	*	*	CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO·) → CO(OH)CH(OH)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02657	*	*	$\text{CH(OH)}_2\text{C(OH)(OO}\cdot\text{)C(OH)}_2\text{CO(O}^-\text{)} \rightarrow$ $\text{CH(OH)}_2\text{COC(OH)}_2\text{CO(O}^-\text{)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02658	*	*	$\text{CO(O}^-\text{)C(OH)}_2\text{CH(OH)CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2}$ $\text{CO(OH)CH(OH)C(OH)}_2\text{CO(O}^-\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02659	*	*	$\text{CO(O}^-\text{)C(OH)}_2\text{CH(OH)CH(OH)(O}\cdot\text{)} \rightarrow$ $\text{CO(O}^-\text{)C(OH)}_2\text{CH(OH)(OO}\cdot\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02660	*	*	$\text{CH(OH)}_2\text{CH(O}\cdot\text{)C(OH)}_2\text{CO(O}^-\text{)} \xrightarrow{\text{O}_2} \text{CH(OH)}_2\text{COC(OH)}_2\text{CO(O}^-\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02661	*	*	$\text{CH(OH)}_2\text{CH(O}\cdot\text{)C(OH)}_2\text{CO(O}^-\text{)} \rightarrow$ $0.500 \text{ CH}\cdot(\text{OH})_2 + 0.500 \text{ CO(O}^-\text{)C(OH)}_2\text{CHO} + 0.500 \text{ CH(OH)}_2\text{CHO} +$ $0.500 \text{ CO(O}^-\text{)C(OH)}_2(\text{OO}\cdot\text{)} - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02662	*	*	$\text{CH(OH)}_2\text{CH(OH)C(OH)(O}\cdot\text{)CO(O}^-\text{)} \rightarrow$ $0.500 \text{ CH(OH)}_2\text{CH(OH)(OO}\cdot\text{)} + 0.500 \text{ CO(OH)CO(O}^-\text{)} +$ $0.500 \text{ CH(OH)}_2\text{CH(OH)CO(OH)} + 0.500 \cdot \text{CO(O}^-\text{)} - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02663	*		$\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CO(O}\cdot\text{)} \rightarrow$ $\text{CH(OH)}_2\text{CH(OH)C(OH)}_2(\text{OO}\cdot\text{)} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02664	*	*	$\text{CH(OH)}_2\text{CH(OH)CH(OH)CO(O}^-\text{)} + \text{OH} \rightarrow$ $0.288 \text{ CO(O}^-\text{)CH(OH)CH(OH)C(OH)}_2(\text{OO}\cdot\text{)} +$ $0.112 \text{ CH(OH)}_2\text{C(OH)(OO}\cdot\text{)CH(OH)CO(O}^-\text{)} +$ $0.106 \text{ CH(OH)}_2\text{CH(OH)C(OH)(OO}\cdot\text{)CO(O}^-\text{)} +$ $0.334 \text{ CO(O}^-\text{)CH(OH)CH(OH)CH(OH)(O}\cdot\text{)} +$ $0.074 \text{ CH(OH)}_2\text{CH(O}\cdot\text{)CH(OH)CO(O}^-\text{)} +$ $0.087 \text{ CH(OH)}_2\text{CH(OH)CH(O}\cdot\text{)CO(O}^-\text{)} + \text{H}_2\text{O} - 0.506 \text{ O}_2$	$1.1 \cdot 10^{+09}$		
R <sub>o</sub> 02665	*		$\text{CH(OH)}_2\text{CH(OH)CH(OH)CO(O}^-\text{)} + \text{NO}_3 \rightarrow$ $\text{CH(OH)}_2\text{CH(OH)CH(OH)CO(O}\cdot\text{)} + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02666	*	*	$\text{CO(O}^-\text{)CH(OH)CH(OH)C(OH)}_2(\text{OO}\cdot\text{)} \rightarrow$ $\text{CO(OH)CH(OH)CH(OH)CO(O}^-\text{)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02667	*	*	$\text{CH(OH)}_2\text{C(OH)(OO}\cdot\text{)CH(OH)CO(O}^-\text{)} \rightarrow$ $\text{CH(OH)}_2\text{COCH(OH)CO(O}^-\text{)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02668	*	*	$\text{CH(OH)}_2\text{CH(OH)C(OH)(OO}\cdot\text{)CO(O}^-\text{)} \rightarrow$ $\text{CH(OH)}_2\text{CH(OH)COCO(O}^-\text{)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02669	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02670	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02671	*		$\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) \rightarrow$ $\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02672	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{OH} \rightarrow$ $0.131 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.048 \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{O}^-) +$ $0.364 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) +$ $0.362 \text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) +$ $0.095 \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) + \text{H}_2\text{O} - 0.179 \text{O}_2$	$1.0 \cdot 10^{+09}$		
R <sub>o</sub> 02673	*		$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02674	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow$ $\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02675	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{O}^-) \rightarrow$ $\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{COCO}(\text{O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02676	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02677	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02678	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CH} \cdot (\text{OH})_2 + 0.500 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^-) +$ $0.500 \text{CH}(\text{OH})_2\text{CO}(\text{OH}) + 0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02679	*		$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) \rightarrow$ $\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00349	*	*	$\text{CH}(\text{OH})_2\text{COCOCO}(\text{O}^-) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{COCO}(\text{O}^-)$	$2.6 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00350	*	*	$\text{CH}(\text{OH})_2\text{COCOCO}(\text{O}^-) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}^-)$	$1.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02680	*	*	CH(OH) <sub>2</sub> COCOCO(O <sup>-</sup> ) $\rightarrow$ 0.250 CHO(OH) + 0.250 HO <sub>2</sub> + 0.250 CO(O <sup>-</sup> )COCO(OO $\cdot$ ) + 0.250 CH(OH) <sub>2</sub> CO(OO $\cdot$ ) + 0.250 CO(O <sup>-</sup> )CO(OO $\cdot$ )	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 02681	*	*	CH(OH) <sub>2</sub> COCOCO(O <sup>-</sup> ) + OH $\rightarrow$ 0.280 CO(O <sup>-</sup> )COCOC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.720 CO(O <sup>-</sup> )COCOCH(OH)(O $\cdot$ ) + H <sub>2</sub> O - 0.280 O <sub>2</sub>	4.5 · 10 <sup>+08</sup>		
R <sub>o</sub> 02682	*		CH(OH) <sub>2</sub> COCOCO(O <sup>-</sup> ) + NO <sub>3</sub> $\rightarrow$ CH(OH) <sub>2</sub> COCOCO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 02683	*	*	CO(O <sup>-</sup> )COCOC(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)COCOCO(O <sup>-</sup> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02684	*	*	CO(O <sup>-</sup> )COCOCH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)COCOCO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02685	*	*	CO(O <sup>-</sup> )COCOCH(OH)(O $\cdot$ ) $\rightarrow$ CO(O <sup>-</sup> )COCO(OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02686	*		CH(OH) <sub>2</sub> COCOCO(O $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> COCO(OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02687	*	*	CH(OH) <sub>2</sub> CH(OH)COCO(O <sup>-</sup> ) + OH $\rightarrow$ 0.356 CO(O <sup>-</sup> )COCH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.072 CH(OH) <sub>2</sub> C(OH)(OO $\cdot$ )COCO(O <sup>-</sup> ) + 0.481 CO(O <sup>-</sup> )COCH(OH)CH(OH)(O $\cdot$ ) + 0.091 CH(OH) <sub>2</sub> CH(O $\cdot$ )COCO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.428 O <sub>2</sub>	7.9 · 10 <sup>+08</sup>		
R <sub>o</sub> 02688	*		CH(OH) <sub>2</sub> CH(OH)COCO(O <sup>-</sup> ) + NO <sub>3</sub> $\rightarrow$ CH(OH) <sub>2</sub> CH(OH)COCO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 02689	*	*	CO(O <sup>-</sup> )COCH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)CH(OH)COCO(O <sup>-</sup> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02690	*	*	CH(OH) <sub>2</sub> C(OH)(OO $\cdot$ )COCO(O <sup>-</sup> ) $\rightarrow$ CH(OH) <sub>2</sub> COCOCO(O <sup>-</sup> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02691	*	*	CO(O <sup>-</sup> )COCH(OH)CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)CH(OH)COCO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02692	*	*	CO(O <sup>-</sup> )COCH(OH)CH(OH)(O $\cdot$ ) $\rightarrow$ CO(O <sup>-</sup> )COCH(OH)(OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02693	*		CH(OH) <sub>2</sub> CH(OH)COCO(O $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> CH(OH)CO(OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02694	*	*	CH(OH) <sub>2</sub> COCH(OH)CO(O <sup>-</sup> ) + OH $\rightarrow$ 0.241 CO(O <sup>-</sup> )CH(OH)COC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.089 CH(OH) <sub>2</sub> COC(OH)(OO $\cdot$ )CO(O <sup>-</sup> ) + 0.532 CO(O <sup>-</sup> )CH(OH)COCH(OH)(O $\cdot$ ) + 0.138 CH(OH) <sub>2</sub> COCH(O $\cdot$ )CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.330 O <sub>2</sub>	6.1 · 10 <sup>+08</sup>		
R <sub>o</sub> 02695	*		CH(OH) <sub>2</sub> COCH(OH)CO(O <sup>-</sup> ) + NO <sub>3</sub> $\rightarrow$ CH(OH) <sub>2</sub> COCH(OH)CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 02696	*	*	CO(O <sup>-</sup> )CH(OH)COC(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)COCH(OH)CO(O <sup>-</sup> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02697	*	*	$\text{CH(OH)}_2\text{COC(OH)(OO}\cdot\text{)CO(O}^-) \rightarrow \text{CH(OH)}_2\text{COCOCO(O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02698	*	*	$\text{CO(O}^-)\text{CH(OH)COCH(OH)(O}\cdot) \xrightarrow{\text{O}_2} \text{CO(OH)COCH(OH)CO(O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02699	*	*	$\text{CO(O}^-)\text{CH(OH)COCH(OH)(O}\cdot) \rightarrow$ $\text{CO(O}^-)\text{CH(OH)CO(OO}\cdot) + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02700	*		$\text{CH(OH)}_2\text{COCH(OH)CO(O}\cdot) \rightarrow \text{CH(OH)}_2\text{COCH(OH)(OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02701	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{COCO(O}^-) \rightarrow$ $0.250 \text{ CHO(OH)} + 0.250 \text{ HO}_2 + 0.250 \text{ CO(O}^-)\text{COC(OH)}_2\text{(OO}\cdot) +$ $0.250 \text{ CH(OH)}_2\text{C(OH)}_2\text{(OO}\cdot) + 0.250 \text{ CO(O}^-)\text{CO(OO}\cdot)$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 02702	*	*	$\text{CH(OH)}_2\text{C(OH)}_2\text{COCO(O}^-) + \text{OH} \rightarrow$ $0.143 \text{ CO(O}^-)\text{COC(OH)}_2\text{C(OH)}_2\text{(OO}\cdot) +$ $0.463 \text{ CO(O}^-)\text{COC(OH)}_2\text{CH(OH)(O}\cdot) +$ $0.394 \text{ CH(OH)}_2\text{C(OH)(O}\cdot)\text{COCO(O}^-) + \text{H}_2\text{O} - 0.143 \text{ O}_2$	$7.8 \cdot 10^{+08}$		
R <sub>o</sub> 02703	*		$\text{CH(OH)}_2\text{C(OH)}_2\text{COCO(O}^-) + \text{NO}_3 \rightarrow$ $\text{CH(OH)}_2\text{C(OH)}_2\text{COCO(O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02704	*	*	$\text{CO(O}^-)\text{COC(OH)}_2\text{C(OH)}_2\text{(OO}\cdot) \rightarrow \text{CO(OH)C(OH)}_2\text{COCO(O}^-) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02705	*	*	$\text{CO(O}^-)\text{COC(OH)}_2\text{CH(OH)(O}\cdot) \xrightarrow{\text{O}_2} \text{CO(OH)C(OH)}_2\text{COCO(O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02706	*	*	$\text{CO(O}^-)\text{COC(OH)}_2\text{CH(OH)(O}\cdot) \rightarrow$ $\text{CO(O}^-)\text{COC(OH)}_2\text{(OO}\cdot) + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02707	*	*	$\text{CH(OH)}_2\text{C(OH)(O}\cdot)\text{COCO(O}^-) \rightarrow$ $0.500 \text{ CH}\cdot\text{(OH)}_2 + 0.500 \text{ CO(OH)COCO(O}^-) + 0.500 \text{ CH(OH)}_2\text{CO(OH)} +$ $0.500 \text{ CO(O}^-)\text{CO(OO}\cdot) - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02708	*		$\text{CH(OH)}_2\text{C(OH)}_2\text{COCO(O}\cdot) \rightarrow \text{CH(OH)}_2\text{C(OH)}_2\text{CO(OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00351	*	*	$\text{CO(O}^-)\text{C(OH)}_2\text{COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)}_2\text{COCO(O}^-)$	$2.6 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00352	*	*	$\text{CO(O}^-)\text{C(OH)}_2\text{COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)}_2\text{C(OH)}_2\text{CO(O}^-)$	$1.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02709	*	*	$\text{CO(O}^-)\text{C(OH)}_2\text{COCHO} \rightarrow 0.250 \text{ CO(O}^-)\text{C(OH)}_2\text{(OO}\cdot) +$ $0.250 \text{ CHOCO(OO}\cdot) + 0.250 \text{ CO(O}^-)\text{C(OH)}_2\text{CO(OO}\cdot) + 0.250 \text{ CHO(OO}\cdot)$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 02710	*	*	$\text{CO(O}^-)\text{C(OH)}_2\text{COCHO} + \text{OH} \rightarrow 0.531 \text{ CO(O}^-)\text{C(OH)}_2\text{COCO(OO}\cdot) +$ $0.469 \text{ CO(O}^-)\text{C(OH)(O}\cdot)\text{COCHO} + \text{H}_2\text{O} - 0.531 \text{ O}_2$	$7.7 \cdot 10^{+08}$		
R <sub>o</sub> 02711	*		$\text{CO(O}^-)\text{C(OH)}_2\text{COCHO} + \text{NO}_3 \rightarrow \text{CHOCOC(OH)}_2\text{CO(O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02712	*	*	$\text{CO(O}^-)\text{C(OH)}_2\text{COCO(OO}\cdot) \rightarrow \text{CO(OH)COC(OH)}_2\text{CO(O}^-) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02713	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{O}\cdot)\text{COCHO} \rightarrow 0.500 \cdot \text{CO}(\text{O}^-) + 0.500 \text{CO}(\text{OH})\text{COCHO} +$ $0.500 \text{CO}(\text{OH})\text{CO}(\text{O}^-) + 0.500 \text{CHOCO}(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02714	*		$\text{CHOCOC}(\text{OH})_2\text{CO}(\text{O}\cdot) \rightarrow \text{CHOCOC}(\text{OH})_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00353	*	*	$\text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{COCO}(\text{O}^-)$	$2.6 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00354	*	*	$\text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}^-)$	$1.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02715	*	*	$\text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CHO} \rightarrow 0.250 \text{CO}(\text{O}^-)\text{CO}(\text{OO}\cdot) +$ $0.250 \text{CHOC}(\text{OH})_2(\text{OO}\cdot) + 0.250 \text{CO}(\text{O}^-)\text{COC}(\text{OH})_2(\text{OO}\cdot) + 0.250 \text{CHO}(\text{OO}\cdot)$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 02716	*	*	$\text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CHO} + \text{OH} \rightarrow 0.550 \text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CO}(\text{OO}\cdot) +$ $0.450 \text{CO}(\text{O}^-)\text{COC}(\text{OH})(\text{O}\cdot)\text{CHO} + \text{H}_2\text{O} - 0.550 \text{O}_2$	$5.9 \cdot 10^{+08}$		
R <sub>o</sub> 02717	*		$\text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CHO} + \text{NO}_3 \rightarrow \text{CHOC}(\text{OH})_2\text{COCO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02718	*	*	$\text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CO}(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{COCO}(\text{O}^-) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02719	*	*	$\text{CO}(\text{O}^-)\text{COC}(\text{OH})(\text{O}\cdot)\text{CHO} \rightarrow$ $0.500 \text{CO}(\text{O}^-)\text{CO}(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CHO} + 0.500 \text{CO}(\text{OH})\text{COCO}(\text{O}^-) +$ $0.500 \text{CH} \cdot (\text{OH})_2 - 0.500 \text{O}_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02720	*		$\text{CHOC}(\text{OH})_2\text{COCO}(\text{O}\cdot) \rightarrow \text{CHOC}(\text{OH})_2\text{CO}(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00355	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{COCO}(\text{O}^-)$	$5.6 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00356	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{O}^-)$	$6.7 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02721	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CHO} + \text{OH} \rightarrow$ $0.036 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{OO}\cdot)\text{CHO} +$ $0.626 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) +$ $0.291 \text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})\text{CHO} +$ $0.047 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CHO} + \text{H}_2\text{O} - 0.661 \text{O}_2$	$1.5 \cdot 10^{+09}$		
R <sub>o</sub> 02722	*		$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CHO} + \text{NO}_3 \rightarrow$ $\text{CHOCH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02723	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{OO}\cdot)\text{CHO} \rightarrow \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02724	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) \rightarrow$ $\text{CO}(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02725	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})\text{CHO} \rightarrow$ $0.500 \cdot \text{CO}(\text{O}^-) + 0.500 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CHO} + 0.500 \text{CO}(\text{OH})\text{CO}(\text{O}^-) +$ $0.500 \text{CHOCH}(\text{OH})(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02726	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CHO} \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02727	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CHO} \rightarrow$ $0.500 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.500 \text{CHOCHO} +$ $0.500 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CHO} + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{O}_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02728	*		$\text{CHOCH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{O}\cdot) \rightarrow \text{CHOCH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00357	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{COCH}(\text{OH})\text{CO}(\text{O}^-)$	$9.7 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00358	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}^-)$	$1.4 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02729	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CHO} + \text{OH} \rightarrow$ $0.050 \text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CHO} +$ $0.460 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) +$ $0.115 \text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CHO} +$ $0.376 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CHO} + \text{H}_2\text{O} - 0.510 \text{O}_2$	$8.2 \cdot 10^{+08}$		
R <sub>o</sub> 02730	*		$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CHO} + \text{NO}_3 \rightarrow$ $\text{CHOC}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02731	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CHO} \rightarrow \text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02732	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) \rightarrow$ $\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02733	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CHO} \rightarrow$ $0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CHO} +$ $0.500 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^-) + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{O}_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02734	*		$\text{CHOC}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) \rightarrow \text{CHOC}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00359	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{COCO}(\text{O}^-)$	$2.6 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00360	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}^-)$	$1.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02735	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CHO} \rightarrow$ $0.250 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.250 \text{CHOC}(\text{OH})_2(\text{OO}\cdot) +$ $0.250 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.250 \text{CHO}(\text{OO}\cdot)$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 02736	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CHO} + \text{OH} \rightarrow$ $0.341 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) +$ $0.381 \text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{O}\cdot)\text{C}(\text{OH})_2\text{CHO} +$ $0.279 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CHO} + \text{H}_2\text{O} - 0.341 \text{O}_2$	$1.1 \cdot 10^{+09}$		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02737	*		$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CHO} + \text{NO}_3 \rightarrow$ $\text{CHOC}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02738	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) \rightarrow$ $\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02739	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{O}\cdot)\text{C}(\text{OH})_2\text{CHO} \rightarrow$ $0.500 \cdot \text{CO}(\text{O}^-) + 0.500 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CHO} + 0.500 \text{CO}(\text{OH})\text{CO}(\text{O}^-) +$ $0.500 \text{CHOC}(\text{OH})_2(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02740	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CHO} \rightarrow$ $0.500 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CHO} +$ $0.500 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{O}_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02741	*		$\text{CHOC}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}\cdot) \rightarrow \text{CHOC}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00361	*	*	$\text{CH}(\text{OH})_2\text{COC}(\text{OH})_2\text{CO}(\text{OH}) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{OH})$	$1.2 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00362	*	*	$\text{CH}(\text{OH})_2\text{COC}(\text{OH})_2\text{CO}(\text{OH}) \rightleftharpoons \text{CH}(\text{OH})_2\text{COC}(\text{OH})_2\text{CO}(\text{O}^-) + \text{H}^+$	$4.5 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02742	*	*	$\text{CH}(\text{OH})_2\text{COC}(\text{OH})_2\text{CO}(\text{OH}) \rightarrow$ $0.250 \text{CHO}(\text{OH}) + 0.250 \text{HO}_2 + 0.250 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) +$ $0.250 \text{CH}(\text{OH})_2\text{CO}(\text{OO}\cdot) + 0.250 \text{CO}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot)$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 02743	*	*	$\text{CH}(\text{OH})_2\text{COC}(\text{OH})_2\text{CO}(\text{OH}) + \text{OH} \rightarrow$ $0.209 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{COC}(\text{OH})_2(\text{OO}\cdot) +$ $0.485 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{COCH}(\text{OH})(\text{O}\cdot) +$ $0.306 \text{CH}(\text{OH})_2\text{COC}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) + \text{H}_2\text{O} - 0.209 \text{O}_2$	$6.7 \cdot 10^{+08}$		
R <sub>o</sub> 02744	*		$\text{CH}(\text{OH})_2\text{COC}(\text{OH})_2\text{CO}(\text{OH}) + \text{NO}_3 \rightarrow$ $0.209 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{COC}(\text{OH})_2(\text{OO}\cdot) +$ $0.485 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{COCH}(\text{OH})(\text{O}\cdot) +$ $0.306 \text{CH}(\text{OH})_2\text{COC}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) + \text{NO}_3^- + \text{H}^+ - 0.209 \text{O}_2$	$7.4 \cdot 10^{+06}$		
R <sub>o</sub> 02745	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{COC}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{COCO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02746	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{COCH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{COCO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02747	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{COCH}(\text{OH})(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02748	*	*	$\text{CH}(\text{OH})_2\text{COC}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) \rightarrow$ $0.500 \text{CH}(\text{OH})_2\text{CO}(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CO}(\text{OH}) +$ $0.500 \text{CH}(\text{OH})_2\text{COCO}(\text{OH}) + 0.500 \cdot \text{CO}(\text{OH}) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00363	*	*	$\text{CH(OH)}_2\text{COC(OH)}_2\text{CO(O}^-) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)}_2\text{COCO(O}^-)$	$2.6 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00364	*	*	$\text{CH(OH)}_2\text{COC(OH)}_2\text{CO(O}^-) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)}_2\text{C(OH)}_2\text{CO(O}^-)$	$1.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02749	*	*	$\text{CH(OH)}_2\text{COC(OH)}_2\text{CO(O}^-) \rightarrow$ $0.250 \text{ CHO(OH)} + 0.250 \text{ HO}_2 + 0.250 \text{ CO(O}^-)\text{C(OH)}_2\text{CO(OO}\cdot) +$ $0.250 \text{ CH(OH)}_2\text{CO(OO}\cdot) + 0.250 \text{ CO(O}^-)\text{C(OH)}_2\text{(OO}\cdot)$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 02750	*	*	$\text{CH(OH)}_2\text{COC(OH)}_2\text{CO(O}^-) + \text{OH} \rightarrow$ $0.170 \text{ CO(O}^-)\text{C(OH)}_2\text{COC(OH)}_2\text{(OO}\cdot) +$ $0.394 \text{ CO(O}^-)\text{C(OH)}_2\text{COCH(OH)(O}\cdot) +$ $0.436 \text{ CH(OH)}_2\text{COC(OH)(O}\cdot)\text{CO(O}^-) + \text{H}_2\text{O} - 0.170 \text{ O}_2$	$8.3 \cdot 10^{+08}$		
R <sub>o</sub> 02751	*		$\text{CH(OH)}_2\text{COC(OH)}_2\text{CO(O}^-) + \text{NO}_3 \rightarrow$ $\text{CH(OH)}_2\text{COC(OH)}_2\text{CO(O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02752	*	*	$\text{CO(O}^-)\text{C(OH)}_2\text{COC(OH)}_2\text{(OO}\cdot) \rightarrow \text{CO(OH)COC(OH)}_2\text{CO(O}^-) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02753	*	*	$\text{CO(O}^-)\text{C(OH)}_2\text{COCH(OH)(O}\cdot) \xrightarrow{\text{O}_2} \text{CO(OH)COC(OH)}_2\text{CO(O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02754	*	*	$\text{CO(O}^-)\text{C(OH)}_2\text{COCH(OH)(O}\cdot) \rightarrow$ $\text{CO(O}^-)\text{C(OH)}_2\text{CO(OO}\cdot) + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02755	*	*	$\text{CH(OH)}_2\text{COC(OH)(O}\cdot)\text{CO(O}^-) \rightarrow$ $0.500 \text{ CH(OH)}_2\text{CO(OO}\cdot) + 0.500 \text{ CO(OH)CO(O}^-) +$ $0.500 \text{ CH(OH)}_2\text{COCO(OH)} + 0.500 \cdot \text{CO(O}^-) - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02756	*		$\text{CH(OH)}_2\text{COC(OH)}_2\text{CO(O}\cdot) \rightarrow \text{CH(OH)}_2\text{COC(OH)}_2\text{(OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00365	*	*	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH(OH)}_2$	$1.2 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02757	*	*	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} + \text{OH} \rightarrow$ $0.114 \text{ CHOCH}_2\text{CH}_2\text{CH}_2\text{(OO}\cdot) + 0.230 \text{ CH}_3\text{CH(OO}\cdot)\text{CH}_2\text{CHO} +$ $0.050 \text{ CH}_3\text{CH}_2\text{CH(OO}\cdot)\text{CHO} + 0.606 \text{ CH}_3\text{CH}_2\text{CH}_2\text{CO(OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$3.9 \cdot 10^{+09}$	-900.0	<i>Hesper</i> (2003)
R <sub>o</sub> 02758	*		$\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} + \text{NO}_3 \rightarrow 0.114 \text{ CHOCH}_2\text{CH}_2\text{CH}_2\text{(OO}\cdot) +$ $0.230 \text{ CH}_3\text{CH(OO}\cdot)\text{CH}_2\text{CHO} + 0.050 \text{ CH}_3\text{CH}_2\text{CH(OO}\cdot)\text{CHO} +$ $0.606 \text{ CH}_3\text{CH}_2\text{CH}_2\text{CO(OO}\cdot) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$5.6 \cdot 10^{+07}$	-2045.0	<i>de Semainville et al.</i> (2007a)
R <sub>o</sub> 02759	*	*	$\text{CHOCH}_2\text{CH}_2\text{CH}_2\text{(OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CHOCH}_2\text{CH}_2\text{CH}_2\text{(O}\cdot) + 0.550 \text{ CHOCH}_2\text{CH}_2\text{CHO} +$ $0.250 \text{ CH}_2\text{(OH)CH}_2\text{CH}_2\text{CHO} + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02760	*	*	CH <sub>3</sub> CH(OO·)CH <sub>2</sub> CHO $\xrightarrow{RO_2}$ 0.200 CH <sub>3</sub> CH(O·)CH <sub>2</sub> CHO + 0.550 CH <sub>3</sub> COCH <sub>2</sub> CHO + 0.250 CH <sub>3</sub> CH(OH)CH <sub>2</sub> CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02761	*	*	CH <sub>3</sub> CH <sub>2</sub> CH(OO·)CHO $\xrightarrow{RO_2}$ 0.200 CH <sub>3</sub> CH <sub>2</sub> CH(O·)CHO + 0.550 CH <sub>3</sub> CH <sub>2</sub> COCHO + 0.250 CH <sub>3</sub> CH <sub>2</sub> CH(OH)CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02762	*	*	CHOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CHOCH <sub>2</sub> CH <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02763	*	*	CHOCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> (O·) → CHOCH <sub>2</sub> CH <sub>2</sub> (OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02764	*	*	CH <sub>3</sub> CH(O·)CH <sub>2</sub> CHO $\xrightarrow{O_2}$ CH <sub>3</sub> COCH <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02765	*	*	CH <sub>3</sub> CH(O·)CH <sub>2</sub> CHO → 0.500 CH <sub>3</sub> (OO·) + 0.500 CHOCH <sub>2</sub> CHO + 0.500 CH <sub>3</sub> CHO + 0.500 CHOCH <sub>2</sub> (OO·) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02766	*	*	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OH) <sub>2</sub> + OH → 0.155 CH(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> (OO·) + 0.364 CH <sub>3</sub> CH(OO·)CH <sub>2</sub> CH(OH) <sub>2</sub> + 0.066 CH <sub>3</sub> CH <sub>2</sub> CH(OO·)CH(OH) <sub>2</sub> + 0.283 CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.132 CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OH)(O·) + H <sub>2</sub> O – 0.868 O <sub>2</sub>	3.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 02767	*		CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.155 CH(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> (OO·) + 0.364 CH <sub>3</sub> CH(OO·)CH <sub>2</sub> CH(OH) <sub>2</sub> + 0.066 CH <sub>3</sub> CH <sub>2</sub> CH(OO·)CH(OH) <sub>2</sub> + 0.283 CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.132 CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.868 O <sub>2</sub>	1.2 · 10 <sup>+07</sup>		
R <sub>o</sub> 02768	*	*	CH(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> (O·) + 0.550 CH(OH) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CHO + 0.250 CH <sub>2</sub> (OH)CH <sub>2</sub> CH <sub>2</sub> CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02769	*	*	CH <sub>3</sub> CH(OO·)CH <sub>2</sub> CH(OH) <sub>2</sub> $\xrightarrow{RO_2}$ 0.200 CH <sub>3</sub> CH(O·)CH <sub>2</sub> CH(OH) <sub>2</sub> + 0.550 CH <sub>3</sub> COCH <sub>2</sub> CH(OH) <sub>2</sub> + 0.250 CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02770	*	*	CH <sub>3</sub> CH <sub>2</sub> CH(OO·)CH(OH) <sub>2</sub> $\xrightarrow{RO_2}$ 0.200 CH <sub>3</sub> CH <sub>2</sub> CH(O·)CH(OH) <sub>2</sub> + 0.550 CH <sub>3</sub> CH <sub>2</sub> COCH(OH) <sub>2</sub> + 0.250 CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02771	*	*	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02772	*	*	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH(OH)(O·) → CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> (OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02773	*	*	$\text{CH(OH)}_2\text{CH}_2\text{CH}_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH(OH)}_2\text{CH}_2\text{CH}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02774	*	*	$\text{CH(OH)}_2\text{CH}_2\text{CH}_2\text{CH}_2(\text{O}\cdot) \rightarrow \text{CH(OH)}_2\text{CH}_2\text{CH}_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00366	*	*	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CO(OH)} \rightleftharpoons \text{CH}_3\text{CH}_2\text{CH}_2\text{CO(O}^-) + \text{H}^+$	$1.7 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02775	*	*	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CO(OH)} + \text{OH} \rightarrow$ $0.369 \text{ CO(OH)CH}_2\text{CH}_2\text{CH}_2(\text{OO}\cdot) + 0.580 \text{ CH}_3\text{CH(OO}\cdot\text{)CH}_2\text{CO(OH)} +$ $0.051 \text{ CH}_3\text{CH}_2\text{CH(OO}\cdot\text{)CO(OH)} + \text{H}_2\text{O} - \text{O}_2$	$2.2 \cdot 10^{+09}$		<i>Scholes and Willson (1967)</i>
R <sub>o</sub> 02776	*		$\text{CH}_3\text{CH}_2\text{CH}_2\text{CO(OH)} + \text{NO}_3 \rightarrow$ $0.369 \text{ CO(OH)CH}_2\text{CH}_2\text{CH}_2(\text{OO}\cdot) + 0.580 \text{ CH}_3\text{CH(OO}\cdot\text{)CH}_2\text{CO(OH)} +$ $0.051 \text{ CH}_3\text{CH}_2\text{CH(OO}\cdot\text{)CO(OH)} + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$2.9 \cdot 10^{+02}$		
R <sub>o</sub> 02777	*	*	$\text{CO(OH)CH}_2\text{CH}_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CO(OH)CH}_2\text{CH}_2\text{CH}_2(\text{O}\cdot) + 0.550 \text{ CO(OH)CH}_2\text{CH}_2\text{CHO} +$ $0.250 \text{ CH}_2(\text{OH)CH}_2\text{CH}_2\text{CO(OH)} + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02778	*	*	$\text{CH}_3\text{CH(OO}\cdot\text{)CH}_2\text{CO(OH)} \xrightarrow{\text{RO}_2}$ $0.200 \text{ CH}_3\text{CH(O}\cdot\text{)CH}_2\text{CO(OH)} + 0.550 \text{ CH}_3\text{COCH}_2\text{CO(OH)} +$ $0.250 \text{ CH}_3\text{CH(OH)CH}_2\text{CO(OH)} + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02779	*	*	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CO(O}^-) + \text{OH} \rightarrow$ $0.236 \text{ CO(O}^-)\text{CH}_2\text{CH}_2\text{CH}_2(\text{OO}\cdot) + 0.652 \text{ CH}_3\text{CH(OO}\cdot\text{)CH}_2\text{CO(O}^-) +$ $0.112 \text{ CH}_3\text{CH}_2\text{CH(OO}\cdot\text{)CO(O}^-) + \text{H}_2\text{O} - \text{O}_2$	$2.0 \cdot 10^{+09}$		<i>Anbar et al. (1966a)</i>
R <sub>o</sub> 02780	*		$\text{CH}_3\text{CH}_2\text{CH}_2\text{CO(O}^-) + \text{NO}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CO(O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 02781	*	*	$\text{CO(O}^-)\text{CH}_2\text{CH}_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CO(O}^-)\text{CH}_2\text{CH}_2\text{CH}_2(\text{O}\cdot) + 0.550 \text{ CO(O}^-)\text{CH}_2\text{CH}_2\text{CHO} +$ $0.250 \text{ CH}_2(\text{OH)CH}_2\text{CH}_2\text{CO(O}^-) + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02782	*	*	$\text{CH}_3\text{CH(OO}\cdot\text{)CH}_2\text{CO(O}^-) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CH}_3\text{CH(O}\cdot\text{)CH}_2\text{CO(O}^-) + 0.550 \text{ CH}_3\text{COCH}_2\text{CO(O}^-) +$ $0.250 \text{ CH}_3\text{CH(OH)CH}_2\text{CO(O}^-) + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02783	*	*	$\text{CH}_3\text{CH}_2\text{CH(OH)CH}_3 + \text{OH} \rightarrow$ $0.144 \text{ CH}_3\text{CH(OH)CH}_2\text{CH}_2(\text{OO}\cdot) + 0.160 \text{ CH}_3\text{CH(OH)CH(OO}\cdot\text{)CH}_3 +$ $0.603 \text{ CH}_3\text{CH}_2\text{C(OH)(OO}\cdot\text{)CH}_3 + 0.061 \text{ CH}_3\text{CH}_2\text{CH(OH)CH}_2(\text{OO}\cdot) +$ $0.032 \text{ CH}_3\text{CH}_2\text{CH(O}\cdot\text{)CH}_3 + \text{H}_2\text{O} - 0.968 \text{ O}_2$	$3.5 \cdot 10^{+09}$	-910.0	<i>Hesper (2003)</i>

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02784	*		CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH <sub>3</sub> + NO <sub>3</sub> → 0.144 CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> (OO·) + 0.160 CH <sub>3</sub> CH(OH)CH(OO·)CH <sub>3</sub> + 0.603 CH <sub>3</sub> CH <sub>2</sub> C(OH)(OO·)CH <sub>3</sub> + 0.061 CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH <sub>2</sub> (OO·) + 0.032 CH <sub>3</sub> CH <sub>2</sub> CH(O·)CH <sub>3</sub> + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.968 O <sub>2</sub>	2.3 · 10 <sup>+06</sup>		
R <sub>o</sub> 02785	*	*	CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> (O·) + 0.550 CH <sub>3</sub> CH(OH)CH <sub>2</sub> CHO + 0.250 CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> (OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02786	*	*	CH <sub>3</sub> CH(OH)CH(OO·)CH <sub>3</sub> $\xrightarrow{RO_2}$ 0.200 CH <sub>3</sub> CH(OH)CH(O·)CH <sub>3</sub> + 0.550 CH <sub>3</sub> CH(OH)COCH <sub>3</sub> + 0.250 CH <sub>3</sub> CH(OH)CH(OH)CH <sub>3</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02787	*	*	CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) + 0.550 CH <sub>3</sub> CH <sub>2</sub> CH(OH)CHO + 0.250 CH <sub>3</sub> CH <sub>2</sub> CH(OH)CH <sub>2</sub> (OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02788	*	*	CH <sub>3</sub> CH <sub>2</sub> CH(O·)CH <sub>3</sub> $\xrightarrow{O_2}$ CH <sub>3</sub> CH <sub>2</sub> COCH <sub>3</sub> + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02789	*	*	CH <sub>3</sub> CH <sub>2</sub> CH(O·)CH <sub>3</sub> → 0.500 CH <sub>3</sub> CH <sub>2</sub> (OO·) + 0.500 CH <sub>3</sub> CHO + 0.500 CH <sub>3</sub> CH <sub>2</sub> CHO + 0.500 CH <sub>3</sub> (OO·) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02790	*	*	CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>3</sub> CH(OH)CH <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02791	*	*	CH <sub>3</sub> CH(OH)CH <sub>2</sub> CH <sub>2</sub> (O·) → CH <sub>3</sub> CH(OH)CH <sub>2</sub> (OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02792	*	*	CH <sub>3</sub> CH(OH)CH(O·)CH <sub>3</sub> $\xrightarrow{O_2}$ CH <sub>3</sub> CH(OH)COCH <sub>3</sub> + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02793	*	*	CH <sub>3</sub> CH(OH)CH(O·)CH <sub>3</sub> → 0.500 CH <sub>3</sub> CH(OH)(OO·) + 0.500 CH <sub>3</sub> CHO + 0.500 CH <sub>3</sub> CH(OH)CHO + 0.500 CH <sub>3</sub> (OO·) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02794	*	*	CH <sub>3</sub> CH(OH)CH(OH)CH <sub>3</sub> + OH → 0.175 CH <sub>3</sub> CH(OH)CH(OH)CH <sub>2</sub> (OO·) + 0.733 CH <sub>3</sub> CH(OH)C(OH)(OO·)CH <sub>3</sub> + 0.092 CH <sub>3</sub> CH(OH)CH(O·)CH <sub>3</sub> + H <sub>2</sub> O - 0.908 O <sub>2</sub>	1.3 · 10 <sup>+09</sup>		Adams et al. (1965a)
R <sub>o</sub> 02795	*		CH <sub>3</sub> CH(OH)CH(OH)CH <sub>3</sub> + NO <sub>3</sub> → 0.175 CH <sub>3</sub> CH(OH)CH(OH)CH <sub>2</sub> (OO·) + 0.733 CH <sub>3</sub> CH(OH)C(OH)(OO·)CH <sub>3</sub> + 0.092 CH <sub>3</sub> CH(OH)CH(O·)CH <sub>3</sub> + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.908 O <sub>2</sub>	2.2 · 10 <sup>+06</sup>		
R <sub>o</sub> 02796	*	*	CH <sub>3</sub> CH(OH)CH(OH)CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>3</sub> CH(OH)CH(OH)CH <sub>2</sub> (O·) + 0.550 CH <sub>3</sub> CH(OH)CH(OH)CHO + 0.250 CH <sub>3</sub> CH(OH)CH(OH)CH <sub>2</sub> (OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02797	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_3 \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{COCH}_3 + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02798	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{COCH}_3 + \text{OH} \rightarrow 0.236 \text{CH}_3\text{COCH}(\text{OH})\text{CH}_2(\text{OO}\cdot) +$ $0.517 \text{CH}_3\text{COC}(\text{OH})(\text{OO}\cdot)\text{CH}_3 + 0.124 \text{CH}_3\text{CH}(\text{OH})\text{COCH}_2(\text{OO}\cdot) +$ $0.123 \text{CH}_3\text{COCH}(\text{O}\cdot)\text{CH}_3 + \text{H}_2\text{O} - 0.877 \text{O}_2$	$2.9 \cdot 10^{+09}$	-1323.0	<i>Hesper</i> (2003)
R <sub>o</sub> 02799	*		$\text{CH}_3\text{CH}(\text{OH})\text{COCH}_3 + \text{NO}_3 \rightarrow 0.236 \text{CH}_3\text{COCH}(\text{OH})\text{CH}_2(\text{OO}\cdot) +$ $0.517 \text{CH}_3\text{COC}(\text{OH})(\text{OO}\cdot)\text{CH}_3 + 0.124 \text{CH}_3\text{CH}(\text{OH})\text{COCH}_2(\text{OO}\cdot) +$ $0.123 \text{CH}_3\text{COCH}(\text{O}\cdot)\text{CH}_3 + \text{NO}_3^- + \text{H}^+ - 0.877 \text{O}_2$	$1.8 \cdot 10^{+06}$		
R <sub>o</sub> 02800	*	*	$\text{CH}_3\text{COCH}(\text{OH})\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_3\text{COCH}(\text{OH})\text{CH}_2(\text{O}\cdot) + 0.550 \text{CH}_3\text{COCH}(\text{OH})\text{CHO} +$ $0.250 \text{CH}_3\text{COCH}(\text{OH})\text{CH}_2(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02801	*	*	$\text{CH}_3\text{COC}(\text{OH})(\text{OO}\cdot)\text{CH}_3 \rightarrow \text{CH}_3\text{COCOCH}_3 + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02802	*	*	$\text{CH}_3\text{CH}(\text{OH})\text{COCH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_3\text{CH}(\text{OH})\text{COCH}_2(\text{O}\cdot) + 0.550 \text{CH}_3\text{CH}(\text{OH})\text{COCHO} +$ $0.250 \text{CH}_3\text{CH}(\text{OH})\text{COCH}_2(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02803	*	*	$\text{CH}_3\text{CH}_2\text{COCH}_3 + \text{OH} \rightarrow 0.554 \text{CH}_3\text{COCH}_2\text{CH}_2(\text{OO}\cdot) +$ $0.323 \text{CH}_3\text{COCH}(\text{OO}\cdot)\text{CH}_3 + 0.123 \text{CH}_3\text{CH}_2\text{COCH}_2(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$1.3 \cdot 10^{+09}$	-1451.0	Average of measurements within MOST
R <sub>o</sub> 02804	*		$\text{CH}_3\text{CH}_2\text{COCH}_3 + \text{NO}_3 \rightarrow 0.554 \text{CH}_3\text{COCH}_2\text{CH}_2(\text{OO}\cdot) +$ $0.323 \text{CH}_3\text{COCH}(\text{OO}\cdot)\text{CH}_3 + 0.123 \text{CH}_3\text{CH}_2\text{COCH}_2(\text{OO}\cdot) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$2.2 \cdot 10^{+07}$	-2887.0	<i>de Semainville et al.</i> (2007a)
R <sub>o</sub> 02805	*	*	$\text{CH}_3\text{COCH}_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2} 0.200 \text{CH}_3\text{COCH}_2\text{CH}_2(\text{O}\cdot) +$ $0.550 \text{CH}_3\text{COCH}_2\text{CH}_2\text{CHO} + 0.250 \text{CH}_3\text{COCH}_2\text{CH}_2(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
E <sub>o</sub> 00367	*	*	$\text{CHOCH}=\text{CHCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{CH}=\text{CHCHO}$	$3.3 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{s}^{-1}$ estimated
E <sub>o</sub> 00368	*	*	$\text{CHOCH}=\text{CHCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{CH}=\text{CHCH}(\text{OH})_2$	$3.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{s}^{-1}$ estimated
R <sub>o</sub> 02806	*	*	$\text{CHOCH}=\text{CHCHO} + \text{OH} \rightarrow 0.062 \text{CHOCH}=\text{CHCO}(\text{OO}\cdot) +$ $0.938 \text{CHOCH}(\text{OH})\text{CH}(\text{OO}\cdot)\text{CHO} + 0.062 \text{H}_2\text{O} - \text{O}_2$	$2.3 \cdot 10^{+10}$		
R <sub>o</sub> 02807			$\text{CHOCH}=\text{CHCHO} + \text{NO}_3 \rightarrow 0.062 \text{CHOCH}=\text{CHCO}(\text{OO}\cdot) +$ $0.938 \text{CHOCH}(\text{ONO}_2)\text{CH}(\text{OO}\cdot)\text{CHO} + 0.062 \text{NO}_3^- + 0.062 \text{H}^+ - \text{O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 02808	*	*	$\text{CHOCH}=\text{CHCO}(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}=\text{CHCHO} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02809			$\text{CHOCH}(\text{ONO}_2)\text{CH}(\text{OO}\cdot)\text{CHO} \xrightarrow{\text{RO}_2}$ $0.200 \text{CHOCH}(\text{ONO}_2)\text{CH}(\text{O}\cdot)\text{CHO} + 0.550 \text{CHOCOCH}(\text{ONO}_2)\text{CHO} +$ $0.250 \text{CHOCH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02810			$\text{CHOCH(ONO}_2\text{)CH(O}\cdot\text{)CHO} \xrightarrow{\text{O}_2} \text{CHOCOCH(ONO}_2\text{)CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02811			$\text{CHOCH(ONO}_2\text{)CH(O}\cdot\text{)CHO} \rightarrow$ $0.500 \text{ CHOCH(ONO}_2\text{)(OO}\cdot\text{)} + 0.500 \text{ CHOCHO} +$ $0.500 \text{ CHOCH(ONO}_2\text{)CHO} + 0.500 \text{ CH}\cdot\text{(OH)}_2 - 0.500 \text{ O}_2 - 0.500 \text{ H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02812			$\text{CHOCH(ONO}_2\text{)(OO}\cdot\text{)} \xrightarrow{\text{RO}_2} 0.200 \text{ CHOCH(ONO}_2\text{)(O}\cdot\text{)} +$ $0.550 \text{ CO(ONO}_2\text{)CHO} + 0.250 \text{ CH(OH)(ONO}_2\text{)CHO} + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02813			$\text{CHOCH(ONO}_2\text{)(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CO(ONO}_2\text{)CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02814			$\text{CHOCH(ONO}_2\text{)(O}\cdot\text{)} \rightarrow \text{CH}\cdot\text{(OH)}_2 + \text{CHO(ONO}_2\text{)} - \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02815	*	*	$\text{CH(OH)}_2\text{CH=CHCH(OH)}_2 + \text{OH} \rightarrow$ $\text{CH(OH)}_2\text{CH(OH)CH(OO}\cdot\text{)CH(OH)}_2 - \text{O}_2$	$6.0 \cdot 10^{+10}$		
R <sub>o</sub> 02816			$\text{CH(OH)}_2\text{CH=CHCH(OH)}_2 + \text{NO}_3 \rightarrow$ $\text{CH(OH)}_2\text{CH(ONO}_2\text{)CH(OO}\cdot\text{)CH(OH)}_2 - \text{O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 02817			$\text{CH(OH)}_2\text{CH(ONO}_2\text{)CH(OO}\cdot\text{)CH(OH)}_2 \xrightarrow{\text{RO}_2}$ $0.200 \text{ CH(OH)}_2\text{CH(ONO}_2\text{)CH(O}\cdot\text{)CH(OH)}_2 +$ $0.550 \text{ CH(OH)}_2\text{COCH(ONO}_2\text{)CH(OH)}_2 +$ $0.250 \text{ CH(OH)}_2\text{CH(OH)CH(ONO}_2\text{)CH(OH)}_2 + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02818			$\text{CH(OH)}_2\text{CH(ONO}_2\text{)CH(O}\cdot\text{)CH(OH)}_2 \xrightarrow{\text{O}_2}$ $\text{CH(OH)}_2\text{COCH(ONO}_2\text{)CH(OH)}_2 + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02819			$\text{CH(OH)}_2\text{CH(ONO}_2\text{)CH(O}\cdot\text{)CH(OH)}_2 \rightarrow$ $0.500 \text{ CH(OH)}_2\text{CH(ONO}_2\text{)(OO}\cdot\text{)} + 0.500 \text{ CH(OH)}_2\text{CHO} +$ $0.500 \text{ CH(OH)}_2\text{CH(ONO}_2\text{)CHO} + 0.500 \text{ CH}\cdot\text{(OH)}_2 - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02820			$\text{CH(OH)}_2\text{CH(ONO}_2\text{)(OO}\cdot\text{)} \xrightarrow{\text{RO}_2}$ $0.200 \text{ CH(OH)}_2\text{CH(ONO}_2\text{)(O}\cdot\text{)} + 0.550 \text{ CH(OH)}_2\text{CO(ONO}_2\text{)} +$ $0.250 \text{ CH(OH)}_2\text{CH(OH)(ONO}_2\text{)} + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02821			$\text{CH(OH)}_2\text{CH(ONO}_2\text{)(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CH(OH)}_2\text{CO(ONO}_2\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02822			$\text{CH(OH)}_2\text{CH(ONO}_2\text{)(O}\cdot\text{)} \rightarrow \text{CH}\cdot\text{(OH)}_2 + \text{CHO(ONO}_2\text{)}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02823	*	*	$\text{CH(OH)}_2\text{CH=CHCHO} + \text{OH} \rightarrow 0.500 \text{ CH(OH)}_2\text{CH(OH)CH(OO}\cdot\text{)CHO} +$ $0.500 \text{ CH(OH)}_2\text{CH(OO}\cdot\text{)CH(OH)CHO} - \text{O}_2$	$3.6 \cdot 10^{+10}$		
R <sub>o</sub> 02824			$\text{CH(OH)}_2\text{CH=CHCHO} + \text{NO}_3 \rightarrow 0.500 \text{ CH(OH)}_2\text{CH(ONO}_2\text{)CH(OO}\cdot\text{)CHO} +$ $0.500 \text{ CH(OH)}_2\text{CH(OO}\cdot\text{)CH(ONO}_2\text{)CHO} - \text{O}_2$	$1.0 \cdot 10^{+07}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02825	*	*	CH(OH) <sub>2</sub> CH(OH)CH(OO·)CHO $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH(OH)CH(O·)CHO + 0.550 CH(OH) <sub>2</sub> CH(OH)COCHO + 0.250 CH(OH) <sub>2</sub> CH(OH)CH(OH)CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02826	*	*	CH(OH) <sub>2</sub> CH(OO·)CH(OH)CHO $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH(O·)CH(OH)CHO + 0.550 CH(OH) <sub>2</sub> COCH(OH)CHO + 0.250 CH(OH) <sub>2</sub> CH(OH)CH(OH)CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02827			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OO·)CHO $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(O·)CHO + 0.550 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCHO + 0.250 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02828			CH(OH) <sub>2</sub> CH(OO·)CH(ONO <sub>2</sub> )CHO $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH(O·)CH(ONO <sub>2</sub> )CHO + 0.550 CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CHO + 0.250 CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02829			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(O·)CHO $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02830			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(O·)CHO → 0.500 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.500 CHOCHO + 0.500 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + 0.500 CH · (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02831			CH(OH) <sub>2</sub> CH(O·)CH(ONO <sub>2</sub> )CHO $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02832			CH(OH) <sub>2</sub> CH(O·)CH(ONO <sub>2</sub> )CHO → 0.500 CH · (OH) <sub>2</sub> + 0.500 CHOCH(ONO <sub>2</sub> )CHO + 0.500 CH(OH) <sub>2</sub> CHO + 0.500 CHOCH(ONO <sub>2</sub> )(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00369			CHOCH(OH)CH(ONO <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub>	1.0 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02833			CHOCH(OH)CH(ONO <sub>2</sub> )CHO + OH → 0.439 CHOCH(ONO <sub>2</sub> )CH(OH)CO(OO·) + 0.044 CHOCH(ONO <sub>2</sub> )C(OH)(OO·)CHO + 0.044 CHOCH(OH)C(ONO <sub>2</sub> )(OO·)CHO + 0.439 CHOCH(OH)CH(ONO <sub>2</sub> )CO(OO·) + 0.033 CHOCH(ONO <sub>2</sub> )CH(O·)CHO + H <sub>2</sub> O - 0.967 O <sub>2</sub>	2.2 · 10 <sup>+09</sup>		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02834			CHOCH(OH)CH(ONO <sub>2</sub> )CHO + NO <sub>3</sub> → 0.439 CHOCH(ONO <sub>2</sub> )CH(OH)CO(OO·) + 0.044 CHOCH(ONO <sub>2</sub> )C(OH)(OO·)CHO + 0.044 CHOCH(OH)C(ONO <sub>2</sub> )(OO·)CHO + 0.439 CHOCH(OH)CH(ONO <sub>2</sub> )CO(OO·) + 0.033 CHOCH(ONO <sub>2</sub> )CH(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.967 O <sub>2</sub>	8.9 · 10 <sup>+06</sup>		
R <sub>o</sub> 02835			CHOCH(ONO <sub>2</sub> )CH(OH)CO(OO·) → CO(OH)CH(OH)CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02836			CHOCH(ONO <sub>2</sub> )C(OH)(OO·)CHO → CHOCOCH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02837			CHOCH(OH)C(ONO <sub>2</sub> )(OO·)CHO $\xrightarrow{RO_2}$ CHOCH(OH)C(ONO <sub>2</sub> )(O·)CHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02838			CHOCH(OH)CH(ONO <sub>2</sub> )CO(OO·) → CO(OH)CH(ONO <sub>2</sub> )CH(OH)CHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02839			CHOCH(OH)C(ONO <sub>2</sub> )(O·)CHO → 0.500 CHOCH(OH)(OO·) + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CO(ONO <sub>2</sub> )CH(OH)CHO + 0.500 CH · (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00370			CHOCOCH(ONO <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub>	9.4 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02840			CHOCOCH(ONO <sub>2</sub> )CHO → 0.500 + 0.500	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 02841			CHOCOCH(ONO <sub>2</sub> )CHO + OH → 0.333 CHOCH(ONO <sub>2</sub> )COCO(OO·) + 0.033 CHOCOC(ONO <sub>2</sub> )(OO·)CHO + 0.634 CHOCOCH(ONO <sub>2</sub> )CO(OO·) + H <sub>2</sub> O - O <sub>2</sub>	1.3 · 10 <sup>+09</sup>		
R <sub>o</sub> 02842			CHOCOCH(ONO <sub>2</sub> )CHO + NO <sub>3</sub> → 0.333 CHOCH(ONO <sub>2</sub> )COCO(OO·) + 0.033 CHOCOC(ONO <sub>2</sub> )(OO·)CHO + 0.634 CHOCOCH(ONO <sub>2</sub> )CO(OO·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	3.5 · 10 <sup>+06</sup>		
R <sub>o</sub> 02843			CHOCH(ONO <sub>2</sub> )CO(OO·) → CO(OH)CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02844			CHOCH(ONO <sub>2</sub> )COCO(OO·) → CO(OH)COCH(ONO <sub>2</sub> )CHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02845			CHOCOC(ONO <sub>2</sub> )(OO·)CHO $\xrightarrow{RO_2}$ CHOCOC(ONO <sub>2</sub> )(O·)CHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02846			CHOCOCH(ONO <sub>2</sub> )CO(OO·) → CO(OH)CH(ONO <sub>2</sub> )COCHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02847			CHOCOC(ONO <sub>2</sub> )(O·)CHO → 0.500 CHOCO(OO·) + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CO(ONO <sub>2</sub> )COCHO + 0.500 CH · (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00371			$\text{CHOCH(ONO}_2\text{)CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{CH(ONO}_2\text{)CH(OH)}_2$	$5.7 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02848			$\text{CHOCH(ONO}_2\text{)CHO} + \text{OH} \rightarrow \text{CHOCH(ONO}_2\text{)CO(OO}\cdot\text{)} + \text{H}_2\text{O} - \text{O}_2$	$1.6 \cdot 10^{+09}$		
R <sub>o</sub> 02849			$\text{CHOCH(ONO}_2\text{)CHO} + \text{NO}_3 \rightarrow$ $\text{CHOCH(ONO}_2\text{)CO(OO}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$3.6 \cdot 10^{+06}$		
E <sub>o</sub> 00372			$\text{CH(OH)(ONO}_2\text{)CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{CH(OH)(ONO}_2\text{)}$	$4.1 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02850			$\text{CH(OH)(ONO}_2\text{)CHO} + \text{OH} \rightarrow$ $0.493 \text{ CHOC(OH)(ONO}_2\text{)(OO}\cdot\text{)} + 0.432 \text{ CH(OH)(ONO}_2\text{)CO(OO}\cdot\text{)} +$ $0.075 \text{ CHOCH(ONO}_2\text{)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.925 \text{ O}_2$	$9.2 \cdot 10^{+08}$		
R <sub>o</sub> 02851			$\text{CH(OH)(ONO}_2\text{)CHO} + \text{NO}_3 \rightarrow$ $0.493 \text{ CHOC(OH)(ONO}_2\text{)(OO}\cdot\text{)} + 0.432 \text{ CH(OH)(ONO}_2\text{)CO(OO}\cdot\text{)} +$ $0.075 \text{ CHOCH(ONO}_2\text{)(O}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - 0.925 \text{ O}_2$	$3.3 \cdot 10^{+06}$		
R <sub>o</sub> 02852			$\text{CHOC(OH)(ONO}_2\text{)(OO}\cdot\text{)} \rightarrow \text{CO(ONO}_2\text{)CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02853			$\text{CH(OH)(ONO}_2\text{)CO(OO}\cdot\text{)} \rightarrow \text{CO(OH)CH(OH)(ONO}_2\text{)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
E <sub>o</sub> 00373			$\text{CO(ONO}_2\text{)CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{CO(ONO}_2\text{)}$	$6.7 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02854			$\text{CO(ONO}_2\text{)CHO} \xrightarrow{\text{H}_2\text{O}} \text{CO(OH)CHO} + \text{H}^+ + \text{NO}_3$	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 02855			$\text{CO(ONO}_2\text{)CHO} + \text{OH} \rightarrow \text{CO(ONO}_2\text{)CO(OO}\cdot\text{)} + \text{H}_2\text{O} - \text{O}_2$	$1.8 \cdot 10^{+08}$		
R <sub>o</sub> 02856			$\text{CO(ONO}_2\text{)CHO} + \text{NO}_3 \rightarrow \text{CO(ONO}_2\text{)CO(OO}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$1.4 \cdot 10^{+06}$		
R <sub>o</sub> 02857			$\text{CO(ONO}_2\text{)CO(OO}\cdot\text{)} \rightarrow \text{CO(OH)CO(ONO}_2\text{)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
E <sub>o</sub> 00374	*	*	$\text{CO(OH)CH=CHCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{CH=CHCO(OH)}$	$1.4 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00375	*	*	$\text{CO(OH)CH=CHCHO} \rightleftharpoons \text{CO(O}^-\text{)CH=CHCHO} + \text{H}^+$	$4.4 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 02858	*	*	$\text{CO(OH)CH=CHCHO} + \text{OH} \rightarrow$ $0.078 \text{ CO(OH)CH=CHCO(OO}\cdot\text{)} + 0.461 \text{ CO(OH)CH(OH)CH(OO}\cdot\text{)CHO} +$ $0.461 \text{ CO(OH)CH(OO}\cdot\text{)CH(OH)CHO} + 0.078 \text{ H}_2\text{O} - \text{O}_2$	$9.2 \cdot 10^{+09}$		
R <sub>o</sub> 02859			$\text{CO(OH)CH=CHCHO} + \text{NO}_3 \rightarrow$ $0.078 \text{ CO(OH)CH=CHCO(OO}\cdot\text{)} + 0.461 \text{ CO(OH)CH(ONO}_2\text{)CH(OO}\cdot\text{)CHO} +$ $0.461 \text{ CO(OH)CH(OO}\cdot\text{)CH(ONO}_2\text{)CHO} + 0.078 \text{ NO}_3^- + 0.078 \text{ H}^+ - \text{O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 02860	*	*	$\text{CO(OH)CH=CHCO(OO}\cdot\text{)} \rightarrow \text{CO(OH)CH=CHCO(OH)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02861	*	*	$\text{CO(OH)CH(OH)CH(OO}\cdot\text{)CHO} \xrightarrow{\text{RO}_2}$ $0.200 \text{ CO(OH)CH(OH)CH(O}\cdot\text{)CHO} + 0.550 \text{ CO(OH)CH(OH)COCHO} +$ $0.250 \text{ CO(OH)CH(OH)CH(OH)CHO} + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02862	*	*	CO(OH)CH(OO·)CH(OH)CHO + CO(OH)CH(OO·)CH(OH)CHO → 2.000 CHOCH(OH)CHO + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 02863	*	*	CO(OH)CH(OO·)CH(OH)CHO $\xrightarrow{RO_2}$ 0.200 CO(OH)CH(O·)CH(OH)CHO + 0.550 CO(OH)COCH(OH)CHO + 0.250 CO(OH)CH(OH)CH(OH)CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02864			CO(OH)CH(ONO <sub>2</sub> )CH(OO·)CHO $\xrightarrow{RO_2}$ 0.200 CO(OH)CH(ONO <sub>2</sub> )CH(O·)CHO + 0.550 CO(OH)CH(ONO <sub>2</sub> )COCHO + 0.250 CO(OH)CH(ONO <sub>2</sub> )CH(OH)CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02865			CO(OH)CH(OO·)CH(ONO <sub>2</sub> )CHO + CO(OH)CH(OO·)CH(ONO <sub>2</sub> )CHO → 2.000 CHOCH(ONO <sub>2</sub> )CHO + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 02866			CO(OH)CH(OO·)CH(ONO <sub>2</sub> )CHO $\xrightarrow{RO_2}$ 0.200 CO(OH)CH(O·)CH(ONO <sub>2</sub> )CHO + 0.550 CO(OH)COCH(ONO <sub>2</sub> )CHO + 0.250 CO(OH)CH(OH)CH(ONO <sub>2</sub> )CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02867			CO(OH)CH(ONO <sub>2</sub> )CH(O·)CHO $\xrightarrow{O_2}$ CO(OH)CH(ONO <sub>2</sub> )COCHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02868			CO(OH)CH(ONO <sub>2</sub> )CH(O·)CHO → 0.500 CO(OH)CH(ONO <sub>2</sub> )(OO·) + 0.500 CHOCHO + 0.500 CO(OH)CH(ONO <sub>2</sub> )CHO + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02869			CO(OH)CH(O·)CH(ONO <sub>2</sub> )CHO $\xrightarrow{O_2}$ CO(OH)COCH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02870			CO(OH)CH(O·)CH(ONO <sub>2</sub> )CHO → 0.500 ·CO(OH) + 0.500 CHOCH(ONO <sub>2</sub> )CHO + 0.500 CO(OH)CHO + 0.500 CHOCH(ONO <sub>2</sub> )(OO·) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02871			CO(OH)CH(ONO <sub>2</sub> )(OO·) + CO(OH)CH(ONO <sub>2</sub> )(OO·) → 2.000 CHO(ONO <sub>2</sub> ) + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 02872			CO(OH)CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CO(OH)CH(ONO <sub>2</sub> )(O·) + 0.550 CO(OH)CO(ONO <sub>2</sub> ) + 0.250 CO(OH)CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02873			CO(OH)CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CO(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02874			CO(OH)CH(ONO <sub>2</sub> )(O·) → ·CO(OH) + CHO(ONO <sub>2</sub> )	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02875			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> → 0.500 + 0.500 + 0.500	$1.0 \cdot 10^{-01}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02876			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> + OH → 0.084 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.202 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.234 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(O·) + 0.233 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH)(O·)CH(OH) <sub>2</sub> + 0.246 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(O·) + H <sub>2</sub> O – 0.287 O <sub>2</sub>	1.5 · 10 <sup>+09</sup>		
R <sub>o</sub> 02877			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.084 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.202 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.234 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(O·) + 0.233 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH)(O·)CH(OH) <sub>2</sub> + 0.246 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.287 O <sub>2</sub>	9.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 02878			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02879			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02880			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02881			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02882			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(O·) → CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02883			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH)(O·)CH(OH) <sub>2</sub> → 0.500 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH) + 0.500 CH · (OH) <sub>2</sub> – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02884			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02885			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(O·) → CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02886			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + 0.550 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.250 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02887			$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(ONO}_2\text{)(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CH(OH)}_2\text{C(OH)}_2\text{CO(ONO}_2\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02888			$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(ONO}_2\text{)(O}\cdot\text{)} \rightarrow$ $\text{CH(OH)}_2\text{C(OH)}_2\text{(OO}\cdot\text{)} + \text{CHO(ONO}_2\text{)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02889			$\text{CH(OH)}_2\text{CH(ONO}_2\text{)CH(OH)}_2 + \text{OH} \rightarrow$ $0.449 \text{ CH(OH)}_2\text{CH(ONO}_2\text{)C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.031 \text{ CH(OH)}_2\text{C(ONO}_2\text{)(OO}\cdot\text{)CH(OH)}_2 +$ $0.520 \text{ CH(OH)}_2\text{CH(ONO}_2\text{)CH(OH)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.480 \text{ O}_2$	$1.5 \cdot 10^{+09}$		
R <sub>o</sub> 02890			$\text{CH(OH)}_2\text{CH(ONO}_2\text{)CH(OH)}_2 + \text{NO}_3 \rightarrow$ $0.449 \text{ CH(OH)}_2\text{CH(ONO}_2\text{)C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.031 \text{ CH(OH)}_2\text{C(ONO}_2\text{)(OO}\cdot\text{)CH(OH)}_2 +$ $0.520 \text{ CH(OH)}_2\text{CH(ONO}_2\text{)CH(OH)(O}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - 0.480 \text{ O}_2$	$9.5 \cdot 10^{+06}$		
R <sub>o</sub> 02891			$\text{CH(OH)}_2\text{C(ONO}_2\text{)(OO}\cdot\text{)CH(OH)}_2 \xrightarrow{\text{RO}_2^-}$ $\text{CH(OH)}_2\text{C(ONO}_2\text{)(O}\cdot\text{)CH(OH)}_2 + 0.500 \text{ O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 02892			$\text{CH(OH)}_2\text{CH(ONO}_2\text{)CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CH(OH)}_2\text{CH(ONO}_2\text{)CO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02893			$\text{CH(OH)}_2\text{CH(ONO}_2\text{)CH(OH)(O}\cdot\text{)} \rightarrow$ $\text{CH(OH)}_2\text{CH(ONO}_2\text{)(OO}\cdot\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02894			$\text{CH(OH)}_2\text{C(ONO}_2\text{)(O}\cdot\text{)CH(OH)}_2 \rightarrow \text{CH}\cdot\text{(OH)}_2 + \text{CH(OH)}_2\text{CO(ONO}_2\text{)}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02895			$\text{CH(OH)}_2\text{CH(OH)CH(ONO}_2\text{)CH(OH)}_2 + \text{OH} \rightarrow$ $0.191 \text{ CH(OH)}_2\text{CH(ONO}_2\text{)CH(OH)C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.063 \text{ CH(OH)}_2\text{CH(ONO}_2\text{)C(OH)(OO}\cdot\text{)CH(OH)}_2 +$ $0.063 \text{ CH(OH)}_2\text{CH(OH)C(ONO}_2\text{)(OO}\cdot\text{)CH(OH)}_2 +$ $0.191 \text{ CH(OH)}_2\text{CH(OH)CH(ONO}_2\text{)C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.221 \text{ CH(OH)}_2\text{CH(ONO}_2\text{)CH(OH)CH(OH)(O}\cdot\text{)} +$ $0.049 \text{ CH(OH)}_2\text{CH(ONO}_2\text{)CH(O}\cdot\text{)CH(OH)}_2 +$ $0.221 \text{ CH(OH)}_2\text{CH(OH)CH(ONO}_2\text{)CH(OH)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.508 \text{ O}_2$	$1.7 \cdot 10^{+09}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02896			CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.191 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> (OO·) + 0.063 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH)(OO·)CH(OH) <sub>2</sub> + 0.063 CH(OH) <sub>2</sub> CH(OH)C(ONO <sub>2</sub> )(OO·)CH(OH) <sub>2</sub> + 0.191 CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.221 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CH(OH)(O·) + 0.049 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(O·)CH(OH) <sub>2</sub> + 0.221 CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.508 O <sub>2</sub>	1.2 · 10 <sup>+07</sup>		
R <sub>o</sub> 02897			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> (OO·) → CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02898			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH)(OO·)CH(OH) <sub>2</sub> → CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02899			CH(OH) <sub>2</sub> CH(OH)C(ONO <sub>2</sub> )(OO·)CH(OH) <sub>2</sub> $\xrightarrow{RO_2}$ CH(OH) <sub>2</sub> CH(OH)C(ONO <sub>2</sub> )(O·)CH(OH) <sub>2</sub> + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02900			CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02901			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CH(OH)(O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02902			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CH(OH)(O·) → CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02903			CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CH(OH)(O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02904			CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CH(OH)(O·) → CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02905			CH(OH) <sub>2</sub> CH(OH)C(ONO <sub>2</sub> )(O·)CH(OH) <sub>2</sub> → 0.500 CH(OH) <sub>2</sub> CH(OH)(OO·) + 0.500 CH(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02906			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(OO·) → CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02907			CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O·) + 0.550 CH(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + 0.250 CH(OH) <sub>2</sub> CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02908			CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02909			CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O·) → CH(OH) <sub>2</sub> CH(OH)(OO·) + CHO(ONO <sub>2</sub> ) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02910			CH(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + OH → 0.132 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.426 CH(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) + 0.365 CH(OH)(ONO <sub>2</sub> )CH(OH)(O·) + 0.077 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O – 0.558 O <sub>2</sub>	1.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 02911			CH(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.132 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.426 CH(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) + 0.365 CH(OH)(ONO <sub>2</sub> )CH(OH)(O·) + 0.077 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.558 O <sub>2</sub>	9.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02912			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CO(OH)CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02913			CH(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) → CH(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02914			CH(OH)(ONO <sub>2</sub> )CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02915			CH(OH)(ONO <sub>2</sub> )CH(OH)(O·) → CHO(ONO <sub>2</sub> ) + CHO(OH) + HO <sub>2</sub> – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00376			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub>	9.4 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02916			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> → 0.500 + 0.500 + 0.500	1.0 · 10 <sup>–01</sup>		
R <sub>o</sub> 02917			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> + OH → 0.125 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + 0.041 CH(OH) <sub>2</sub> COC(ONO <sub>2</sub> )(OO·)CH(OH) <sub>2</sub> + 0.238 CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.275 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCH(OH)(O·) + 0.321 CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CH(OH)(O·) + H <sub>2</sub> O – 0.404 O <sub>2</sub>	1.2 · 10 <sup>+09</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02918			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.125 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + 0.041 CH(OH) <sub>2</sub> COC(ONO <sub>2</sub> )(OO·)CH(OH) <sub>2</sub> + 0.238 CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.275 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCH(OH)(O·) + 0.321 CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.404 O <sub>2</sub>	9.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 02919			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OO·) → CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02920			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) → CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02921			CH(OH) <sub>2</sub> COC(ONO <sub>2</sub> )(OO·)CH(OH) <sub>2</sub> $\xrightarrow{RO_2}$ CH(OH) <sub>2</sub> COC(ONO <sub>2</sub> )(O·)CH(OH) <sub>2</sub> + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02922			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02923			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCH(OH)(O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02924			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCH(OH)(O·) → CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02925			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CH(OH)(O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02926			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CH(OH)(O·) → CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02927			CH(OH) <sub>2</sub> COC(ONO <sub>2</sub> )(O·)CH(OH) <sub>2</sub> → 0.500 CH(OH) <sub>2</sub> CO(OO·) + 0.500 CH(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02928			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O·) + 0.550 CH(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + 0.250 CH(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02929			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02930			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O·) → CH(OH) <sub>2</sub> CO(OO·) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02931			$\text{CH(OH)}_2\text{CO(ONO}_2\text{)} \xrightarrow{\text{H}_2\text{O}} \text{CH(OH)}_2\text{CO(OH)} + \text{H}^+ + \text{NO}_3$	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 02932			$\text{CH(OH)}_2\text{CO(ONO}_2\text{)} + \text{OH} \rightarrow 0.160 \text{ CO(ONO}_2\text{)C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.840 \text{ CO(ONO}_2\text{)CH(OH)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.160 \text{ O}_2$	$3.9 \cdot 10^{+08}$		
R <sub>o</sub> 02933			$\text{CH(OH)}_2\text{CO(ONO}_2\text{)} + \text{NO}_3 \rightarrow 0.160 \text{ CO(ONO}_2\text{)C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.840 \text{ CO(ONO}_2\text{)CH(OH)(O}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - 0.160 \text{ O}_2$	$7.4 \cdot 10^{+06}$		
R <sub>o</sub> 02934			$\text{CO(ONO}_2\text{)C(OH)}_2\text{(OO}\cdot\text{)} \rightarrow \text{CO(OH)CO(ONO}_2\text{)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02935			$\text{CO(ONO}_2\text{)CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CO(OH)CO(ONO}_2\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02936			$\text{CO(ONO}_2\text{)CH(OH)(O}\cdot\text{)} \rightarrow \text{CO} + \text{CHO(OH)} + \text{NO}_3$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00377			$\text{CH(OH)}_2\text{CH(OH)CH(ONO}_2\text{)CHO} \xrightleftharpoons{\text{H}_2\text{O}}$ $\text{CH(OH)}_2\text{CH(OH)CH(ONO}_2\text{)CH(OH)}_2$	$1.0 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02937			$\text{CH(OH)}_2\text{CH(OH)CH(ONO}_2\text{)CHO} + \text{OH} \rightarrow$ $0.168 \text{ CHOCH(ONO}_2\text{)CH(OH)C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.048 \text{ CH(OH)}_2\text{C(OH)(OO}\cdot\text{)CH(ONO}_2\text{)CHO} +$ $0.057 \text{ CH(OH)}_2\text{CH(OH)C(ONO}_2\text{)(OO}\cdot\text{)CHO} +$ $0.488 \text{ CH(OH)}_2\text{CH(OH)CH(ONO}_2\text{)CO(OO}\cdot\text{)} +$ $0.195 \text{ CHOCH(ONO}_2\text{)CH(OH)CH(OH)(O}\cdot\text{)} +$ $0.043 \text{ CH(OH)}_2\text{CH(O}\cdot\text{)CH(ONO}_2\text{)CHO} + \text{H}_2\text{O} - 0.762 \text{ O}_2$	$2.0 \cdot 10^{+09}$		
R <sub>o</sub> 02938			$\text{CH(OH)}_2\text{CH(OH)CH(ONO}_2\text{)CHO} + \text{NO}_3 \rightarrow$ $0.168 \text{ CHOCH(ONO}_2\text{)CH(OH)C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.048 \text{ CH(OH)}_2\text{C(OH)(OO}\cdot\text{)CH(ONO}_2\text{)CHO} +$ $0.057 \text{ CH(OH)}_2\text{CH(OH)C(ONO}_2\text{)(OO}\cdot\text{)CHO} +$ $0.488 \text{ CH(OH)}_2\text{CH(OH)CH(ONO}_2\text{)CO(OO}\cdot\text{)} +$ $0.195 \text{ CHOCH(ONO}_2\text{)CH(OH)CH(OH)(O}\cdot\text{)} +$ $0.043 \text{ CH(OH)}_2\text{CH(O}\cdot\text{)CH(ONO}_2\text{)CHO} + \text{NO}_3^- + \text{H}^+ - 0.762 \text{ O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 02939			$\text{CHOCH(ONO}_2\text{)CH(OH)C(OH)}_2\text{(OO}\cdot\text{)} \rightarrow$ $\text{CO(OH)CH(OH)CH(ONO}_2\text{)CHO} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02940			$\text{CH(OH)}_2\text{C(OH)(OO}\cdot\text{)CH(ONO}_2\text{)CHO} \rightarrow$ $\text{CH(OH)}_2\text{COCH(ONO}_2\text{)CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 02941			$\text{CH(OH)}_2\text{CH(OH)C(ONO}_2\text{)(OO}\cdot\text{)CHO} \xrightarrow{\text{RO}_2}$ $\text{CH(OH)}_2\text{CH(OH)C(ONO}_2\text{)(O}\cdot\text{)CHO} + 0.500 \text{ O}_2$	$1.0 \cdot 10^{+06}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02942			CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CO(OO·) → CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02943			CHOCH(ONO <sub>2</sub> )CH(OH)CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH(OH)CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02944			CHOCH(ONO <sub>2</sub> )CH(OH)CH(OH)(O·) → CHOCH(ONO <sub>2</sub> )CH(OH)(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02945			CH(OH) <sub>2</sub> CH(OH)C(ONO <sub>2</sub> )(O·)CHO → 0.500 CH(OH) <sub>2</sub> CH(OH)(OO·) + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CH(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + 0.500 CH · (OH) <sub>2</sub> – 0.500 O <sub>2</sub> – 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02946			CHOCH(ONO <sub>2</sub> )CH(OH)(OO·) → CHOCH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00378			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub>	9.4 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02947			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CHO → 0.500 + 0.500 + 0.500	1.0 · 10 <sup>–01</sup>		
R <sub>o</sub> 02948			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CHO + OH → 0.110 CHOCH(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + 0.037 CH(OH) <sub>2</sub> COC(ONO <sub>2</sub> )(OO·)CHO + 0.609 CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CO(OO·) + 0.243 CHOCH(ONO <sub>2</sub> )COCH(OH)(O·) + H <sub>2</sub> O – 0.757 O <sub>2</sub>	1.3 · 10 <sup>+09</sup>		
R <sub>o</sub> 02949			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CHO + NO <sub>3</sub> → 0.110 CHOCH(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + 0.037 CH(OH) <sub>2</sub> COC(ONO <sub>2</sub> )(OO·)CHO + 0.609 CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CO(OO·) + 0.243 CHOCH(ONO <sub>2</sub> )COCH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.757 O <sub>2</sub>	8.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02950			CHOCH(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) → CO(OH)COCH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02951			CH(OH) <sub>2</sub> COC(ONO <sub>2</sub> )(OO·)CHO $\xrightarrow{RO_2}$ CH(OH) <sub>2</sub> COC(ONO <sub>2</sub> )(O·)CHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02952			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CO(OO·) → CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02953			CHOCH(ONO <sub>2</sub> )COCH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)COCH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02954			CHOCH(ONO <sub>2</sub> )COCH(OH)(O·) → CHOCH(ONO <sub>2</sub> )CO(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02955			CH(OH) <sub>2</sub> COC(ONO <sub>2</sub> )(O·)CHO → 0.500 CH(OH) <sub>2</sub> CO(OO·) + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CH(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + 0.500 CH·(OH) <sub>2</sub> – 0.500 O <sub>2</sub> – 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00379			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub>	1.0 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02956			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CHO + OH → 0.170 CHOCH(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.048 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CH(OH)CHO + 0.057 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH)(OO·)CHO + 0.491 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CO(OO·) + 0.196 CHOCH(OH)CH(ONO <sub>2</sub> )CH(OH)(O·) + 0.037 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(O·)CHO + H <sub>2</sub> O – 0.766 O <sub>2</sub>	1.9 · 10 <sup>+09</sup>		
R <sub>o</sub> 02957			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CHO + NO <sub>3</sub> → 0.170 CHOCH(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.048 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CH(OH)CHO + 0.057 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH)(OO·)CHO + 0.491 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CO(OO·) + 0.196 CHOCH(OH)CH(ONO <sub>2</sub> )CH(OH)(O·) + 0.037 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(O·)CHO + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.766 O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 02958			CHOCH(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CO(OH)CH(ONO <sub>2</sub> )CH(OH)CHO + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02959			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CH(OH)CHO $\xrightarrow{RO_2}$ CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O·)CH(OH)CHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02960			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH)(OO·)CHO → CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02961			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CO(OO·) → CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CO(OH) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02962			CHOCH(OH)CH(ONO <sub>2</sub> )CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH(ONO <sub>2</sub> )CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02963			CHOCH(OH)CH(ONO <sub>2</sub> )CH(OH)(O·) → CHOCH(OH)CH(ONO <sub>2</sub> )(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02964			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O·)CH(OH)CHO → 0.500 CH·(OH) <sub>2</sub> + 0.500 CO(ONO <sub>2</sub> )CH(OH)CHO + 0.500 CH(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 CHOCH(OH)(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02965			CHOCH(OH)CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CHOCH(OH)CH(ONO <sub>2</sub> )(O·) + 0.550 CO(ONO <sub>2</sub> )CH(OH)CHO + 0.250 CH(OH)(ONO <sub>2</sub> )CH(OH)CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 02966			CHOCH(OH)CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02967			CHOCH(OH)CH(ONO <sub>2</sub> )(O·) → CHOCH(OH)(OO·) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00380			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub>	9.4 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02968			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCHO → 0.500 + 0.500	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 02969			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCHO + OH → 0.248 CHOCOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.037 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)COCHO + 0.379 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCO(OO·) + 0.336 CHOCOCH(ONO <sub>2</sub> )CH(OH)(O·) + H <sub>2</sub> O - 0.664 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 02970			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCHO + NO <sub>3</sub> → 0.248 CHOCOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.037 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)COCHO + 0.379 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCO(OO·) + 0.336 CHOCOCH(ONO <sub>2</sub> )CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.664 O <sub>2</sub>	7.9 · 10 <sup>+06</sup>		
R <sub>o</sub> 02971			CHOCOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CO(OH)CH(ONO <sub>2</sub> )COCHO + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02972			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)COCHO $\xrightarrow{RO_2}$ CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O·)COCHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02973			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCO(OO·) → CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 02974			CHOCOCH(ONO <sub>2</sub> )CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH(ONO <sub>2</sub> )COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 02975			CHOCOCH(ONO <sub>2</sub> )CH(OH)(O·) → CHOCOCH(ONO <sub>2</sub> )(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 02976			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O·)COCHO → 0.500 CH·(OH) <sub>2</sub> + 0.500 CO(ONO <sub>2</sub> )COCHO + 0.500 CH(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 CHOCO(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02977			CHOCOCH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CHOCOCH(ONO <sub>2</sub> )(O·) + 0.550 CO(ONO <sub>2</sub> )COCHO + 0.250 CH(OH)(ONO <sub>2</sub> )COCHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02978			CHOCOCH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )COCHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02979			CHOCOCH(ONO <sub>2</sub> )(O·) $\rightarrow$ CHOCO(OO·) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00381			CO(ONO <sub>2</sub> )COCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> COCO(ONO <sub>2</sub> )	$3.2 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00382			CO(ONO <sub>2</sub> )COCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> )	$4.0 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02980			CO(ONO <sub>2</sub> )COCHO $\xrightarrow{H_2O}$ CO(OH)COCHO + H <sup>+</sup> + NO <sub>3</sub>	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 02981			CO(ONO <sub>2</sub> )COCHO + OH $\rightarrow$ CO(ONO <sub>2</sub> )COCO(OO·) + H <sub>2</sub> O - O <sub>2</sub>	$3.7 \cdot 10^{+08}$		
R <sub>o</sub> 02982			CO(ONO <sub>2</sub> )COCHO + NO <sub>3</sub> $\rightarrow$ CO(ONO <sub>2</sub> )COCO(OO·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	$1.4 \cdot 10^{+06}$		
R <sub>o</sub> 02983			CO(ONO <sub>2</sub> )COCO(OO·) $\rightarrow$ CO(OH)COCO(ONO <sub>2</sub> ) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
E <sub>o</sub> 00383			CO(ONO <sub>2</sub> )CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> )	$3.7 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02984			CO(ONO <sub>2</sub> )CH(OH)CHO $\xrightarrow{H_2O}$ CO(OH)CH(OH)CHO + H <sup>+</sup> + NO <sub>3</sub>	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 02985			CO(ONO <sub>2</sub> )CH(OH)CHO + OH $\rightarrow$ 0.929 CO(ONO <sub>2</sub> )CH(OH)CO(OO·) + 0.071 CO(ONO <sub>2</sub> )CH(O·)CHO + H <sub>2</sub> O - 0.929 O <sub>2</sub>	$8.8 \cdot 10^{+08}$		
R <sub>o</sub> 02986			CO(ONO <sub>2</sub> )CH(OH)CHO + NO <sub>3</sub> $\rightarrow$ 0.929 CO(ONO <sub>2</sub> )CH(OH)CO(OO·) + 0.071 CO(ONO <sub>2</sub> )CH(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.929 O <sub>2</sub>	$3.6 \cdot 10^{+06}$		
R <sub>o</sub> 02987			CO(ONO <sub>2</sub> )CH(OH)CO(OO·) $\rightarrow$ CO(OH)CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 02988			CO(ONO <sub>2</sub> )CH(O·)CHO $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )COCHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02989			CO(ONO <sub>2</sub> )CH(O·)CHO $\rightarrow$ 0.500 CO + 0.500 CHOCHO + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CH·(OH) <sub>2</sub> + 0.500 NO <sub>3</sub> - 0.500 H <sub>2</sub> O	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00384			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub>	$5.7 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 02990			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + OH $\rightarrow$ 0.174 CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.590 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OO·) + 0.236 CHOCH(ONO <sub>2</sub> )CH(OH)(O·) + H <sub>2</sub> O - 0.764 O <sub>2</sub>	$1.6 \cdot 10^{+09}$		
R <sub>o</sub> 02991			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + NO <sub>3</sub> $\rightarrow$ 0.174 CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.590 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OO·) + 0.236 CHOCH(ONO <sub>2</sub> )CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.764 O <sub>2</sub>	$7.9 \cdot 10^{+06}$		
R <sub>o</sub> 02992			CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) $\rightarrow$ CO(OH)CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 02993			$\text{CHOCH(ONO}_2\text{)CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CO(OH)CH(ONO}_2\text{)CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 02994			$\text{CHOCH(ONO}_2\text{)CH(OH)(O}\cdot\text{)} \rightarrow \text{CHOCH(ONO}_2\text{)(OO}\cdot\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 02995	*	*	$\text{CO(O}^-\text{)CH=CHCHO} + \text{OH} \rightarrow 0.500 \text{CO(O}^-\text{)CH(OH)CH(OO}\cdot\text{)CHO} +$ $0.500 \text{CO(O}^-\text{)CH(OO}\cdot\text{)CH(OH)CHO} - \text{O}_2$	$3.6 \cdot 10^{+10}$		
R <sub>o</sub> 02996			$\text{CO(O}^-\text{)CH=CHCHO} + \text{NO}_3 \rightarrow 0.500 \text{CO(O}^-\text{)CH(ONO}_2\text{)CH(OO}\cdot\text{)CHO} +$ $0.500 \text{CO(O}^-\text{)CH(OO}\cdot\text{)CH(ONO}_2\text{)CHO} - \text{O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 02997			$\text{CO(O}^-\text{)CH(ONO}_2\text{)CH(OO}\cdot\text{)CHO} \xrightarrow{\text{RO}_2^{\cdot}}$ $0.200 \text{CO(O}^-\text{)CH(ONO}_2\text{)CH(O}\cdot\text{)CHO} + 0.550 \text{CO(O}^-\text{)CH(ONO}_2\text{)COCHO} +$ $0.250 \text{CO(O}^-\text{)CH(ONO}_2\text{)CH(OH)CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 02998			$\text{CO(O}^-\text{)CH(OO}\cdot\text{)CH(ONO}_2\text{)CHO} + \text{CO(O}^-\text{)CH(OO}\cdot\text{)CH(ONO}_2\text{)CHO} \rightarrow$ $2.000 \text{CHOCH(ONO}_2\text{)CHO} + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 02999			$\text{CO(O}^-\text{)CH(OO}\cdot\text{)CH(ONO}_2\text{)CHO} \xrightarrow{\text{RO}_2^{\cdot}}$ $0.200 \text{CO(O}^-\text{)CH(O}\cdot\text{)CH(ONO}_2\text{)CHO} + 0.550 \text{CO(O}^-\text{)COCH(ONO}_2\text{)CHO} +$ $0.250 \text{CO(O}^-\text{)CH(OH)CH(ONO}_2\text{)CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03000			$\text{CO(O}^-\text{)CH(ONO}_2\text{)CH(O}\cdot\text{)CHO} \xrightarrow{\text{O}_2} \text{CO(O}^-\text{)CH(ONO}_2\text{)COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03001			$\text{CO(O}^-\text{)CH(ONO}_2\text{)CH(O}\cdot\text{)CHO} \rightarrow$ $0.500 \text{CO(O}^-\text{)CH(ONO}_2\text{)(OO}\cdot\text{)} + 0.500 \text{CHOCHO} +$ $0.500 \text{CO(O}^-\text{)CH(ONO}_2\text{)CHO} + 0.500 \text{CH}\cdot\text{(OH)}_2 - 0.500 \text{O}_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03002			$\text{CO(O}^-\text{)CH(O}\cdot\text{)CH(ONO}_2\text{)CHO} \xrightarrow{\text{O}_2} \text{CO(O}^-\text{)COCH(ONO}_2\text{)CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03003			$\text{CO(O}^-\text{)CH(O}\cdot\text{)CH(ONO}_2\text{)CHO} \rightarrow$ $0.500 \cdot \text{CO(O}^-\text{)} + 0.500 \text{CHOCH(ONO}_2\text{)CHO} + 0.500 \text{CO(O}^-\text{)CHO} +$ $0.500 \text{CHOCH(ONO}_2\text{)(OO}\cdot\text{)} - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03004			$\text{CO(O}^-\text{)CH(ONO}_2\text{)(OO}\cdot\text{)} + \text{CO(O}^-\text{)CH(ONO}_2\text{)(OO}\cdot\text{)} \rightarrow$ $2.000 \text{CHO(ONO}_2\text{)} + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03005			$\text{CO(O}^-\text{)CH(ONO}_2\text{)(OO}\cdot\text{)} \xrightarrow{\text{RO}_2^{\cdot}}$ $0.200 \text{CO(O}^-\text{)CH(ONO}_2\text{)(O}\cdot\text{)} + 0.550 \text{CO(O}^-\text{)CO(ONO}_2\text{)} +$ $0.250 \text{CO(O}^-\text{)CH(OH)(ONO}_2\text{)} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03006			$\text{CO(O}^-\text{)CH(ONO}_2\text{)(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CO(O}^-\text{)CO(ONO}_2\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03007			$\text{CO(O}^-\text{)CH(ONO}_2\text{)(O}\cdot\text{)} \rightarrow \cdot\text{CO(O}^-\text{)} + \text{CHO(ONO}_2\text{)}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00385	*	*	$\text{CH(OH)}_2\text{CH=CHCO(OH)} \rightleftharpoons \text{CH(OH)}_2\text{CH=CHCO(O}^-\text{)} + \text{H}^+$	$8.0 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03008	*	*	CH(OH) <sub>2</sub> CH=CHCO(OH) + OH $\rightarrow$ 0.045 CO(OH)CH=CHC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.477 CH(OH) <sub>2</sub> CH(OH)CH(OO $\cdot$ )CO(OH) + 0.477 CH(OH) <sub>2</sub> CH(OO $\cdot$ )CH(OH)CO(OH) + 0.045 H <sub>2</sub> O – O <sub>2</sub>	1.5 · 10 <sup>+10</sup>		
R <sub>o</sub> 03009			CH(OH) <sub>2</sub> CH=CHCO(OH) + NO <sub>3</sub> $\rightarrow$ 0.045 CO(OH)CH=CHC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.477 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OO $\cdot$ )CO(OH) + 0.477 CH(OH) <sub>2</sub> CH(OO $\cdot$ )CH(ONO <sub>2</sub> )CO(OH) + 0.045 NO <sub>3</sub> <sup>–</sup> + 0.045 H <sup>+</sup> – O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03010	*	*	CO(OH)CH=CHC(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)CH=CHCO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03011	*	*	CH(OH) <sub>2</sub> CH(OH)CH(OO $\cdot$ )CO(OH) + CH(OH) <sub>2</sub> CH(OH)CH(OO $\cdot$ )CO(OH) $\rightarrow$ 2.000 CH(OH) <sub>2</sub> CH(OH)CHO + 2.000 CO <sub>2</sub> + –O <sub>2</sub> –	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03012	*	*	CH(OH) <sub>2</sub> CH(OH)CH(OO $\cdot$ )CO(OH) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH(OH)CH(O $\cdot$ )CO(OH) + 0.550 CH(OH) <sub>2</sub> CH(OH)COCO(OH) + 0.250 CH(OH) <sub>2</sub> CH(OH)CH(OH)CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03013			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OO $\cdot$ )CO(OH) + CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OO $\cdot$ )CO(OH) $\rightarrow$ 2.000 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + 2.000 CO <sub>2</sub> + –O <sub>2</sub> –	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03014			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OO $\cdot$ )CO(OH) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(O $\cdot$ )CO(OH) + 0.550 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCO(OH) + 0.250 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03015			CH(OH) <sub>2</sub> CH(OO $\cdot$ )CH(ONO <sub>2</sub> )CO(OH) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH(O $\cdot$ )CH(ONO <sub>2</sub> )CO(OH) + 0.550 CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CO(OH) + 0.250 CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03016			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(O $\cdot$ )CO(OH) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03017			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(O $\cdot$ )CO(OH) $\rightarrow$ 0.500 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.500 CO(OH)CHO + 0.500 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + 0.500 · CO(OH) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03018			$\text{CH(OH)}_2\text{CH(O}\cdot\text{)CH(ONO}_2\text{)CO(OH)} \xrightarrow{\text{O}_2}$ $\text{CH(OH)}_2\text{COCH(ONO}_2\text{)CO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03019			$\text{CH(OH)}_2\text{CH(O}\cdot\text{)CH(ONO}_2\text{)CO(OH)} \rightarrow$ $0.500 \text{ CH} \cdot (\text{OH})_2 + 0.500 \text{ CO(OH)CH(ONO}_2\text{)CHO} + 0.500 \text{ CH(OH)}_2\text{CHO} +$ $0.500 \text{ CO(OH)CH(ONO}_2\text{)(OO}\cdot\text{)} - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00386			$\text{CO(OH)CH(ONO}_2\text{)COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)}_2\text{CH(ONO}_2\text{)CO(OH)}$	$2.1 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00387			$\text{CO(OH)CH(ONO}_2\text{)COCHO} \rightleftharpoons \text{CO(O}^-\text{)CH(ONO}_2\text{)COCHO} + \text{H}^+$	$6.5 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03020			$\text{CO(OH)CH(ONO}_2\text{)COCHO} + \text{OH} \rightarrow$ $0.031 \text{ CO(OH)C(ONO}_2\text{)(OO}\cdot\text{)COCHO} +$ $0.969 \text{ CO(OH)CH(ONO}_2\text{)COCO(OO}\cdot\text{)} + \text{H}_2\text{O} - \text{O}_2$	$4.4 \cdot 10^{+08}$		
R <sub>o</sub> 03021			$\text{CO(OH)CH(ONO}_2\text{)COCHO} + \text{NO}_3 \rightarrow$ $0.031 \text{ CO(OH)C(ONO}_2\text{)(OO}\cdot\text{)COCHO} +$ $0.969 \text{ CO(OH)CH(ONO}_2\text{)COCO(OO}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$3.8 \cdot 10^{+06}$		
R <sub>o</sub> 03022			$\text{CO(OH)C(ONO}_2\text{)(OO}\cdot\text{)COCHO} + \text{CO(OH)C(ONO}_2\text{)(OO}\cdot\text{)COCHO} \rightarrow$ $2.000 \text{ CO(ONO}_2\text{)COCHO} + 2.000 \text{ CO}_2 + -\text{O}_2 -$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03023			$\text{CO(OH)C(ONO}_2\text{)(OO}\cdot\text{)COCHO} \xrightarrow{\text{RO}_2}$ $\text{CO(OH)C(ONO}_2\text{)(O}\cdot\text{)COCHO} + 0.500 \text{ O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03024			$\text{CO(OH)CH(ONO}_2\text{)COCO(OO}\cdot\text{)} \rightarrow$ $\text{CO(OH)COCH(ONO}_2\text{)CO(OH)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 03025			$\text{CO(OH)C(ONO}_2\text{)(O}\cdot\text{)COCHO} \rightarrow$ $0.500 \cdot \text{CO(OH)} + 0.500 \text{ CO(ONO}_2\text{)COCHO} + 0.500 \text{ CO(OH)CO(ONO}_2\text{)} +$ $0.500 \text{ CHOCO(OO}\cdot\text{)} - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00388			$\text{CO(OH)COCH(ONO}_2\text{)CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{CH(ONO}_2\text{)C(OH)}_2\text{CO(OH)}$	$5.4 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00389			$\text{CO(OH)COCH(ONO}_2\text{)CHO} \rightleftharpoons \text{CO(O}^-\text{)COCH(ONO}_2\text{)CHO} + \text{H}^+$	$5.3 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03026			$\text{CO(OH)COCH(ONO}_2\text{)CHO} + \text{OH} \rightarrow$ $0.039 \text{ CO(OH)COC(ONO}_2\text{)(OO}\cdot\text{)CHO} +$ $0.961 \text{ CO(OH)COCH(ONO}_2\text{)CO(OO}\cdot\text{)} + \text{H}_2\text{O} - \text{O}_2$	$8.5 \cdot 10^{+08}$		
R <sub>o</sub> 03027			$\text{CO(OH)COCH(ONO}_2\text{)CHO} + \text{NO}_3 \rightarrow$ $0.039 \text{ CO(OH)COC(ONO}_2\text{)(OO}\cdot\text{)CHO} +$ $0.961 \text{ CO(OH)COCH(ONO}_2\text{)CO(OO}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$3.8 \cdot 10^{+06}$		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03028			CO(OH)COC(ONO <sub>2</sub> )(OO·)CHO $\xrightarrow{RO_2}$ CO(OH)COC(ONO <sub>2</sub> )(O·)CHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03029			CO(OH)COCH(ONO <sub>2</sub> )CO(OO·) → CO(OH)COCH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03030			CO(OH)COC(ONO <sub>2</sub> )(O·)CHO → 0.500 CO(OH)CO(OO·) + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CO(OH)COCO(ONO <sub>2</sub> ) + 0.500 CH·(OH) <sub>2</sub> – 0.500 O <sub>2</sub> – 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00390			CO(OH)CH(ONO <sub>2</sub> )CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CO(OH)	9.7 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00391			CO(OH)CH(ONO <sub>2</sub> )CH(OH)CHO $\rightleftharpoons$ CO(O <sup>–</sup> )CH(ONO <sub>2</sub> )CH(OH)CHO + H <sup>+</sup>	3.2 · 10 <sup>–04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03031			CO(OH)CH(ONO <sub>2</sub> )CH(OH)CHO + OH → 0.067 CO(OH)CH(ONO <sub>2</sub> )C(OH)(OO·)CHO + 0.867 CO(OH)CH(ONO <sub>2</sub> )CH(OH)CO(OO·) + 0.066 CO(OH)CH(ONO <sub>2</sub> )CH(O·)CHO + H <sub>2</sub> O – 0.934 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 03032			CO(OH)CH(ONO <sub>2</sub> )CH(OH)CHO + NO <sub>3</sub> → 0.067 CO(OH)CH(ONO <sub>2</sub> )C(OH)(OO·)CHO + 0.867 CO(OH)CH(ONO <sub>2</sub> )CH(OH)CO(OO·) + 0.066 CO(OH)CH(ONO <sub>2</sub> )CH(O·)CHO + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.934 O <sub>2</sub>	9.9 · 10 <sup>+06</sup>		
R <sub>o</sub> 03033			CO(OH)CH(ONO <sub>2</sub> )C(OH)(OO·)CHO → CO(OH)CH(ONO <sub>2</sub> )COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03034			CO(OH)CH(ONO <sub>2</sub> )CH(OH)CO(OO·) → CO(OH)CH(OH)CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
E <sub>o</sub> 00392			CO(OH)CH(OH)CH(ONO <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CO(OH)	3.7 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00393			CO(OH)CH(OH)CH(ONO <sub>2</sub> )CHO $\rightleftharpoons$ CO(O <sup>–</sup> )CH(OH)CH(ONO <sub>2</sub> )CHO + H <sup>+</sup>	1.6 · 10 <sup>–04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03035			CO(OH)CH(OH)CH(ONO <sub>2</sub> )CHO + OH → 0.068 CO(OH)CH(OH)C(ONO <sub>2</sub> )(OO·)CHO + 0.880 CO(OH)CH(OH)CH(ONO <sub>2</sub> )CO(OO·) + 0.052 CO(OH)CH(O·)CH(ONO <sub>2</sub> )CHO + H <sub>2</sub> O – 0.948 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03036			CO(OH)CH(OH)CH(ONO <sub>2</sub> )CHO + NO <sub>3</sub> → 0.068 CO(OH)CH(OH)C(ONO <sub>2</sub> )(OO·)CHO + 0.880 CO(OH)CH(OH)CH(ONO <sub>2</sub> )CO(OO·) + 0.052 CO(OH)CH(O·)CH(ONO <sub>2</sub> )CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.948 O <sub>2</sub>	9.9 · 10 <sup>+06</sup>		
R <sub>o</sub> 03037			CO(OH)CH(OH)C(ONO <sub>2</sub> )(OO·)CHO $\xrightarrow{RO_2}$ CO(OH)CH(OH)C(ONO <sub>2</sub> )(O·)CHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03038			CO(OH)CH(OH)CH(ONO <sub>2</sub> )CO(OO·) → CO(OH)CH(OH)CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03039			CO(OH)CH(OH)C(ONO <sub>2</sub> )(O·)CHO → 0.500 CO(OH)CH(OH)(OO·) + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CO(OH)CH(OH)CO(ONO <sub>2</sub> ) + 0.500 CH · (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00394			CO(OH)CH(ONO <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH)	7.6 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00395			CO(OH)CH(ONO <sub>2</sub> )CHO $\rightleftharpoons$ CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CHO + H <sup>+</sup>	4.8 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03040			CO(OH)CH(ONO <sub>2</sub> )CHO + OH → CO(OH)CH(ONO <sub>2</sub> )CO(OO·) + H <sub>2</sub> O - O <sub>2</sub>	6.4 · 10 <sup>+08</sup>		
R <sub>o</sub> 03041			CO(OH)CH(ONO <sub>2</sub> )CHO + NO <sub>3</sub> → CO(OH)CH(ONO <sub>2</sub> )CO(OO·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	3.9 · 10 <sup>+06</sup>		
R <sub>o</sub> 03042			CO(OH)CH(ONO <sub>2</sub> )CO(OO·) → CO(OH)CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
E <sub>o</sub> 00396			CO(OH)CO(ONO <sub>2</sub> ) $\rightleftharpoons$ CO(O <sup>-</sup> )CO(ONO <sub>2</sub> ) + H <sup>+</sup>	3.8 · 10 <sup>-03</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03043			CO(OH)CO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CO(OH)CO(OH) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>-06</sup>	6600.0	
R <sub>o</sub> 03044			CO(OH)CO(ONO <sub>2</sub> ) + OH → CO(ONO <sub>2</sub> )CO(O·) + H <sub>2</sub> O	7.0 · 10 <sup>+05</sup>		
R <sub>o</sub> 03045			CO(OH)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> → CO(ONO <sub>2</sub> )CO(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	8.4 · 10 <sup>+06</sup>		
R <sub>o</sub> 03046			CO(ONO <sub>2</sub> )CO(O·) → CO + CO <sub>2</sub> + NO <sub>3</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00397			CO(OH)CH(OH)(ONO <sub>2</sub> ) $\rightleftharpoons$ CO(O <sup>-</sup> )CH(OH)(ONO <sub>2</sub> ) + H <sup>+</sup>	3.3 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03047			CO(OH)CH(OH)(ONO <sub>2</sub> ) + OH → 0.730 CO(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.270 CO(OH)CH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O - 0.730 O <sub>2</sub>	2.0 · 10 <sup>+08</sup>		
R <sub>o</sub> 03048			CO(OH)CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.730 CO(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.270 CO(OH)CH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.730 O <sub>2</sub>	9.4 · 10 <sup>+05</sup>		
R <sub>o</sub> 03049			CO(OH)C(OH)(ONO <sub>2</sub> )(OO·) → CO(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00398	*	*	CO(OH)CH=CHCO(OH) $\rightleftharpoons$ CO(OH)CH=CHCO(O <sup>-</sup> ) + H <sup>+</sup>	1.9 · 10 <sup>-03</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03050	*	*	CO(OH)CH=CHCO(OH) + OH → CO(OH)CH(OH)CH(OO·)CO(OH) - O <sub>2</sub>	6.0 · 10 <sup>+09</sup>		Cabelli and Bielski (1985)

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03051			CO(OH)CH=CHCO(OH) + NO <sub>3</sub> → CO(OH)CH(ONO <sub>2</sub> )CH(OO·)CO(OH) – O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		<i>Neta and Huie (1986)</i>
R <sub>o</sub> 03052			CO(OH)CH(ONO <sub>2</sub> )CH(OO·)CO(OH) + CO(OH)CH(ONO <sub>2</sub> )CH(OO·)CO(OH) → 2.000 CO(OH)CH(ONO <sub>2</sub> )CHO + 2.000 CO <sub>2</sub> + –O <sub>2</sub> –	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03053			CO(OH)CH(ONO <sub>2</sub> )CH(OO·)CO(OH) $\xrightarrow{RO_2}$ 0.200 CO(OH)CH(ONO <sub>2</sub> )CH(O·)CO(OH) + 0.550 CO(OH)COCH(ONO <sub>2</sub> )CO(OH) + 0.250 CO(OH)CH(OH)CH(ONO <sub>2</sub> )CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03054			CO(OH)CH(ONO <sub>2</sub> )CH(O·)CO(OH) $\xrightarrow{O_2}$ CO(OH)COCH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03055			CO(OH)CH(ONO <sub>2</sub> )CH(O·)CO(OH) → 0.500 CO(OH)CH(ONO <sub>2</sub> )(OO·) + 0.500 CO(OH)CHO + 0.500 CO(OH)CH(ONO <sub>2</sub> )CHO + 0.500 · CO(OH) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03056			CH(OH) <sub>2</sub> CH(OH)CH(OH)(ONO <sub>2</sub> ) + OH → 0.170 CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> (OO·) + 0.548 CH(OH) <sub>2</sub> CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.197 CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)(O·) + 0.044 CH(OH) <sub>2</sub> CH(O·)CH(OH)(ONO <sub>2</sub> ) + 0.041 CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O – 0.718 O <sub>2</sub>	1.9 · 10 <sup>+09</sup>		
R <sub>o</sub> 03057			CH(OH) <sub>2</sub> CH(OH)CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.170 CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> (OO·) + 0.548 CH(OH) <sub>2</sub> CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.197 CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)(O·) + 0.044 CH(OH) <sub>2</sub> CH(O·)CH(OH)(ONO <sub>2</sub> ) + 0.041 CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.718 O <sub>2</sub>	1.2 · 10 <sup>+07</sup>		
R <sub>o</sub> 03058			CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> (OO·) → CO(OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03059			CH(OH) <sub>2</sub> CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) → CH(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03060			$\text{CH(OH)(ONO}_2\text{)CH(OH)CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2}$ $\text{CO(OH)CH(OH)CH(OH)(ONO}_2\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03061			$\text{CH(OH)(ONO}_2\text{)CH(OH)CH(OH)(O}\cdot\text{)} \rightarrow$ $\text{CH(OH)(ONO}_2\text{)CH(OH)(OO}\cdot\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03062			$\text{CH(OH)}_2\text{CH(O}\cdot\text{)CH(OH)(ONO}_2\text{)} \xrightarrow{\text{O}_2} \text{CH(OH)}_2\text{COCH(OH)(ONO}_2\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03063			$\text{CH(OH)}_2\text{CH(O}\cdot\text{)CH(OH)(ONO}_2\text{)} \rightarrow$ $0.500 \text{CH}\cdot\text{(OH)}_2 + 0.500 \text{CH(OH)(ONO}_2\text{)CHO} + 0.500 \text{CH(OH)}_2\text{CHO} +$ $0.500 \text{CHO(ONO}_2\text{)} + 0.500 \text{HO}_2 - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03064			$\text{CH(OH)(ONO}_2\text{)CH(OH)(OO}\cdot\text{)} \rightarrow \text{CH(OH)(ONO}_2\text{)CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03065			$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)(ONO}_2\text{)} + \text{OH} \rightarrow$ $0.096 \text{CH(OH)(ONO}_2\text{)C(OH)}_2\text{C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.312 \text{CH(OH)}_2\text{C(OH)}_2\text{C(OH)(ONO}_2\text{)(OO}\cdot\text{)} +$ $0.269 \text{CH(OH)(ONO}_2\text{)C(OH)}_2\text{CH(OH)(O}\cdot\text{)} +$ $0.267 \text{CH(OH)}_2\text{C(OH)(O}\cdot\text{)CH(OH)(ONO}_2\text{)} +$ $0.057 \text{CH(OH)}_2\text{C(OH)}_2\text{CH(ONO}_2\text{)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.408 \text{O}_2$	$1.4 \cdot 10^{+09}$		
R <sub>o</sub> 03066			$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)(ONO}_2\text{)} + \text{NO}_3 \rightarrow$ $0.096 \text{CH(OH)(ONO}_2\text{)C(OH)}_2\text{C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.312 \text{CH(OH)}_2\text{C(OH)}_2\text{C(OH)(ONO}_2\text{)(OO}\cdot\text{)} +$ $0.269 \text{CH(OH)(ONO}_2\text{)C(OH)}_2\text{CH(OH)(O}\cdot\text{)} +$ $0.267 \text{CH(OH)}_2\text{C(OH)(O}\cdot\text{)CH(OH)(ONO}_2\text{)} +$ $0.057 \text{CH(OH)}_2\text{C(OH)}_2\text{CH(ONO}_2\text{)(O}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - 0.408 \text{O}_2$	$9.0 \cdot 10^{+06}$		
R <sub>o</sub> 03067			$\text{CH(OH)(ONO}_2\text{)C(OH)}_2\text{C(OH)}_2\text{(OO}\cdot\text{)} \rightarrow$ $\text{CO(OH)C(OH)}_2\text{CH(OH)(ONO}_2\text{)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 03068			$\text{CH(OH)}_2\text{C(OH)}_2\text{C(OH)(ONO}_2\text{)(OO}\cdot\text{)} \rightarrow$ $\text{CH(OH)}_2\text{C(OH)}_2\text{CO(ONO}_2\text{)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03069			$\text{CH(OH)(ONO}_2\text{)C(OH)}_2\text{CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2}$ $\text{CO(OH)C(OH)}_2\text{CH(OH)(ONO}_2\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03070			$\text{CH(OH)(ONO}_2\text{)C(OH)}_2\text{CH(OH)(O}\cdot\text{)} \rightarrow$ $\text{CH(OH)(ONO}_2\text{)C(OH)}_2\text{(OO}\cdot\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03071			CH(OH) <sub>2</sub> C(OH)(O·)CH(OH)(ONO <sub>2</sub> ) → 0.500 CH·(OH) <sub>2</sub> + 0.500 CO(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00399			CH(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> )	1.2 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03072			CH(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) + OH → 0.145 CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + 0.468 CH(OH) <sub>2</sub> COC(OH)(ONO <sub>2</sub> )(OO·) + 0.319 CH(OH)(ONO <sub>2</sub> )COCH(OH)(O·) + 0.067 CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O – 0.613 O <sub>2</sub>	1.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 03073			CH(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.145 CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + 0.468 CH(OH) <sub>2</sub> COC(OH)(ONO <sub>2</sub> )(OO·) + 0.319 CH(OH)(ONO <sub>2</sub> )COCH(OH)(O·) + 0.067 CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.613 O <sub>2</sub>	8.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 03074			CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) → CO(OH)COCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03075			CH(OH) <sub>2</sub> COC(OH)(ONO <sub>2</sub> )(OO·) → CH(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03076			CH(OH)(ONO <sub>2</sub> )COCH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)COCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03077			CH(OH)(ONO <sub>2</sub> )COCH(OH)(O·) → CH(OH)(ONO <sub>2</sub> )CO(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03078			CH(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CH(OH) <sub>2</sub> COCO(OH) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>–06</sup>	6600.0	
R <sub>o</sub> 03079			CH(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + OH → 0.280 CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + 0.720 CO(ONO <sub>2</sub> )COCH(OH)(O·) + H <sub>2</sub> O – 0.280 O <sub>2</sub>	4.5 · 10 <sup>+08</sup>		
R <sub>o</sub> 03080			CH(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.280 CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + 0.720 CO(ONO <sub>2</sub> )COCH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.280 O <sub>2</sub>	7.4 · 10 <sup>+06</sup>		
R <sub>o</sub> 03081			CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) → CO(OH)COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03082			CO(ONO <sub>2</sub> )COCH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03083			CO(ONO <sub>2</sub> )COCH(OH)(O·) → CO(ONO <sub>2</sub> )CO(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03084			CH(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CH(OH) <sub>2</sub> CH(OH)CO(OH) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>–06</sup>	6600.0	

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03085			CH(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + OH → 0.383 CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> (OO·) + 0.518 CO(ONO <sub>2</sub> )CH(OH)CH(OH)(O·) + 0.098 CH(OH) <sub>2</sub> CH(O·)CO(ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.383 O <sub>2</sub>	7.4 · 10 <sup>+08</sup>		
R <sub>o</sub> 03086			CH(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.383 CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> (OO·) + 0.518 CO(ONO <sub>2</sub> )CH(OH)CH(OH)(O·) + 0.098 CH(OH) <sub>2</sub> CH(O·)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.383 O <sub>2</sub>	9.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 03087			CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> (OO·) → CO(OH)CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03088			CO(ONO <sub>2</sub> )CH(OH)CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03089			CO(ONO <sub>2</sub> )CH(OH)CH(OH)(O·) → CO(ONO <sub>2</sub> )CH(OH)(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03090			CH(OH) <sub>2</sub> CH(O·)CO(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03091			CH(OH) <sub>2</sub> CH(O·)CO(ONO <sub>2</sub> ) → 0.500 CH·(OH) <sub>2</sub> + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CH(OH) <sub>2</sub> CHO + 0.500 CO + 0.500 NO <sub>3</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03092			CO(ONO <sub>2</sub> )CH(OH)(OO·) → CO(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03093			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>–06</sup>	6600.0	
R <sub>o</sub> 03094			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + OH → 0.143 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.463 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(O·) + 0.394 CH(OH) <sub>2</sub> C(OH)(O·)CO(ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.143 O <sub>2</sub>	7.8 · 10 <sup>+08</sup>		
R <sub>o</sub> 03095			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.143 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.463 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(O·) + 0.394 CH(OH) <sub>2</sub> C(OH)(O·)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.143 O <sub>2</sub>	7.4 · 10 <sup>+06</sup>		
R <sub>o</sub> 03096			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CO(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03097			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03098			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(O·) → CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03099			CH(OH) <sub>2</sub> C(OH)(O·)CO(ONO <sub>2</sub> ) → 0.500 CH·(OH) <sub>2</sub> + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CO + 0.500 NO <sub>3</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00400			$\text{CH(OH)(ONO}_2\text{)COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)(ONO}_2\text{)}$	$1.2 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03100			$\text{CH(OH)(ONO}_2\text{)COCHO} + \text{OH} \rightarrow$ $0.451 \text{ CHOCOC(OH)(ONO}_2\text{)(OO}\cdot\text{)} + 0.473 \text{ CH(OH)(ONO}_2\text{)COCO(OO}\cdot\text{)} +$ $0.076 \text{ CHOCOCH(ONO}_2\text{)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.924 \text{ O}_2$	$9.1 \cdot 10^{+08}$		
R <sub>o</sub> 03101			$\text{CH(OH)(ONO}_2\text{)COCHO} + \text{NO}_3 \rightarrow$ $0.451 \text{ CHOCOC(OH)(ONO}_2\text{)(OO}\cdot\text{)} + 0.473 \text{ CH(OH)(ONO}_2\text{)COCO(OO}\cdot\text{)} +$ $0.076 \text{ CHOCOCH(ONO}_2\text{)(O}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - 0.924 \text{ O}_2$	$3.3 \cdot 10^{+06}$		
R <sub>o</sub> 03102			$\text{CHOCOC(OH)(ONO}_2\text{)(OO}\cdot\text{)} \rightarrow \text{CO(ONO}_2\text{)COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03103			$\text{CH(OH)(ONO}_2\text{)COCO(OO}\cdot\text{)} \rightarrow \text{CO(OH)COCH(OH)(ONO}_2\text{)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
E <sub>o</sub> 00401			$\text{CH(OH)(ONO}_2\text{)CH(OH)CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{CH(OH)CH(OH)(ONO}_2\text{)}$	$7.6 \cdot 10^{+01}$		
R <sub>o</sub> 03104			$\text{CH(OH)(ONO}_2\text{)CH(OH)CHO} + \text{OH} \rightarrow$ $0.452 \text{ CHOCH(OH)C(OH)(ONO}_2\text{)(OO}\cdot\text{)} +$ $0.473 \text{ CH(OH)(ONO}_2\text{)CH(OH)CO(OO}\cdot\text{)} +$ $0.040 \text{ CHOCH(OH)CH(ONO}_2\text{)(O}\cdot\text{)} + 0.036 \text{ CH(OH)(ONO}_2\text{)CH(O}\cdot\text{)CHO} +$ $\text{H}_2\text{O} - 0.924 \text{ O}_2$	$2.0 \cdot 10^{+09}$		
R <sub>o</sub> 03105			$\text{CH(OH)(ONO}_2\text{)CH(OH)CHO} + \text{NO}_3 \rightarrow$ $0.452 \text{ CHOCH(OH)C(OH)(ONO}_2\text{)(OO}\cdot\text{)} +$ $0.473 \text{ CH(OH)(ONO}_2\text{)CH(OH)CO(OO}\cdot\text{)} +$ $0.040 \text{ CHOCH(OH)CH(ONO}_2\text{)(O}\cdot\text{)} + 0.036 \text{ CH(OH)(ONO}_2\text{)CH(O}\cdot\text{)CHO} +$ $\text{NO}_3^- + \text{H}^+ - 0.924 \text{ O}_2$	$1.1 \cdot 10^{+07}$		
R <sub>o</sub> 03106			$\text{CHOCH(OH)C(OH)(ONO}_2\text{)(OO}\cdot\text{)} \rightarrow \text{CO(ONO}_2\text{)CH(OH)CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03107			$\text{CH(OH)(ONO}_2\text{)CH(OH)CO(OO}\cdot\text{)} \rightarrow$ $\text{CO(OH)CH(OH)CH(OH)(ONO}_2\text{)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 03108			$\text{CH(OH)(ONO}_2\text{)CH(O}\cdot\text{)CHO} \xrightarrow{\text{O}_2} \text{CH(OH)(ONO}_2\text{)COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03109			$\text{CH(OH)(ONO}_2\text{)CH(O}\cdot\text{)CHO} \rightarrow$ $0.500 \text{ CHO(ONO}_2\text{)} + 0.500 \text{ CHOCHO} + 0.500 \text{ CH(OH)(ONO}_2\text{)CHO} +$ $0.500 \text{ CH}\cdot\text{(OH)}_2 + 0.500 \text{ HO}_2 - 0.500 \text{ O}_2 - 0.500 \text{ H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03110	*	*	$\text{CH(OH)}_2\text{CH=CHCO(O}^-\text{)} + \text{OH} \rightarrow$ $0.500 \text{ CH(OH)}_2\text{CH(OH)CH(OO}\cdot\text{)CO(O}^-\text{)} +$ $0.500 \text{ CH(OH)}_2\text{CH(OO}\cdot\text{)CH(OH)CO(O}^-\text{)} - \text{O}_2$	$6.0 \cdot 10^{+10}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03111			CH(OH) <sub>2</sub> CH=CHCO(O <sup>-</sup> ) + NO <sub>3</sub> → 0.500 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OO·)CO(O <sup>-</sup> ) + 0.500 CH(OH) <sub>2</sub> CH(OO·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) - O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03112			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OO·)CO(O <sup>-</sup> ) + CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OO·)CO(O <sup>-</sup> ) → 2.000 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + 2.000 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2.000 OH <sup>-</sup> - 2.000 H <sub>2</sub> O	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03113			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OO·)CO(O <sup>-</sup> ) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(O·)CO(O <sup>-</sup> ) + 0.550 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCO(O <sup>-</sup> ) + 0.250 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CO(O <sup>-</sup> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03114			CH(OH) <sub>2</sub> CH(OO·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH(O·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + 0.550 CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + 0.250 CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03115			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(O·)CO(O <sup>-</sup> ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03116			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(O·)CO(O <sup>-</sup> ) → 0.500 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.500 CO(O <sup>-</sup> )CHO + 0.500 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + 0.500 · CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03117			CH(OH) <sub>2</sub> CH(O·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03118			CH(OH) <sub>2</sub> CH(O·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) → 0.500 CH · (OH) <sub>2</sub> + 0.500 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CHO + 0.500 CH(OH) <sub>2</sub> CHO + 0.500 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00402			CO(O <sup>-</sup> )CH(OH)CH(ONO <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CO(O <sup>-</sup> )	1.4 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03119			CO(O <sup>-</sup> )CH(OH)CH(ONO <sub>2</sub> )CHO + OH → 0.081 CO(O <sup>-</sup> )C(OH)(OO·)CH(ONO <sub>2</sub> )CHO + 0.101 CO(O <sup>-</sup> )CH(OH)C(ONO <sub>2</sub> )(OO·)CHO + 0.741 CO(O <sup>-</sup> )CH(OH)CH(ONO <sub>2</sub> )CO(OO·) + 0.077 CO(O <sup>-</sup> )CH(O·)CH(ONO <sub>2</sub> )CHO + H <sub>2</sub> O - 0.923 O <sub>2</sub>	1.3 · 10 <sup>+09</sup>		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03120			CO(O <sup>-</sup> )CH(OH)CH(ONO <sub>2</sub> )CHO + NO <sub>3</sub> → CHOCH(ONO <sub>2</sub> )CH(OH)CO(O <sup>·</sup> ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03121			CO(O <sup>-</sup> )C(OH)(OO <sup>·</sup> )CH(ONO <sub>2</sub> )CHO → CO(O <sup>-</sup> )COCH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03122			CO(O <sup>-</sup> )CH(OH)C(ONO <sub>2</sub> )(OO <sup>·</sup> )CHO $\xrightarrow{RO_2}$ CO(O <sup>-</sup> )CH(OH)C(ONO <sub>2</sub> )(O <sup>·</sup> )CHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03123			CO(O <sup>-</sup> )CH(OH)CH(ONO <sub>2</sub> )CO(OO <sup>·</sup> ) → CO(OH)CH(ONO <sub>2</sub> )CH(OH)CO(O <sup>-</sup> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03124			CHOCH(ONO <sub>2</sub> )CH(OH)CO(O <sup>·</sup> ) → CHOCH(ONO <sub>2</sub> )CH(OH)(OO <sup>·</sup> ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03125			CO(O <sup>-</sup> )CH(OH)C(ONO <sub>2</sub> )(O <sup>·</sup> )CHO → 0.500 CO(O <sup>-</sup> )CH(OH)(OO <sup>·</sup> ) + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CO(O <sup>-</sup> )CH(OH)CO(ONO <sub>2</sub> ) + 0.500 CH · (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00403			CO(O <sup>-</sup> )COCH(ONO <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCO(O <sup>-</sup> )	3.0 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00404			CO(O <sup>-</sup> )COCH(ONO <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O <sup>-</sup> )	3.3 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03126			CO(O <sup>-</sup> )COCH(ONO <sub>2</sub> )CHO + OH → 0.067 CO(O <sup>-</sup> )COC(ONO <sub>2</sub> )(OO <sup>·</sup> )CHO + 0.933 CO(O <sup>-</sup> )COCH(ONO <sub>2</sub> )CO(OO <sup>·</sup> ) + H <sub>2</sub> O - O <sub>2</sub>	8.8 · 10 <sup>+08</sup>		
R <sub>o</sub> 03127			CO(O <sup>-</sup> )COCH(ONO <sub>2</sub> )CHO + NO <sub>3</sub> → CHOCH(ONO <sub>2</sub> )COCO(O <sup>·</sup> ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03128			CO(O <sup>-</sup> )COC(ONO <sub>2</sub> )(OO <sup>·</sup> )CHO $\xrightarrow{RO_2}$ CO(O <sup>-</sup> )COC(ONO <sub>2</sub> )(O <sup>·</sup> )CHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03129			CO(O <sup>-</sup> )COCH(ONO <sub>2</sub> )CO(OO <sup>·</sup> ) → CO(OH)CH(ONO <sub>2</sub> )COCO(O <sup>-</sup> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03130			CHOCH(ONO <sub>2</sub> )COCO(O <sup>·</sup> ) → CHOCH(ONO <sub>2</sub> )CO(OO <sup>·</sup> ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03131			CO(O <sup>-</sup> )COC(ONO <sub>2</sub> )(O <sup>·</sup> )CHO → 0.500 CO(O <sup>-</sup> )CO(OO <sup>·</sup> ) + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CO(O <sup>-</sup> )COCO(ONO <sub>2</sub> ) + 0.500 CH · (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00405			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> )	3.7 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03132			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH(OH)CHO + OH → 0.083 CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO·)CH(OH)CHO + 0.103 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH)(OO·)CHO + 0.757 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH(OH)CO(OO·) + 0.057 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH(O·)CHO + H <sub>2</sub> O - 0.943 O <sub>2</sub>	1.3 · 10 <sup>+09</sup>		
R <sub>o</sub> 03133			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH(OH)CHO + NO <sub>3</sub> → CHOCH(OH)CH(ONO <sub>2</sub> )CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03134			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO·)CH(OH)CHO + CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO·)CH(OH)CHO → 2.000 CO(ONO <sub>2</sub> )CH(OH)CHO + 2.000 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2.000 OH <sup>-</sup> - 2.000 H <sub>2</sub> O	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03135			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO·)CH(OH)CHO $\xrightarrow{RO_2}$ CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(O·)CH(OH)CHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03136			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH)(OO·)CHO → CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03137			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH(OH)CO(OO·) → CO(OH)CH(OH)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03138			CHOCH(OH)CH(ONO <sub>2</sub> )CO(O·) → CHOCH(OH)CH(ONO <sub>2</sub> )(OO·) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03139			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(O·)CH(OH)CHO → 0.500 · CO(O <sup>-</sup> ) + 0.500 CO(ONO <sub>2</sub> )CH(OH)CHO + 0.500 CO(O <sup>-</sup> )CO(ONO <sub>2</sub> ) + 0.500 CHOCH(OH)(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00406			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )COCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CO(O <sup>-</sup> )	3.2 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00407			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )COCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O <sup>-</sup> )	4.0 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03140			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )COCHO + OH → 0.098 CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO·)COCHO + 0.902 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )COCO(OO·) + H <sub>2</sub> O - O <sub>2</sub>	4.8 · 10 <sup>+08</sup>		
R <sub>o</sub> 03141			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )COCHO + NO <sub>3</sub> → CHOCOCH(ONO <sub>2</sub> )CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03142			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO·)COCHO + CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO·)COCHO → 2.000 CO(ONO <sub>2</sub> )COCHO + 2.000 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2.000 OH <sup>-</sup> - 2.000 H <sub>2</sub> O	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03143			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO·)COCHO $\xrightarrow{RO_2}$ CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(O·)COCHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03144			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )COCO(OO $\cdot$ ) $\rightarrow$ CO(OH)COCH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03145			CHOCOCH(ONO <sub>2</sub> )CO(O $\cdot$ ) $\rightarrow$ CHOCOCH(ONO <sub>2</sub> )(OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03146			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(O $\cdot$ )COCHO $\rightarrow$ 0.500 · CO(O <sup>-</sup> ) + 0.500 CO(ONO <sub>2</sub> )COCHO + 0.500 CO(O <sup>-</sup> )CO(ONO <sub>2</sub> ) + 0.500 CHOCO(OO $\cdot$ ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00408			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O <sup>-</sup> )	6.7 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03147			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CHO + OH $\rightarrow$ 0.045 CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO $\cdot$ )CHO + 0.955 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CO(OO $\cdot$ ) + H <sub>2</sub> O - O <sub>2</sub>	1.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 03148			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CHO + NO <sub>3</sub> $\rightarrow$ CHOCH(ONO <sub>2</sub> )CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03149			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO $\cdot$ )CHO + CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO $\cdot$ )CHO $\rightarrow$ 2.000 CO(ONO <sub>2</sub> )CHO + 2.000 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2.000 OH <sup>-</sup> - 2.000 H <sub>2</sub> O	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03150			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO $\cdot$ )CHO $\xrightarrow{RO_2}$ CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(O $\cdot$ )CHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03151			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CO(OO $\cdot$ ) $\rightarrow$ CO(OH)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03152			CHOCH(ONO <sub>2</sub> )CO(O $\cdot$ ) $\rightarrow$ CHOCH(ONO <sub>2</sub> )(OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03153			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(O $\cdot$ )CHO $\rightarrow$ 0.500 · CO(O <sup>-</sup> ) + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CO(O <sup>-</sup> )CO(ONO <sub>2</sub> ) + 0.500 CH · (OH) <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03154			CO(O <sup>-</sup> )CH(OH)(ONO <sub>2</sub> ) + OH $\rightarrow$ 0.841 CO(O <sup>-</sup> )C(OH)(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.159 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )(O $\cdot$ ) + H <sub>2</sub> O - 0.841 O <sub>2</sub>	5.9 · 10 <sup>+08</sup>		
R <sub>o</sub> 03155			CO(O <sup>-</sup> )CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> $\rightarrow$ CH(OH)(ONO <sub>2</sub> )CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03156			CO(O <sup>-</sup> )C(OH)(ONO <sub>2</sub> )(OO $\cdot$ ) $\rightarrow$ CO(O <sup>-</sup> )CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03157			CH(OH)(ONO <sub>2</sub> )CO(O $\cdot$ ) $\rightarrow$ CHO(ONO <sub>2</sub> ) + CO <sub>2</sub> + HO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03158			CO(O <sup>-</sup> )CO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CO(OH)CO(O <sup>-</sup> ) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>-06</sup>	6600.0	
R <sub>o</sub> 03159			CO(O <sup>-</sup> )CO(ONO <sub>2</sub> ) + NO <sub>3</sub> $\rightarrow$ CO(ONO <sub>2</sub> )CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	0.0 · 10 <sup>+00</sup>		
E <sub>o</sub> 00409	*	*	CO(OH)CH=CHCO(O <sup>-</sup> ) $\rightleftharpoons$ CO(O <sup>-</sup> )CH=CHCO(O <sup>-</sup> ) + H <sup>+</sup>	7.9 · 10 <sup>-06</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03160	*	*	CO(OH)CH=CHCO(O <sup>-</sup> ) + OH $\rightarrow$ 0.500 CO(OH)CH(OH)CH(OO $\cdot$ )CO(O <sup>-</sup> ) + 0.500 CO(OH)CH(OO $\cdot$ )CH(OH)CO(O <sup>-</sup> ) - O <sub>2</sub>	1.4 · 10 <sup>+10</sup>		
R <sub>o</sub> 03161			CO(OH)CH=CHCO(O <sup>-</sup> ) + NO <sub>3</sub> $\rightarrow$ 0.500 CO(OH)CH(ONO <sub>2</sub> )CH(OO $\cdot$ )CO(O <sup>-</sup> ) + 0.500 CO(OH)CH(OO $\cdot$ )CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) - O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03162			CO(OH)CH(ONO <sub>2</sub> )CH(OO·)CO(O <sup>-</sup> ) + CO(OH)CH(ONO <sub>2</sub> )CH(OO·)CO(O <sup>-</sup> ) → 2.000 CO(OH)CH(ONO <sub>2</sub> )CHO + 2.000 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2.000 OH <sup>-</sup> - 2.000 H <sub>2</sub> O	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03163			CO(OH)CH(ONO <sub>2</sub> )CH(OO·)CO(O <sup>-</sup> ) $\xrightarrow{RO_2}$ 0.200 CO(OH)CH(ONO <sub>2</sub> )CH(O·)CO(O <sup>-</sup> ) + 0.550 CO(OH)CH(ONO <sub>2</sub> )COCO(O <sup>-</sup> ) + 0.250 CO(OH)CH(ONO <sub>2</sub> )CH(OH)CO(O <sup>-</sup> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03164			CO(OH)CH(OO·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + CO(OH)CH(OO·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) → 2.000 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CHO + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03165			CO(OH)CH(OO·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) $\xrightarrow{RO_2}$ 0.200 CO(OH)CH(O·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + 0.550 CO(OH)COCH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + 0.250 CO(OH)CH(OH)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03166			CO(OH)CH(ONO <sub>2</sub> )CH(O·)CO(O <sup>-</sup> ) $\xrightarrow{O_2}$ CO(OH)CH(ONO <sub>2</sub> )COCO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03167			CO(OH)CH(ONO <sub>2</sub> )CH(O·)CO(O <sup>-</sup> ) → 0.500 CO(OH)CH(ONO <sub>2</sub> )(OO·) + 0.500 CO(O <sup>-</sup> )CHO + 0.500 CO(OH)CH(ONO <sub>2</sub> )CHO + 0.500 · CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03168			CO(OH)CH(O·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) $\xrightarrow{O_2}$ CO(OH)COCH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03169			CO(OH)CH(O·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) → 0.500 · CO(OH) + 0.500 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CHO + 0.500 CO(OH)CHO + 0.500 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00410			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CO(OH) $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH)	2.1 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00411			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CO(OH) $\rightleftharpoons$ CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + H <sup>+</sup>	5.2 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03170			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CO(OH) + OH → 0.302 CO(OH)CH(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + 0.033 CH(OH) <sub>2</sub> COC(ONO <sub>2</sub> )(OO·)CO(OH) + 0.666 CO(OH)CH(ONO <sub>2</sub> )COCH(OH)(O·) + H <sub>2</sub> O - 0.334 O <sub>2</sub>	4.9 · 10 <sup>+08</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03171			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CO(OH) + NO <sub>3</sub> → 0.302 CO(OH)CH(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + 0.033 CH(OH) <sub>2</sub> COC(ONO <sub>2</sub> )(OO·)CO(OH) + 0.666 CO(OH)CH(ONO <sub>2</sub> )COCH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.334 O <sub>2</sub>	8.1 · 10 <sup>+06</sup>		
R <sub>o</sub> 03172			CO(OH)CH(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) → CO(OH)COCH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03173			CH(OH) <sub>2</sub> COC(ONO <sub>2</sub> )(OO·)CO(OH) + CH(OH) <sub>2</sub> COC(ONO <sub>2</sub> )(OO·)CO(OH) → 2.000 CH(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03174			CH(OH) <sub>2</sub> COC(ONO <sub>2</sub> )(OO·)CO(OH) $\xrightarrow{RO_2}$ CH(OH) <sub>2</sub> COC(ONO <sub>2</sub> )(O·)CO(OH) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03175			CO(OH)CH(ONO <sub>2</sub> )COCH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)COCH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03176			CO(OH)CH(ONO <sub>2</sub> )COCH(OH)(O·) → CO(OH)CH(ONO <sub>2</sub> )CO(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03177			CH(OH) <sub>2</sub> COC(ONO <sub>2</sub> )(O·)CO(OH) → 0.500 CH(OH) <sub>2</sub> CO(OO·) + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + 0.500 · CO(OH) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00412			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCO(OH) $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OH)	5.4 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00413			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCO(OH) $\rightleftharpoons$ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCO(O <sup>-</sup> ) + H <sup>+</sup>	3.1 · 10 <sup>-01</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03178			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCO(OH) + OH → 0.405 CO(OH)COCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.047 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)COCO(OH) + 0.548 CO(OH)COCH(ONO <sub>2</sub> )CH(OH)(O·) + H <sub>2</sub> O - 0.452 O <sub>2</sub>	7.0 · 10 <sup>+08</sup>		
R <sub>o</sub> 03179			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCO(OH) + NO <sub>3</sub> → 0.405 CO(OH)COCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.047 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)COCO(OH) + 0.548 CO(OH)COCH(ONO <sub>2</sub> )CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.452 O <sub>2</sub>	8.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03180			CO(OH)COCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CO(OH)COCH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03181			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)COCO(OH) $\xrightarrow{RO_2}$ CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O·)COCO(OH) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03182			CO(OH)COCH(ONO <sub>2</sub> )CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)COCH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03183			CO(OH)COCH(ONO <sub>2</sub> )CH(OH)(O·) → CO(OH)COCH(ONO <sub>2</sub> )(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03184			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O·)COCO(OH) → 0.500 CH · (OH) <sub>2</sub> + 0.500 CO(OH)COCO(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 CO(OH)CO(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03185			CO(OH)COCH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CO(OH)COCH(ONO <sub>2</sub> )(O·) + 0.550 CO(OH)COCO(ONO <sub>2</sub> ) + 0.250 CO(OH)COCH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03186			CO(OH)COCH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CO(OH)COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03187			CO(OH)COCH(ONO <sub>2</sub> )(O·) → CO(OH)CO(OO·) + CHO(ONO <sub>2</sub> ) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00414			CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CO(OH) ⇌ CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CO(O <sup>–</sup> ) + H <sup>+</sup>	2.5 · 10 <sup>–04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03188			CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CO(OH) + OH → 0.365 CO(OH)CH(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> (OO·) + 0.080 CH(OH) <sub>2</sub> C(OH)(OO·)CH(ONO <sub>2</sub> )CO(OH) + 0.039 CH(OH) <sub>2</sub> CH(OH)C(ONO <sub>2</sub> )(OO·)CO(OH) + 0.422 CO(OH)CH(ONO <sub>2</sub> )CH(OH)CH(OH)(O·) + 0.094 CH(OH) <sub>2</sub> CH(O·)CH(ONO <sub>2</sub> )CO(OH) + H <sub>2</sub> O – 0.484 O <sub>2</sub>	9.0 · 10 <sup>+08</sup>		
R <sub>o</sub> 03189			CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CO(OH) + NO <sub>3</sub> → 0.365 CO(OH)CH(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> (OO·) + 0.080 CH(OH) <sub>2</sub> C(OH)(OO·)CH(ONO <sub>2</sub> )CO(OH) + 0.039 CH(OH) <sub>2</sub> CH(OH)C(ONO <sub>2</sub> )(OO·)CO(OH) + 0.422 CO(OH)CH(ONO <sub>2</sub> )CH(OH)CH(OH)(O·) + 0.094 CH(OH) <sub>2</sub> CH(O·)CH(ONO <sub>2</sub> )CO(OH) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.484 O <sub>2</sub>	1.1 · 10 <sup>+07</sup>		
R <sub>o</sub> 03190			CO(OH)CH(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> (OO·) → CO(OH)CH(OH)CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03191			CH(OH) <sub>2</sub> C(OH)(OO·)CH(ONO <sub>2</sub> )CO(OH) → CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03192			CH(OH) <sub>2</sub> CH(OH)C(ONO <sub>2</sub> )(OO·)CO(OH) + CH(OH) <sub>2</sub> CH(OH)C(ONO <sub>2</sub> )(OO·)CO(OH) → 2.000 CH(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03193			CH(OH) <sub>2</sub> CH(OH)C(ONO <sub>2</sub> )(OO·)CO(OH) $\xrightarrow{RO_2}$ CH(OH) <sub>2</sub> CH(OH)C(ONO <sub>2</sub> )(O·)CO(OH) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03194			CO(OH)CH(ONO <sub>2</sub> )CH(OH)CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH(OH)CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03195			CO(OH)CH(ONO <sub>2</sub> )CH(OH)CH(OH)(O·) → CO(OH)CH(ONO <sub>2</sub> )CH(OH)(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03196			CH(OH) <sub>2</sub> CH(OH)C(ONO <sub>2</sub> )(O·)CO(OH) → 0.500 CH(OH) <sub>2</sub> CH(OH)(OO·) + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + 0.500 · CO(OH) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03197			CO(OH)CH(ONO <sub>2</sub> )CH(OH)(OO·) → CO(OH)CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00415			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CO(OH) ⇌ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CO(O <sup>-</sup> ) + H <sup>+</sup>	1.3 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03198			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CO(OH) + OH → 0.376 CO(OH)CH(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.083 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CH(OH)CO(OH) + 0.041 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH)(OO·)CO(OH) + 0.436 CO(OH)CH(OH)CH(ONO <sub>2</sub> )CH(OH)(O·) + 0.064 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(O·)CO(OH) + H <sub>2</sub> O - 0.500 O <sub>2</sub>	8.7 · 10 <sup>+08</sup>		
R <sub>o</sub> 03199			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CO(OH) + NO <sub>3</sub> → 0.376 CO(OH)CH(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.083 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CH(OH)CO(OH) + 0.041 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH)(OO·)CO(OH) + 0.436 CO(OH)CH(OH)CH(ONO <sub>2</sub> )CH(OH)(O·) + 0.064 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(O·)CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.500 O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03200			CO(OH)CH(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CO(OH)CH(OH)CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03201			$\text{CH(OH)}_2\text{C(ONO}_2\text{)(OO}\cdot\text{)CH(OH)CO(OH)} \xrightarrow{RO_2}$ $\text{CH(OH)}_2\text{C(ONO}_2\text{)(O}\cdot\text{)CH(OH)CO(OH)} + 0.500 \text{ O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03202			$\text{CH(OH)}_2\text{CH(ONO}_2\text{)C(OH)(OO}\cdot\text{)CO(OH)} \rightarrow$ $\text{CH(OH)}_2\text{CH(ONO}_2\text{)COCO(OH)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03203			$\text{CO(OH)CH(OH)CH(ONO}_2\text{)CH(OH)(O}\cdot\text{)} \xrightarrow{O_2}$ $\text{CO(OH)CH(OH)CH(ONO}_2\text{)CO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03204			$\text{CO(OH)CH(OH)CH(ONO}_2\text{)CH(OH)(O}\cdot\text{)} \rightarrow$ $\text{CO(OH)CH(OH)CH(ONO}_2\text{)(OO}\cdot\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03205			$\text{CH(OH)}_2\text{C(ONO}_2\text{)(O}\cdot\text{)CH(OH)CO(OH)} \rightarrow$ $0.500 \text{ CH}\cdot\text{(OH)}_2 + 0.500 \text{ CO(OH)CH(OH)CO(ONO}_2\text{)} +$ $0.500 \text{ CH(OH)}_2\text{CO(ONO}_2\text{)} + 0.500 \text{ CO(OH)CH(OH)(OO}\cdot\text{)} - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03206			$\text{CO(OH)CH(OH)CH(ONO}_2\text{)(OO}\cdot\text{)} \xrightarrow{RO_2}$ $0.200 \text{ CO(OH)CH(OH)CH(ONO}_2\text{)(O}\cdot\text{)} + 0.550 \text{ CO(OH)CH(OH)CO(ONO}_2\text{)} +$ $0.250 \text{ CO(OH)CH(OH)CH(OH)(ONO}_2\text{)} + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03207			$\text{CO(OH)CH(OH)CH(ONO}_2\text{)(O}\cdot\text{)} \xrightarrow{O_2} \text{CO(OH)CH(OH)CO(ONO}_2\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03208			$\text{CO(OH)CH(OH)CH(ONO}_2\text{)(O}\cdot\text{)} \rightarrow$ $\text{CO(OH)CH(OH)(OO}\cdot\text{)} + \text{CHO(ONO}_2\text{)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00416			$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(ONO}_2\text{)CO(OH)} \rightleftharpoons$ $\text{CH(OH)}_2\text{C(OH)}_2\text{CH(ONO}_2\text{)CO(O}^-\text{)} + \text{H}^+$	$3.7 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03209			$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(ONO}_2\text{)CO(OH)} + \text{OH} \rightarrow$ $0.153 \text{ CO(OH)CH(ONO}_2\text{)C(OH)}_2\text{C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.425 \text{ CO(OH)CH(ONO}_2\text{)C(OH)}_2\text{CH(OH)(O}\cdot\text{)} +$ $0.422 \text{ CH(OH)}_2\text{C(OH)(O}\cdot\text{)CH(ONO}_2\text{)CO(OH)} + \text{H}_2\text{O} - 0.153 \text{ O}_2$	$8.5 \cdot 10^{+08}$		
R <sub>o</sub> 03210			$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(ONO}_2\text{)CO(OH)} + \text{NO}_3 \rightarrow$ $0.153 \text{ CO(OH)CH(ONO}_2\text{)C(OH)}_2\text{C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.425 \text{ CO(OH)CH(ONO}_2\text{)C(OH)}_2\text{CH(OH)(O}\cdot\text{)} +$ $0.422 \text{ CH(OH)}_2\text{C(OH)(O}\cdot\text{)CH(ONO}_2\text{)CO(OH)} + \text{NO}_3^- + \text{H}^+ - 0.153 \text{ O}_2$	$8.2 \cdot 10^{+06}$		
R <sub>o</sub> 03211			$\text{CO(OH)CH(ONO}_2\text{)C(OH)}_2\text{C(OH)}_2\text{(OO}\cdot\text{)} \rightarrow$ $\text{CO(OH)C(OH)}_2\text{CH(ONO}_2\text{)CO(OH)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 03212			$\text{CO(OH)CH(ONO}_2\text{)C(OH)}_2\text{CH(OH)(O}\cdot\text{)} \xrightarrow{O_2}$ $\text{CO(OH)C(OH)}_2\text{CH(ONO}_2\text{)CO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03213			CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(O·) → CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03214			CH(OH) <sub>2</sub> C(OH)(O·)CH(ONO <sub>2</sub> )CO(OH) → 0.500 CH·(OH) <sub>2</sub> + 0.500 CO(OH)CH(ONO <sub>2</sub> )CO(OH) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CO(OH)CH(ONO <sub>2</sub> )(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03215			CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CO(OH)CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
E <sub>o</sub> 00417			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OH) ⇌ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O <sup>–</sup> ) + H <sup>+</sup>	3.3 · 10 <sup>–04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03216			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OH) + OH → 0.335 CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.408 CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(O·) + 0.257 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH)(O·)CO(OH) + H <sub>2</sub> O – 0.335 O <sub>2</sub>	9.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03217			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OH) + NO <sub>3</sub> → 0.335 CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.408 CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(O·) + 0.257 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH)(O·)CO(OH) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.335 O <sub>2</sub>	8.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03218			CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03219			CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03220			CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(O·) → CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03221			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH)(O·)CO(OH) → 0.500 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.500 CO(OH)CO(OH) + 0.500 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH) + 0.500 · CO(OH) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03222			CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + 0.550 CO(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.250 CO(OH)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03223			CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03224			CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) → CO(OH)C(OH) <sub>2</sub> (OO·) + CHO(ONO <sub>2</sub> ) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00418			$\text{CO(OH)CH(OH)CO(ONO}_2\text{)} \rightleftharpoons \text{CO(O}^-\text{)CH(OH)CO(ONO}_2\text{)} + \text{H}^+$	$9.4 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03225			$\text{CO(OH)CH(OH)CO(ONO}_2\text{)} \xrightarrow{\text{H}_2\text{O}} \text{CO(OH)CH(OH)CO(OH)} + \text{H}^+ + \text{NO}_3$	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 03226			$\text{CO(OH)CH(OH)CO(ONO}_2\text{)} + \text{OH} \rightarrow$ $0.122 \text{ CO(OH)C(OH)(OO}\cdot\text{)CO(ONO}_2\text{)} + 0.878 \text{ CO(OH)CH(O}\cdot\text{)CO(ONO}_2\text{)} +$ $\text{H}_2\text{O} - 0.122 \text{ O}_2$	$5.5 \cdot 10^{+07}$		
R <sub>o</sub> 03227			$\text{CO(OH)CH(OH)CO(ONO}_2\text{)} + \text{NO}_3 \rightarrow$ $0.122 \text{ CO(OH)C(OH)(OO}\cdot\text{)CO(ONO}_2\text{)} + 0.878 \text{ CO(OH)CH(O}\cdot\text{)CO(ONO}_2\text{)} +$ $\text{NO}_3^- + \text{H}^+ - 0.122 \text{ O}_2$	$3.4 \cdot 10^{+05}$		
R <sub>o</sub> 03228			$\text{CO(OH)C(OH)(OO}\cdot\text{)CO(ONO}_2\text{)} \rightarrow \text{CO(OH)COCO(ONO}_2\text{)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03229			$\text{CO(OH)CH(O}\cdot\text{)CO(ONO}_2\text{)} \xrightarrow{\text{O}_2} \text{CO(OH)COCO(ONO}_2\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03230			$\text{CO(OH)CH(O}\cdot\text{)CO(ONO}_2\text{)} \rightarrow 0.500 \cdot \text{CO(OH)} + 0.500 \text{ CO(ONO}_2\text{)CHO} +$ $0.500 \text{ CO(OH)CHO} + 0.500 \text{ CO} + 0.500 \text{ NO}_3$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00419			$\text{CO(OH)COCO(ONO}_2\text{)} \xrightarrow{\text{H}_2\text{O}} \text{CO(OH)C(OH)}_2\text{CO(ONO}_2\text{)}$	$9.1 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00420			$\text{CO(OH)COCO(ONO}_2\text{)} \rightleftharpoons \text{CO(O}^-\text{)COCO(ONO}_2\text{)} + \text{H}^+$	$1.5 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03231			$\text{CO(OH)COCO(ONO}_2\text{)} \xrightarrow{\text{H}_2\text{O}} \text{CO(OH)COCO(OH)} + \text{H}^+ + \text{NO}_3$	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 03232			$\text{CO(OH)COCO(ONO}_2\text{)} + \text{OH} \rightarrow \text{CO(ONO}_2\text{)COCO(O}\cdot\text{)} + \text{H}_2\text{O}$	$7.0 \cdot 10^{+05}$		
R <sub>o</sub> 03233			$\text{CO(OH)COCO(ONO}_2\text{)} + \text{NO}_3 \rightarrow \text{CO(ONO}_2\text{)COCO(O}\cdot\text{)} + \text{NO}_3^- + \text{H}^+$	$8.4 \cdot 10^{+06}$		
R <sub>o</sub> 03234			$\text{CO(ONO}_2\text{)COCO(O}\cdot\text{)} \rightarrow \text{CO(ONO}_2\text{)CO(OO}\cdot\text{)} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00421			$\text{CH(OH)}_2\text{CH(ONO}_2\text{)CO(OH)} \rightleftharpoons \text{CH(OH)}_2\text{CH(ONO}_2\text{)CO(O}^-\text{)} + \text{H}^+$	$2.7 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03235			$\text{CH(OH)}_2\text{CH(ONO}_2\text{)CO(OH)} + \text{OH} \rightarrow$ $0.365 \text{ CO(OH)CH(ONO}_2\text{)C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.635 \text{ CO(OH)CH(ONO}_2\text{)CH(OH)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.365 \text{ O}_2$	$6.0 \cdot 10^{+08}$		
R <sub>o</sub> 03236			$\text{CH(OH)}_2\text{CH(ONO}_2\text{)CO(OH)} + \text{NO}_3 \rightarrow$ $0.365 \text{ CO(OH)CH(ONO}_2\text{)C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.635 \text{ CO(OH)CH(ONO}_2\text{)CH(OH)(O}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - 0.365 \text{ O}_2$	$8.1 \cdot 10^{+06}$		
R <sub>o</sub> 03237			$\text{CO(OH)CH(ONO}_2\text{)CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CO(OH)CH(ONO}_2\text{)CO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03238			$\text{CO(OH)CH(ONO}_2\text{)CH(OH)(O}\cdot\text{)} \rightarrow$ $\text{CO(OH)CH(ONO}_2\text{)(OO}\cdot\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00422			$\text{CO(OH)CH(OH)CH(ONO}_2\text{)CO(OH)} \rightleftharpoons$ $\text{CO(OH)CH(ONO}_2\text{)CH(OH)CO(O}^-\text{)} + \text{H}^+$	$1.6 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00423			CO(OH)CH(OH)CH(ONO <sub>2</sub> )CO(OH) $\rightleftharpoons$ CO(OH)CH(OH)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + H <sup>+</sup>	$3.1 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03239			CO(OH)CH(OH)CH(ONO <sub>2</sub> )CO(OH) + OH $\rightarrow$ 0.228 CO(OH)CH(ONO <sub>2</sub> )C(OH)(OO $\cdot$ )CO(OH) + 0.228 CO(OH)CH(OH)C(ONO <sub>2</sub> )(OO $\cdot$ )CO(OH) + 0.544 CO(OH)CH(ONO <sub>2</sub> )CH(O $\cdot$ )CO(OH) + H <sub>2</sub> O - 0.456 O <sub>2</sub>	$1.0 \cdot 10^{+08}$		
R <sub>o</sub> 03240			CO(OH)CH(OH)CH(ONO <sub>2</sub> )CO(OH) + NO <sub>3</sub> $\rightarrow$ 0.228 CO(OH)CH(ONO <sub>2</sub> )C(OH)(OO $\cdot$ )CO(OH) + 0.228 CO(OH)CH(OH)C(ONO <sub>2</sub> )(OO $\cdot$ )CO(OH) + 0.544 CO(OH)CH(ONO <sub>2</sub> )CH(O $\cdot$ )CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.456 O <sub>2</sub>	$2.9 \cdot 10^{+04}$		
R <sub>o</sub> 03241			CO(OH)CH(ONO <sub>2</sub> )C(OH)(OO $\cdot$ )CO(OH) $\rightarrow$ CO(OH)COCH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03242			CO(OH)CH(OH)C(ONO <sub>2</sub> )(OO $\cdot$ )CO(OH) + CO(OH)CH(OH)C(ONO <sub>2</sub> )(OO $\cdot$ )CO(OH) $\rightarrow$ 2.000 CO(OH)CH(OH)CO(ONO <sub>2</sub> ) + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03243			CO(OH)CH(OH)C(ONO <sub>2</sub> )(OO $\cdot$ )CO(OH) $\xrightarrow{RO_2}$ CO(OH)CH(OH)C(ONO <sub>2</sub> )(O $\cdot$ )CO(OH) + 0.500 O <sub>2</sub>	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03244			CO(OH)CH(OH)C(ONO <sub>2</sub> )(O $\cdot$ )CO(OH) $\rightarrow$ 0.500 CO(OH)CH(OH)(OO $\cdot$ ) + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CO(OH)CH(OH)CO(ONO <sub>2</sub> ) + 0.500 $\cdot$ CO(OH) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00424			CO(OH)COCH(ONO <sub>2</sub> )CO(OH) $\xrightleftharpoons{H_2O}$ CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH)	$1.0 \cdot 10^{+03}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00425			CO(OH)COCH(ONO <sub>2</sub> )CO(OH) $\rightleftharpoons$ CO(OH)CH(ONO <sub>2</sub> )COCO(O <sup>-</sup> ) + H <sup>+</sup>	$5.1 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
E <sub>o</sub> 00426			CO(OH)COCH(ONO <sub>2</sub> )CO(OH) $\rightleftharpoons$ CO(OH)COCH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + H <sup>+</sup>	$6.4 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03245			CO(OH)COCH(ONO <sub>2</sub> )CO(OH) + OH $\rightarrow$ 0.884 CO(OH)COC(ONO <sub>2</sub> )(OO $\cdot$ )CO(OH) + 0.058 CO(OH)CH(ONO <sub>2</sub> )COCO(O $\cdot$ ) + 0.058 CO(OH)COCH(ONO <sub>2</sub> )CO(O $\cdot$ ) + H <sub>2</sub> O - 0.884 O <sub>2</sub>	$1.2 \cdot 10^{+07}$		
R <sub>o</sub> 03246			CO(OH)COCH(ONO <sub>2</sub> )CO(OH) + NO <sub>3</sub> $\rightarrow$ 0.884 CO(OH)COC(ONO <sub>2</sub> )(OO $\cdot$ )CO(OH) + 0.058 CO(OH)CH(ONO <sub>2</sub> )COCO(O $\cdot$ ) + 0.058 CO(OH)COCH(ONO <sub>2</sub> )CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.884 O <sub>2</sub>	$6.8 \cdot 10^{+05}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03247			CO(OH)COC(ONO <sub>2</sub> )(OO·)CO(OH) + CO(OH)COC(ONO <sub>2</sub> )(OO·)CO(OH) → 2.000 CO(OH)COCO(ONO <sub>2</sub> ) + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03248			CO(OH)COC(ONO <sub>2</sub> )(OO·)CO(OH) $\xrightarrow{RO_2}$ CO(OH)COC(ONO <sub>2</sub> )(O·)CO(OH) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03249			CO(OH)CH(ONO <sub>2</sub> )COCO(O·) → CO(OH)CH(ONO <sub>2</sub> )CO(OO·) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03250			CO(OH)COCH(ONO <sub>2</sub> )CO(O·) → CO(OH)COCH(ONO <sub>2</sub> )(OO·) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03251			CO(OH)COC(ONO <sub>2</sub> )(O·)CO(OH) → 0.500 CO(OH)CO(OO·) + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CO(OH)COCO(ONO <sub>2</sub> ) + 0.500 · CO(OH) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00427			CO(OH)CH(ONO <sub>2</sub> )CO(OH) ⇌ CO(OH)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + H <sup>+</sup>	2.3 · 10 <sup>-03</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03252			CO(OH)CH(ONO <sub>2</sub> )CO(OH) + OH → 0.775 CO(OH)C(ONO <sub>2</sub> )(OO·)CO(OH) + 0.225 CO(OH)CH(ONO <sub>2</sub> )CO(O·) + H <sub>2</sub> O - 0.775 O <sub>2</sub>	6.2 · 10 <sup>+06</sup>		
R <sub>o</sub> 03253			CO(OH)CH(ONO <sub>2</sub> )CO(OH) + NO <sub>3</sub> → 0.775 CO(OH)C(ONO <sub>2</sub> )(OO·)CO(OH) + 0.225 CO(OH)CH(ONO <sub>2</sub> )CO(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.775 O <sub>2</sub>	6.1 · 10 <sup>+05</sup>		
R <sub>o</sub> 03254			CO(OH)C(ONO <sub>2</sub> )(OO·)CO(OH) + CO(OH)C(ONO <sub>2</sub> )(OO·)CO(OH) → 2.000 CO(OH)CO(ONO <sub>2</sub> ) + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03255			CO(OH)C(ONO <sub>2</sub> )(OO·)CO(OH) $\xrightarrow{RO_2}$ CO(OH)C(ONO <sub>2</sub> )(O·)CO(OH) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03256			CO(OH)CH(ONO <sub>2</sub> )CO(O·) → CO(OH)CH(ONO <sub>2</sub> )(OO·) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03257			CO(OH)C(ONO <sub>2</sub> )(O·)CO(OH) → ·CO(OH) + CO(OH)CO(ONO <sub>2</sub> )	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03258			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + OH → 0.145 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.053 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) + 0.402 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(O·) + 0.400 CH(OH) <sub>2</sub> C(OH)(O·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.198 O <sub>2</sub>	9.0 · 10 <sup>+08</sup>		
R <sub>o</sub> 03259			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03260			$\text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow$ $\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CO}(\text{O}^-) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 03261			$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CO}(\text{O}^-) +$ $\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CO}(\text{O}^-) \rightarrow$ $2.000 \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- -$ $2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03262			$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{RO}_2}$ $\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{CO}(\text{O}^-) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03263			$\text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03264			$\text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03265			$\text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{ONO}_2)\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CH}\cdot(\text{OH})_2 + 0.500 \text{CO}(\text{OH})\text{CH}(\text{ONO}_2)\text{CO}(\text{O}^-) +$ $0.500 \text{CH}(\text{OH})_2\text{CO}(\text{OH}) + 0.500 \text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03266			$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CO}(\text{O}\cdot) \rightarrow$ $\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03267			$\text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CH}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.500 \text{CO}(\text{O}^-)\text{CO}(\text{ONO}_2) +$ $0.500 \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) + 0.500 \cdot \text{CO}(\text{O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03268			$\text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}(\text{ONO}_2)\text{CO}(\text{O}^-) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 03269			$\text{CH}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{OH} \rightarrow$ $0.268 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.043 \text{CH}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{O}^-) +$ $0.327 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{O}\cdot) +$ $0.362 \text{CH}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{O}^-) + \text{H}_2\text{O} - 0.312 \text{O}_2$	$1.2 \cdot 10^{+09}$		
R <sub>o</sub> 03270			$\text{CH}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $\text{CH}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 03271			$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow$ $\text{CO}(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03272			$\text{CH(OH)}_2\text{C(ONO}_2\text{)(OO}\cdot\text{)C(OH)}_2\text{CO(O}^-) \xrightarrow{RO_2}$ $\text{CH(OH)}_2\text{C(ONO}_2\text{)(O}\cdot\text{)C(OH)}_2\text{CO(O}^-) + 0.500 \text{ O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03273			$\text{CO(O}^-)\text{C(OH)}_2\text{CH(ONO}_2\text{)CH(OH)(O}\cdot\text{) } \xrightarrow{O_2}$ $\text{CO(OH)CH(ONO}_2\text{)C(OH)}_2\text{CO(O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03274			$\text{CO(O}^-)\text{C(OH)}_2\text{CH(ONO}_2\text{)CH(OH)(O}\cdot\text{) } \rightarrow$ $\text{CO(O}^-)\text{C(OH)}_2\text{CH(ONO}_2\text{)(OO}\cdot\text{) } + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03275			$\text{CH(OH)}_2\text{CH(ONO}_2\text{)C(OH)(O}\cdot\text{)CO(O}^-) \rightarrow$ $0.500 \text{ CH(OH)}_2\text{CH(ONO}_2\text{)(OO}\cdot\text{) } + 0.500 \text{ CO(OH)CO(O}^-) +$ $0.500 \text{ CH(OH)}_2\text{CH(ONO}_2\text{)CO(OH)} + 0.500 \cdot \text{CO(O}^-) - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03276			$\text{CH(OH)}_2\text{CH(ONO}_2\text{)C(OH)}_2\text{CO(O}\cdot\text{) } \rightarrow$ $\text{CH(OH)}_2\text{CH(ONO}_2\text{)C(OH)}_2\text{(OO}\cdot\text{) } + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03277			$\text{CH(OH)}_2\text{C(ONO}_2\text{)(O}\cdot\text{)C(OH)}_2\text{CO(O}^-) \rightarrow$ $0.500 \text{ CH} \cdot (\text{OH})_2 + 0.500 \text{ CO(O}^-)\text{C(OH)}_2\text{CO(ONO}_2) +$ $0.500 \text{ CH(OH)}_2\text{CO(ONO}_2) + 0.500 \text{ CO(O}^-)\text{C(OH)}_2\text{(OO}\cdot\text{) } - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03278			$\text{CO(O}^-)\text{C(OH)}_2\text{CH(ONO}_2\text{)(OO}\cdot\text{) } \xrightarrow{RO_2}$ $0.200 \text{ CO(O}^-)\text{C(OH)}_2\text{CH(ONO}_2\text{)(O}\cdot\text{) } + 0.550 \text{ CO(O}^-)\text{C(OH)}_2\text{CO(ONO}_2) +$ $0.250 \text{ CO(O}^-)\text{C(OH)}_2\text{CH(OH)(ONO}_2) + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03279			$\text{CO(O}^-)\text{C(OH)}_2\text{CH(ONO}_2\text{)(O}\cdot\text{) } \xrightarrow{O_2} \text{CO(O}^-)\text{C(OH)}_2\text{CO(ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03280			$\text{CO(O}^-)\text{C(OH)}_2\text{CH(ONO}_2\text{)(O}\cdot\text{) } \rightarrow$ $\text{CO(O}^-)\text{C(OH)}_2\text{(OO}\cdot\text{) } + \text{CHO(ONO}_2) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03281			$\text{CH(OH)}_2\text{CH(OH)CH(ONO}_2\text{)CO(O}^-) + \text{OH} \rightarrow$ $0.315 \text{ CO(O}^-)\text{CH(ONO}_2\text{)CH(OH)C(OH)}_2\text{(OO}\cdot\text{) } +$ $0.122 \text{ CH(OH)}_2\text{C(OH)(OO}\cdot\text{)CH(ONO}_2\text{)CO(O}^-) +$ $0.116 \text{ CH(OH)}_2\text{CH(OH)C(ONO}_2\text{)(OO}\cdot\text{)CO(O}^-) +$ $0.365 \text{ CO(O}^-)\text{CH(ONO}_2\text{)CH(OH)CH(OH)(O}\cdot\text{) } +$ $0.081 \text{ CH(OH)}_2\text{CH(O}\cdot\text{)CH(ONO}_2\text{)CO(O}^-) + \text{H}_2\text{O} - 0.554 \text{ O}_2$	$1.0 \cdot 10^{+09}$		
R <sub>o</sub> 03282			$\text{CH(OH)}_2\text{CH(OH)CH(ONO}_2\text{)CO(O}^-) + \text{NO}_3 \rightarrow$ $\text{CH(OH)}_2\text{CH(OH)CH(ONO}_2\text{)CO(O}\cdot\text{) } + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 03283			$\text{CO(O}^-)\text{CH(ONO}_2\text{)CH(OH)C(OH)}_2\text{(OO}\cdot\text{) } \rightarrow$ $\text{CO(OH)CH(OH)CH(ONO}_2\text{)CO(O}^-) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03284			CH(OH) <sub>2</sub> C(OH)(OO·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) → CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03285			CH(OH) <sub>2</sub> CH(OH)C(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) + CH(OH) <sub>2</sub> CH(OH)C(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) → 2.000 CH(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + 2.000 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2.000 OH <sup>-</sup> - 2.000 H <sub>2</sub> O	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03286			CH(OH) <sub>2</sub> CH(OH)C(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) $\xrightarrow{RO_2}$ CH(OH) <sub>2</sub> CH(OH)C(ONO <sub>2</sub> )(O·)CO(O <sup>-</sup> ) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03287			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH(OH)CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH(OH)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03288			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH(OH)CH(OH)(O·) → CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH(OH)(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03289			CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CO(O·) → CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(OO·) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03290			CH(OH) <sub>2</sub> CH(OH)C(ONO <sub>2</sub> )(O·)CO(O <sup>-</sup> ) → 0.500 CH(OH) <sub>2</sub> CH(OH)(OO·) + 0.500 CO(O <sup>-</sup> )CO(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + 0.500 · CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03291			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH(OH)(OO·) → CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03292			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + OH → 0.280 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + 0.103 CH(OH) <sub>2</sub> COC(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) + 0.617 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )COCH(OH)(O·) + H <sub>2</sub> O - 0.383 O <sub>2</sub>	5.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03293			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03294			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) → CO(OH)COCH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03295			CH(OH) <sub>2</sub> COC(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) + CH(OH) <sub>2</sub> COC(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) → 2.000 CH(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + 2.000 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2.000 OH <sup>-</sup> - 2.000 H <sub>2</sub> O	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03296			CH(OH) <sub>2</sub> COC(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) $\xrightarrow{RO_2}$ CH(OH) <sub>2</sub> COC(ONO <sub>2</sub> )(O·)CO(O <sup>-</sup> ) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03297			$\text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{COCH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CO}(\text{OH})\text{COCH}(\text{ONO}_2)\text{CO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03298			$\text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{COCH}(\text{OH})(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{CO}(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03299			$\text{CH}(\text{OH})_2\text{COCH}(\text{ONO}_2)\text{CO}(\text{O}\cdot) \rightarrow$ $\text{CH}(\text{OH})_2\text{COCH}(\text{ONO}_2)(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03300			$\text{CH}(\text{OH})_2\text{COC}(\text{ONO}_2)(\text{O}\cdot)\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CH}(\text{OH})_2\text{CO}(\text{OO}\cdot) + 0.500 \text{CO}(\text{O}^-)\text{CO}(\text{ONO}_2) +$ $0.500 \text{CH}(\text{OH})_2\text{COCO}(\text{ONO}_2) + 0.500 \cdot \text{CO}(\text{O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03301			$\text{CH}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{OH} \rightarrow$ $0.311 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.120 \text{CH}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) +$ $0.115 \text{CH}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{O}^-) +$ $0.360 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{O}\cdot) +$ $0.093 \text{CH}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) + \text{H}_2\text{O} - 0.546 \text{O}_2$	$1.1 \cdot 10^{+09}$		
R <sub>o</sub> 03302			$\text{CH}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $\text{CH}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 03303			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow$ $\text{CO}(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 03304			$\text{CH}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) \xrightarrow{\text{RO}_2}$ $\text{CH}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03305			$\text{CH}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{O}^-) \rightarrow$ $\text{CH}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{COCO}(\text{O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03306			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CO}(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03307			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03308			$\text{CH}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) \rightarrow$ $\text{CH}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03309			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O·)CH(OH)CO(O <sup>-</sup> ) → 0.500 CH·(OH) <sub>2</sub> + 0.500 CO(O <sup>-</sup> )CH(OH)CO(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 CO(O <sup>-</sup> )CH(OH)(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03310			CO(O <sup>-</sup> )CH(OH)CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CO(O <sup>-</sup> )CH(OH)CH(ONO <sub>2</sub> )(O·) + 0.550 CO(O <sup>-</sup> )CH(OH)CO(ONO <sub>2</sub> ) + 0.250 CO(O <sup>-</sup> )CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03311			CO(O <sup>-</sup> )CH(OH)CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CO(O <sup>-</sup> )CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03312			CO(O <sup>-</sup> )CH(OH)CH(ONO <sub>2</sub> )(O·) → CO(O <sup>-</sup> )CH(OH)(OO·) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03313			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCO(O <sup>-</sup> ) + OH → 0.391 CO(O <sup>-</sup> )COCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.080 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)COCO(O <sup>-</sup> ) + 0.529 CO(O <sup>-</sup> )COCH(ONO <sub>2</sub> )CH(OH)(O·) + H <sub>2</sub> O - 0.471 O <sub>2</sub>	7.2 · 10 <sup>+08</sup>		
R <sub>o</sub> 03314			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCO(O <sup>-</sup> ) + NO <sub>3</sub> → CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03315			CO(O <sup>-</sup> )COCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CO(OH)CH(ONO <sub>2</sub> )COCO(O <sup>-</sup> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03316			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)COCO(O <sup>-</sup> ) $\xrightarrow{RO_2}$ CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O·)COCO(O <sup>-</sup> ) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03317			CO(O <sup>-</sup> )COCH(ONO <sub>2</sub> )CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH(ONO <sub>2</sub> )COCO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03318			CO(O <sup>-</sup> )COCH(ONO <sub>2</sub> )CH(OH)(O·) → CO(O <sup>-</sup> )COCH(ONO <sub>2</sub> )(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03319			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCO(O·) → CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OO·) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03320			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O·)COCO(O <sup>-</sup> ) → 0.500 CH·(OH) <sub>2</sub> + 0.500 CO(O <sup>-</sup> )COCO(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 CO(O <sup>-</sup> )CO(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03321			CO(O <sup>-</sup> )COCH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CO(O <sup>-</sup> )COCH(ONO <sub>2</sub> )(O·) + 0.550 CO(O <sup>-</sup> )COCO(ONO <sub>2</sub> ) + 0.250 CO(O <sup>-</sup> )COCH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03322			$\text{CO}(\text{O}^-)\text{COCH}(\text{ONO}_2)(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{COCO}(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03323			$\text{CO}(\text{O}^-)\text{COCH}(\text{ONO}_2)(\text{O}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{CO}(\text{OO}\cdot) + \text{CHO}(\text{ONO}_2) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03324			$\text{CH}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CO}(\text{O}^-) + \text{OH} \rightarrow$ $0.471 \text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.062 \text{CH}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CO}(\text{O}^-) +$ $0.466 \text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.534 \text{O}_2$	$8.2 \cdot 10^{+08}$		
R <sub>o</sub> 03325			$\text{CH}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $\text{CH}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 03326			$\text{CH}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CH}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CO}(\text{O}^-) \rightarrow$ $2.000 \text{CH}(\text{OH})_2\text{CO}(\text{ONO}_2) + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03327			$\text{CH}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{RO}_2\cdot}$ $\text{CH}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{CO}(\text{O}^-) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03328			$\text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{CH}(\text{ONO}_2)\text{CO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03329			$\text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03330			$\text{CH}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CO}(\text{O}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03331			$\text{CH}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{CO}(\text{O}^-) \rightarrow 0.500 \text{CH}\cdot(\text{OH})_2 +$ $0.500 \text{CO}(\text{O}^-)\text{CO}(\text{ONO}_2) + 0.500 \text{CH}(\text{OH})_2\text{CO}(\text{ONO}_2) + 0.500 \cdot \text{CO}(\text{O}^-)$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00428			$\text{CO}(\text{O}^-)\text{COCO}(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}} \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2)$	$2.1 \cdot 10^{-01}$		$k_b = 5.69 \cdot 10^{-3} \text{s}^{-1}$ estimated
R <sub>o</sub> 03332			$\text{CO}(\text{O}^-)\text{COCO}(\text{ONO}_2) \xrightarrow{\text{H}_2\text{O}} \text{CO}(\text{OH})\text{COCO}(\text{O}^-) + \text{H}^+ + \text{NO}_3$	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 03333			$\text{CO}(\text{O}^-)\text{COCO}(\text{ONO}_2) + \text{NO}_3 \rightarrow \text{CO}(\text{ONO}_2)\text{COCO}(\text{O}\cdot) + \text{NO}_3^-$	$0.0 \cdot 10^{+00}$		
R <sub>o</sub> 03334			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) \xrightarrow{\text{H}_2\text{O}} \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{H}^+ + \text{NO}_3$	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 03335			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) + \text{OH} \rightarrow$ $0.213 \text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{ONO}_2) + 0.787 \text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{CO}(\text{ONO}_2) +$ $\text{H}_2\text{O} - 0.213 \text{O}_2$	$1.1 \cdot 10^{+08}$		
R <sub>o</sub> 03336			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) + \text{NO}_3 \rightarrow \text{CO}(\text{ONO}_2)\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 03337			$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{ONO}_2) \rightarrow \text{CO}(\text{O}^-)\text{COCO}(\text{ONO}_2) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03338			$\text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{CO}(\text{ONO}_2) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{COCO}(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03339			$\text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{CO}(\text{ONO}_2) \rightarrow 0.500 \cdot \text{CO}(\text{O}^-) + 0.500 \text{CO}(\text{ONO}_2)\text{CHO} +$ $0.500 \text{CO}(\text{O}^-)\text{CHO} + 0.500 \text{CO} + 0.500 \text{NO}_3$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03340			$\text{CO(ONO}_2\text{)CH(OH)CO(O}\cdot\text{)} \rightarrow \text{CO(ONO}_2\text{)CH(OH)(OO}\cdot\text{)} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03341	*	*	$\text{CO(O}^-\text{)CH=CHCO(O}^-\text{)} + \text{OH} \rightarrow \text{CO(O}^-\text{)CH(OH)CH(OO}\cdot\text{)CO(O}^-\text{)} - \text{O}_2$	$6.0 \cdot 10^{+10}$		
R <sub>o</sub> 03342			$\text{CO(O}^-\text{)CH=CHCO(O}^-\text{)} + \text{NO}_3 \rightarrow$ $\text{CO(O}^-\text{)CH(ONO}_2\text{)CH(OO}\cdot\text{)CO(O}^-\text{)} - \text{O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 03343			$\text{CO(O}^-\text{)CH(ONO}_2\text{)CH(OO}\cdot\text{)CO(O}^-\text{)} +$ $\text{CO(O}^-\text{)CH(ONO}_2\text{)CH(OO}\cdot\text{)CO(O}^-\text{)} \rightarrow$ $2.000 \text{ CO(O}^-\text{)CH(ONO}_2\text{)CHO} + 2.000 \text{ CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{ OH}^- - 2.000 \text{ H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03344			$\text{CO(O}^-\text{)CH(ONO}_2\text{)CH(OO}\cdot\text{)CO(O}^-\text{)} \xrightarrow{\text{RO}_2^-}$ $0.200 \text{ CO(O}^-\text{)CH(ONO}_2\text{)CH(O}\cdot\text{)CO(O}^-\text{)} +$ $0.550 \text{ CO(O}^-\text{)COCH(ONO}_2\text{)CO(O}^-\text{)} +$ $0.250 \text{ CO(O}^-\text{)CH(OH)CH(ONO}_2\text{)CO(O}^-\text{)} + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03345			$\text{CO(O}^-\text{)CH(ONO}_2\text{)CH(O}\cdot\text{)CO(O}^-\text{)} \xrightarrow{\text{O}_2}$ $\text{CO(O}^-\text{)COCH(ONO}_2\text{)CO(O}^-\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03346			$\text{CO(O}^-\text{)CH(ONO}_2\text{)CH(O}\cdot\text{)CO(O}^-\text{)} \rightarrow$ $0.500 \text{ CO(O}^-\text{)CH(ONO}_2\text{)(OO}\cdot\text{)} + 0.500 \text{ CO(O}^-\text{)CHO} +$ $0.500 \text{ CO(O}^-\text{)CH(ONO}_2\text{)CHO} + 0.500 \cdot \text{CO(O}^-\text{)} - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00429			$\text{CO(OH)COCH(ONO}_2\text{)CO(O}^-\text{)} \xrightleftharpoons{\text{H}_2\text{O}} \text{CO(OH)C(OH)}_2\text{CH(ONO}_2\text{)CO(O}^-\text{)}$	$9.1 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00430			$\text{CO(OH)COCH(ONO}_2\text{)CO(O}^-\text{)} \rightleftharpoons \text{CO(O}^-\text{)COCH(ONO}_2\text{)CO(O}^-\text{)} + \text{H}^+$	$1.5 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03347			$\text{CO(OH)COCH(ONO}_2\text{)CO(O}^-\text{)} + \text{OH} \rightarrow$ $\text{CO(OH)COC(ONO}_2\text{)(OO}\cdot\text{)CO(O}^-\text{)} + \text{H}_2\text{O} - \text{O}_2$	$3.6 \cdot 10^{+07}$		
R <sub>o</sub> 03348			$\text{CO(OH)COCH(ONO}_2\text{)CO(O}^-\text{)} + \text{NO}_3 \rightarrow$ $\text{CO(OH)COCH(ONO}_2\text{)CO(O}\cdot\text{)} + \text{NO}_3^-$	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 03349			$\text{CO(OH)COC(ONO}_2\text{)(OO}\cdot\text{)CO(O}^-\text{)} +$ $\text{CO(OH)COC(ONO}_2\text{)(OO}\cdot\text{)CO(O}^-\text{)} \rightarrow$ $2.000 \text{ CO(OH)COCO(ONO}_2\text{)} + 2.000 \text{ CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{ OH}^- - 2.000 \text{ H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03350			$\text{CO(OH)COC(ONO}_2\text{)(OO}\cdot\text{)CO(O}^-\text{)} \xrightarrow{\text{RO}_2^-}$ $\text{CO(OH)COC(ONO}_2\text{)(O}\cdot\text{)CO(O}^-\text{)} + 0.500 \text{ O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03351			$\text{CO(OH)COC(ONO}_2\text{)(O}\cdot\text{)CO(O}^-\text{)} \rightarrow$ $0.500 \text{ CO(OH)CO(OO}\cdot\text{)} + 0.500 \text{ CO(O}^-\text{)CO(ONO}_2\text{)} +$ $0.500 \text{ CO(OH)COCO(ONO}_2\text{)} + 0.500 \cdot \text{CO(O}^-\text{)} - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00431			$\text{CO(OH)CH(OH)CH(ONO}_2\text{)CO(O}^-) \rightleftharpoons$ $\text{CO(O}^-)\text{CH(OH)CH(ONO}_2\text{)CO(O}^-) + \text{H}^+$	$9.4 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03352			$\text{CO(OH)CH(OH)CH(ONO}_2\text{)CO(O}^-) + \text{OH} \rightarrow$ $0.232 \text{ CO(OH)C(OH)(OO}\cdot\text{)CH(ONO}_2\text{)CO(O}^-) +$ $0.453 \text{ CO(OH)CH(OH)C(ONO}_2\text{)(OO}\cdot\text{)CO(O}^-) +$ $0.315 \text{ CO(OH)CH(O}\cdot\text{)CH(ONO}_2\text{)CO(O}^-) + \text{H}_2\text{O} - 0.685 \text{ O}_2$	$1.8 \cdot 10^{+08}$		
R <sub>o</sub> 03353			$\text{CO(OH)CH(OH)CH(ONO}_2\text{)CO(O}^-) + \text{NO}_3 \rightarrow$ $\text{CO(OH)CH(OH)CH(ONO}_2\text{)CO(O}\cdot\text{) + NO}_3^-$	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 03354			$\text{CO(OH)C(OH)(OO}\cdot\text{)CH(ONO}_2\text{)CO(O}^-) \rightarrow$ $\text{CO(OH)COCH(ONO}_2\text{)CO(O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03355			$\text{CO(OH)CH(OH)C(ONO}_2\text{)(OO}\cdot\text{)CO(O}^-) +$ $\text{CO(OH)CH(OH)C(ONO}_2\text{)(OO}\cdot\text{)CO(O}^-) \rightarrow$ $2.000 \text{ CO(OH)CH(OH)CO(ONO}_2\text{) + 2.000 CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{ OH}^- -$ $2.000 \text{ H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03356			$\text{CO(OH)CH(OH)C(ONO}_2\text{)(OO}\cdot\text{)CO(O}^-) \xrightarrow{\text{RO}_2}$ $\text{CO(OH)CH(OH)C(ONO}_2\text{)(O}\cdot\text{)CO(O}^-) + 0.500 \text{ O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03357			$\text{CO(OH)CH(OH)CH(ONO}_2\text{)CO(O}\cdot\text{) \rightarrow}$ $\text{CO(OH)CH(OH)CH(ONO}_2\text{)(OO}\cdot\text{) + CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03358			$\text{CO(OH)CH(OH)C(ONO}_2\text{)(O}\cdot\text{)CO(O}^-) \rightarrow$ $0.500 \text{ CO(OH)CH(OH)(OO}\cdot\text{) + 0.500 CO(O}^-)\text{CO(ONO}_2\text{) +}$ $0.500 \text{ CO(OH)CH(OH)CO(ONO}_2\text{) + 0.500}\cdot\text{CO(O}^-) - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00432			$\text{CO(OH)CH(ONO}_2\text{)COCO(O}^-) \xrightleftharpoons{\text{H}_2\text{O}} \text{CO(OH)CH(ONO}_2\text{)C(OH)}_2\text{CO(O}^-)$	$2.4 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00433			$\text{CO(OH)CH(ONO}_2\text{)COCO(O}^-) \rightleftharpoons \text{CO(O}^-)\text{COCH(ONO}_2\text{)CO(O}^-) + \text{H}^+$	$3.9 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03359			$\text{CO(OH)CH(ONO}_2\text{)COCO(O}^-) + \text{OH} \rightarrow$ $0.964 \text{ CO(OH)C(ONO}_2\text{)(OO}\cdot\text{)COCO(O}^-) +$ $0.036 \text{ CO(O}^-)\text{COCH(ONO}_2\text{)CO(O}\cdot\text{) + H}_2\text{O} - 0.964 \text{ O}_2$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03360			$\text{CO(OH)CH(ONO}_2\text{)COCO(O}^-) + \text{NO}_3 \rightarrow$ $\text{CO(OH)CH(ONO}_2\text{)COCO(O}\cdot\text{) + NO}_3^-$	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 03361			$\text{CO(OH)C(ONO}_2\text{)(OO}\cdot\text{)COCO(O}^-) +$ $\text{CO(OH)C(ONO}_2\text{)(OO}\cdot\text{)COCO(O}^-) \rightarrow$ $2.000 \text{ CO(O}^-)\text{COCO(ONO}_2\text{) + 2.000 CO}_2 + -\text{O}_2-$	$1.9 \cdot 10^{+07}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03362			$\text{CO(OH)C(ONO}_2\text{)(OO}\cdot\text{)COCO(O}^-\text{)} \xrightarrow{RO_2}$	$1.0 \cdot 10^{+06}$		
			$\text{CO(OH)C(ONO}_2\text{)(O}\cdot\text{)COCO(O}^-\text{)} + 0.500 \text{ O}_2$			
R <sub>o</sub> 03363			$\text{CO(O}^-\text{)COCH(ONO}_2\text{)CO(O}\cdot\text{)} \rightarrow \text{CO(O}^-\text{)COCH(ONO}_2\text{)(OO}\cdot\text{)} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03364			$\text{CO(OH)C(ONO}_2\text{)(O}\cdot\text{)COCO(O}^-\text{)} \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \cdot \text{CO(OH)} + 0.500 \text{ CO(O}^-\text{)COCO(ONO}_2\text{)} +$			
			$0.500 \text{ CO(OH)CO(ONO}_2\text{)} + 0.500 \text{ CO(O}^-\text{)CO(OO}\cdot\text{)} - 0.500 \text{ O}_2$			
E <sub>o</sub> 00434			$\text{CO(OH)CH(ONO}_2\text{)CH(OH)CO(O}^-\text{)} \rightleftharpoons$	$1.9 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
			$\text{CO(O}^-\text{)CH(OH)CH(ONO}_2\text{)CO(O}^-\text{)} + \text{H}^+$			
R <sub>o</sub> 03365			$\text{CO(OH)CH(ONO}_2\text{)CH(OH)CO(O}^-\text{)} + \text{OH} \rightarrow$	$2.2 \cdot 10^{+08}$		
			$0.187 \text{ CO(OH)C(ONO}_2\text{)(OO}\cdot\text{)CH(OH)CO(O}^-\text{)} +$			
			$0.366 \text{ CO(OH)CH(ONO}_2\text{)C(OH)(OO}\cdot\text{)CO(O}^-\text{)} +$			
			$0.447 \text{ CO(OH)CH(ONO}_2\text{)CH(O}\cdot\text{)CO(O}^-\text{)} + \text{H}_2\text{O} - 0.553 \text{ O}_2$			
R <sub>o</sub> 03366			$\text{CO(OH)CH(ONO}_2\text{)CH(OH)CO(O}^-\text{)} + \text{NO}_3 \rightarrow$	$2.5 \cdot 10^{+07}$		
			$\text{CO(OH)CH(ONO}_2\text{)CH(OH)CO(O}\cdot\text{)} + \text{NO}_3^-$			
R <sub>o</sub> 03367			$\text{CO(OH)C(ONO}_2\text{)(OO}\cdot\text{)CH(OH)CO(O}^-\text{)} +$	$1.9 \cdot 10^{+07}$		
			$\text{CO(OH)C(ONO}_2\text{)(OO}\cdot\text{)CH(OH)CO(O}^-\text{)} \rightarrow$			
			$2.000 \text{ CO(O}^-\text{)CH(OH)CO(ONO}_2\text{)} + 2.000 \text{ CO}_2 + -\text{O}_2-$			
R <sub>o</sub> 03368			$\text{CO(OH)C(ONO}_2\text{)(OO}\cdot\text{)CH(OH)CO(O}^-\text{)} \xrightarrow{RO_2}$	$1.0 \cdot 10^{+06}$		
			$\text{CO(OH)C(ONO}_2\text{)(O}\cdot\text{)CH(OH)CO(O}^-\text{)} + 0.500 \text{ O}_2$			
R <sub>o</sub> 03369			$\text{CO(OH)CH(ONO}_2\text{)C(OH)(OO}\cdot\text{)CO(O}^-\text{)} \rightarrow$	$2.0 \cdot 10^{+02}$		
			$\text{CO(OH)CH(ONO}_2\text{)COCO(O}^-\text{)} + \text{HO}_2$			
R <sub>o</sub> 03370			$\text{CO(OH)CH(ONO}_2\text{)CH(OH)CO(O}\cdot\text{)} \rightarrow$	$5.0 \cdot 10^{+02}$		
			$\text{CO(OH)CH(ONO}_2\text{)CH(OH)(OO}\cdot\text{)} + \text{CO}_2 - \text{O}_2$			
R <sub>o</sub> 03371			$\text{CO(OH)C(ONO}_2\text{)(O}\cdot\text{)CH(OH)CO(O}^-\text{)} \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \cdot \text{CO(OH)} + 0.500 \text{ CO(O}^-\text{)CH(OH)CO(ONO}_2\text{)} +$			
			$0.500 \text{ CO(OH)CO(ONO}_2\text{)} + 0.500 \text{ CO(O}^-\text{)CH(OH)(OO}\cdot\text{)} - 0.500 \text{ O}_2$			
E <sub>o</sub> 00435			$\text{CO(OH)CH(ONO}_2\text{)CO(O}^-\text{)} \rightleftharpoons \text{CO(O}^-\text{)CH(ONO}_2\text{)CO(O}^-\text{)} + \text{H}^+$	$1.3 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03372			$\text{CO(OH)CH(ONO}_2\text{)CO(O}^-\text{)} + \text{OH} \rightarrow$	$1.7 \cdot 10^{+07}$		
			$0.959 \text{ CO(OH)C(ONO}_2\text{)(OO}\cdot\text{)CO(O}^-\text{)} + 0.041 \text{ CO(O}^-\text{)CH(ONO}_2\text{)CO(O}\cdot\text{)} +$			
			$\text{H}_2\text{O} - 0.959 \text{ O}_2$			
R <sub>o</sub> 03373			$\text{CO(OH)CH(ONO}_2\text{)CO(O}^-\text{)} + \text{NO}_3 \rightarrow \text{CO(OH)CH(ONO}_2\text{)CO(O}\cdot\text{)} + \text{NO}_3^-$	$2.5 \cdot 10^{+07}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03374			$\text{CO(OH)C(ONO}_2\text{)(OO}\cdot\text{)CO(O}^-\text{)} + \text{CO(OH)C(ONO}_2\text{)(OO}\cdot\text{)CO(O}^-\text{)} \rightarrow$ $2.000 \text{CO(O}^-\text{)CO(ONO}_2\text{)} + 2.000 \text{CO}_2 + -\text{O}_2 -$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03375			$\text{CO(OH)C(ONO}_2\text{)(OO}\cdot\text{)CO(O}^-\text{)} \xrightarrow{RO_2}$ $\text{CO(OH)C(ONO}_2\text{)(O}\cdot\text{)CO(O}^-\text{)} + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03376			$\text{CO(O}^-\text{)CH(ONO}_2\text{)CO(O}\cdot\text{)} \rightarrow \text{CO(O}^-\text{)CH(ONO}_2\text{)(OO}\cdot\text{)} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03377			$\text{CO(OH)C(ONO}_2\text{)(O}\cdot\text{)CO(O}^-\text{)} \rightarrow 0.500 \cdot \text{CO(OH)} +$ $0.500 \text{CO(O}^-\text{)CO(ONO}_2\text{)} + 0.500 \text{CO(OH)CO(ONO}_2\text{)} + 0.500 \cdot \text{CO(O}^-\text{)}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00436			$\text{CO(OH)C(OH)}_2\text{CO(ONO}_2\text{)} \rightleftharpoons \text{CO(O}^-\text{)C(OH)}_2\text{CO(ONO}_2\text{)} + \text{H}^+$	$2.2 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03378			$\text{CO(OH)C(OH)}_2\text{CO(ONO}_2\text{)} \xrightarrow{H_2O} \text{CO(OH)C(OH)}_2\text{CO(OH)} + \text{H}^+ + \text{NO}_3$	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 03379			$\text{CO(OH)C(OH)}_2\text{CO(ONO}_2\text{)} + \text{OH} \rightarrow \text{CO(OH)C(OH)(O}\cdot\text{)CO(ONO}_2\text{)} + \text{H}_2\text{O}$	$2.1 \cdot 10^{+08}$		
R <sub>o</sub> 03380			$\text{CO(OH)C(OH)}_2\text{CO(ONO}_2\text{)} + \text{NO}_3 \rightarrow$ $\text{CO(OH)C(OH)(O}\cdot\text{)CO(ONO}_2\text{)} + \text{NO}_3^- + \text{H}^+$	$5.9 \cdot 10^{+06}$		
R <sub>o</sub> 03381			$\text{CO(OH)C(OH)(O}\cdot\text{)CO(ONO}_2\text{)} \rightarrow 0.500 \cdot \text{CO(OH)} +$ $0.500 \text{CO(OH)CO(ONO}_2\text{)} + 0.500 \text{CO(OH)CO(OH)} + 0.500 \text{CO} + 0.500 \text{NO}_3$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00437			$\text{CO(OH)COCH(OH)(ONO}_2\text{)} \xrightarrow{H_2O} \text{CO(OH)C(OH)}_2\text{CH(OH)(ONO}_2\text{)}$	$5.6 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{s}^{-1}$ estimated
E <sub>o</sub> 00438			$\text{CO(OH)COCH(OH)(ONO}_2\text{)} \rightleftharpoons \text{CO(O}^-\text{)COCH(OH)(ONO}_2\text{)} + \text{H}^+$	$3.7 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03382			$\text{CO(OH)COCH(OH)(ONO}_2\text{)} + \text{OH} \rightarrow$ $0.822 \text{CO(OH)COC(OH)(ONO}_2\text{)(OO}\cdot\text{)} + 0.178 \text{CO(OH)COCH(ONO}_2\text{)(O}\cdot\text{)} +$ $\text{H}_2\text{O} - 0.822 \text{O}_2$	$3.9 \cdot 10^{+08}$		
R <sub>o</sub> 03383			$\text{CO(OH)COCH(OH)(ONO}_2\text{)} + \text{NO}_3 \rightarrow$ $0.822 \text{CO(OH)COC(OH)(ONO}_2\text{)(OO}\cdot\text{)} + 0.178 \text{CO(OH)COCH(ONO}_2\text{)(O}\cdot\text{)} +$ $\text{NO}_3^- + \text{H}^+ - 0.822 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03384			$\text{CO(OH)COC(OH)(ONO}_2\text{)(OO}\cdot\text{)} \rightarrow \text{CO(OH)COCO(ONO}_2\text{)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
E <sub>o</sub> 00439			$\text{CO(OH)C(OH)}_2\text{CH(OH)(ONO}_2\text{)} \rightleftharpoons \text{CO(O}^-\text{)C(OH)}_2\text{CH(OH)(ONO}_2\text{)} + \text{H}^+$	$3.6 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03385			$\text{CO(OH)C(OH)}_2\text{CH(OH)(ONO}_2\text{)} + \text{OH} \rightarrow$ $0.470 \text{CO(OH)C(OH)}_2\text{C(OH)(ONO}_2\text{)(OO}\cdot\text{)} +$ $0.402 \text{CO(OH)C(OH)(O}\cdot\text{)CH(OH)(ONO}_2\text{)} +$ $0.128 \text{CO(OH)C(OH)}_2\text{CH(ONO}_2\text{)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.470 \text{O}_2$	$6.0 \cdot 10^{+08}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03386			CO(OH)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.470 CO(OH)C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) + 0.402 CO(OH)C(OH)(O·)CH(OH)(ONO <sub>2</sub> ) + 0.128 CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.470 O <sub>2</sub>	7.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 03387			CO(OH)C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) → CO(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03388			CO(OH)C(OH)(O·)CH(OH)(ONO <sub>2</sub> ) → 0.500 · CO(OH) + 0.500 CO(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CO(OH)CO(OH) + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00440			CO(OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) ⇌ CO(O <sup>-</sup> )CH(OH)CH(OH)(ONO <sub>2</sub> ) + H <sup>+</sup>	1.4 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03389			CO(OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) + OH → 0.838 CO(OH)CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.067 CO(OH)CH(O·)CH(OH)(ONO <sub>2</sub> ) + 0.095 CO(OH)CH(OH)CH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O - 0.838 O <sub>2</sub>	8.5 · 10 <sup>+08</sup>		
R <sub>o</sub> 03390			CO(OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.838 CO(OH)CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.067 CO(OH)CH(O·)CH(OH)(ONO <sub>2</sub> ) + 0.095 CO(OH)CH(OH)CH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.838 O <sub>2</sub>	2.2 · 10 <sup>+04</sup>		
R <sub>o</sub> 03391			CO(OH)CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) → CO(OH)CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03392			CO(OH)CH(O·)CH(OH)(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CO(OH)COCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03393			CO(OH)CH(O·)CH(OH)(ONO <sub>2</sub> ) → 0.500 · CO(OH) + 0.500 CH(OH)(ONO <sub>2</sub> )CHO + 0.500 CO(OH)CHO + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00441			CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH) ⇌ CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + H <sup>+</sup>	4.2 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
E <sub>o</sub> 00442			CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH) ⇌ CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + H <sup>+</sup>	4.5 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03394			CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH) + OH → 0.037 CO(OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CO(OH) + 0.963 CO(OH)CH(ONO <sub>2</sub> )C(OH)(O·)CO(OH) + H <sub>2</sub> O - 0.037 O <sub>2</sub>	2.5 · 10 <sup>+08</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03395			CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH) + NO <sub>3</sub> → 0.037 CO(OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CO(OH) + 0.963 CO(OH)CH(ONO <sub>2</sub> )C(OH)(O·)CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.037 O <sub>2</sub>	6.8 · 10 <sup>+06</sup>		
R <sub>o</sub> 03396			CO(OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CO(OH) + CO(OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CO(OH) → 2.000 CO(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03397			CO(OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CO(OH) $\xrightarrow{RO_2}$ CO(OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O·)CO(OH) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03398			CO(OH)CH(ONO <sub>2</sub> )C(OH)(O·)CO(OH) → 0.500 CO(OH)CH(ONO <sub>2</sub> )(OO·) + 0.500 CO(OH)CO(OH) + 0.500 CO(OH)CH(ONO <sub>2</sub> )CO(OH) + 0.500 · CO(OH) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03399			CO(OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O·)CO(OH) → 0.500 CO(OH)C(OH) <sub>2</sub> (OO·) + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CO(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 · CO(OH) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00443			CO(O <sup>-</sup> )COCH(OH)(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> )	1.3 · 10 <sup>+00</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03400			CO(O <sup>-</sup> )COCH(OH)(ONO <sub>2</sub> ) + OH → 0.891 CO(O <sup>-</sup> )COC(OH)(ONO <sub>2</sub> )(OO·) + 0.109 CO(O <sup>-</sup> )COCH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O - 0.891 O <sub>2</sub>	6.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03401			CO(O <sup>-</sup> )COCH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → CH(OH)(ONO <sub>2</sub> )COCO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03402			CO(O <sup>-</sup> )COC(OH)(ONO <sub>2</sub> )(OO·) → CO(O <sup>-</sup> )COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03403			CH(OH)(ONO <sub>2</sub> )COCO(O·) → CH(OH)(ONO <sub>2</sub> )CO(OO·) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03404			CO(O <sup>-</sup> )CH(OH)CH(OH)(ONO <sub>2</sub> ) + OH → 0.035 CO(O <sup>-</sup> )C(OH)(OO·)CH(OH)(ONO <sub>2</sub> ) + 0.844 CO(O <sup>-</sup> )CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.067 CO(O <sup>-</sup> )CH(O·)CH(OH)(ONO <sub>2</sub> ) + 0.055 CO(O <sup>-</sup> )CH(OH)CH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O - 0.878 O <sub>2</sub>	1.5 · 10 <sup>+09</sup>		
R <sub>o</sub> 03405			CO(O <sup>-</sup> )CH(OH)CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → CH(OH)(ONO <sub>2</sub> )CH(OH)CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03406			CO(O <sup>-</sup> )C(OH)(OO·)CH(OH)(ONO <sub>2</sub> ) → CO(O <sup>-</sup> )COCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		



**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03407			CO(O <sup>-</sup> )CH(OH)C(OH)(ONO <sub>2</sub> )(OO $\cdot$ ) $\rightarrow$ CO(O <sup>-</sup> )CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03408			CO(O <sup>-</sup> )CH(O $\cdot$ )CH(OH)(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CO(O <sup>-</sup> )COCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03409			CO(O <sup>-</sup> )CH(O $\cdot$ )CH(OH)(ONO <sub>2</sub> ) $\rightarrow$ 0.500 · CO(O <sup>-</sup> ) + 0.500 CH(OH)(ONO <sub>2</sub> )CHO + 0.500 CO(O <sup>-</sup> )CHO + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03410			CH(OH)(ONO <sub>2</sub> )CH(OH)CO(O $\cdot$ ) $\rightarrow$ CH(OH)(ONO <sub>2</sub> )CH(OH)(OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03411			CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + OH $\rightarrow$ 0.497 CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.426 CO(O <sup>-</sup> )C(OH)(O $\cdot$ )CH(OH)(ONO <sub>2</sub> ) + 0.077 CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O $\cdot$ ) + H <sub>2</sub> O - 0.497 O <sub>2</sub>	$9.9 \cdot 10^{+08}$		
R <sub>o</sub> 03412			CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> $\rightarrow$ CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 03413			CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO $\cdot$ ) $\rightarrow$ CO(O <sup>-</sup> )C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03414			CO(O <sup>-</sup> )C(OH)(O $\cdot$ )CH(OH)(ONO <sub>2</sub> ) $\rightarrow$ 0.500 · CO(O <sup>-</sup> ) + 0.500 CO(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CO(OH)CO(O <sup>-</sup> ) + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03415			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O $\cdot$ ) $\rightarrow$ CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03416			CO(O <sup>-</sup> )C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CO(OH)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + H <sup>+</sup> + NO <sub>3</sub>	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 03417			CO(O <sup>-</sup> )C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + OH $\rightarrow$ CO(O <sup>-</sup> )C(OH)(O $\cdot$ )CO(ONO <sub>2</sub> ) + H <sub>2</sub> O	$3.6 \cdot 10^{+08}$		
R <sub>o</sub> 03418			CO(O <sup>-</sup> )C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + NO <sub>3</sub> $\rightarrow$ CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 03419			CO(O <sup>-</sup> )C(OH)(O $\cdot$ )CO(ONO <sub>2</sub> ) $\rightarrow$ 0.500 · CO(O <sup>-</sup> ) + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CO(OH)CO(O <sup>-</sup> ) + 0.500 CO + 0.500 NO <sub>3</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03420			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O $\cdot$ ) $\rightarrow$ CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03421			CO(O <sup>-</sup> )CH(OH)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + OH $\rightarrow$ 0.371 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH)(OO $\cdot$ )CO(O <sup>-</sup> ) + 0.371 CO(O <sup>-</sup> )CH(OH)C(ONO <sub>2</sub> )(OO $\cdot$ )CO(O <sup>-</sup> ) + 0.258 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH(O $\cdot$ )CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.742 O <sub>2</sub>	$3.8 \cdot 10^{+08}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03422			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $0.500 \text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})\text{CO}(\text{O}^\cdot) +$ $0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CO}(\text{O}^\cdot) + \text{NO}_3^-$	$7.8 \cdot 10^{+07}$		
R <sub>o</sub> 03423			$\text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{C}(\text{OH})(\text{OO}^\cdot)\text{CO}(\text{O}^-) \rightarrow$ $\text{CO}(\text{O}^-)\text{COCH}(\text{ONO}_2)\text{CO}(\text{O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03424			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{ONO}_2)(\text{OO}^\cdot)\text{CO}(\text{O}^-) +$ $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{ONO}_2)(\text{OO}^\cdot)\text{CO}(\text{O}^-) \rightarrow$ $2.000 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- -$ $2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03425			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{ONO}_2)(\text{OO}^\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{RO}_2}$ $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{ONO}_2)(\text{O}^\cdot)\text{CO}(\text{O}^-) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03426			$\text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})\text{CO}(\text{O}^\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}^\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03427			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CO}(\text{O}^\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)(\text{OO}^\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03428			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{ONO}_2)(\text{O}^\cdot)\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})(\text{OO}^\cdot) + 0.500 \text{CO}(\text{O}^-)\text{CO}(\text{ONO}_2) +$ $0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) + 0.500 \cdot \text{CO}(\text{O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00444			$\text{CO}(\text{O}^-)\text{COCH}(\text{ONO}_2)\text{CO}(\text{O}^-) \xrightleftharpoons{\text{H}_2\text{O}} \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CO}(\text{O}^-)$	$2.1 \cdot 10^{-01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03429			$\text{CO}(\text{O}^-)\text{COCH}(\text{ONO}_2)\text{CO}(\text{O}^-) + \text{OH} \rightarrow$ $\text{CO}(\text{O}^-)\text{COC}(\text{ONO}_2)(\text{OO}^\cdot)\text{CO}(\text{O}^-) + \text{H}_2\text{O} - \text{O}_2$	$6.4 \cdot 10^{+07}$		
R <sub>o</sub> 03430			$\text{CO}(\text{O}^-)\text{COCH}(\text{ONO}_2)\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $0.500 \text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{COCO}(\text{O}^\cdot) +$ $0.500 \text{CO}(\text{O}^-)\text{COCH}(\text{ONO}_2)\text{CO}(\text{O}^\cdot) + \text{NO}_3^-$	$7.8 \cdot 10^{+07}$		
R <sub>o</sub> 03431			$\text{CO}(\text{O}^-)\text{COC}(\text{ONO}_2)(\text{OO}^\cdot)\text{CO}(\text{O}^-) +$ $\text{CO}(\text{O}^-)\text{COC}(\text{ONO}_2)(\text{OO}^\cdot)\text{CO}(\text{O}^-) \rightarrow$ $2.000 \text{CO}(\text{O}^-)\text{COCO}(\text{ONO}_2) + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03432			$\text{CO}(\text{O}^-)\text{COC}(\text{ONO}_2)(\text{OO}^\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{RO}_2}$ $\text{CO}(\text{O}^-)\text{COC}(\text{ONO}_2)(\text{O}^\cdot)\text{CO}(\text{O}^-) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03433			$\text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{COCO}(\text{O}^\cdot) \rightarrow \text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{CO}(\text{OO}^\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03434			CO(O <sup>-</sup> )COC(ONO <sub>2</sub> )(O $\cdot$ )CO(O <sup>-</sup> ) $\rightarrow$ 0.500 CO(O <sup>-</sup> )CO(OO $\cdot$ ) + 0.500 CO(O <sup>-</sup> )CO(ONO <sub>2</sub> ) + 0.500 CO(O <sup>-</sup> )COCO(ONO <sub>2</sub> ) + 0.500 $\cdot$ CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03435			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + OH $\rightarrow$ CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO $\cdot$ )CO(O <sup>-</sup> ) + H <sub>2</sub> O - O <sub>2</sub>	$5.7 \cdot 10^{+07}$		
R <sub>o</sub> 03436			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + NO <sub>3</sub> $\rightarrow$ 0.500 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CO(O $\cdot$ ) + 0.500 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + NO <sub>3</sub> <sup>-</sup>	$7.8 \cdot 10^{+07}$		
R <sub>o</sub> 03437			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO $\cdot$ )CO(O <sup>-</sup> ) + CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO $\cdot$ )CO(O <sup>-</sup> ) $\rightarrow$ 2.000 CO(O <sup>-</sup> )CO(ONO <sub>2</sub> ) + 2.000 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2.000 OH <sup>-</sup> - 2.000 H <sub>2</sub> O	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03438			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO $\cdot$ )CO(O <sup>-</sup> ) $\xrightarrow{RO_2^{\cdot}}$ CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(O $\cdot$ )CO(O <sup>-</sup> ) + 0.500 O <sub>2</sub>	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03439			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(O $\cdot$ )CO(O <sup>-</sup> ) $\rightarrow$ $\cdot$ CO(O <sup>-</sup> ) + CO(O <sup>-</sup> )CO(ONO <sub>2</sub> )	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00445			CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O <sup>-</sup> ) $\rightleftharpoons$ CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + H <sup>+</sup>	$2.7 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03440			CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + OH $\rightarrow$ 0.037 CO(OH)C(ONO <sub>2</sub> )(OO $\cdot$ )C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + 0.963 CO(OH)CH(ONO <sub>2</sub> )C(OH)(O $\cdot$ )CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.037 O <sub>2</sub>	$4.4 \cdot 10^{+08}$		
R <sub>o</sub> 03441			CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + NO <sub>3</sub> $\rightarrow$ CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 03442			CO(OH)C(ONO <sub>2</sub> )(OO $\cdot$ )C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + CO(OH)C(ONO <sub>2</sub> )(OO $\cdot$ )C(OH) <sub>2</sub> CO(O <sup>-</sup> ) $\rightarrow$ 2.000 CO(O <sup>-</sup> )C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03443			CO(OH)C(ONO <sub>2</sub> )(OO $\cdot$ )C(OH) <sub>2</sub> CO(O <sup>-</sup> ) $\xrightarrow{RO_2^{\cdot}}$ CO(OH)C(ONO <sub>2</sub> )(O $\cdot$ )C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + 0.500 O <sub>2</sub>	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03444			CO(OH)CH(ONO <sub>2</sub> )C(OH)(O $\cdot$ )CO(O <sup>-</sup> ) $\rightarrow$ 0.500 CO(OH)CH(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.500 CO(OH)CO(O <sup>-</sup> ) + 0.500 CO(OH)CH(ONO <sub>2</sub> )CO(OH) + 0.500 $\cdot$ CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03445			CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O $\cdot$ ) $\rightarrow$ CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03446			CO(OH)C(ONO <sub>2</sub> )(O·)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) → 0.500 · CO(OH) + 0.500 CO(O <sup>-</sup> )C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CO(O <sup>-</sup> )C(OH) <sub>2</sub> (OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00446			CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) ⇌ CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + H <sup>+</sup>	2.2 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03447			CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + OH → 0.118 CO(OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) + 0.882 CO(OH)C(OH)(O·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.118 O <sub>2</sub>	2.7 · 10 <sup>+08</sup>		
R <sub>o</sub> 03448			CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + NO <sub>3</sub> → CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.5 · 10 <sup>+07</sup>		
R <sub>o</sub> 03449			CO(OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) + CO(OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) → 2.000 CO(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 2.000 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2.000 OH <sup>-</sup> - 2.000 H <sub>2</sub> O	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03450			CO(OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) $\xrightarrow{RO_2}$ CO(OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O·)CO(O <sup>-</sup> ) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03451			CO(OH)C(OH)(O·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) → 0.500 · CO(OH) + 0.500 CO(OH)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + 0.500 CO(OH)CO(OH) + 0.500 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03452			CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O·) → CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03453			CO(OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O·)CO(O <sup>-</sup> ) → 0.500 CO(OH)C(OH) <sub>2</sub> (OO·) + 0.500 CO(O <sup>-</sup> )CO(ONO <sub>2</sub> ) + 0.500 CO(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 · CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03454			CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + OH → 0.118 CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) + 0.882 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH)(O·)CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.118 O <sub>2</sub>	4.8 · 10 <sup>+08</sup>		
R <sub>o</sub> 03455			CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + NO <sub>3</sub> → 0.500 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O·) + 0.500 CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O·) + NO <sub>3</sub> <sup>-</sup>	7.8 · 10 <sup>+07</sup>		

**Table G.13 (continued)** Aqueous phase processes in CAPRAM 3.5

C3.5 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A/R^b$	Reference/comment
R <sub>o</sub> 03456			CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO $\cdot$ )CO(O <sup>-</sup> ) + CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO $\cdot$ )CO(O <sup>-</sup> ) $\rightarrow$ 2.000 CO(O <sup>-</sup> )C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 2.000 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2.000 OH <sup>-</sup> - 2.000 H <sub>2</sub> O	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03457			CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO $\cdot$ )CO(O <sup>-</sup> ) $\xrightarrow{RO_3}$ CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O $\cdot$ )CO(O <sup>-</sup> ) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03458			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH)(O $\cdot$ )CO(O <sup>-</sup> ) $\rightarrow$ 0.500 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.500 CO(OH)CO(O <sup>-</sup> ) + 0.500 CO(OH)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + 0.500 $\cdot$ CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03459			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O $\cdot$ ) $\rightarrow$ CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03460			CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O $\cdot$ ) $\rightarrow$ CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03461			CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O $\cdot$ )CO(O <sup>-</sup> ) $\rightarrow$ 0.500 CO(O <sup>-</sup> )C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.500 CO(O <sup>-</sup> )CO(ONO <sub>2</sub> ) + 0.500 CO(O <sup>-</sup> )C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 $\cdot$ CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03462			CHO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ HCO(OH) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>-06</sup>	6600.0	

<sup>a</sup> $k_{298}$  is given for non-reversible reactions (labelled with R<sub>o</sub>XXXX in the first column) in M<sup>1-n</sup> s<sup>-1</sup>,  $K$  is given for equilibria (labelled with E<sub>o</sub>XXXX in the first column) in M<sup>m-n</sup> with n being the order of the forward reaction and m the order of the backward reaction. For more convenience,  $K$  values are printed italic.

<sup>b</sup>in K

**Table G.14** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A/R^b$	Reference/comment
E <sub>o</sub> 00447	*	*	CH <sub>3</sub> C(CO(OH))=CH <sub>2</sub> $\rightleftharpoons$ CH <sub>3</sub> C(CO(O <sup>-</sup> ))=CH <sub>2</sub> + H <sup>+</sup>	7.9 · 10 <sup>-06</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03463	*	*	CH <sub>3</sub> C(CO(OH))=CH <sub>2</sub> + OH $\rightarrow$ 0.083 CH <sub>2</sub> =C(CO(OH))CH <sub>2</sub> (OO $\cdot$ ) + 0.917 CH <sub>3</sub> C(OO $\cdot$ )(CH <sub>2</sub> (OH))CO(OH) + 0.083 H <sub>2</sub> O - O <sub>2</sub>	1.2 · 10 <sup>+10</sup>	-1323.0	TROPOS measurements
R <sub>o</sub> 03464			CH <sub>3</sub> C(CO(OH))=CH <sub>2</sub> + NO <sub>3</sub> $\rightarrow$ 0.083 CH <sub>2</sub> =C(CO(OH))CH <sub>2</sub> (OO $\cdot$ ) + 0.917 CH <sub>3</sub> C(OO $\cdot$ )(CH <sub>2</sub> (ONO <sub>2</sub> ))CO(OH) + 0.083 NO <sub>3</sub> <sup>-</sup> + 0.083 H <sup>+</sup> - O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03465	*	*	$\text{CH}_2=\text{C}(\text{CO}(\text{OH}))\text{CH}_2(\text{OO}\cdot) \xrightarrow{RO_2}$ 0.200 $\text{CH}_2=\text{C}(\text{CO}(\text{OH}))\text{CH}_2(\text{O}\cdot) + 0.550 \text{CO}(\text{OH})\text{C}(\text{CHO})=\text{CH}_2 +$ 0.250 $\text{CH}_2(\text{OH})\text{C}(\text{CO}(\text{OH}))=\text{CH}_2 + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03466	*	*	$\text{CH}_3\text{C}(\text{OO}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{OH}) + \text{CH}_3\text{C}(\text{OO}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{OH}) \rightarrow$ $2.000 \text{CH}_3\text{COCH}_2(\text{OH}) + 2.000 \text{CO}_2 + -\text{O}_2-$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03467	*	*	$\text{CH}_3\text{C}(\text{OO}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{OH}) \xrightarrow{RO_2}$ $\text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{OH}) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03468			$\text{CH}_3\text{C}(\text{OO}\cdot)(\text{CO}(\text{OH}))\text{CH}_2(\text{ONO}_2) + \text{CH}_3\text{C}(\text{OO}\cdot)(\text{CO}(\text{OH}))\text{CH}_2(\text{ONO}_2) \rightarrow$ $2.000 \text{CH}_3\text{COCH}_2(\text{ONO}_2) + 2.000 \text{CO}_2 + -\text{O}_2-$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03469			$\text{CH}_3\text{C}(\text{OO}\cdot)(\text{CO}(\text{OH}))\text{CH}_2(\text{ONO}_2) \xrightarrow{RO_2}$ $\text{CH}_3\text{C}(\text{O}\cdot)(\text{CO}(\text{OH}))\text{CH}_2(\text{ONO}_2) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03470	*	*	$\text{CH}_2=\text{C}(\text{CO}(\text{OH}))\text{CH}_2(\text{O}\cdot) \xrightarrow{O_2} \text{CO}(\text{OH})\text{C}(\text{CHO})=\text{CH}_2 + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03471	*	*	$\text{CH}_2=\text{C}(\text{CO}(\text{OH}))\text{CH}_2(\text{O}\cdot) \rightarrow$	$5.0 \cdot 10^{+02}$		Reaction currently obsolete due to missing fragments in the monomolecular decay
R <sub>o</sub> 03472	*	*	$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{OH}) \rightarrow$ $0.333 \text{CH}_3(\text{OO}\cdot) + 0.333 \text{CH}_2(\text{OH})\text{COCO}(\text{OH}) + 0.333 \text{CH}_3\text{COCO}(\text{OH}) +$ $0.333 \text{CH}_2(\text{OH})\cdot + 0.333 \text{CH}_3\text{COCH}_2(\text{OH}) + 0.333 \cdot\text{CO}(\text{OH}) - 0.333 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03473			$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CO}(\text{OH}))\text{CH}_2(\text{ONO}_2) \rightarrow 0.333 \text{CH}_3(\text{OO}\cdot) +$ $0.333 \text{CO}(\text{OH})\text{COCH}_2(\text{ONO}_2) + 0.333 \text{CH}_3\text{COCH}_2(\text{ONO}_2) +$ $0.333 \cdot\text{CO}(\text{OH}) + 0.333 \text{CH}_3\text{COCO}(\text{OH}) + 0.333 \text{CH}_2\text{O} + 0.333 \text{NO}_2 - 0.333 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00448			$\text{CH}_3\text{COCH}_2(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2)$	$2.1 \cdot 10^{-01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03474			$\text{CH}_3\text{COCH}_2(\text{ONO}_2) + \text{OH} \rightarrow$ $0.194 \text{CH}_2(\text{ONO}_2)\text{COCH}_2(\text{OO}\cdot) + 0.806 \text{CH}_3\text{COCH}(\text{ONO}_2)(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$4.4 \cdot 10^{+08}$		
R <sub>o</sub> 03475			$\text{CH}_3\text{COCH}_2(\text{ONO}_2) + \text{NO}_3 \rightarrow 0.194 \text{CH}_2(\text{ONO}_2)\text{COCH}_2(\text{OO}\cdot) +$ $0.806 \text{CH}_3\text{COCH}(\text{ONO}_2)(\text{OO}\cdot) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$1.3 \cdot 10^{+06}$		
R <sub>o</sub> 03476			$\text{CH}_2(\text{ONO}_2)\text{COCH}_2(\text{OO}\cdot) \xrightarrow{RO_2}$ $0.200 \text{CH}_2(\text{ONO}_2)\text{COCH}_2(\text{O}\cdot) + 0.550 \text{CH}_2(\text{ONO}_2)\text{COCHO} +$ $0.250 \text{CH}_2(\text{OH})\text{COCH}_2(\text{ONO}_2) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03477			$\text{CH}_3\text{COCH}(\text{ONO}_2)(\text{OO}\cdot) \xrightarrow{RO_2}$ 0.200 $\text{CH}_3\text{COCH}(\text{ONO}_2)(\text{O}\cdot) + 0.550 \text{CH}_3\text{COCO}(\text{ONO}_2) +$ 0.250 $\text{CH}_3\text{COCH}(\text{OH})(\text{ONO}_2) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03478			$\text{CH}_2(\text{ONO}_2)\text{COCH}_2(\text{O}\cdot) \xrightarrow{O_2} \text{CH}_2(\text{ONO}_2)\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03479			$\text{CH}_2(\text{ONO}_2)\text{COCH}_2(\text{O}\cdot) \rightarrow \text{CH}_2(\text{ONO}_2)\text{CO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03480			$\text{CH}_3\text{COCH}(\text{ONO}_2)(\text{O}\cdot) \xrightarrow{O_2} \text{CH}_3\text{COCO}(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03481			$\text{CH}_3\text{COCH}(\text{ONO}_2)(\text{O}\cdot) \rightarrow \text{CH}_3\text{CO}(\text{OO}\cdot) + \text{CHO}(\text{ONO}_2) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03482			$\text{CH}_2(\text{ONO}_2)\text{CO}(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}_2(\text{ONO}_2) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 03483	*	*	$\text{CH}_3\text{C}(\text{CO}(\text{O}^-))=\text{CH}_2 + \text{OH} \rightarrow 0.969 \text{CH}_3\text{C}(\text{OO}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) +$ $0.031 \text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) - \text{O}_2$	$1.2 \cdot 10^{+10}$	-1443.0	TROPOS measurements
R <sub>o</sub> 03484			$\text{CH}_3\text{C}(\text{CO}(\text{O}^-))=\text{CH}_2 + \text{NO}_3 \rightarrow 0.969 \text{CH}_3\text{C}(\text{OO}\cdot)(\text{CH}_2(\text{ONO}_2))\text{CO}(\text{O}^-) +$ $0.031 \text{CH}_3\text{C}(\text{O}03481)(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) - \text{O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 03485	*	*	$\text{CH}_3\text{C}(\text{OO}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) + \text{CH}_3\text{C}(\text{OO}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) \rightarrow$ $2.000 \text{CH}_3\text{COCH}_2(\text{OH}) + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03486	*	*	$\text{CH}_3\text{C}(\text{OO}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) \xrightarrow{RO_2}$ $\text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03487	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) \xrightarrow{RO_2}$ $0.200 \text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) + 0.550 \text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CHO} +$ $0.250 \text{CH}_3\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03488			$\text{CH}_3\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) + \text{CH}_3\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) \rightarrow$ $2.000 \text{CH}_3\text{COCH}_2(\text{ONO}_2) + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03489			$\text{CH}_3\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) \xrightarrow{RO_2}$ $\text{CH}_3\text{C}(\text{O}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03490			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) \xrightarrow{RO_2}$ $0.200 \text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) + 0.550 \text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CHO} +$ $0.250 \text{CH}_3\text{C}(\text{ONO}_2)(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03491	*	*	$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) \rightarrow$ $0.333 \text{CH}_3(\text{OO}\cdot) + 0.333 \text{CH}_2(\text{OH})\text{COCO}(\text{O}^-) + 0.333 \text{CH}_3\text{COCO}(\text{O}^-) +$ $0.333 \text{CH}_2(\text{OH})\cdot + 0.333 \text{CH}_3\text{COCH}_2(\text{OH}) + 0.333 \cdot \text{CO}(\text{O}^-) - 0.333 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03492	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \xrightarrow{O_2} \text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03493	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \rightarrow \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03494			$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) \rightarrow 0.333 \text{CH}_3(\text{OO}\cdot) +$ $0.333 \text{CO}(\text{O}^-)\text{COCH}_2(\text{ONO}_2) + 0.333 \text{CH}_3\text{COCH}_2(\text{ONO}_2) + 0.333 \cdot \text{CO}(\text{O}^-) +$ $0.333 \text{CH}_3\text{COCO}(\text{O}^-) + 0.333 \text{CH}_2\text{O} + 0.333 \text{NO}_2 - 0.333 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03495			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03496			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CH}_3\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03497			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CH}_3\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CO}(\text{O}^-) \rightarrow$ $2.000 \text{CH}_3\text{CO}(\text{ONO}_2) + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03498			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{RO}_2} \text{CH}_3\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{CO}(\text{O}^-) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03499			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{CO}(\text{O}^-) \rightarrow 0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CO}(\text{O}^-)\text{CO}(\text{ONO}_2) +$ $0.500 \text{CH}_3\text{CO}(\text{ONO}_2) + 0.500 \cdot \text{CO}(\text{O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00449	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{CO}(\text{OH}))=\text{CH}_2 \rightleftharpoons \text{CH}_2(\text{OH})\text{C}(\text{CO}(\text{O}^-))=\text{CH}_2 + \text{H}^+$	$1.3 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03500	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{CO}(\text{OH}))=\text{CH}_2 + \text{OH} \rightarrow$ $0.062 \text{CH}_2=\text{C}(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.938 \text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{OH}) + 0.062 \text{H}_2\text{O} - \text{O}_2$	$9.5 \cdot 10^{+09}$		
R <sub>o</sub> 03501			$\text{CH}_2(\text{OH})\text{C}(\text{CO}(\text{OH}))=\text{CH}_2 + \text{NO}_3 \rightarrow$ $0.062 \text{CH}_2=\text{C}(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.938 \text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{OH}))\text{CH}_2(\text{ONO}_2) + 0.062 \text{NO}_3^- + 0.062 \text{H}^+ - \text{O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 03502	*	*	$\text{CH}_2=\text{C}(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{C}(\text{CHO})=\text{CH}_2 + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03503	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{OH}) +$ $\text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{OH}) \rightarrow$ $2.000 \text{CH}_2(\text{OH})\text{COCH}_2(\text{OH}) + 2.000 \text{CO}_2 + -\text{O}_2-$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03504	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{OH}) \xrightarrow{\text{RO}_2}$ $\text{CH}_2(\text{OH})\text{C}(\text{O}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{OH}) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03505			$\text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{OH}))\text{CH}_2(\text{ONO}_2) +$ $\text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{OH}))\text{CH}_2(\text{ONO}_2) \rightarrow$ $2.000 \text{CH}_2(\text{OH})\text{COCH}_2(\text{ONO}_2) + 2.000 \text{CO}_2 + -\text{O}_2-$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03506			$\text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{OH}))\text{CH}_2(\text{ONO}_2) \xrightarrow{\text{RO}_2}$ $\text{CH}_2(\text{OH})\text{C}(\text{O}\cdot)(\text{CO}(\text{OH}))\text{CH}_2(\text{ONO}_2) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03507	*	*	CH <sub>2</sub> (OH)C(O·)(CH <sub>2</sub> (OH))CO(OH) → 0.667 CH <sub>2</sub> (OH)· + 0.667 CH <sub>2</sub> (OH)COCO(OH) + 0.333 CH <sub>2</sub> (OH)COCH <sub>2</sub> (OH) + 0.333 ·CO(OH)	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03508			CH <sub>2</sub> (OH)C(O·)(CO(OH))CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.333 CH <sub>2</sub> (OH)· + 0.333 CO(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + 0.333 CH <sub>2</sub> (OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + 0.333 ·CO(OH) + 0.333 CH <sub>2</sub> (OH)COCO(OH) + 0.333 CH <sub>2</sub> O + 0.333 NO <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00450	*	*	CO(OH)C(CHO)=CH <sub>2</sub> $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(CO(OH))=CH <sub>2</sub>	3.6 · 10 <sup>-01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00451	*	*	CO(OH)C(CHO)=CH <sub>2</sub> $\rightleftharpoons$ CO(O <sup>-</sup> )C(CHO)=CH <sub>2</sub> + H <sup>+</sup>	4.0 · 10 <sup>-05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03509	*	*	CO(OH)C(CHO)=CH <sub>2</sub> + OH → 0.050 CH <sub>2</sub> =C(CO(OH))CO(OO·) + 0.950 CH <sub>2</sub> (OH)C(OO·)(CO(OH))CHO + 0.050 H <sub>2</sub> O - O <sub>2</sub>	1.4 · 10 <sup>+10</sup>		
R <sub>o</sub> 03510			CO(OH)C(CHO)=CH <sub>2</sub> + NO <sub>3</sub> → 0.050 CH <sub>2</sub> =C(CO(OH))CO(OO·) + 0.950 CH <sub>2</sub> (ONO <sub>2</sub> )C(OO·)(CO(OH))CHO + 0.050 NO <sub>3</sub> <sup>-</sup> + 0.050 H <sup>+</sup> - O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03511	*	*	CH <sub>2</sub> =C(CO(OH))CO(OO·) → CO(OH)C(CO(OH))=CH <sub>2</sub> + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03512	*	*	CH <sub>2</sub> (OH)C(OO·)(CO(OH))CHO + CH <sub>2</sub> (OH)C(OO·)(CO(OH))CHO → 2.000 CH <sub>2</sub> (OH)COCHO + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03513	*	*	CH <sub>2</sub> (OH)C(OO·)(CO(OH))CHO $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)C(O·)(CO(OH))CHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03514			CO(OH)C(OO·)(CH <sub>2</sub> (ONO <sub>2</sub> ))CHO + CO(OH)C(OO·)(CH <sub>2</sub> (ONO <sub>2</sub> ))CHO → 2.000 CH <sub>2</sub> (ONO <sub>2</sub> )COCHO + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03515			CO(OH)C(OO·)(CH <sub>2</sub> (ONO <sub>2</sub> ))CHO $\xrightarrow{RO_2}$ CO(OH)C(O·)(CH <sub>2</sub> (ONO <sub>2</sub> ))CHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03516	*	*	CH <sub>2</sub> (OH)C(O·)(CO(OH))CHO → 0.333 CH <sub>2</sub> (OH)· + 0.333 CO(OH)COCHO + 0.333 CH <sub>2</sub> (OH)COCHO + 0.333 ·CO(OH) + 0.333 CH <sub>2</sub> (OH)COCO(OH) + 0.333 CH·(OH) <sub>2</sub> - 0.333 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03517			CO(OH)C(O·)(CH <sub>2</sub> (ONO <sub>2</sub> ))CHO → 0.333 ·CO(OH) + 0.333 CH <sub>2</sub> (ONO <sub>2</sub> )COCHO + 0.333 CO(OH)COCHO + 0.333 CH <sub>2</sub> O + 0.333 CO(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + 0.333 CH·(OH) <sub>2</sub> + 0.333 NO <sub>2</sub> - 0.333 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00452			CO(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> )	9.1 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00453			CO(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) $\rightleftharpoons$ CO(O <sup>-</sup> )COCH <sub>2</sub> (ONO <sub>2</sub> ) + H <sup>+</sup>	1.5 · 10 <sup>-01</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03518			CO(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + OH → CO(OH)COCH(ONO <sub>2</sub> )(OO·) + H <sub>2</sub> O - O <sub>2</sub>	2.1 · 10 <sup>+08</sup>		
R <sub>o</sub> 03519			CO(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → CO(OH)COCH(ONO <sub>2</sub> )(OO·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	8.2 · 10 <sup>+05</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03520			CH <sub>3</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + OH → 0.093 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (OO·) + 0.384 CH <sub>3</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.523 CH <sub>3</sub> C(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.477 O <sub>2</sub>	8.0 · 10 <sup>+08</sup>		
R <sub>o</sub> 03521			CH <sub>3</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.093 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (OO·) + 0.384 CH <sub>3</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.523 CH <sub>3</sub> C(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.477 O <sub>2</sub>	8.2 · 10 <sup>+06</sup>		
R <sub>o</sub> 03522			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.550 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + 0.250 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03523			CH <sub>3</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>3</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + 0.550 CH <sub>3</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.250 CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03524			CH <sub>3</sub> C(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CH <sub>3</sub> (OO·) + 0.500 CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CH <sub>3</sub> CO(OH) + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03525			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03526			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O·) → CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03527			CH <sub>3</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CH <sub>3</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03528			CH <sub>3</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) → CH <sub>3</sub> C(OH) <sub>2</sub> (OO·) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03529			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
E <sub>o</sub> 00454			CH <sub>3</sub> COCH(OH)(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> )	1.3 · 10 <sup>+00</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03530			CH <sub>3</sub> COCH(OH)(ONO <sub>2</sub> ) + OH → 0.118 CH(OH)(ONO <sub>2</sub> )COCH <sub>2</sub> (OO·) + 0.781 CH <sub>3</sub> COC(OH)(ONO <sub>2</sub> )(OO·) + 0.101 CH <sub>3</sub> COCH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O - 0.899 O <sub>2</sub>	6.8 · 10 <sup>+08</sup>		
R <sub>o</sub> 03531			CH <sub>3</sub> COCH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.118 CH(OH)(ONO <sub>2</sub> )COCH <sub>2</sub> (OO·) + 0.781 CH <sub>3</sub> COC(OH)(ONO <sub>2</sub> )(OO·) + 0.101 CH <sub>3</sub> COCH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.899 O <sub>2</sub>	1.3 · 10 <sup>+06</sup>		
R <sub>o</sub> 03532			CH(OH)(ONO <sub>2</sub> )COCH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH(OH)(ONO <sub>2</sub> )COCH <sub>2</sub> (O·) + 0.550 CH(OH)(ONO <sub>2</sub> )COCHO + 0.250 CH <sub>2</sub> (OH)COCH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03533			$\text{CH}_3\text{COC}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) \rightarrow \text{CH}_3\text{COCO}(\text{ONO}_2) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03534			$\text{CH}(\text{OH})(\text{ONO}_2)\text{COCH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}(\text{OH})(\text{ONO}_2)\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03535			$\text{CH}(\text{OH})(\text{ONO}_2)\text{COCH}_2(\text{O}\cdot) \rightarrow \text{CH}(\text{OH})(\text{ONO}_2)\text{CO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00455			$\text{CH}_3\text{COCO}(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2)$	$2.1 \cdot 10^{-01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03536			$\text{CH}_3\text{COCO}(\text{ONO}_2) \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{COCO}(\text{OH}) + \text{H}^+ + \text{NO}_3$	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 03537			$\text{CH}_3\text{COCO}(\text{ONO}_2) + \text{OH} \rightarrow \text{CO}(\text{ONO}_2)\text{COCH}_2(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$6.9 \cdot 10^{+07}$		
R <sub>o</sub> 03538			$\text{CH}_3\text{COCO}(\text{ONO}_2) + \text{NO}_3 \rightarrow \text{CO}(\text{ONO}_2)\text{COCH}_2(\text{OO}\cdot) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$1.2 \cdot 10^{+06}$		
R <sub>o</sub> 03539			$\text{CO}(\text{ONO}_2)\text{COCH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CO}(\text{ONO}_2)\text{COCH}_2(\text{O}\cdot) + 0.550 \text{ CO}(\text{ONO}_2)\text{COCHO} +$ $0.250 \text{ CH}_2(\text{OH})\text{COCO}(\text{ONO}_2) + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03540			$\text{CO}(\text{ONO}_2)\text{COCH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{ONO}_2)\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03541			$\text{CO}(\text{ONO}_2)\text{COCH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{ONO}_2)\text{CO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00456			$\text{CH}_2(\text{OH})\text{COCH}_2(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2)$	$1.3 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03542			$\text{CH}_2(\text{OH})\text{COCH}_2(\text{ONO}_2) + \text{OH} \rightarrow$ $0.449 \text{ CH}_2(\text{ONO}_2)\text{COCH}(\text{OH})(\text{OO}\cdot) + 0.449 \text{ CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)(\text{OO}\cdot) +$ $0.102 \text{ CH}_2(\text{ONO}_2)\text{COCH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.898 \text{ O}_2$	$7.4 \cdot 10^{+08}$		
R <sub>o</sub> 03543			$\text{CH}_2(\text{OH})\text{COCH}_2(\text{ONO}_2) + \text{NO}_3 \rightarrow$ $0.449 \text{ CH}_2(\text{ONO}_2)\text{COCH}(\text{OH})(\text{OO}\cdot) + 0.449 \text{ CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)(\text{OO}\cdot) +$ $0.102 \text{ CH}_2(\text{ONO}_2)\text{COCH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.898 \text{ O}_2$	$1.3 \cdot 10^{+06}$		
R <sub>o</sub> 03544			$\text{CH}_2(\text{ONO}_2)\text{COCH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{ONO}_2)\text{COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03545			$\text{CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)(\text{O}\cdot) + 0.550 \text{ CH}_2(\text{OH})\text{COCO}(\text{ONO}_2) +$ $0.250 \text{ CH}_2(\text{OH})\text{COCH}(\text{OH})(\text{ONO}_2) + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03546			$\text{CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCO}(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03547			$\text{CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CO}(\text{OO}\cdot) + \text{CHO}(\text{ONO}_2) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00457			$\text{CH}_2(\text{ONO}_2)\text{COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{COCH}_2(\text{ONO}_2)$	$3.2 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00458			$\text{CH}_2(\text{ONO}_2)\text{COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2)$	$4.0 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03548			$\text{CH}_2(\text{ONO}_2)\text{COCHO} + \text{OH} \rightarrow$ $0.375 \text{ CHOCOCH}(\text{ONO}_2)(\text{OO}\cdot) + 0.625 \text{ CH}_2(\text{ONO}_2)\text{COCO}(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$7.2 \cdot 10^{+08}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03549			$\text{CH}_2(\text{ONO}_2)\text{COCHO} + \text{NO}_3 \rightarrow 0.375 \text{CHOCOCH}(\text{ONO}_2)(\text{OO}\cdot) +$ $0.625 \text{CH}_2(\text{ONO}_2)\text{COCO}(\text{OO}\cdot) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$3.6 \cdot 10^{+06}$		
R <sub>o</sub> 03550			$\text{CH}_2(\text{ONO}_2)\text{COCO}(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{COCH}_2(\text{ONO}_2) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 03551	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{CHO})=\text{CH}_2 + \text{OH} \rightarrow 0.969 \text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CHO} +$ $0.031 \text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{CHO})\text{CH}_2(\text{OO}\cdot) - \text{O}_2$	$6.1 \cdot 10^{+10}$		
R <sub>o</sub> 03552			$\text{CO}(\text{O}^-)\text{C}(\text{CHO})=\text{CH}_2 + \text{NO}_3 \rightarrow 0.969 \text{CO}(\text{O}^-)\text{C}(\text{OO}\cdot)(\text{CH}_2(\text{ONO}_2))\text{CHO} +$ $0.031 \text{CO}(\text{O}^-)\text{C}(\text{ONO}_2)(\text{CHO})\text{CH}_2(\text{OO}\cdot) - \text{O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 03553	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CHO} + \text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CHO} \rightarrow$ $2.000 \text{CH}_2(\text{OH})\text{COCHO} + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03554	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CHO} \xrightarrow{\text{RO}_2}$ $\text{CH}_2(\text{OH})\text{C}(\text{O}\cdot)(\text{CO}(\text{O}^-))\text{CHO} + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03555	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{CHO})\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{CHO})\text{CH}_2(\text{O}\cdot) + 0.550 \text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{CHO})\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03556			$\text{CO}(\text{O}^-)\text{C}(\text{OO}\cdot)(\text{CH}_2(\text{ONO}_2))\text{CHO} + \text{CO}(\text{O}^-)\text{C}(\text{OO}\cdot)(\text{CH}_2(\text{ONO}_2))\text{CHO} \rightarrow$ $2.000 \text{CH}_2(\text{ONO}_2)\text{COCHO} + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03557			$\text{CO}(\text{O}^-)\text{C}(\text{OO}\cdot)(\text{CH}_2(\text{ONO}_2))\text{CHO} \xrightarrow{\text{RO}_2}$ $\text{CO}(\text{O}^-)\text{C}(\text{O}\cdot)(\text{CH}_2(\text{ONO}_2))\text{CHO} + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03558			$\text{CO}(\text{O}^-)\text{C}(\text{ONO}_2)(\text{CHO})\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CO}(\text{O}^-)\text{C}(\text{ONO}_2)(\text{CHO})\text{CH}_2(\text{O}\cdot) +$ $0.550 \text{CO}(\text{O}^-)\text{C}(\text{ONO}_2)(\text{CHO})\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03559	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{O}\cdot)(\text{CO}(\text{O}^-))\text{CHO} \rightarrow$ $0.333 \text{CH}_2(\text{OH})\cdot + 0.333 \text{CO}(\text{O}^-)\text{COCHO} + 0.333 \text{CH}_2(\text{OH})\text{COCHO} +$ $0.333 \cdot \text{CO}(\text{O}^-) + 0.333 \text{CH}_2(\text{OH})\text{COCO}(\text{O}^-) + 0.333 \text{CH}\cdot(\text{OH})_2 - 0.333 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03560	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{CHO})\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{CHO})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03561	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{CHO})\text{CH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{OO}\cdot)\text{CHO} + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03562			$\text{CO}(\text{O}^-)\text{C}(\text{O}\cdot)(\text{CH}_2(\text{ONO}_2))\text{CHO} \rightarrow 0.333 \cdot \text{CO}(\text{O}^-) +$ $0.333 \text{CH}_2(\text{ONO}_2)\text{COCHO} + 0.333 \text{CO}(\text{O}^-)\text{COCHO} + 0.333 \text{CH}_2\text{O} +$ $0.333 \text{CO}(\text{O}^-)\text{COCH}_2(\text{ONO}_2) + 0.333 \text{CH}\cdot(\text{OH})_2 + 0.333 \text{NO}_2 - 0.333 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03563			$\text{CO}(\text{O}^-)\text{C}(\text{ONO}_2)(\text{CHO})\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{C}(\text{ONO}_2)(\text{CHO})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03564			$\text{CO}(\text{O}^-)\text{C}(\text{ONO}_2)(\text{CHO})\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CHO} + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03565	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{CO}(\text{O}^-))=\text{CH}_2 + \text{OH} \rightarrow$ $0.969 \text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) +$ $0.031 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) - \text{O}_2$	$3.9 \cdot 10^{+10}$		
R <sub>o</sub> 03566			$\text{CH}_2(\text{OH})\text{C}(\text{CO}(\text{O}^-))=\text{CH}_2 + \text{NO}_3 \rightarrow$ $0.969 \text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) +$ $0.031 \text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) - \text{O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 03567	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) +$ $\text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) \rightarrow$ $2.000 \text{CH}_2(\text{OH})\text{COCH}_2(\text{OH}) + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03568	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) \xrightarrow{\text{RO}_2^\ddagger}$ $\text{CH}_2(\text{OH})\text{C}(\text{O}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03569	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2^\ddagger}$ $0.200 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) +$ $0.550 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03570			$\text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) +$ $\text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) \rightarrow$ $2.000 \text{CH}_2(\text{OH})\text{COCH}_2(\text{ONO}_2) + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03571			$\text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) \xrightarrow{\text{RO}_2^\ddagger}$ $\text{CH}_2(\text{OH})\text{C}(\text{O}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03572			$\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2^\ddagger}$ $0.200 \text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) +$ $0.550 \text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03573	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{O}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) \rightarrow 0.667 \text{CH}_2(\text{OH})\cdot +$ $0.667 \text{CH}_2(\text{OH})\text{COCO}(\text{O}^-) + 0.333 \text{CH}_2(\text{OH})\text{COCH}_2(\text{OH}) + 0.333 \cdot \text{CO}(\text{O}^-)$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03574	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03575	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03576			$\text{CH}_2(\text{OH})\text{C}(\text{O}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) \rightarrow 0.333 \text{CH}_2(\text{OH})\cdot +$ $0.333 \text{CO}(\text{O}^-)\text{COCH}_2(\text{ONO}_2) + 0.333 \text{CH}_2(\text{OH})\text{COCH}_2(\text{ONO}_2) +$ $0.333 \cdot \text{CO}(\text{O}^-) + 0.333 \text{CH}_2(\text{OH})\text{COCO}(\text{O}^-) + 0.333 \text{CH}_2\text{O} + 0.333 \text{NO}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03577			$\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03578			$\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03579			$\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CO}(\text{O}^-) \rightarrow$ $2.000 \text{CH}_2(\text{OH})\text{CO}(\text{ONO}_2) + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03580			$\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{RO}_2}$ $\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{CO}(\text{O}^-) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03581			$\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{CO}(\text{O}^-) \rightarrow 0.500 \text{CH}_2(\text{OH})\cdot +$ $0.500 \text{CO}(\text{O}^-)\text{CO}(\text{ONO}_2) + 0.500 \text{CH}_2(\text{OH})\text{CO}(\text{ONO}_2) + 0.500 \cdot \text{CO}(\text{O}^-)$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00459	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CO}(\text{OH}) \rightleftharpoons \text{CH}_3\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) + \text{H}^+$	$4.0 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03582	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) + \text{OH} \rightarrow$ $0.165 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) +$ $0.683 \text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.086 \text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) + 0.066 \text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) +$ $\text{H}_2\text{O} - 0.848 \text{O}_2$	$1.3 \cdot 10^{+09}$		
R <sub>o</sub> 03583	*		$\text{CH}_3\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $\text{CH}_3\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 03584	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03585	*		$\text{CH}_3\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2(\text{OH}) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00460			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{CH}_2(\text{OH}))\text{CO}(\text{OH}) \rightleftharpoons$ $\text{CH}_3\text{C}(\text{ONO}_2)(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) + \text{H}^+$	$1.7 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03586			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) + \text{OH} \rightarrow$ $0.180 \text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) +$ $0.748 \text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.072 \text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.928 \text{O}_2$	$1.2 \cdot 10^{+09}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R_o03587			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $\text{CH}_3\text{C}(\text{ONO}_2)(\text{CH}_2(\text{OH}))\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R_o03588			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow$ $\text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R_o03589			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{CH}_2(\text{OH}))\text{CO}(\text{O}\cdot) \rightarrow$ $\text{CH}_3\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CH}_2(\text{OH}) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R_o03590			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CH}_2(\text{OH}) \xrightarrow{\text{RO}_2} \text{CH}_3\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{CH}_2(\text{OH}) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R_o03591			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{CH}_2(\text{OH}) \rightarrow$ $0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CH}_2(\text{OH})\text{CO}(\text{ONO}_2) + 0.500 \text{CH}_3\text{CO}(\text{ONO}_2) +$ $0.500 \text{CH}_2(\text{OH})\cdot - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E_o00461			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C}(\text{ONO}_2)(\text{CH}(\text{OH})_2)\text{CO}(\text{O}^-)$	$6.7 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{s}^{-1}$ estimated
E_o00462			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CHO} \rightleftharpoons \text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CHO} + \text{H}^+$	$5.2 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R_o03592			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CHO} + \text{OH} \rightarrow$ $0.126 \text{CO}(\text{O}^-)\text{C}(\text{ONO}_2)(\text{CHO})\text{CH}_2(\text{OO}\cdot) +$ $0.874 \text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CO}(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$1.3 \cdot 10^{+09}$		
R_o03593			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CHO} + \text{NO}_3 \rightarrow$ $\text{CH}_3\text{C}(\text{ONO}_2)(\text{CHO})\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R_o03594			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CO}(\text{OO}\cdot) \rightarrow$ $\text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R_o03595			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{CHO})\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_3\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CHO} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R_o03596			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CHO} \xrightarrow{\text{RO}_2} \text{CH}_3\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{CHO} + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R_o03597			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{CHO} \rightarrow 0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CO}(\text{ONO}_2)\text{CHO} +$ $0.500 \text{CH}_3\text{CO}(\text{ONO}_2) + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{O}_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
E_o00463			$\text{CO}(\text{O}^-)\text{COCH}_2(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}} \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2)$	$2.1 \cdot 10^{-01}$		$k_b = 5.69 \cdot 10^{-3} \text{s}^{-1}$ estimated
R_o03598			$\text{CO}(\text{O}^-)\text{COCH}_2(\text{ONO}_2) + \text{OH} \rightarrow \text{CO}(\text{O}^-)\text{COCH}(\text{ONO}_2)(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$3.7 \cdot 10^{+08}$		
R_o03599			$\text{CO}(\text{O}^-)\text{COCH}_2(\text{ONO}_2) + \text{NO}_3 \rightarrow \text{CH}_2(\text{ONO}_2)\text{COCO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R_o03600			$\text{CH}_2(\text{ONO}_2)\text{COCO}(\text{O}\cdot) \rightarrow \text{CH}_2(\text{ONO}_2)\text{CO}(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E_o00464	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{CO}(\text{O}^-)$	$7.4 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{s}^{-1}$ estimated
E_o00465	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CHO} \rightleftharpoons \text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CHO} + \text{H}^+$	$1.3 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03601	*	*	CH <sub>3</sub> C(OH)(CO(O <sup>-</sup> ))CHO + OH → 0.119 CO(O <sup>-</sup> )C(OH)(CHO)CH <sub>2</sub> (OO·) + 0.819 CH <sub>3</sub> C(OH)(CO(O <sup>-</sup> ))CO(OO·) + 0.062 CH <sub>3</sub> C(O·)(CO(O <sup>-</sup> ))CHO + H <sub>2</sub> O - 0.938 O <sub>2</sub>	1.4 · 10 <sup>+09</sup>		
R <sub>o</sub> 03602	*		CH <sub>3</sub> C(OH)(CO(O <sup>-</sup> ))CHO + NO <sub>3</sub> → CH <sub>3</sub> C(OH)(CHO)CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03603	*	*	CH <sub>3</sub> C(OH)(CO(O <sup>-</sup> ))CO(OO·) → CH <sub>3</sub> C(OH)(CO(OH))CO(O <sup>-</sup> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03604	*	*	CH <sub>3</sub> C(O·)(CO(O <sup>-</sup> ))CHO → 0.333 CH <sub>3</sub> (OO·) + 0.333 CO(O <sup>-</sup> )COCHO + 0.333 CH <sub>3</sub> COCHO + 0.333 ·CO(O <sup>-</sup> ) + 0.333 CH <sub>3</sub> COCO(O <sup>-</sup> ) + 0.333 CH · (OH) <sub>2</sub> - 0.333 O <sub>2</sub> - 0.333 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03605	*		CH <sub>3</sub> C(OH)(CHO)CO(O·) → CH <sub>3</sub> C(OH)(OO·)CHO + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00466	*	*	CH(OH) <sub>2</sub> C(CO(OH))=CH <sub>2</sub> ⇌ CH(OH) <sub>2</sub> C(CO(O <sup>-</sup> ))=CH <sub>2</sub> + H <sup>+</sup>	2.0 · 10 <sup>-05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03606	*	*	CH(OH) <sub>2</sub> C(CO(OH))=CH <sub>2</sub> + OH → 0.969 CH <sub>2</sub> (OH)C(OO·)(CH(OH) <sub>2</sub> )CO(OH) + 0.031 CH(OH) <sub>2</sub> C(OH)(CO(OH))CH <sub>2</sub> (OO·) - O <sub>2</sub>	2.4 · 10 <sup>+10</sup>		
R <sub>o</sub> 03607			CH(OH) <sub>2</sub> C(CO(OH))=CH <sub>2</sub> + NO <sub>3</sub> → 0.969 CH(OH) <sub>2</sub> C(OO·)(CO(OH))CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.031 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (OO·) - O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03608	*	*	CH <sub>2</sub> (OH)C(OO·)(CH(OH) <sub>2</sub> )CO(OH) + CH <sub>2</sub> (OH)C(OO·)(CH(OH) <sub>2</sub> )CO(OH) → 2.000 CH <sub>2</sub> (OH)COCH(OH) <sub>2</sub> + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03609	*	*	CH <sub>2</sub> (OH)C(OO·)(CH(OH) <sub>2</sub> )CO(OH) $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)C(O·)(CH(OH) <sub>2</sub> )CO(OH) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03610	*	*	CH(OH) <sub>2</sub> C(OH)(CO(OH))CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> C(OH)(CO(OH))CH <sub>2</sub> (O·) + 0.550 CH(OH) <sub>2</sub> C(OH)(CO(OH))CHO + 0.250 CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03611			CH(OH) <sub>2</sub> C(OO·)(CO(OH))CH <sub>2</sub> (ONO <sub>2</sub> ) + CH(OH) <sub>2</sub> C(OO·)(CO(OH))CH <sub>2</sub> (ONO <sub>2</sub> ) → 2.000 CH(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	1.9 · 10 <sup>+07</sup>		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03612			$\text{CH(OH)}_2\text{C(OO}\cdot\text{)}(\text{CO(OH)})\text{CH}_2(\text{ONO}_2) \xrightarrow{RO_2}$ $\text{CH(OH)}_2\text{C(O}\cdot\text{)}(\text{CO(OH)})\text{CH}_2(\text{ONO}_2) + 0.500 \text{ O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03613			$\text{CH(OH)}_2\text{C(ONO}_2\text{)}(\text{CO(OH)})\text{CH}_2(\text{OO}\cdot\text{)} \xrightarrow{RO_2}$ $0.200 \text{ CH(OH)}_2\text{C(ONO}_2\text{)}(\text{CO(OH)})\text{CH}_2(\text{O}\cdot\text{)} +$ $0.550 \text{ CH(OH)}_2\text{C(ONO}_2\text{)}(\text{CO(OH)})\text{CHO} +$ $0.250 \text{ CH}_2(\text{OH})\text{C(ONO}_2\text{)}(\text{CH(OH)}_2)\text{CO(OH)} + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03614	*	*	$\text{CH}_2(\text{OH})\text{C(O}\cdot\text{)}(\text{CH(OH)}_2)\text{CO(OH)} \rightarrow$ $0.333 \text{ CH}_2(\text{OH})\cdot + 0.333 \text{ CH(OH)}_2\text{COCO(OH)} + 0.333 \text{ CH}_2(\text{OH})\text{COCO(OH)} +$ $0.333 \text{ CH}\cdot(\text{OH})_2 + 0.333 \text{ CH}_2(\text{OH})\text{COCH(OH)}_2 + 0.333 \cdot\text{CO(OH)}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03615	*	*	$\text{CH(OH)}_2\text{C(OH)}(\text{CO(OH)})\text{CH}_2(\text{O}\cdot\text{)} \xrightarrow{O_2}$ $\text{CH(OH)}_2\text{C(OH)}(\text{CO(OH)})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03616	*	*	$\text{CH(OH)}_2\text{C(OH)}(\text{CO(OH)})\text{CH}_2(\text{O}\cdot\text{)} \rightarrow$ $\text{CH(OH)}_2\text{C(OH)}(\text{OO}\cdot\text{)}\text{CO(OH)} + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03617			$\text{CH(OH)}_2\text{C(O}\cdot\text{)}(\text{CO(OH)})\text{CH}_2(\text{ONO}_2) \rightarrow 0.333 \text{ CH}\cdot(\text{OH})_2 +$ $0.333 \text{ CO(OH)COCH}_2(\text{ONO}_2) + 0.333 \text{ CH(OH)}_2\text{COCH}_2(\text{ONO}_2) +$ $0.333 \cdot\text{CO(OH)} + 0.333 \text{ CH(OH)}_2\text{COCO(OH)} + 0.333 \text{ CH}_2\text{O} + 0.333 \text{ NO}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03618			$\text{CH(OH)}_2\text{C(ONO}_2\text{)}(\text{CO(OH)})\text{CH}_2(\text{O}\cdot\text{)} \xrightarrow{O_2}$ $\text{CH(OH)}_2\text{C(ONO}_2\text{)}(\text{CO(OH)})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03619			$\text{CH(OH)}_2\text{C(ONO}_2\text{)}(\text{CO(OH)})\text{CH}_2(\text{O}\cdot\text{)} \rightarrow$ $\text{CH(OH)}_2\text{C(ONO}_2\text{)}(\text{OO}\cdot\text{)}\text{CO(OH)} + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03620	*	*	$\text{CH(OH)}_2\text{C(OH)}(\text{OO}\cdot\text{)}\text{CO(OH)} \rightarrow \text{CH(OH)}_2\text{COCO(OH)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03621			$\text{CH(OH)}_2\text{C(ONO}_2\text{)}(\text{OO}\cdot\text{)}\text{CO(OH)} + \text{CH(OH)}_2\text{C(ONO}_2\text{)}(\text{OO}\cdot\text{)}\text{CO(OH)} \rightarrow$ $2.000 \text{ CH(OH)}_2\text{CO(ONO}_2\text{)} + 2.000 \text{ CO}_2 + -\text{O}_2 -$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03622			$\text{CH(OH)}_2\text{C(ONO}_2\text{)}(\text{OO}\cdot\text{)}\text{CO(OH)} \xrightarrow{RO_2}$ $\text{CH(OH)}_2\text{C(ONO}_2\text{)}(\text{O}\cdot\text{)}\text{CO(OH)} + 0.500 \text{ O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03623			$\text{CH(OH)}_2\text{C(ONO}_2\text{)}(\text{O}\cdot\text{)}\text{CO(OH)} \rightarrow 0.500 \text{ CH}\cdot(\text{OH})_2 +$ $0.500 \text{ CO(OH)CO(ONO}_2\text{)} + 0.500 \text{ CH(OH)}_2\text{CO(ONO}_2\text{)} + 0.500 \cdot\text{CO(OH)}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00467			$\text{CO(OH)C(OH)}_2\text{CH}_2(\text{ONO}_2) \rightleftharpoons \text{CO(O}^-\text{)}\text{C(OH)}_2\text{CH}_2(\text{ONO}_2) + \text{H}^+$	$2.2 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03624			$\text{CO(OH)C(OH)}_2\text{CH}_2(\text{ONO}_2) + \text{OH} \rightarrow$ $0.423 \text{ CO(OH)C(OH)}_2\text{CH(ONO}_2\text{)}(\text{OO}\cdot\text{)} +$ $0.577 \text{ CO(OH)C(OH)}(\text{O}\cdot\text{)}\text{CH}_2(\text{ONO}_2) + \text{H}_2\text{O} - 0.423 \text{ O}_2$	$4.4 \cdot 10^{+08}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03625			CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.423 CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.577 CO(OH)C(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.423 O <sub>2</sub>	6.8 · 10 <sup>+06</sup>		
R <sub>o</sub> 03626			CO(OH)C(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 · CO(OH) + 0.500 CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CO(OH)CO(OH) + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00468			CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) ⇌ CO(O <sup>-</sup> )CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sup>+</sup>	1.5 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03627			CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + OH → CO(OH)CH(ONO <sub>2</sub> )(OO·) + H <sub>2</sub> O - O <sub>2</sub>	9.6 · 10 <sup>+07</sup>		
R <sub>o</sub> 03628			CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → CO(OH)CH(ONO <sub>2</sub> )(OO·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	7.1 · 10 <sup>+05</sup>		
E <sub>o</sub> 00469	*	*	CO(OH)C(CO(OH))=CH <sub>2</sub> ⇌ CO(OH)C(CO(O <sup>-</sup> ))=CH <sub>2</sub> + H <sup>+</sup>	1.8 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03629	*	*	CO(OH)C(CO(OH))=CH <sub>2</sub> + OH → 0.969 CH <sub>2</sub> (OH)C(OO·)(CO(OH))CO(OH) + 0.031 CO(OH)C(OH)(CO(OH))CH <sub>2</sub> (OO·) - O <sub>2</sub>	5.5 · 10 <sup>+09</sup>		
R <sub>o</sub> 03630			CO(OH)C(CO(OH))=CH <sub>2</sub> + NO <sub>3</sub> → 0.969 CO(OH)C(OO·)(CO(OH))CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.031 CO(OH)C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (OO·) - O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03631	*	*	CH <sub>2</sub> (OH)C(OO·)(CO(OH))CO(OH) + CH <sub>2</sub> (OH)C(OO·)(CO(OH))CO(OH) → 2.000 CH <sub>2</sub> (OH)COCO(OH) + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03632	*	*	CH <sub>2</sub> (OH)C(OO·)(CO(OH))CO(OH) $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)C(O·)(CO(OH))CO(OH) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03633	*	*	CO(OH)C(OH)(CO(OH))CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CO(OH)C(OH)(CO(OH))CH <sub>2</sub> (O·) + 0.550 CO(OH)C(OH)(CO(OH))CHO + 0.250 CH <sub>2</sub> (OH)C(OH)(CO(OH))CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03634			CO(OH)C(OO·)(CO(OH))CH <sub>2</sub> (ONO <sub>2</sub> ) + CO(OH)C(OO·)(CO(OH))CH <sub>2</sub> (ONO <sub>2</sub> ) → 2.000 CO(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03635			CO(OH)C(OO·)(CO(OH))CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{RO_2}$ CO(OH)C(O·)(CO(OH))CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03636			CO(OH)C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CO(OH)C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (O·) + 0.550 CO(OH)C(ONO <sub>2</sub> )(CO(OH))CHO + 0.250 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03637	*	*	CH <sub>2</sub> (OH)C(O·)(CO(OH))CO(OH) → 0.333 CH <sub>2</sub> (OH)· + 0.333 CO(OH)COCO(OH) + 0.667 CH <sub>2</sub> (OH)COCO(OH) + 0.667 ·CO(OH)	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03638	*	*	CO(OH)C(OH)(CO(OH))CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(OH)C(OH)(CO(OH))CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03639	*	*	CO(OH)C(OH)(CO(OH))CH <sub>2</sub> (O·) → CO(OH)C(OH)(OO·)CO(OH) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03640			CO(OH)C(O·)(CO(OH))CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.667 ·CO(OH) + 0.667 CO(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + 0.333 CO(OH)COCO(OH) + 0.333 CH <sub>2</sub> O + 0.333 NO <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03641			CO(OH)C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(OH)C(ONO <sub>2</sub> )(CO(OH))CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03642			CO(OH)C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (O·) → CO(OH)C(ONO <sub>2</sub> )(OO·)CO(OH) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03643			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + OH → 0.118 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.240 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.314 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(O·) + 0.327 CH(OH) <sub>2</sub> C(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.359 O <sub>2</sub>	1.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 03644			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.118 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.240 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.314 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(O·) + 0.327 CH(OH) <sub>2</sub> C(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.359 O <sub>2</sub>	8.1 · 10 <sup>+06</sup>		
R <sub>o</sub> 03645			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03646			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03647			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(O·) → CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03648			CH(OH) <sub>2</sub> C(OH)(O $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) $\rightarrow$ 0.500 CH $\cdot$ (OH) <sub>2</sub> + 0.500 CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03649			CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + OH $\rightarrow$ 0.070 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (OO $\cdot$ ) + 0.461 CH <sub>3</sub> C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.394 CH <sub>3</sub> C(OH)(O $\cdot$ )CH(OH)(ONO <sub>2</sub> ) + 0.075 CH <sub>3</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O $\cdot$ ) + H <sub>2</sub> O – 0.531 O <sub>2</sub>	1.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 03650			CH <sub>3</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> $\rightarrow$ 0.070 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (OO $\cdot$ ) + 0.461 CH <sub>3</sub> C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.394 CH <sub>3</sub> C(OH)(O $\cdot$ )CH(OH)(ONO <sub>2</sub> ) + 0.075 CH <sub>3</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O $\cdot$ ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.531 O <sub>2</sub>	9.1 · 10 <sup>+06</sup>		
R <sub>o</sub> 03651			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (OO $\cdot$ ) $\xrightarrow{RO_2}$ 0.200 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) + 0.550 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + 0.250 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03652			CH <sub>3</sub> C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO $\cdot$ ) $\rightarrow$ CH <sub>3</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03653			CH <sub>3</sub> C(OH)(O $\cdot$ )CH(OH)(ONO <sub>2</sub> ) $\rightarrow$ 0.500 CH <sub>3</sub> (OO $\cdot$ ) + 0.500 CO(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CH <sub>3</sub> CO(OH) + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03654			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) $\xrightarrow{O_2}$ CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03655			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) $\rightarrow$ CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO $\cdot$ ) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03656			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + OH $\rightarrow$ 0.274 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO $\cdot$ ) + 0.274 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.079 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) + 0.373 CH <sub>2</sub> (OH)C(OH)(O $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.548 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03657			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.274 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO·) + 0.274 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.079 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.373 CH <sub>2</sub> (OH)C(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.548 O <sub>2</sub>	8.9 · 10 <sup>+06</sup>		
R <sub>o</sub> 03658			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO·) → CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03659			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + 0.550 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.250 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03660			CH <sub>2</sub> (OH)C(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03661			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03662			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO·) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03663			CH(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) + OH → 0.195 CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + 0.395 CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(OO·) + 0.410 CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)(O·) + H <sub>2</sub> O - 0.590 O <sub>2</sub>	8.0 · 10 <sup>+08</sup>		
R <sub>o</sub> 03664			CH(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.195 CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + 0.395 CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(OO·) + 0.410 CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.590 O <sub>2</sub>	8.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03665			CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) → CO(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03666			CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03667			CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)(O·) → CH <sub>2</sub> (ONO <sub>2</sub> )CO(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00470			CH <sub>2</sub> (OH)COCO(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> )	1.3 · 10 <sup>+00</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03668			CH <sub>2</sub> (OH)COCO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CH <sub>2</sub> (OH)COCO(OH) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>-06</sup>	6600.0	
R <sub>o</sub> 03669			CH <sub>2</sub> (OH)COCO(ONO <sub>2</sub> ) + OH → 0.782 CO(ONO <sub>2</sub> )COCH(OH)(OO·) + 0.218 CO(ONO <sub>2</sub> )COCH <sub>2</sub> (O·) + H <sub>2</sub> O - 0.782 O <sub>2</sub>	3.5 · 10 <sup>+08</sup>		
R <sub>o</sub> 03670			CH <sub>2</sub> (OH)COCO(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.782 CO(ONO <sub>2</sub> )COCH(OH)(OO·) + 0.218 CO(ONO <sub>2</sub> )COCH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.782 O <sub>2</sub>	1.1 · 10 <sup>+06</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03671			$\text{CO(ONO}_2\text{)COCH(OH)(OO}\cdot\text{)} \rightarrow \text{CO(ONO}_2\text{)COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
E <sub>o</sub> 00471			$\text{CH}_2(\text{OH})\text{COCH(OH)(ONO}_2\text{)} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{C(OH)}_2\text{CH(OH)(ONO}_2\text{)}$	$7.9 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03672			$\text{CH}_2(\text{OH})\text{COCH(OH)(ONO}_2\text{)} + \text{OH} \rightarrow$ $0.328 \text{ CH(OH)(ONO}_2\text{)COCH(OH)(OO}\cdot\text{)} +$ $0.522 \text{ CH}_2(\text{OH})\text{COC(OH)(ONO}_2\text{)(OO}\cdot\text{)} +$ $0.078 \text{ CH(OH)(ONO}_2\text{)COCH}_2(\text{O}\cdot\text{)} + 0.072 \text{ CH}_2(\text{OH})\text{COCH(ONO}_2\text{)(O}\cdot\text{)} +$ $\text{H}_2\text{O} - 0.850 \text{ O}_2$	$9.6 \cdot 10^{+08}$		
R <sub>o</sub> 03673			$\text{CH}_2(\text{OH})\text{COCH(OH)(ONO}_2\text{)} + \text{NO}_3 \rightarrow$ $0.328 \text{ CH(OH)(ONO}_2\text{)COCH(OH)(OO}\cdot\text{)} +$ $0.522 \text{ CH}_2(\text{OH})\text{COC(OH)(ONO}_2\text{)(OO}\cdot\text{)} +$ $0.078 \text{ CH(OH)(ONO}_2\text{)COCH}_2(\text{O}\cdot\text{)} + 0.072 \text{ CH}_2(\text{OH})\text{COCH(ONO}_2\text{)(O}\cdot\text{)} +$ $\text{NO}_3^- + \text{H}^+ - 0.850 \text{ O}_2$	$1.3 \cdot 10^{+06}$		
R <sub>o</sub> 03674			$\text{CH(OH)(ONO}_2\text{)COCH(OH)(OO}\cdot\text{)} \rightarrow \text{CH(OH)(ONO}_2\text{)COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03675			$\text{CH}_2(\text{OH})\text{COC(OH)(ONO}_2\text{)(OO}\cdot\text{)} \rightarrow \text{CH}_2(\text{OH})\text{COCO(ONO}_2\text{)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03676			$\text{CH}_3\text{C(OH)}_2\text{CO(ONO}_2\text{)} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{C(OH)}_2\text{CO(OH)} + \text{H}^+ + \text{NO}_3$	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 03677			$\text{CH}_3\text{C(OH)}_2\text{CO(ONO}_2\text{)} + \text{OH} \rightarrow 0.150 \text{ CO(ONO}_2\text{)C(OH)}_2\text{CH}_2(\text{OO}\cdot\text{)} +$ $0.850 \text{ CH}_3\text{C(OH)(O}\cdot\text{)CO(ONO}_2\text{)} + \text{H}_2\text{O} - 0.150 \text{ O}_2$	$4.1 \cdot 10^{+08}$		
R <sub>o</sub> 03678			$\text{CH}_3\text{C(OH)}_2\text{CO(ONO}_2\text{)} + \text{NO}_3 \rightarrow 0.150 \text{ CO(ONO}_2\text{)C(OH)}_2\text{CH}_2(\text{OO}\cdot\text{)} +$ $0.850 \text{ CH}_3\text{C(OH)(O}\cdot\text{)CO(ONO}_2\text{)} + \text{NO}_3^- + \text{H}^+ - 0.150 \text{ O}_2$	$7.8 \cdot 10^{+06}$		
R <sub>o</sub> 03679			$\text{CO(ONO}_2\text{)C(OH)}_2\text{CH}_2(\text{OO}\cdot\text{)} \xrightarrow{\text{RO}_2}$ $0.200 \text{ CO(ONO}_2\text{)C(OH)}_2\text{CH}_2(\text{O}\cdot\text{)} + 0.550 \text{ CO(ONO}_2\text{)C(OH)}_2\text{CHO} +$ $0.250 \text{ CH}_2(\text{OH})\text{C(OH)}_2\text{CO(ONO}_2\text{)} + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03680			$\text{CH}_3\text{C(OH)(O}\cdot\text{)CO(ONO}_2\text{)} \rightarrow 0.500 \text{ CH}_3(\text{OO}\cdot\text{)} + 0.500 \text{ CO(OH)CO(ONO}_2\text{)} +$ $0.500 \text{ CH}_3\text{CO(OH)} + 0.500 \text{ CO} + 0.500 \text{ NO}_3 - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03681			$\text{CO(ONO}_2\text{)C(OH)}_2\text{CH}_2(\text{O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CO(ONO}_2\text{)C(OH)}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03682			$\text{CO(ONO}_2\text{)C(OH)}_2\text{CH}_2(\text{O}\cdot\text{)} \rightarrow \text{CO(ONO}_2\text{)C(OH)}_2(\text{OO}\cdot\text{)} + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03683			$\text{CH}_2(\text{OH})\text{CO(ONO}_2\text{)} \xrightarrow{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{CO(OH)} + \text{H}^+ + \text{NO}_3$	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 03684			$\text{CH}_2(\text{OH})\text{CO(ONO}_2\text{)} + \text{OH} \rightarrow$ $0.637 \text{ CO(ONO}_2\text{)CH(OH)(OO}\cdot\text{)} + 0.363 \text{ CO(ONO}_2\text{)CH}_2(\text{O}\cdot\text{)} + \text{H}_2\text{O} - 0.637 \text{ O}_2$	$2.1 \cdot 10^{+08}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03685			$\text{CH}_2(\text{OH})\text{CO}(\text{ONO}_2) + \text{NO}_3 \rightarrow 0.637 \text{CO}(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}\cdot) + 0.363 \text{CO}(\text{ONO}_2)\text{CH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.637 \text{O}_2$	$1.1 \cdot 10^{+06}$		
R <sub>o</sub> 03686			$\text{CO}(\text{ONO}_2)\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{ONO}_2)\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03687			$\text{CO}(\text{ONO}_2)\text{CH}_2(\text{O}\cdot) \rightarrow \text{CO} + \text{CH}_2\text{O} + \text{NO}_3$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00472			$\text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{COCH}_2(\text{ONO}_2)$	$3.2 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00473			$\text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2)$	$4.0 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03688			$\text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CHO} + \text{OH} \rightarrow 0.248 \text{CHOC}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{OO}\cdot) + 0.414 \text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) + 0.338 \text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})(\text{O}\cdot)\text{CHO} + \text{H}_2\text{O} - 0.662 \text{O}_2$	$9.6 \cdot 10^{+08}$		
R <sub>o</sub> 03689			$\text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CHO} + \text{NO}_3 \rightarrow 0.248 \text{CHOC}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{OO}\cdot) + 0.414 \text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) + 0.338 \text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})(\text{O}\cdot)\text{CHO} + \text{NO}_3^- + \text{H}^+ - 0.662 \text{O}_2$	$6.7 \cdot 10^{+06}$		
R <sub>o</sub> 03690			$\text{CHOC}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{OO}\cdot) \xrightarrow{\text{RO}_2} 0.200 \text{CHOC}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{O}\cdot) + 0.550 \text{CO}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CHO} + 0.250 \text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2\text{CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03691			$\text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 03692			$\text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})(\text{O}\cdot)\text{CHO} \rightarrow 0.500 \text{CH}_2\text{O} + 0.500 \text{CO}(\text{OH})\text{CHO} + 0.500 \text{CO}(\text{OH})\text{CH}_2(\text{ONO}_2) + 0.500 \text{CH} \cdot (\text{OH})_2 + 0.500 \text{NO}_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03693			$\text{CHOC}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03694			$\text{CHOC}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{O}\cdot) \rightarrow \text{CHOC}(\text{OH})_2(\text{OO}\cdot) + \text{CHO}(\text{ONO}_2) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03695	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{CO}(\text{O}^-))=\text{CH}_2 + \text{OH} \rightarrow 0.969 \text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CH}(\text{OH})_2)\text{CO}(\text{O}^-) + 0.031 \text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) - \text{O}_2$	$1.0 \cdot 10^{+11}$		
R <sub>o</sub> 03696			$\text{CH}(\text{OH})_2\text{C}(\text{CO}(\text{O}^-))=\text{CH}_2 + \text{NO}_3 \rightarrow 0.969 \text{CH}(\text{OH})_2\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) + 0.031 \text{CH}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) - \text{O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 03697	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CH}(\text{OH})_2)\text{CO}(\text{O}^-) + \text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CH}(\text{OH})_2)\text{CO}(\text{O}^-) \rightarrow 2.000 \text{CH}_2(\text{OH})\text{COCH}(\text{OH})_2 + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03698	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CH}(\text{OH})_2)\text{CO}(\text{O}^-) \xrightarrow{\text{RO}_2^{\cdot}}$ $\text{CH}_2(\text{OH})\text{C}(\text{O}\cdot)(\text{CH}(\text{OH})_2)\text{CO}(\text{O}^-) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03699	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2^{\cdot}}$ $0.200 \text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) +$ $0.550 \text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03700			$\text{CH}(\text{OH})_2\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) +$ $\text{CH}(\text{OH})_2\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) \rightarrow$ $2.000 \text{CH}(\text{OH})_2\text{COCH}_2(\text{ONO}_2) + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03701			$\text{CH}(\text{OH})_2\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) \xrightarrow{\text{RO}_2^{\cdot}}$ $\text{CH}(\text{OH})_2\text{C}(\text{O}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03702			$\text{CH}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2^{\cdot}}$ $0.200 \text{CH}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) +$ $0.550 \text{CH}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CH}(\text{OH})_2)\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03703	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{O}\cdot)(\text{CH}(\text{OH})_2)\text{CO}(\text{O}^-) \rightarrow$ $0.333 \text{CH}_2(\text{OH})\cdot + 0.333 \text{CH}(\text{OH})_2\text{COCO}(\text{O}^-) + 0.333 \text{CH}_2(\text{OH})\text{COCO}(\text{O}^-) +$ $0.333 \text{CH}\cdot(\text{OH})_2 + 0.333 \text{CH}_2(\text{OH})\text{COCH}(\text{OH})_2 + 0.333 \cdot\text{CO}(\text{O}^-)$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03704	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03705	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03706			$\text{CH}(\text{OH})_2\text{C}(\text{O}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) \rightarrow 0.333 \text{CH}\cdot(\text{OH})_2 +$ $0.333 \text{CO}(\text{O}^-)\text{COCH}_2(\text{ONO}_2) + 0.333 \text{CH}(\text{OH})_2\text{COCH}_2(\text{ONO}_2) +$ $0.333 \cdot\text{CO}(\text{O}^-) + 0.333 \text{CH}(\text{OH})_2\text{COCO}(\text{O}^-) + 0.333 \text{CH}_2\text{O} + 0.333 \text{NO}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03707			$\text{CH}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CH}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03708			$\text{CH}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CH}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00474	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{CO}(\text{OH}) \rightleftharpoons \text{CH}_3\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{CO}(\text{O}^-) + \text{H}^+$	$6.4 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03709	*	*	CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CO(O <sup>-</sup> ) + OH → 0.185 CH(OH) <sub>2</sub> C(OH)(CO(O <sup>-</sup> ))CH <sub>2</sub> (OO·) + 0.379 CH <sub>3</sub> C(OH)(CO(O <sup>-</sup> ))C(OH) <sub>2</sub> (OO·) + 0.097 CH <sub>3</sub> C(O·)(CH(OH) <sub>2</sub> )CO(O <sup>-</sup> ) + 0.339 CH <sub>3</sub> C(OH)(CO(O <sup>-</sup> ))CH(OH)(O·) + H <sub>2</sub> O - 0.564 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 03710	*		CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03711	*	*	CH <sub>3</sub> C(OH)(CO(O <sup>-</sup> ))C(OH) <sub>2</sub> (OO·) → CH <sub>3</sub> C(OH)(CO(OH))CO(O <sup>-</sup> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03712	*	*	CH <sub>3</sub> C(O·)(CH(OH) <sub>2</sub> )CO(O <sup>-</sup> ) → 0.333 CH <sub>3</sub> (OO·) + 0.333 CH(OH) <sub>2</sub> COCO(O <sup>-</sup> ) + 0.333 CH <sub>3</sub> COCO(O <sup>-</sup> ) + 0.333 CH·(OH) <sub>2</sub> + 0.333 CH <sub>3</sub> COCH(OH) <sub>2</sub> + 0.333 ·CO(O <sup>-</sup> ) - 0.333 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03713	*	*	CH <sub>3</sub> C(OH)(CO(O <sup>-</sup> ))CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>3</sub> C(OH)(CO(OH))CO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03714	*	*	CH <sub>3</sub> C(OH)(CO(O <sup>-</sup> ))CH(OH)(O·) → CH <sub>3</sub> C(OH)(OO·)CO(O <sup>-</sup> ) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03715	*		CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CO(O·) → CH <sub>3</sub> C(OH)(OO·)CH(OH) <sub>2</sub> + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00475	*	*	CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CO(OH) ⇌ CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CO(O <sup>-</sup> ) + H <sup>+</sup>	6.4 · 10 <sup>-05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03716	*	*	CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CO(O <sup>-</sup> ) + OH → 0.858 CH <sub>2</sub> (OH)C(OH)(CO(O <sup>-</sup> ))CH(OH)(OO·) + 0.088 CH <sub>2</sub> (OH)C(OH)(CO(O <sup>-</sup> ))CH <sub>2</sub> (O·) + 0.054 CH <sub>2</sub> (OH)C(O·)(CH <sub>2</sub> (OH))CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.858 O <sub>2</sub>	1.9 · 10 <sup>+09</sup>		
R <sub>o</sub> 03717	*		CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03718	*	*	CH <sub>2</sub> (OH)C(OH)(CO(O <sup>-</sup> ))CH(OH)(OO·) → CH <sub>2</sub> (OH)C(OH)(CO(O <sup>-</sup> ))CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03719	*		CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CO(O·) → CH <sub>2</sub> (OH)C(OH)(OO·)CH <sub>2</sub> (OH) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00476			CH <sub>3</sub> C(ONO <sub>2</sub> )(CH(OH) <sub>2</sub> )CO(OH) ⇌ CH <sub>3</sub> C(ONO <sub>2</sub> )(CH(OH) <sub>2</sub> )CO(O <sup>-</sup> ) + H <sup>+</sup>	2.6 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03720			CH <sub>3</sub> C(ONO <sub>2</sub> )(CH(OH) <sub>2</sub> )CO(O <sup>-</sup> ) + OH → 0.205 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CH <sub>2</sub> (OO·) + 0.420 CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))C(OH) <sub>2</sub> (OO·) + 0.375 CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CH(OH)(O·) + H <sub>2</sub> O - 0.625 O <sub>2</sub>	9.7 · 10 <sup>+08</sup>		
R <sub>o</sub> 03721			CH <sub>3</sub> C(ONO <sub>2</sub> )(CH(OH) <sub>2</sub> )CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>3</sub> C(ONO <sub>2</sub> )(CH(OH) <sub>2</sub> )CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03722			CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))C(OH) <sub>2</sub> (OO·) → CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CO(O <sup>-</sup> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03723			CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03724			CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CH(OH)(O·) → CH <sub>3</sub> C(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03725			CH <sub>3</sub> C(ONO <sub>2</sub> )(CH(OH) <sub>2</sub> )CO(O·) → CH <sub>3</sub> C(ONO <sub>2</sub> )(OO·)CH(OH) <sub>2</sub> + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03726			CH <sub>3</sub> C(ONO <sub>2</sub> )(OO·)CH(OH) <sub>2</sub> $\xrightarrow{RO_2}$ CH <sub>3</sub> C(ONO <sub>2</sub> )(O·)CH(OH) <sub>2</sub> + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03727			CH <sub>3</sub> C(ONO <sub>2</sub> )(O·)CH(OH) <sub>2</sub> → 0.500 CH <sub>3</sub> (OO·) + 0.500 CH(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 CH <sub>3</sub> CO(ONO <sub>2</sub> ) + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00477			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CH <sub>2</sub> (OH))CO(OH) ⇌ CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CH <sub>2</sub> (OH))CO(O <sup>-</sup> ) + H <sup>+</sup>	2.6 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03728			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CH <sub>2</sub> (OH))CO(O <sup>-</sup> ) + OH → 0.907 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CH(OH)(OO·) + 0.093 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CH <sub>2</sub> (O·) + H <sub>2</sub> O - 0.907 O <sub>2</sub>	1.8 · 10 <sup>+09</sup>		
R <sub>o</sub> 03729			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CH <sub>2</sub> (OH))CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CH <sub>2</sub> (OH))CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03730			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CH(OH)(OO·) → CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03731			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CH <sub>2</sub> (OH))CO(O·) → CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)CH <sub>2</sub> (OH) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03732			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)CH <sub>2</sub> (OH) $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(O·)CH <sub>2</sub> (OH) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03733			$\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{CH}_2(\text{OH}) \rightarrow \text{CH}_2(\text{OH})\cdot + \text{CH}_2(\text{OH})\text{CO}(\text{ONO}_2)$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00478			$\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}}$ $\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CH}(\text{OH})_2)\text{CO}(\text{O}^-)$	$1.4 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00479			$\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CHO} \rightleftharpoons$ $\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CHO} + \text{H}^+$	$8.2 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03734			$\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CHO} + \text{OH} \rightarrow$ $0.358 \text{ CO}(\text{O}^-)\text{C}(\text{ONO}_2)(\text{CHO})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.597 \text{ CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CO}(\text{OO}\cdot) +$ $0.045 \text{ CO}(\text{O}^-)\text{C}(\text{ONO}_2)(\text{CHO})\text{CH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.955 \text{ O}_2$	$1.9 \cdot 10^{+09}$		
R <sub>o</sub> 03735			$\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CHO} + \text{NO}_3 \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CHO})\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 03736			$\text{CO}(\text{O}^-)\text{C}(\text{ONO}_2)(\text{CHO})\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{C}(\text{ONO}_2)(\text{CHO})\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03737			$\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CO}(\text{OO}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 03738			$\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CHO})\text{CO}(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CHO} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03739			$\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CHO} \xrightarrow{\text{RO}_2} \text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{CHO} + 0.500 \text{ O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03740			$\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{CHO} \rightarrow 0.500 \text{ CH}_2(\text{OH})\cdot + 0.500 \text{ CO}(\text{ONO}_2)\text{CHO} +$ $0.500 \text{ CH}_2(\text{OH})\text{CO}(\text{ONO}_2) + 0.500 \text{ CH}\cdot(\text{OH})_2 - 0.500 \text{ H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00480			$\text{CO}(\text{O}^-)\text{C}(\text{ONO}_2)(\text{CHO})\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{CH}(\text{OH})_2)\text{CO}(\text{O}^-)$	$5.7 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00481			$\text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CHO})\text{CHO} \rightleftharpoons \text{CO}(\text{O}^-)\text{C}(\text{ONO}_2)(\text{CHO})\text{CHO} + \text{H}^+$	$2.6 \cdot 10^{-03}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03741			$\text{CO}(\text{O}^-)\text{C}(\text{ONO}_2)(\text{CHO})\text{CHO} + \text{OH} \rightarrow$ $\text{CO}(\text{O}^-)\text{C}(\text{ONO}_2)(\text{CHO})\text{CO}(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$1.8 \cdot 10^{+09}$		
R <sub>o</sub> 03742			$\text{CO}(\text{O}^-)\text{C}(\text{ONO}_2)(\text{CHO})\text{CHO} + \text{NO}_3 \rightarrow$ $\text{CHOC}(\text{ONO}_2)(\text{CHO})\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 03743			$\text{CO}(\text{O}^-)\text{C}(\text{ONO}_2)(\text{CHO})\text{CO}(\text{OO}\cdot) \rightarrow$ $\text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CHO} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 03744			$\text{CHOC}(\text{ONO}_2)(\text{CHO})\text{CO}(\text{O}\cdot) \rightarrow \text{CHOC}(\text{ONO}_2)(\text{OO}\cdot)\text{CHO} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03745			$\text{CHOC}(\text{ONO}_2)(\text{OO}\cdot)\text{CHO} \xrightarrow{\text{RO}_2} \text{CHOC}(\text{ONO}_2)(\text{O}\cdot)\text{CHO} + 0.500 \text{ O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03746			$\text{CHOC}(\text{ONO}_2)(\text{O}\cdot)\text{CHO} \rightarrow \text{CH}\cdot(\text{OH})_2 + \text{CO}(\text{ONO}_2)\text{CHO} - \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03747			CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + OH → 0.423 CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.577 CO(O <sup>-</sup> )C(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.423 O <sub>2</sub>	7.7 · 10 <sup>+08</sup>		
R <sub>o</sub> 03748			CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03749			CO(O <sup>-</sup> )C(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 · CO(O <sup>-</sup> ) + 0.500 CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CO(OH)CO(O <sup>-</sup> ) + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03750			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O·) → CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03751			CO(O <sup>-</sup> )CH <sub>2</sub> (ONO <sub>2</sub> ) + OH → CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )(OO·) + H <sub>2</sub> O - O <sub>2</sub>	3.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03752			CO(O <sup>-</sup> )CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → CH <sub>2</sub> (ONO <sub>2</sub> )CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03753			CH <sub>2</sub> (ONO <sub>2</sub> )CO(O·) → CH <sub>2</sub> O + CO <sub>2</sub> + NO <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00482	*	*	CH <sub>2</sub> (OH)C(OH)(CO(O <sup>-</sup> ))CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CO(O <sup>-</sup> )	1.5 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00483	*	*	CH <sub>2</sub> (OH)C(OH)(CO(OH))CHO $\rightleftharpoons$ CH <sub>2</sub> (OH)C(OH)(CO(O <sup>-</sup> ))CHO + H <sup>+</sup>	2.0 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03754	*	*	CH <sub>2</sub> (OH)C(OH)(CO(O <sup>-</sup> ))CHO + OH → 0.343 CO(O <sup>-</sup> )C(OH)(CHO)CH(OH)(OO·) + 0.571 CH <sub>2</sub> (OH)C(OH)(CO(O <sup>-</sup> ))CO(OO·) + 0.043 CO(O <sup>-</sup> )C(OH)(CHO)CH <sub>2</sub> (O·) + 0.043 CH <sub>2</sub> (OH)C(O·)(CO(O <sup>-</sup> ))CHO + H <sub>2</sub> O - 0.914 O <sub>2</sub>	1.9 · 10 <sup>+09</sup>		
R <sub>o</sub> 03755	*		CH <sub>2</sub> (OH)C(OH)(CO(O <sup>-</sup> ))CHO + NO <sub>3</sub> → CH <sub>2</sub> (OH)C(OH)(CHO)CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03756	*	*	CO(O <sup>-</sup> )C(OH)(CHO)CH(OH)(OO·) → CO(O <sup>-</sup> )C(OH)(CHO)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03757	*	*	CH <sub>2</sub> (OH)C(OH)(CO(O <sup>-</sup> ))CO(OO·) → CH <sub>2</sub> (OH)C(OH)(CO(OH))CO(O <sup>-</sup> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03758	*		CH <sub>2</sub> (OH)C(OH)(CHO)CO(O·) → CH <sub>2</sub> (OH)C(OH)(OO·)CHO + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00484	*	*	CO(O <sup>-</sup> )C(OH)(CHO)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CO(O <sup>-</sup> )	6.3 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00485	*	*	CO(OH)C(OH)(CHO)CHO $\rightleftharpoons$ CO(O <sup>-</sup> )C(OH)(CHO)CHO + H <sup>+</sup>	6.2 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03759	*	*	CO(O <sup>-</sup> )C(OH)(CHO)CHO + OH → 0.963 CO(O <sup>-</sup> )C(OH)(CHO)CO(OO·) + 0.037 CO(O <sup>-</sup> )C(O·)(CHO)CHO + H <sub>2</sub> O - 0.963 O <sub>2</sub>	1.9 · 10 <sup>+09</sup>		
R <sub>o</sub> 03760	*		CO(O <sup>-</sup> )C(OH)(CHO)CHO + NO <sub>3</sub> → CHOC(OH)(CHO)CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03761	*	*	CO(O <sup>-</sup> )C(OH)(CHO)CO(OO·) → CO(OH)C(OH)(CO(O <sup>-</sup> ))CHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03762	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{O}\cdot)(\text{CHO})\text{CHO} \rightarrow 0.333 \cdot \text{CO}(\text{O}^-) + 0.333 \text{CHOCOCHO} +$ $0.667 \text{CO}(\text{O}^-)\text{COCHO} + 0.667 \text{CH} \cdot (\text{OH})_2 - 0.667 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03763	*		$\text{CHOC}(\text{OH})(\text{CHO})\text{CO}(\text{O}\cdot) \rightarrow \text{CHOC}(\text{OH})(\text{OO}\cdot)\text{CHO} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03764	*	*	$\text{CHOC}(\text{OH})(\text{OO}\cdot)\text{CHO} \rightarrow \text{CHOCOCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
E <sub>o</sub> 00486	*	*	$\text{CO}(\text{OH})\text{C}(\text{CO}(\text{O}^-))=\text{CH}_2 \rightleftharpoons \text{CO}(\text{O}^-)\text{C}(\text{CO}(\text{O}^-))=\text{CH}_2 + \text{H}^+$	$7.9 \cdot 10^{-06}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03765	*	*	$\text{CO}(\text{OH})\text{C}(\text{CO}(\text{O}^-))=\text{CH}_2 + \text{OH} \rightarrow$ $0.969 \text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) +$ $0.031 \text{CO}(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) - \text{O}_2$	$2.4 \cdot 10^{+10}$		
R <sub>o</sub> 03766			$\text{CO}(\text{OH})\text{C}(\text{CO}(\text{O}^-))=\text{CH}_2 + \text{NO}_3 \rightarrow$ $0.969 \text{CO}(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) +$ $0.031 \text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) - \text{O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 03767	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) +$ $\text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) \rightarrow$ $2.000 \text{CH}_2(\text{OH})\text{COCO}(\text{O}^-) + 2.000 \text{CO}_2 + -\text{O}_2-$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03768	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) \xrightarrow{\text{RO}_2}$ $\text{CH}_2(\text{OH})\text{C}(\text{O}\cdot)(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03769	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CO}(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) +$ $0.550 \text{CO}(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03770			$\text{CO}(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) +$ $\text{CO}(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) \rightarrow$ $2.000 \text{CO}(\text{O}^-)\text{COCH}_2(\text{ONO}_2) + 2.000 \text{CO}_2 + -\text{O}_2-$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03771			$\text{CO}(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) \xrightarrow{\text{RO}_2}$ $\text{CO}(\text{OH})\text{C}(\text{O}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03772			$\text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) +$ $0.550 \text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03773	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{O}\cdot)(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) \rightarrow$ $0.333 \text{CH}_2(\text{OH})\cdot + 0.333 \text{CO}(\text{OH})\text{COCO}(\text{O}^-) + 0.333 \text{CH}_2(\text{OH})\text{COCO}(\text{O}^-) +$ $0.333 \cdot \text{CO}(\text{OH}) + 0.333 \text{CH}_2(\text{OH})\text{COCO}(\text{OH}) + 0.333 \cdot \text{CO}(\text{O}^-)$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03774	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CO}(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03775	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03776			$\text{CO}(\text{OH})\text{C}(\text{O}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) \rightarrow 0.333 \cdot \text{CO}(\text{OH}) +$ $0.333 \text{CO}(\text{O}^-)\text{COCH}_2(\text{ONO}_2) + 0.333 \text{CO}(\text{OH})\text{COCH}_2(\text{ONO}_2) +$ $0.333 \cdot \text{CO}(\text{O}^-) + 0.333 \text{CO}(\text{OH})\text{COCO}(\text{O}^-) + 0.333 \text{CH}_2\text{O} + 0.333 \text{NO}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03777			$\text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03778			$\text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00487	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) \rightleftharpoons \text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CO}(\text{O}^-) + \text{H}^+$	$2.5 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
E <sub>o</sub> 00488	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CO}(\text{OH}) \rightleftharpoons \text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + \text{H}^+$	$1.2 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03779	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + \text{OH} \rightarrow$ $0.656 \text{CO}(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) +$ $0.344 \text{CH}_3\text{C}(\text{O}\cdot)(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + \text{H}_2\text{O} - 0.656 \text{O}_2$	$2.0 \cdot 10^{+08}$		
R <sub>o</sub> 03780	*		$\text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $\text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 03781	*	*	$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) \rightarrow$ $0.333 \text{CH}_3(\text{OO}\cdot) + 0.333 \text{CO}(\text{OH})\text{COCO}(\text{O}^-) + 0.333 \text{CH}_3\text{COCO}(\text{O}^-) +$ $0.333 \cdot \text{CO}(\text{OH}) + 0.333 \text{CH}_3\text{COCO}(\text{OH}) + 0.333 \cdot \text{CO}(\text{O}^-) - 0.333 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03782	*		$\text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{OH}) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00489			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) \rightleftharpoons \text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CO}(\text{O}^-) + \text{H}^+$	$1.0 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
E <sub>o</sub> 00490			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CO}(\text{OH}) \rightleftharpoons \text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + \text{H}^+$	$5.1 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03783			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + \text{OH} \rightarrow$ $\text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$1.3 \cdot 10^{+08}$		
R <sub>o</sub> 03784			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $\text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.5 \cdot 10^{+07}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03785			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_3\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CO}(\text{OH}) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03786			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CO}(\text{OH}) + \text{CH}_3\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CO}(\text{OH}) \rightarrow$ $2.000 \text{CH}_3\text{CO}(\text{ONO}_2) + 2.000 \text{CO}_2 + -\text{O}_2 -$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03787			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CO}(\text{OH}) \xrightarrow{\text{RO}_2} \text{CH}_3\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{CO}(\text{OH}) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03788			$\text{CH}_3\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{CO}(\text{OH}) \rightarrow 0.500 \text{CH}_3(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CO}(\text{ONO}_2) +$ $0.500 \text{CH}_3\text{CO}(\text{ONO}_2) + 0.500 \cdot \text{CO}(\text{OH}) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00491	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{CO}(\text{OH}) \rightleftharpoons$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{CO}(\text{O}^-) + \text{H}^+$	$1.0 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03789	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{CO}(\text{OH}) + \text{OH} \rightarrow$ $0.380 \text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.187 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.072 \text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CH}_2(\text{O}\cdot) +$ $0.048 \text{CH}_2(\text{OH})\text{C}(\text{O}\cdot)(\text{CH}(\text{OH})_2)\text{CO}(\text{OH}) +$ $0.313 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.567 \text{O}_2$	$1.2 \cdot 10^{+09}$		
R <sub>o</sub> 03790	*		$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{CO}(\text{OH}) + \text{NO}_3 \rightarrow$ $0.380 \text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.187 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.072 \text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CH}_2(\text{O}\cdot) +$ $0.048 \text{CH}_2(\text{OH})\text{C}(\text{O}\cdot)(\text{CH}(\text{OH})_2)\text{CO}(\text{OH}) +$ $0.313 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.567 \text{O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 03791	*	*	$\text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow$ $\text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03792	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 03793	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03794	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{OH}) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03795	*	*	CH <sub>3</sub> C(OH)(CH <sub>2</sub> (OH))CO(OH) + OH → 0.157 CH <sub>2</sub> (OH)C(OH)(CO(OH))CH <sub>2</sub> (OO·) + 0.651 CH <sub>3</sub> C(OH)(CO(OH))CH(OH)(OO·) + 0.082 CH <sub>3</sub> C(O·)(CH <sub>2</sub> (OH))CO(OH) + 0.110 CH <sub>3</sub> C(OH)(CO(OH))CH <sub>2</sub> (O·) + H <sub>2</sub> O – 0.807 O <sub>2</sub>	7.6 · 10 <sup>+08</sup>		
R <sub>o</sub> 03796	*		CH <sub>3</sub> C(OH)(CH <sub>2</sub> (OH))CO(OH) + NO <sub>3</sub> → 0.157 CH <sub>2</sub> (OH)C(OH)(CO(OH))CH <sub>2</sub> (OO·) + 0.651 CH <sub>3</sub> C(OH)(CO(OH))CH(OH)(OO·) + 0.082 CH <sub>3</sub> C(O·)(CH <sub>2</sub> (OH))CO(OH) + 0.110 CH <sub>3</sub> C(OH)(CO(OH))CH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.807 O <sub>2</sub>	1.5 · 10 <sup>+03</sup>		
R <sub>o</sub> 03797	*	*	CH <sub>2</sub> (OH)C(OH)(CO(OH))CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)C(OH)(CO(OH))CH <sub>2</sub> (O·) + 0.550 CH <sub>2</sub> (OH)C(OH)(CO(OH))CHO + 0.250 CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03798	*	*	CH <sub>3</sub> C(OH)(CO(OH))CH(OH)(OO·) → CH <sub>3</sub> C(OH)(CO(OH))CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03799	*	*	CH <sub>3</sub> C(OH)(CO(OH))CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>3</sub> C(OH)(CO(OH))CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03800	*	*	CH <sub>3</sub> C(OH)(CO(OH))CH <sub>2</sub> (O·) → CH <sub>3</sub> C(OH)(OO·)CO(OH) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03801	*	*	CH <sub>2</sub> (OH)C(OH)(CO(OH))CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(OH)(CO(OH))CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03802	*	*	CH <sub>2</sub> (OH)C(OH)(CO(OH))CH <sub>2</sub> (O·) → CH <sub>2</sub> (OH)C(OH)(OO·)CO(OH) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00492			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CH(OH) <sub>2</sub> )CO(OH) ⇌ CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CH(OH) <sub>2</sub> )CO(O <sup>–</sup> ) + H <sup>+</sup>	4.2 · 10 <sup>–04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03803			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CH(OH) <sub>2</sub> )CO(OH) + OH → 0.399 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CH(OH)(OO·) + 0.197 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))C(OH) <sub>2</sub> (OO·) + 0.076 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (O·) + 0.328 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CH(OH)(O·) + H <sub>2</sub> O – 0.596 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03804			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CH(OH) <sub>2</sub> )CO(OH) + NO <sub>3</sub> → 0.399 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CH(OH)(OO·) + 0.197 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))C(OH) <sub>2</sub> (OO·) + 0.076 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (O·) + 0.328 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.596 O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03805			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CH(OH)(OO·) → CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03806			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))C(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03807			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03808			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CH(OH)(O·) → CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)CO(OH) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03809			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)CO(OH) + CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)CO(OH) → 2.000 CH <sub>2</sub> (OH)CO(ONO <sub>2</sub> ) + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03810			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)CO(OH) $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(O·)CO(OH) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03811			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(O·)CO(OH) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CO(ONO <sub>2</sub> ) + 0.500 ·CO(OH)	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00493			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CH(OH) <sub>2</sub> )CO(OH)	6.5 · 10 <sup>+03</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00494			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CHO = CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CHO + H <sup>+</sup>	1.3 · 10 <sup>-03</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03812			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CHO + OH → 0.156 CO(OH)C(ONO <sub>2</sub> )(CHO)C(OH) <sub>2</sub> (OO·) + 0.527 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CO(OO·) + 0.318 CO(OH)C(ONO <sub>2</sub> )(CHO)CH(OH)(O·) + H <sub>2</sub> O - 0.682 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 03813			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CHO + NO <sub>3</sub> → 0.156 CO(OH)C(ONO <sub>2</sub> )(CHO)C(OH) <sub>2</sub> (OO·) + 0.527 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CO(OO·) + 0.318 CO(OH)C(ONO <sub>2</sub> )(CHO)CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.682 O <sub>2</sub>	8.0 · 10 <sup>+06</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03814			CO(OH)C(ONO <sub>2</sub> )(CHO)C(OH) <sub>2</sub> (OO·) → CO(OH)C(ONO <sub>2</sub> )(CO(OH))CHO + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03815			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CO(OO·) → CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03816			CO(OH)C(ONO <sub>2</sub> )(CHO)CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(ONO <sub>2</sub> )(CO(OH))CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03817			CO(OH)C(ONO <sub>2</sub> )(CHO)CH(OH)(O·) → CO(OH)C(ONO <sub>2</sub> )(OO·)CHO + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03818			CO(OH)C(ONO <sub>2</sub> )(OO·)CHO + CO(OH)C(ONO <sub>2</sub> )(OO·)CHO → 2.000 CO(ONO <sub>2</sub> )CHO + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 03819			CO(OH)C(ONO <sub>2</sub> )(OO·)CHO $\xrightarrow{RO_2}$ CO(OH)C(ONO <sub>2</sub> )(O·)CHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03820			CO(OH)C(ONO <sub>2</sub> )(O·)CHO → 0.500 · CO(OH) + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CH · (OH) <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00495			CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CHO $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> C(ONO <sub>2</sub> )(CH(OH) <sub>2</sub> )CO(OH)	7.6 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03821			CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CHO + OH → 0.126 CO(OH)C(ONO <sub>2</sub> )(CHO)CH <sub>2</sub> (OO·) + 0.874 CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CO(OO·) + H <sub>2</sub> O - O <sub>2</sub>	7.7 · 10 <sup>+08</sup>		
R <sub>o</sub> 03822			CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CHO + NO <sub>3</sub> → 0.126 CO(OH)C(ONO <sub>2</sub> )(CHO)CH <sub>2</sub> (OO·) + 0.874 CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CO(OO·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	1.1 · 10 <sup>+07</sup>		
R <sub>o</sub> 03823			CO(OH)C(ONO <sub>2</sub> )(CHO)CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CO(OH)C(ONO <sub>2</sub> )(CHO)CH <sub>2</sub> (O·) + 0.550 CO(OH)C(ONO <sub>2</sub> )(CHO)CHO + 0.250 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03824			CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CO(OO·) → CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03825			CO(OH)C(ONO <sub>2</sub> )(CHO)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(OH)C(ONO <sub>2</sub> )(CHO)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03826			CO(OH)C(ONO <sub>2</sub> )(CHO)CH <sub>2</sub> (O·) → CO(OH)C(ONO <sub>2</sub> )(OO·)CHO + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03827			CH <sub>3</sub> C(ONO <sub>2</sub> )(CH <sub>2</sub> (OH))CO(OH) + OH → 0.171 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (OO·) + 0.709 CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CH(OH)(OO·) + 0.120 CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (O·) + H <sub>2</sub> O – 0.880 O <sub>2</sub>	6.9 · 10 <sup>+08</sup>		
R <sub>o</sub> 03828			CH <sub>3</sub> C(ONO <sub>2</sub> )(CH <sub>2</sub> (OH))CO(OH) + NO <sub>3</sub> → 0.171 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (OO·) + 0.709 CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CH(OH)(OO·) + 0.120 CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.880 O <sub>2</sub>	1.5 · 10 <sup>+03</sup>		
R <sub>o</sub> 03829			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (OO·) $\xrightarrow{RO_2^-}$ 0.200 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (O·) + 0.550 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CHO + 0.250 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CH <sub>2</sub> (OH))CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03830			CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CH(OH)(OO·) → CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03831			CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03832			CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (O·) → CH <sub>3</sub> C(ONO <sub>2</sub> )(OO·)CO(OH) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03833			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03834			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (O·) → CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)CO(OH) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00496	*	*	CH(OH) <sub>2</sub> C(OH)(CO(OH))CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CO(OH)	7.1 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00497	*	*	CH(OH) <sub>2</sub> C(OH)(CO(OH))CHO $\rightleftharpoons$ CH(OH) <sub>2</sub> C(OH)(CO(O <sup>–</sup> ))CHO + H <sup>+</sup>	3.2 · 10 <sup>–04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03835	*	*	CH(OH) <sub>2</sub> C(OH)(CO(OH))CHO + OH → 0.150 CO(OH)C(OH)(CHO)C(OH) <sub>2</sub> (OO·) + 0.506 CH(OH) <sub>2</sub> C(OH)(CO(OH))CO(OO·) + 0.306 CO(OH)C(OH)(CHO)CH(OH)(O·) + 0.038 CH(OH) <sub>2</sub> C(O·)(CO(OH))CHO + H <sub>2</sub> O – 0.656 O <sub>2</sub>	1.2 · 10 <sup>+09</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03836	*		CH(OH) <sub>2</sub> C(OH)(CO(OH))CHO + NO <sub>3</sub> → 0.150 CO(OH)C(OH)(CHO)C(OH) <sub>2</sub> (OO·) + 0.506 CH(OH) <sub>2</sub> C(OH)(CO(OH))CO(OO·) + 0.306 CO(OH)C(OH)(CHO)CH(OH)(O·) + 0.038 CH(OH) <sub>2</sub> C(O·)(CO(OH))CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.656 O <sub>2</sub>	8.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03837	*	*	CO(OH)C(OH)(CHO)C(OH) <sub>2</sub> (OO·) → CO(OH)C(OH)(CO(OH))CHO + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03838	*	*	CH(OH) <sub>2</sub> C(OH)(CO(OH))CO(OO·) → CH(OH) <sub>2</sub> C(OH)(CO(OH))CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03839	*	*	CO(OH)C(OH)(CHO)CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(OH)(CO(OH))CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03840	*	*	CO(OH)C(OH)(CHO)CH(OH)(O·) → CO(OH)C(OH)(OO·)CHO + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03841	*	*	CH(OH) <sub>2</sub> C(O·)(CO(OH))CHO → 0.333 CH · (OH) <sub>2</sub> + 0.333 CO(OH)COCHO + 0.333 CH(OH) <sub>2</sub> COCHO + 0.333 · CO(OH) + 0.333 CH(OH) <sub>2</sub> COCO(OH) + 0.333 CH · (OH) <sub>2</sub> - 0.333 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03842	*	*	CO(OH)C(OH)(OO·)CHO → CO(OH)COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00498	*	*	CH <sub>3</sub> C(OH)(CO(OH))CHO $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CO(OH)	8.3 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03843	*	*	CH <sub>3</sub> C(OH)(CO(OH))CHO + OH → 0.119 CO(OH)C(OH)(CHO)CH <sub>2</sub> (OO·) + 0.819 CH <sub>3</sub> C(OH)(CO(OH))CO(OO·) + 0.062 CH <sub>3</sub> C(O·)(CO(OH))CHO + H <sub>2</sub> O - 0.938 O <sub>2</sub>	8.2 · 10 <sup>+08</sup>		
R <sub>o</sub> 03844	*		CH <sub>3</sub> C(OH)(CO(OH))CHO + NO <sub>3</sub> → 0.119 CO(OH)C(OH)(CHO)CH <sub>2</sub> (OO·) + 0.819 CH <sub>3</sub> C(OH)(CO(OH))CO(OO·) + 0.062 CH <sub>3</sub> C(O·)(CO(OH))CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.938 O <sub>2</sub>	1.1 · 10 <sup>+07</sup>		
R <sub>o</sub> 03845	*	*	CO(OH)C(OH)(CHO)CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CO(OH)C(OH)(CHO)CH <sub>2</sub> (O·) + 0.550 CO(OH)C(OH)(CHO)CHO + 0.250 CH <sub>2</sub> (OH)C(OH)(CO(OH))CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03846	*	*	CH <sub>3</sub> C(OH)(CO(OH))CO(OO·) → CH <sub>3</sub> C(OH)(CO(OH))CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03847	*	*	$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CO}(\text{OH}))\text{CHO} \rightarrow 0.333 \text{CH}_3(\text{OO}\cdot) + 0.333 \text{CO}(\text{OH})\text{COCHO} +$ $0.333 \text{CH}_3\text{COCHO} + 0.333 \cdot \text{CO}(\text{OH}) + 0.333 \text{CH}_3\text{COCO}(\text{OH}) +$ $0.333 \text{CH} \cdot (\text{OH})_2 - 0.333 \text{O}_2 - 0.333 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03848	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})(\text{CHO})\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{C}(\text{OH})(\text{CHO})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03849	*	*	$\text{CO}(\text{OH})\text{C}(\text{OH})(\text{CHO})\text{CH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CHO} + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00499			$\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CO}(\text{OH}) \rightleftharpoons$ $\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + \text{H}^+$	$3.9 \cdot 10^{-03}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03850			$\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CO}(\text{OH}) + \text{OH} \rightarrow$ $0.779 \text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.221 \text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.779 \text{O}_2$	$3.8 \cdot 10^{+08}$		
R <sub>o</sub> 03851			$\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CO}(\text{OH}) + \text{NO}_3 \rightarrow$ $0.779 \text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.221 \text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.779 \text{O}_2$	$2.8 \cdot 10^{+04}$		
R <sub>o</sub> 03852			$\text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow$ $\text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
E <sub>o</sub> 00500			$\text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}}$ $\text{CH}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CO}(\text{OH})$	$8.6 \cdot 10^{+03}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00501			$\text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CHO} \rightleftharpoons \text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CHO} + \text{H}^+$	$1.2 \cdot 10^{-02}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03853			$\text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CHO} + \text{OH} \rightarrow$ $\text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CO}(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$4.0 \cdot 10^{+08}$		
R <sub>o</sub> 03854			$\text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CHO} + \text{NO}_3 \rightarrow$ $\text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CO}(\text{OO}\cdot) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$4.1 \cdot 10^{+06}$		
R <sub>o</sub> 03855			$\text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CO}(\text{OO}\cdot) \rightarrow$ $\text{CO}(\text{OH})\text{C}(\text{ONO}_2)(\text{CO}(\text{OH}))\text{CO}(\text{OH}) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
E <sub>o</sub> 00502	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CO}(\text{OH}) \rightleftharpoons$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + \text{H}^+$	$9.3 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03856	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CO}(\text{OH}) + \text{OH} \rightarrow$ $0.709 \text{CO}(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.201 \text{CO}(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{OH}))\text{CH}_2(\text{O}\cdot) +$ $0.090 \text{CH}_2(\text{OH})\text{C}(\text{O}\cdot)(\text{CO}(\text{OH}))\text{CO}(\text{OH}) + \text{H}_2\text{O} - 0.709 \text{O}_2$	$4.1 \cdot 10^{+08}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03857	*		CH <sub>2</sub> (OH)C(OH)(CO(OH))CO(OH) + NO <sub>3</sub> → 0.709 CO(OH)C(OH)(CO(OH))CH(OH)(OO·) + 0.201 CO(OH)C(OH)(CO(OH))CH <sub>2</sub> (O·) + 0.090 CH <sub>2</sub> (OH)C(O·)(CO(OH))CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.709 O <sub>2</sub>	2.8 · 10 <sup>+04</sup>		
R <sub>o</sub> 03858	*	*	CO(OH)C(OH)(CO(OH))CH(OH)(OO·) → CO(OH)C(OH)(CO(OH))CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00503	*	*	CO(OH)C(OH)(CO(OH))CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH)(CO(OH))CO(OH)	9.4 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00504	*	*	CO(OH)C(OH)(CO(OH))CHO $\rightleftharpoons$ CO(OH)C(OH)(CO(O <sup>-</sup> ))CHO + H <sup>+</sup>	2.9 · 10 <sup>-03</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03859	*	*	CO(OH)C(OH)(CO(OH))CHO + OH → 0.929 CO(OH)C(OH)(CO(OH))CO(OO·) + 0.071 CO(OH)C(O·)(CO(OH))CHO + H <sub>2</sub> O - 0.929 O <sub>2</sub>	4.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 03860	*		CO(OH)C(OH)(CO(OH))CHO + NO <sub>3</sub> → 0.929 CO(OH)C(OH)(CO(OH))CO(OO·) + 0.071 CO(OH)C(O·)(CO(OH))CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.929 O <sub>2</sub>	3.9 · 10 <sup>+06</sup>		
R <sub>o</sub> 03861	*	*	CO(OH)C(OH)(CO(OH))CO(OO·) → CO(OH)C(OH)(CO(OH))CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03862	*	*	CO(OH)C(O·)(CO(OH))CHO → 0.667 · CO(OH) + 0.667 CO(OH)COCHO + 0.333 CO(OH)COCO(OH) + 0.333 CH · (OH) <sub>2</sub> - 0.333 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03863			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + OH → 0.221 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO·) + 0.351 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) + 0.066 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.301 CH <sub>2</sub> (OH)C(OH)(O·)CH(OH)(ONO <sub>2</sub> ) + 0.061 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O - 0.572 O <sub>2</sub>	1.3 · 10 <sup>+09</sup>		
R <sub>o</sub> 03864			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.221 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO·) + 0.351 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) + 0.066 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.301 CH <sub>2</sub> (OH)C(OH)(O·)CH(OH)(ONO <sub>2</sub> ) + 0.061 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.572 O <sub>2</sub>	9.9 · 10 <sup>+06</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03865			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO·) → CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03866			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03867			CH <sub>2</sub> (OH)C(OH)(O·)CH(OH)(ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03868			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CO(OH) + H <sup>+</sup> + NO <sub>3</sub>	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 03869			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + OH → 0.369 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO·) + 0.129 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.502 CH <sub>2</sub> (OH)C(OH)(O·)CO(ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.369 O <sub>2</sub>	$6.5 \cdot 10^{+08}$		
R <sub>o</sub> 03870			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.369 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO·) + 0.129 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.502 CH <sub>2</sub> (OH)C(OH)(O·)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.369 O <sub>2</sub>	$8.1 \cdot 10^{+06}$		
R <sub>o</sub> 03871			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO·) → CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03872			CH <sub>2</sub> (OH)C(OH)(O·)CO(ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CO + 0.500 NO <sub>3</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00505			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> COCO(ONO <sub>2</sub> )	$3.2 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00506			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> )	$4.0 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03873			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO $\xrightarrow{H_2O}$ CO(OH)C(OH) <sub>2</sub> CHO + H <sup>+</sup> + NO <sub>3</sub>	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 03874			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + OH → 0.550 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) + 0.450 CO(ONO <sub>2</sub> )C(OH)(O·)CHO + H <sub>2</sub> O - 0.550 O <sub>2</sub>	$5.9 \cdot 10^{+08}$		
R <sub>o</sub> 03875			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + NO <sub>3</sub> → 0.550 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) + 0.450 CO(ONO <sub>2</sub> )C(OH)(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.550 O <sub>2</sub>	$5.6 \cdot 10^{+06}$		
R <sub>o</sub> 03876			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) → CO(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 03877			CO(ONO <sub>2</sub> )C(OH)(O·)CHO → 0.500 CO + 0.500 CO(OH)CHO + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CH·(OH) <sub>2</sub> + 0.500 NO <sub>3</sub> - 0.500 H <sub>2</sub> O	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00507			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> )	$1.2 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03878			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + OH → 0.321 CHOC(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) + 0.336 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) + 0.068 CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + 0.275 CH(OH)(ONO <sub>2</sub> )C(OH)(O·)CHO + H <sub>2</sub> O – 0.657 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 03879			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + NO <sub>3</sub> → 0.321 CHOC(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) + 0.336 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) + 0.068 CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + 0.275 CH(OH)(ONO <sub>2</sub> )C(OH)(O·)CHO + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.657 O <sub>2</sub>	7.4 · 10 <sup>+06</sup>		
R <sub>o</sub> 03880			CHOC(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) → CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03881			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) → CO(OH)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03882			CH(OH)(ONO <sub>2</sub> )C(OH)(O·)CHO → 0.500 CHO(ONO <sub>2</sub> ) + 0.500 CO(OH)CHO + 0.500 CO(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CH·(OH) <sub>2</sub> + 0.500 HO <sub>2</sub> – 0.500 O <sub>2</sub> – 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00508	*	*	CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CO(OH) ⇌ CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CO(O <sup>–</sup> ) + H <sup>+</sup>	1.6 · 10 <sup>–04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03883	*	*	CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CO(O <sup>–</sup> ) + OH → 0.471 CH(OH) <sub>2</sub> C(OH)(CO(O <sup>–</sup> ))C(OH) <sub>2</sub> (OO·) + 0.469 CH(OH) <sub>2</sub> C(OH)(CO(O <sup>–</sup> ))CH(OH)(O·) + 0.060 CH(OH) <sub>2</sub> C(O·)(CH(OH) <sub>2</sub> )CO(O <sup>–</sup> ) + H <sub>2</sub> O – 0.471 O <sub>2</sub>	1.5 · 10 <sup>+09</sup>		
R <sub>o</sub> 03884	*		CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CO(O <sup>–</sup> ) + NO <sub>3</sub> → CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CO(O·) + NO <sub>3</sub> <sup>–</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03885	*	*	CH(OH) <sub>2</sub> C(OH)(CO(O <sup>–</sup> ))C(OH) <sub>2</sub> (OO·) → CH(OH) <sub>2</sub> C(OH)(CO(OH))CO(O <sup>–</sup> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03886	*	*	CH(OH) <sub>2</sub> C(OH)(CO(O <sup>–</sup> ))CH(OH)(O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> C(OH)(CO(OH))CO(O <sup>–</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03887	*	*	CH(OH) <sub>2</sub> C(OH)(CO(O <sup>–</sup> ))CH(OH)(O·) → CH(OH) <sub>2</sub> C(OH)(OO·)CO(O <sup>–</sup> ) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03888	*	*	$\text{CH(OH)}_2\text{C(O}\cdot\text{)(CH(OH)}_2\text{CO(O}^-\text{))} \rightarrow 0.667 \text{CH}\cdot\text{(OH)}_2 +$ $0.667 \text{CH(OH)}_2\text{COCO(O}^-\text{)} + 0.333 \text{CH(OH)}_2\text{COCH(OH)}_2 + 0.333 \cdot\text{CO(O}^-\text{)}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03889	*		$\text{CH(OH)}_2\text{C(OH)(CH(OH)}_2\text{CO(O}\cdot\text{))} \rightarrow$ $\text{CH(OH)}_2\text{C(OH)(OO}\cdot\text{)CH(OH)}_2 + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03890	*	*	$\text{CH(OH)}_2\text{C(OH)(OO}\cdot\text{)CH(OH)}_2 \rightarrow \text{CH(OH)}_2\text{COCH(OH)}_2 + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03891	*	*	$\text{CH}_2(\text{OH})\text{C(OH)(CH(OH)}_2\text{CO(O}^-\text{))} + \text{OH} \rightarrow$ $0.456 \text{CH(OH)}_2\text{C(OH)(CO(O}^-\text{))CH(OH)(OO}\cdot\text{)} +$ $0.224 \text{CH}_2(\text{OH})\text{C(OH)(CO(O}^-\text{))C(OH)}_2(\text{OO}\cdot\text{)} +$ $0.049 \text{CH(OH)}_2\text{C(OH)(CO(O}^-\text{))CH}_2(\text{O}\cdot\text{)} +$ $0.058 \text{CH}_2(\text{OH})\text{C(O}\cdot\text{)(CH(OH)}_2\text{CO(O}^-\text{))} +$ $0.213 \text{CH}_2(\text{OH})\text{C(OH)(CO(O}^-\text{))CH(OH)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.680 \text{O}_2$	$1.7 \cdot 10^{+09}$		
R <sub>o</sub> 03892	*		$\text{CH}_2(\text{OH})\text{C(OH)(CH(OH)}_2\text{CO(O}^-\text{))} + \text{NO}_3 \rightarrow$ $\text{CH}_2(\text{OH})\text{C(OH)(CH(OH)}_2\text{CO(O}\cdot\text{))} + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 03893	*	*	$\text{CH(OH)}_2\text{C(OH)(CO(O}^-\text{))CH(OH)(OO}\cdot\text{)} \rightarrow$ $\text{CH(OH)}_2\text{C(OH)(CO(O}^-\text{))CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03894	*	*	$\text{CH}_2(\text{OH})\text{C(OH)(CO(O}^-\text{))C(OH)}_2(\text{OO}\cdot\text{)} \rightarrow$ $\text{CH}_2(\text{OH})\text{C(OH)(CO(OH))CO(O}^-\text{)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 03895	*	*	$\text{CH}_2(\text{OH})\text{C(OH)(CO(O}^-\text{))CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2}$ $\text{CH}_2(\text{OH})\text{C(OH)(CO(OH))CO(O}^-\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03896	*	*	$\text{CH}_2(\text{OH})\text{C(OH)(CO(O}^-\text{))CH(OH)(O}\cdot\text{)} \rightarrow$ $\text{CH}_2(\text{OH})\text{C(OH)(OO}\cdot\text{)CO(O}^-\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03897	*		$\text{CH}_2(\text{OH})\text{C(OH)(CH(OH)}_2\text{CO(O}\cdot\text{))} \rightarrow$ $\text{CH}_2(\text{OH})\text{C(OH)(OO}\cdot\text{)CH(OH)}_2 + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00509			$\text{CH(OH)}_2\text{C(ONO}_2\text{)(CH(OH)}_2\text{CO(OH))} \rightleftharpoons$ $\text{CH(OH)}_2\text{C(ONO}_2\text{)(CH(OH)}_2\text{CO(O}^-\text{))} + \text{H}^+$	$6.6 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03898			$\text{CH(OH)}_2\text{C(ONO}_2\text{)(CH(OH)}_2\text{CO(O}^-\text{))} + \text{OH} \rightarrow$ $0.501 \text{CH(OH)}_2\text{C(ONO}_2\text{)(CO(O}^-\text{))C(OH)}_2(\text{OO}\cdot\text{)} +$ $0.499 \text{CH(OH)}_2\text{C(ONO}_2\text{)(CO(O}^-\text{))CH(OH)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.501 \text{O}_2$	$1.5 \cdot 10^{+09}$		
R <sub>o</sub> 03899			$\text{CH(OH)}_2\text{C(ONO}_2\text{)(CH(OH)}_2\text{CO(O}^-\text{))} + \text{NO}_3 \rightarrow$ $\text{CH(OH)}_2\text{C(ONO}_2\text{)(CH(OH)}_2\text{CO(O}\cdot\text{))} + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03900			$\text{CH(OH)}_2\text{C(ONO}_2\text{)(CO(O}^-\text{))C(OH)}_2\text{(OO}\cdot\text{)} \rightarrow$ $\text{CH(OH)}_2\text{C(ONO}_2\text{)(CO(OH))CO(O}^-\text{)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 03901			$\text{CH(OH)}_2\text{C(ONO}_2\text{)(CO(O}^-\text{))CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2}$ $\text{CH(OH)}_2\text{C(ONO}_2\text{)(CO(OH))CO(O}^-\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03902			$\text{CH(OH)}_2\text{C(ONO}_2\text{)(CO(O}^-\text{))CH(OH)(O}\cdot\text{)} \rightarrow$ $\text{CH(OH)}_2\text{C(ONO}_2\text{)(OO}\cdot\text{)CO(O}^-\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03903			$\text{CH(OH)}_2\text{C(ONO}_2\text{)(CH(OH)}_2\text{)CO(O}\cdot\text{)} \rightarrow$ $\text{CH(OH)}_2\text{C(ONO}_2\text{)(OO}\cdot\text{)CH(OH)}_2 + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03904			$\text{CH}_2\text{(OH)C(ONO}_2\text{)(CH(OH)}_2\text{)CO(O}^-\text{)} + \text{OH} \rightarrow$ $0.484 \text{CH(OH)}_2\text{C(ONO}_2\text{)(CO(O}^-\text{))CH(OH)(OO}\cdot\text{)} +$ $0.238 \text{CH}_2\text{(OH)C(ONO}_2\text{)(CO(O}^-\text{))C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.052 \text{CH(OH)}_2\text{C(ONO}_2\text{)(CO(O}^-\text{))CH}_2\text{(O}\cdot\text{)} +$ $0.226 \text{CH}_2\text{(OH)C(ONO}_2\text{)(CO(O}^-\text{))CH(OH)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.722 \text{O}_2$	$1.6 \cdot 10^{+09}$		
R <sub>o</sub> 03905			$\text{CH}_2\text{(OH)C(ONO}_2\text{)(CH(OH)}_2\text{)CO(O}^-\text{)} + \text{NO}_3 \rightarrow$ $\text{CH}_2\text{(OH)C(ONO}_2\text{)(CH(OH)}_2\text{)CO(O}\cdot\text{)} + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 03906			$\text{CH(OH)}_2\text{C(ONO}_2\text{)(CO(O}^-\text{))CH(OH)(OO}\cdot\text{)} \rightarrow$ $\text{CH(OH)}_2\text{C(ONO}_2\text{)(CO(O}^-\text{))CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03907			$\text{CH}_2\text{(OH)C(ONO}_2\text{)(CO(O}^-\text{))C(OH)}_2\text{(OO}\cdot\text{)} \rightarrow$ $\text{CH}_2\text{(OH)C(ONO}_2\text{)(CO(OH))CO(O}^-\text{)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 03908			$\text{CH}_2\text{(OH)C(ONO}_2\text{)(CO(O}^-\text{))CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2}$ $\text{CH}_2\text{(OH)C(ONO}_2\text{)(CO(OH))CO(O}^-\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03909			$\text{CH}_2\text{(OH)C(ONO}_2\text{)(CO(O}^-\text{))CH(OH)(O}\cdot\text{)} \rightarrow$ $\text{CH}_2\text{(OH)C(ONO}_2\text{)(OO}\cdot\text{)CO(O}^-\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03910			$\text{CH}_2\text{(OH)C(ONO}_2\text{)(CH(OH)}_2\text{)CO(O}\cdot\text{)} \rightarrow$ $\text{CH}_2\text{(OH)C(ONO}_2\text{)(OO}\cdot\text{)CH(OH)}_2 + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03911			$\text{CH}_2\text{(OH)C(ONO}_2\text{)(OO}\cdot\text{)CH(OH)}_2 \xrightarrow{\text{RO}_2}$ $\text{CH}_2\text{(OH)C(ONO}_2\text{)(O}\cdot\text{)CH(OH)}_2 + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03912			$\text{CH}_2\text{(OH)C(ONO}_2\text{)(O}\cdot\text{)CH(OH)}_2 \rightarrow 0.500 \text{CH}_2\text{(OH)}\cdot +$ $0.500 \text{CH(OH)}_2\text{CO(ONO}_2\text{)} + 0.500 \text{CH}_2\text{(OH)CO(ONO}_2\text{)} + 0.500 \text{CH} \cdot \text{(OH)}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00510			$\text{CH(OH)}_2\text{C(ONO}_2\text{)(CO(O}^-\text{))CHO} \xrightleftharpoons{\text{H}_2\text{O}}$ $\text{CH(OH)}_2\text{C(ONO}_2\text{)(CH(OH)}_2\text{)CO(O}^-\text{)}$	$5.7 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03913			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CHO + OH → 0.180 CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CHO)C(OH) <sub>2</sub> (OO·) + 0.610 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(OO·) + 0.210 CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CHO)CH(OH)(O·) + H <sub>2</sub> O - 0.790 O <sub>2</sub>	1.7 · 10 <sup>+09</sup>		
R <sub>o</sub> 03914			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CHO + NO <sub>3</sub> → CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CHO)CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03915			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CHO)C(OH) <sub>2</sub> (OO·) → CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CHO + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03916			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(OO·) → CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CO(O <sup>-</sup> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03917			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CHO)CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03918			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CHO)CH(OH)(O·) → CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO·)CHO + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03919			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CHO)CO(O·) → CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CHO + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03920			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CHO $\xrightarrow{RO_2}$ CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O·)CHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03921			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O·)CHO → 0.500 CH·(OH) <sub>2</sub> + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CH(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 CH·(OH) <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00511	*	*	CH(OH) <sub>2</sub> C(OH)(CO(O <sup>-</sup> ))CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CO(O <sup>-</sup> )	6.3 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03922	*	*	CH(OH) <sub>2</sub> C(OH)(CO(O <sup>-</sup> ))CHO + OH → 0.172 CO(O <sup>-</sup> )C(OH)(CHO)C(OH) <sub>2</sub> (OO·) + 0.583 CH(OH) <sub>2</sub> C(OH)(CO(O <sup>-</sup> ))CO(OO·) + 0.200 CO(O <sup>-</sup> )C(OH)(CHO)CH(OH)(O·) + 0.044 CH(OH) <sub>2</sub> C(O·)(CO(O <sup>-</sup> ))CHO + H <sub>2</sub> O - 0.755 O <sub>2</sub>	1.8 · 10 <sup>+09</sup>		
R <sub>o</sub> 03923	*		CH(OH) <sub>2</sub> C(OH)(CO(O <sup>-</sup> ))CHO + NO <sub>3</sub> → CH(OH) <sub>2</sub> C(OH)(CHO)CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03924	*	*	CO(O <sup>-</sup> )C(OH)(CHO)C(OH) <sub>2</sub> (OO·) → CO(OH)C(OH)(CO(O <sup>-</sup> ))CHO + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03925	*	*	$\text{CH(OH)}_2\text{C(OH)(CO(O}^-))\text{CO(OO}\cdot) \rightarrow$ $\text{CH(OH)}_2\text{C(OH)(CO(OH))CO(O}^-) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 03926	*	*	$\text{CO(O}^-)\text{C(OH)(CHO)CH(OH)(O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CO(OH)C(OH)(CO(O}^-))\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03927	*	*	$\text{CO(O}^-)\text{C(OH)(CHO)CH(OH)(O}\cdot) \rightarrow$ $\text{CO(O}^-)\text{C(OH)(OO}\cdot)\text{CHO} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03928	*	*	$\text{CH(OH)}_2\text{C(O}\cdot)\text{(CO(O}^-))\text{CHO} \rightarrow$ $0.333 \text{ CH}\cdot(\text{OH})_2 + 0.333 \text{ CO(O}^-)\text{COCHO} + 0.333 \text{ CH(OH)}_2\text{COCHO} +$ $0.333 \cdot \text{CO(O}^-) + 0.333 \text{ CH(OH)}_2\text{COCO(O}^-) + 0.333 \text{ CH}\cdot(\text{OH})_2 - 0.333 \text{ H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03929	*		$\text{CH(OH)}_2\text{C(OH)(CHO)CO(O}\cdot) \rightarrow \text{CH(OH)}_2\text{C(OH)(OO}\cdot)\text{CHO} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03930	*	*	$\text{CH(OH)}_2\text{C(OH)(OO}\cdot)\text{CHO} \rightarrow \text{CH(OH)}_2\text{COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03931			$\text{CH}_3\text{C(ONO}_2\text{)(CO(O}^-))\text{CO(O}^-) + \text{OH} \rightarrow$ $\text{CO(O}^-)\text{C(ONO}_2\text{)(CO(O}^-))\text{CH}_2(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$2.3 \cdot 10^{+08}$		
R <sub>o</sub> 03932			$\text{CH}_3\text{C(ONO}_2\text{)(CO(O}^-))\text{CO(O}^-) + \text{NO}_3 \rightarrow$ $0.500 \text{ CH}_3\text{C(ONO}_2\text{)(CO(O}^-))\text{CO(O}\cdot) +$ $0.500 \text{ CH}_3\text{C(ONO}_2\text{)(CO(O}^-))\text{CO(O}\cdot) + \text{NO}_3^-$	$7.8 \cdot 10^{+07}$		
R <sub>o</sub> 03933			$\text{CO(O}^-)\text{C(ONO}_2\text{)(CO(O}^-))\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CO(O}^-)\text{C(ONO}_2\text{)(CO(O}^-))\text{CH}_2(\text{O}\cdot) +$ $0.550 \text{ CO(O}^-)\text{C(ONO}_2\text{)(CO(O}^-))\text{CHO} +$ $0.250 \text{ CH}_2(\text{OH})\text{C(ONO}_2\text{)(CO(O}^-))\text{CO(O}^-) + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03934			$\text{CH}_3\text{C(ONO}_2\text{)(CO(O}^-))\text{CO(O}\cdot) \rightarrow \text{CH}_3\text{C(ONO}_2\text{)(OO}\cdot)\text{CO(O}^-) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03935			$\text{CO(O}^-)\text{C(ONO}_2\text{)(CO(O}^-))\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CO(O}^-)\text{C(ONO}_2\text{)(CO(O}^-))\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03936			$\text{CO(O}^-)\text{C(ONO}_2\text{)(CO(O}^-))\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CO(O}^-)\text{C(ONO}_2\text{)(OO}\cdot)\text{CO(O}^-) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03937	*	*	$\text{CH}_3\text{C(OH)(CO(O}^-))\text{CO(O}^-) + \text{OH} \rightarrow$ $0.656 \text{ CO(O}^-)\text{C(OH)(CO(O}^-))\text{CH}_2(\text{OO}\cdot) +$ $0.344 \text{ CH}_3\text{C(O}\cdot)\text{(CO(O}^-))\text{CO(O}^-) + \text{H}_2\text{O} - 0.656 \text{ O}_2$	$3.6 \cdot 10^{+08}$		
R <sub>o</sub> 03938	*		$\text{CH}_3\text{C(OH)(CO(O}^-))\text{CO(O}^-) + \text{NO}_3 \rightarrow$ $0.500 \text{ CH}_3\text{C(OH)(CO(O}^-))\text{CO(O}\cdot) + 0.500 \text{ CH}_3\text{C(OH)(CO(O}^-))\text{CO(O}\cdot) +$ $\text{NO}_3^-$	$7.8 \cdot 10^{+07}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03939	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) \xrightarrow{RO_2}$ 0.200 $\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) +$ 0.550 $\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CHO} +$ 0.250 $\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 03940	*	*	$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CO}(\text{O}^-))\text{CO}(\text{O}^-) \rightarrow$ 0.333 $\text{CH}_3(\text{OO}\cdot) + 0.333 \text{CO}(\text{O}^-)\text{COCO}(\text{O}^-) + 0.667 \text{CH}_3\text{COCO}(\text{O}^-) +$ 0.667 $\cdot\text{CO}(\text{O}^-) - 0.333 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03941	*		$\text{CH}_3\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03942	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \xrightarrow{O_2} \text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03943	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03944	*	*	$\text{CO}(\text{O}^-)\text{C}(\text{CO}(\text{O}^-))=\text{CH}_2 + \text{OH} \rightarrow$ 0.969 $\text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CO}(\text{O}^-) +$ 0.031 $\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) - \text{O}_2$	$1.0 \cdot 10^{+11}$		
R <sub>o</sub> 03945			$\text{CO}(\text{O}^-)\text{C}(\text{CO}(\text{O}^-))=\text{CH}_2 + \text{NO}_3 \rightarrow$ 0.969 $\text{CO}(\text{O}^-)\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) +$ 0.031 $\text{CO}(\text{O}^-)\text{C}(\text{ONO}_2)(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) - \text{O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 03946	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CO}(\text{O}^-) + \text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CO}(\text{O}^-) \rightarrow$ 2.000 $\text{CH}_2(\text{OH})\text{COCO}(\text{O}^-) + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03947	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CO}(\text{O}^-) \xrightarrow{RO_2}$ $\text{CH}_2(\text{OH})\text{C}(\text{O}\cdot)(\text{CO}(\text{O}^-))\text{CO}(\text{O}^-) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03948			$\text{CO}(\text{O}^-)\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) +$ $\text{CO}(\text{O}^-)\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) \rightarrow$ 2.000 $\text{CO}(\text{O}^-)\text{COCH}_2(\text{ONO}_2) + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 03949			$\text{CO}(\text{O}^-)\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) \xrightarrow{RO_2}$ $\text{CO}(\text{O}^-)\text{C}(\text{O}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 03950	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{O}\cdot)(\text{CO}(\text{O}^-))\text{CO}(\text{O}^-) \rightarrow 0.333 \text{CH}_2(\text{OH})\cdot +$ 0.333 $\text{CO}(\text{O}^-)\text{COCO}(\text{O}^-) + 0.667 \text{CH}_2(\text{OH})\text{COCO}(\text{O}^-) + 0.667 \cdot\text{CO}(\text{O}^-)$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03951			$\text{CO}(\text{O}^-)\text{C}(\text{O}\cdot)(\text{CO}(\text{O}^-))\text{CH}_2(\text{ONO}_2) \rightarrow$ 0.667 $\cdot\text{CO}(\text{O}^-) + 0.667 \text{CO}(\text{O}^-)\text{COCH}_2(\text{ONO}_2) +$ 0.333 $\text{CO}(\text{O}^-)\text{COCO}(\text{O}^-) + 0.333 \text{CH}_2\text{O} + 0.333 \text{NO}_2$	$5.0 \cdot 10^{+02}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00512	*	*	$\text{CO(OH)C(OH)(CO(O}^-))\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)(CO(OH))CO(O}^-)$	$8.3 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00513	*	*	$\text{CO(OH)C(OH)(CO(O}^-))\text{CHO} \rightleftharpoons \text{CO(O}^-)\text{C(OH)(CO(O}^-))\text{CHO} + \text{H}^+$	$1.3 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03952	*	*	$\text{CO(OH)C(OH)(CO(O}^-))\text{CHO} + \text{OH} \rightarrow$ $0.929 \text{ CO(OH)C(OH)(CO(O}^-))\text{CO(OO}\cdot) +$ $0.071 \text{ CO(OH)C(O}\cdot\text{)(CO(O}^-))\text{CHO} + \text{H}_2\text{O} - 0.929 \text{ O}_2$	$7.6 \cdot 10^{+08}$		
R <sub>o</sub> 03953	*		$\text{CO(OH)C(OH)(CO(O}^-))\text{CHO} + \text{NO}_3 \rightarrow$ $\text{CO(OH)C(OH)(CHO)CO(O}\cdot) + \text{NO}_3^-$	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 03954	*	*	$\text{CO(OH)C(OH)(CO(O}^-))\text{CO(OO}\cdot) \rightarrow$ $\text{CO(OH)C(OH)(CO(OH))CO(O}^-) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 03955	*	*	$\text{CO(OH)C(O}\cdot\text{)(CO(O}^-))\text{CHO} \rightarrow$ $0.333 \cdot \text{CO(OH)} + 0.333 \text{ CO(O}^-)\text{COCHO} + 0.333 \text{ CO(OH)COCHO} +$ $0.333 \cdot \text{CO(O}^-) + 0.333 \text{ CO(OH)COCO(O}^-) + 0.333 \text{ CH} \cdot (\text{OH})_2 - 0.333 \text{ H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03956	*		$\text{CO(OH)C(OH)(CHO)CO(O}\cdot) \rightarrow \text{CO(OH)C(OH)(OO}\cdot\text{)CHO} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00514	*	*	$\text{CH}_2(\text{OH})\text{C(OH)(CO(OH))CO(O}^-) \rightleftharpoons$ $\text{CH}_2(\text{OH})\text{C(OH)(CO(O}^-))\text{CO(O}^-) + \text{H}^+$	$4.0 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03957	*	*	$\text{CH}_2(\text{OH})\text{C(OH)(CO(OH))CO(O}^-) + \text{OH} \rightarrow$ $0.777 \text{ CO(OH)C(OH)(CO(O}^-))\text{CH(OH)(OO}\cdot) +$ $0.125 \text{ CO(OH)C(OH)(CO(O}^-))\text{CH}_2(\text{O}\cdot) +$ $0.098 \text{ CH}_2(\text{OH})\text{C(O}\cdot\text{)(CO(OH))CO(O}^-) + \text{H}_2\text{O} - 0.777 \text{ O}_2$	$6.7 \cdot 10^{+08}$		
R <sub>o</sub> 03958	*		$\text{CH}_2(\text{OH})\text{C(OH)(CO(OH))CO(O}^-) + \text{NO}_3 \rightarrow$ $\text{CH}_2(\text{OH})\text{C(OH)(CO(OH))CO(O}\cdot) + \text{NO}_3^-$	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 03959	*	*	$\text{CO(OH)C(OH)(CO(O}^-))\text{CH(OH)(OO}\cdot) \rightarrow$ $\text{CO(OH)C(OH)(CO(O}^-))\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03960	*		$\text{CH}_2(\text{OH})\text{C(OH)(CO(OH))CO(O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{C(OH)(OO}\cdot\text{)CO(OH)} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00515			$\text{CO(OH)C(ONO}_2\text{)(CO(O}^-))\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}}$ $\text{CH(OH)}_2\text{C(ONO}_2\text{)(CO(OH))CO(O}^-)$	$7.6 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00516			$\text{CO(OH)C(ONO}_2\text{)(CO(O}^-))\text{CHO} \rightleftharpoons \text{CO(O}^-)\text{C(ONO}_2\text{)(CO(O}^-))\text{CHO} + \text{H}^+$	$5.2 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03961			$\text{CO(OH)C(ONO}_2\text{)(CO(O}^-))\text{CHO} + \text{OH} \rightarrow$ $\text{CO(OH)C(ONO}_2\text{)(CO(O}^-))\text{CO(OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$7.0 \cdot 10^{+08}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03962			CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CHO + NO <sub>3</sub> → CO(OH)C(ONO <sub>2</sub> )(CHO)CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	2.5 · 10 <sup>+07</sup>		
R <sub>o</sub> 03963			CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(OO $\cdot$ ) → CO(OH)C(ONO <sub>2</sub> )(CO(OH))CO(O <sup>-</sup> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03964			CO(OH)C(ONO <sub>2</sub> )(CHO)CO(O $\cdot$ ) → CO(OH)C(ONO <sub>2</sub> )(OO $\cdot$ )CHO + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00517			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CO(O <sup>-</sup> ) ⇌ CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + H <sup>+</sup>	1.7 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 03965			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CO(O <sup>-</sup> ) + OH → 0.861 CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CH(OH)(OO $\cdot$ ) + 0.139 CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CH <sub>2</sub> (O $\cdot$ ) + H <sub>2</sub> O - 0.861 O <sub>2</sub>	6.0 · 10 <sup>+08</sup>		
R <sub>o</sub> 03966			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	2.5 · 10 <sup>+07</sup>		
R <sub>o</sub> 03967			CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CH(OH)(OO $\cdot$ ) → CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03968			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CO(O $\cdot$ ) → CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO $\cdot$ )CO(OH) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03969	*	*	CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CO(OH) + OH → 0.347 CH(OH) <sub>2</sub> C(OH)(CO(OH))C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.608 CH(OH) <sub>2</sub> C(OH)(CO(OH))CH(OH)(O $\cdot$ ) + 0.045 CH(OH) <sub>2</sub> C(O $\cdot$ )(CH(OH) <sub>2</sub> )CO(OH) + H <sub>2</sub> O - 0.347 O <sub>2</sub>	1.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 03970	*		CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CO(OH) + NO <sub>3</sub> → 0.347 CH(OH) <sub>2</sub> C(OH)(CO(OH))C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.608 CH(OH) <sub>2</sub> C(OH)(CO(OH))CH(OH)(O $\cdot$ ) + 0.045 CH(OH) <sub>2</sub> C(O $\cdot$ )(CH(OH) <sub>2</sub> )CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.347 O <sub>2</sub>	9.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 03971	*	*	CH(OH) <sub>2</sub> C(OH)(CO(OH))C(OH) <sub>2</sub> (OO $\cdot$ ) → CH(OH) <sub>2</sub> C(OH)(CO(OH))CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03972	*	*	CH(OH) <sub>2</sub> C(OH)(CO(OH))CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> C(OH)(CO(OH))CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03973	*	*	CH(OH) <sub>2</sub> C(OH)(CO(OH))CH(OH)(O $\cdot$ ) → CH(OH) <sub>2</sub> C(OH)(OO $\cdot$ )CO(OH) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03974	*	*	$\text{CH(OH)}_2\text{C(O}\cdot\text{)(CH(OH)}_2\text{)CO(OH)} \rightarrow 0.667 \text{CH}\cdot\text{(OH)}_2 +$ $0.667 \text{CH(OH)}_2\text{COCO(OH)} + 0.333 \text{CH(OH)}_2\text{COCH(OH)}_2 + 0.333 \cdot\text{CO(OH)}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03975	*	*	$\text{CH}_2\text{(OH)C(OH)(CH}_2\text{(OH))CO(OH)} + \text{OH} \rightarrow$ $0.804 \text{CH}_2\text{(OH)C(OH)(CO(OH))CH(OH)(OO}\cdot\text{)} +$ $0.145 \text{CH}_2\text{(OH)C(OH)(CO(OH))CH}_2\text{(O}\cdot\text{)} +$ $0.051 \text{CH}_2\text{(OH)C(O}\cdot\text{)(CH}_2\text{(OH))CO(OH)} + \text{H}_2\text{O} - 0.804 \text{O}_2$	$1.2 \cdot 10^{+09}$		
R <sub>o</sub> 03976	*		$\text{CH}_2\text{(OH)C(OH)(CH}_2\text{(OH))CO(OH)} + \text{NO}_3 \rightarrow$ $0.804 \text{CH}_2\text{(OH)C(OH)(CO(OH))CH(OH)(OO}\cdot\text{)} +$ $0.145 \text{CH}_2\text{(OH)C(OH)(CO(OH))CH}_2\text{(O}\cdot\text{)} +$ $0.051 \text{CH}_2\text{(OH)C(O}\cdot\text{)(CH}_2\text{(OH))CO(OH)} + \text{NO}_3^- + \text{H}^+ - 0.804 \text{O}_2$	$1.7 \cdot 10^{+03}$		
R <sub>o</sub> 03977	*	*	$\text{CH}_2\text{(OH)C(OH)(CO(OH))CH(OH)(OO}\cdot\text{)} \rightarrow$ $\text{CH}_2\text{(OH)C(OH)(CO(OH))CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 03978	*	*	$\text{CH}_3\text{C(OH)(CH(OH)}_2\text{)CO(OH)} + \text{OH} \rightarrow$ $0.148 \text{CH(OH)}_2\text{C(OH)(CO(OH))CH}_2\text{(OO}\cdot\text{)} +$ $0.302 \text{CH}_3\text{C(OH)(CO(OH))C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.077 \text{CH}_3\text{C(O}\cdot\text{)(CH(OH)}_2\text{)CO(OH)} +$ $0.473 \text{CH}_3\text{C(OH)(CO(OH))CH(OH)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.449 \text{O}_2$	$7.7 \cdot 10^{+08}$		
R <sub>o</sub> 03979	*		$\text{CH}_3\text{C(OH)(CH(OH)}_2\text{)CO(OH)} + \text{NO}_3 \rightarrow$ $0.148 \text{CH(OH)}_2\text{C(OH)(CO(OH))CH}_2\text{(OO}\cdot\text{)} +$ $0.302 \text{CH}_3\text{C(OH)(CO(OH))C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.077 \text{CH}_3\text{C(O}\cdot\text{)(CH(OH)}_2\text{)CO(OH)} +$ $0.473 \text{CH}_3\text{C(OH)(CO(OH))CH(OH)(O}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - 0.449 \text{O}_2$	$9.6 \cdot 10^{+06}$		
R <sub>o</sub> 03980	*	*	$\text{CH}_3\text{C(OH)(CO(OH))C(OH)}_2\text{(OO}\cdot\text{)} \rightarrow \text{CH}_3\text{C(OH)(CO(OH))CO(OH)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 03981	*	*	$\text{CH}_3\text{C(O}\cdot\text{)(CH(OH)}_2\text{)CO(OH)} \rightarrow$ $0.333 \text{CH}_3\text{(OO}\cdot\text{)} + 0.333 \text{CH(OH)}_2\text{COCO(OH)} + 0.333 \text{CH}_3\text{COCO(OH)} +$ $0.333 \text{CH}\cdot\text{(OH)}_2 + 0.333 \text{CH}_3\text{COCH(OH)}_2 + 0.333 \cdot\text{CO(OH)} - 0.333 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 03982	*	*	$\text{CH}_3\text{C(OH)(CO(OH))CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CH}_3\text{C(OH)(CO(OH))CO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 03983	*	*	$\text{CH}_3\text{C(OH)(CO(OH))CH(OH)(O}\cdot\text{)} \rightarrow$ $\text{CH}_3\text{C(OH)(OO}\cdot\text{)CO(OH)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03984			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CH(OH) <sub>2</sub> )CO(OH) + OH $\rightarrow$ 0.364 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.636 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CH(OH)(O $\cdot$ ) + H <sub>2</sub> O - 0.364 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 03985			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CH(OH) <sub>2</sub> )CO(OH) + NO <sub>3</sub> $\rightarrow$ 0.364 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.636 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CH(OH)(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.364 O <sub>2</sub>	9.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 03986			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03987			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 03988			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CH(OH)(O $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO $\cdot$ )CO(OH) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00518			CO(OH)C(ONO <sub>2</sub> )(CHO)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CH(OH) <sub>2</sub> )CO(OH)	6.5 · 10 <sup>+03</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03989			CO(OH)C(ONO <sub>2</sub> )(CHO)CHO + OH $\rightarrow$ CO(OH)C(ONO <sub>2</sub> )(CHO)CO(OO $\cdot$ ) + H <sub>2</sub> O - O <sub>2</sub>	1.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 03990			CO(OH)C(ONO <sub>2</sub> )(CHO)CHO + NO <sub>3</sub> $\rightarrow$ CO(OH)C(ONO <sub>2</sub> )(CHO)CO(OO $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	3.9 · 10 <sup>+06</sup>		
R <sub>o</sub> 03991			CO(OH)C(ONO <sub>2</sub> )(CHO)CO(OO $\cdot$ ) $\rightarrow$ CO(OH)C(ONO <sub>2</sub> )(CO(OH))CHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
E <sub>o</sub> 00519			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CH(OH) <sub>2</sub> )CO(OH)	1.6 · 10 <sup>+03</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 03992			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CHO + OH $\rightarrow$ 0.346 CO(OH)C(ONO <sub>2</sub> )(CHO)CH(OH)(OO $\cdot$ ) + 0.577 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CO(OO $\cdot$ ) + 0.076 CO(OH)C(ONO <sub>2</sub> )(CHO)CH <sub>2</sub> (O $\cdot$ ) + H <sub>2</sub> O - 0.924 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 03993			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CHO + NO <sub>3</sub> $\rightarrow$ 0.346 CO(OH)C(ONO <sub>2</sub> )(CHO)CH(OH)(OO $\cdot$ ) + 0.577 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CO(OO $\cdot$ ) + 0.076 CO(OH)C(ONO <sub>2</sub> )(CHO)CH <sub>2</sub> (O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.924 O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 03994			CO(OH)C(ONO <sub>2</sub> )(CHO)CH(OH)(OO $\cdot$ ) $\rightarrow$ CO(OH)C(ONO <sub>2</sub> )(CHO)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 03995			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CO(OO·) → CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CO(OH) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 03996			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CH <sub>2</sub> (OH))CO(OH) + OH → 0.847 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CH(OH)(OO·) + 0.153 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (O·) + H <sub>2</sub> O – 0.847 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 03997			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CH <sub>2</sub> (OH))CO(OH) + NO <sub>3</sub> → 0.847 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CH(OH)(OO·) + 0.153 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.847 O <sub>2</sub>	1.7 · 10 <sup>+03</sup>		
R <sub>o</sub> 03998			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CH(OH)(OO·) → CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(OH))CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 03999			CH <sub>3</sub> C(ONO <sub>2</sub> )(CH(OH) <sub>2</sub> )CO(OH) + OH → 0.160 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (OO·) + 0.327 CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))C(OH) <sub>2</sub> (OO·) + 0.513 CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CH(OH)(O·) + H <sub>2</sub> O – 0.487 O <sub>2</sub>	7.1 · 10 <sup>+08</sup>		
R <sub>o</sub> 04000			CH <sub>3</sub> C(ONO <sub>2</sub> )(CH(OH) <sub>2</sub> )CO(OH) + NO <sub>3</sub> → 0.160 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (OO·) + 0.327 CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))C(OH) <sub>2</sub> (OO·) + 0.513 CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.487 O <sub>2</sub>	9.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 04001			CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))C(OH) <sub>2</sub> (OO·) → CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04002			CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04003			CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CH(OH)(O·) → CH <sub>3</sub> C(ONO <sub>2</sub> )(OO·)CO(OH) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00520	*	*	CO(OH)C(OH)(CHO)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CO(OH)	7.1 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04004	*	*	CO(OH)C(OH)(CHO)CHO + OH → 0.963 CO(OH)C(OH)(CHO)CO(OO·) + 0.037 CO(OH)C(O·)(CHO)CHO + H <sub>2</sub> O – 0.963 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04005	*		CO(OH)C(OH)(CHO)CHO + NO <sub>3</sub> → 0.963 CO(OH)C(OH)(CHO)CO(OO·) + 0.037 CO(OH)C(O·)(CHO)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.963 O <sub>2</sub>	3.5 · 10 <sup>+06</sup>		
R <sub>o</sub> 04006	*	*	CO(OH)C(OH)(CHO)CO(OO·) → CO(OH)C(OH)(CO(OH))CHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04007	*	*	CO(OH)C(O·)(CHO)CHO → 0.333 · CO(OH) + 0.333 CHOCOCHO + 0.667 CO(OH)COCHO + 0.667 CH · (OH) <sub>2</sub> - 0.667 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00521	*	*	CH <sub>2</sub> (OH)C(OH)(CO(OH))CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CO(OH)	1.7 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04008	*	*	CH <sub>2</sub> (OH)C(OH)(CO(OH))CHO + OH → 0.332 CO(OH)C(OH)(CHO)CH(OH)(OO·) + 0.553 CH <sub>2</sub> (OH)C(OH)(CO(OH))CO(OO·) + 0.073 CO(OH)C(OH)(CHO)CH <sub>2</sub> (O·) + 0.042 CH <sub>2</sub> (OH)C(O·)(CO(OH))CHO + H <sub>2</sub> O - 0.885 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 04009	*		CH <sub>2</sub> (OH)C(OH)(CO(OH))CHO + NO <sub>3</sub> → 0.332 CO(OH)C(OH)(CHO)CH(OH)(OO·) + 0.553 CH <sub>2</sub> (OH)C(OH)(CO(OH))CO(OO·) + 0.073 CO(OH)C(OH)(CHO)CH <sub>2</sub> (O·) + 0.042 CH <sub>2</sub> (OH)C(O·)(CO(OH))CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.885 O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 04010	*	*	CO(OH)C(OH)(CHO)CH(OH)(OO·) → CO(OH)C(OH)(CHO)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04011	*	*	CH <sub>2</sub> (OH)C(OH)(CO(OH))CO(OO·) → CH <sub>2</sub> (OH)C(OH)(CO(OH))CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
E <sub>o</sub> 00522	*	*	CO(OH)C(OH)(CO(OH))CO(OH) ⇌ CO(OH)C(OH)(CO(OH))CO(O <sup>-</sup> ) + H <sup>+</sup>	7.1 · 10 <sup>-03</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04012	*	*	CO(OH)C(OH)(CO(OH))CO(OH) + OH → 0.918 CO(OH)C(O·)(CO(OH))CO(OH) + 0.082 CO(OH)C(OH)(CO(OH))CO(O·) + H <sub>2</sub> O	2.6 · 10 <sup>+07</sup>		
R <sub>o</sub> 04013	*		CO(OH)C(OH)(CO(OH))CO(OH) + NO <sub>3</sub> → 0.918 CO(OH)C(O·)(CO(OH))CO(OH) + 0.082 CO(OH)C(OH)(CO(OH))CO(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	6.2 · 10 <sup>+05</sup>		
R <sub>o</sub> 04014	*	*	CO(OH)C(O·)(CO(OH))CO(OH) → ·CO(OH) + CO(OH)COCO(OH)	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04015	*	*	CO(OH)C(OH)(CO(OH))CO(O $\cdot$ ) $\rightarrow$ CO(OH)C(OH)(OO $\cdot$ )CO(OH) + CO <sub>2</sub> - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00523			CO(OH)C(ONO <sub>2</sub> )(CO(OH))CO(OH) $\rightleftharpoons$ CO(OH)C(ONO <sub>2</sub> )(CO(OH))CO(O $\cdot$ ) + H <sup>+</sup>	$2.9 \cdot 10^{-02}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04016			CO(OH)C(ONO <sub>2</sub> )(CO(OH))CO(OH) + OH $\rightarrow$ CO(OH)C(ONO <sub>2</sub> )(CO(OH))CO(O $\cdot$ ) + H <sub>2</sub> O	$2.1 \cdot 10^{+06}$		
R <sub>o</sub> 04017			CO(OH)C(ONO <sub>2</sub> )(CO(OH))CO(OH) + NO <sub>3</sub> $\rightarrow$ CO(OH)C(ONO <sub>2</sub> )(CO(OH))CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	$6.2 \cdot 10^{+05}$		
R <sub>o</sub> 04018			CO(OH)C(ONO <sub>2</sub> )(CO(OH))CO(O $\cdot$ ) $\rightarrow$ CO(OH)C(ONO <sub>2</sub> )(OO $\cdot$ )CO(OH) + CO <sub>2</sub> - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00524	*	*	CH(OH) <sub>2</sub> C(OH)(CO(OH))CO(OH) $\rightleftharpoons$ CH(OH) <sub>2</sub> C(OH)(CO(OH))CO(O $\cdot$ ) + H <sup>+</sup>	$1.5 \cdot 10^{-03}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04019	*	*	CH(OH) <sub>2</sub> C(OH)(CO(OH))CO(OH) + OH $\rightarrow$ 0.258 CO(OH)C(OH)(CO(OH))C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.676 CO(OH)C(OH)(CO(OH))CH(OH)(O $\cdot$ ) + 0.066 CH(OH) <sub>2</sub> C(O $\cdot$ )(CO(OH))CO(OH) + H <sub>2</sub> O - 0.258 O <sub>2</sub>	$5.4 \cdot 10^{+08}$		
R <sub>o</sub> 04020	*		CH(OH) <sub>2</sub> C(OH)(CO(OH))CO(OH) + NO <sub>3</sub> $\rightarrow$ 0.258 CO(OH)C(OH)(CO(OH))C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.676 CO(OH)C(OH)(CO(OH))CH(OH)(O $\cdot$ ) + 0.066 CH(OH) <sub>2</sub> C(O $\cdot$ )(CO(OH))CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.258 O <sub>2</sub>	$8.1 \cdot 10^{+06}$		
R <sub>o</sub> 04021	*	*	CO(OH)C(OH)(CO(OH))C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)C(OH)(CO(OH))CO(OH) + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04022	*	*	CO(OH)C(OH)(CO(OH))CH(OH)(O $\cdot$ ) $\xrightarrow{\text{O}_2}$ CO(OH)C(OH)(CO(OH))CO(OH) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04023	*	*	CO(OH)C(OH)(CO(OH))CH(OH)(O $\cdot$ ) $\rightarrow$ CO(OH)C(OH)(OO $\cdot$ )CO(OH) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04024	*	*	CH(OH) <sub>2</sub> C(O $\cdot$ )(CO(OH))CO(OH) $\rightarrow$ 0.333 CH $\cdot$ (OH) <sub>2</sub> + 0.333 CO(OH)COCO(OH) + 0.667 CH(OH) <sub>2</sub> COCO(OH) + 0.667 $\cdot$ CO(OH)	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00525			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CO(OH) $\rightleftharpoons$ CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CO(O $\cdot$ ) + H <sup>+</sup>	$6.1 \cdot 10^{-03}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04025			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CO(OH) + OH → 0.276 CO(OH)C(ONO <sub>2</sub> )(CO(OH))C(OH) <sub>2</sub> (OO·) + 0.724 CO(OH)C(ONO <sub>2</sub> )(CO(OH))CH(OH)(O·) + H <sub>2</sub> O – 0.276 O <sub>2</sub>	5.0 · 10 <sup>+08</sup>		
R <sub>o</sub> 04026			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CO(OH) + NO <sub>3</sub> → 0.276 CO(OH)C(ONO <sub>2</sub> )(CO(OH))C(OH) <sub>2</sub> (OO·) + 0.724 CO(OH)C(ONO <sub>2</sub> )(CO(OH))CH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.276 O <sub>2</sub>	8.1 · 10 <sup>+06</sup>		
R <sub>o</sub> 04027			CO(OH)C(ONO <sub>2</sub> )(CO(OH))C(OH) <sub>2</sub> (OO·) → CO(OH)C(ONO <sub>2</sub> )(CO(OH))CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04028			CO(OH)C(ONO <sub>2</sub> )(CO(OH))CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(ONO <sub>2</sub> )(CO(OH))CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04029			CO(OH)C(ONO <sub>2</sub> )(CO(OH))CH(OH)(O·) → CO(OH)C(ONO <sub>2</sub> )(OO·)CO(OH) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04030			CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CO(OH) + OH → CO(OH)C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (OO·) + H <sub>2</sub> O – O <sub>2</sub>	7.5 · 10 <sup>+07</sup>		
R <sub>o</sub> 04031			CH <sub>3</sub> C(ONO <sub>2</sub> )(CO(OH))CO(OH) + NO <sub>3</sub> → CO(OH)C(ONO <sub>2</sub> )(CO(OH))CH <sub>2</sub> (OO·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – O <sub>2</sub>	2.3 · 10 <sup>+04</sup>		
R <sub>o</sub> 04032	*	*	CH <sub>3</sub> C(OH)(CO(OH))CO(OH) + OH → 0.656 CO(OH)C(OH)(CO(OH))CH <sub>2</sub> (OO·) + 0.344 CH <sub>3</sub> C(O·)(CO(OH))CO(OH) + H <sub>2</sub> O – 0.656 O <sub>2</sub>	1.2 · 10 <sup>+08</sup>		
R <sub>o</sub> 04033	*		CH <sub>3</sub> C(OH)(CO(OH))CO(OH) + NO <sub>3</sub> → 0.656 CO(OH)C(OH)(CO(OH))CH <sub>2</sub> (OO·) + 0.344 CH <sub>3</sub> C(O·)(CO(OH))CO(OH) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.656 O <sub>2</sub>	2.3 · 10 <sup>+04</sup>		
R <sub>o</sub> 04034	*	*	CH <sub>3</sub> C(O·)(CO(OH))CO(OH) → 0.333 CH <sub>3</sub> (OO·) + 0.333 CO(OH)COCO(OH) + 0.667 CH <sub>3</sub> COCO(OH) + 0.667 · CO(OH) – 0.333 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04035	*	*	CH <sub>2</sub> (OH)C(OH)(CO(O <sup>–</sup> ))CO(O <sup>–</sup> ) + OH → 0.821 CO(O <sup>–</sup> )C(OH)(CO(O <sup>–</sup> ))CH(OH)(OO·) + 0.075 CO(O <sup>–</sup> )C(OH)(CO(O <sup>–</sup> ))CH <sub>2</sub> (O·) + 0.104 CH <sub>2</sub> (OH)C(O·)(CO(O <sup>–</sup> ))CO(O <sup>–</sup> ) + H <sub>2</sub> O – 0.821 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04036	*		CH <sub>2</sub> (OH)C(OH)(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + NO <sub>3</sub> → 0.500 CH <sub>2</sub> (OH)C(OH)(CO(O <sup>-</sup> ))CO(O <sup>·</sup> ) + 0.500 CH <sub>2</sub> (OH)C(OH)(CO(O <sup>-</sup> ))CO(O <sup>·</sup> ) + NO <sub>3</sub> <sup>-</sup>	7.8 · 10 <sup>+07</sup>		
R <sub>o</sub> 04037	*	*	CO(O <sup>-</sup> )C(OH)(CO(O <sup>-</sup> ))CH(OH)(OO <sup>·</sup> ) → CO(O <sup>-</sup> )C(OH)(CO(O <sup>-</sup> ))CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04038	*		CH <sub>2</sub> (OH)C(OH)(CO(O <sup>-</sup> ))CO(O <sup>·</sup> ) → CH <sub>2</sub> (OH)C(OH)(OO <sup>·</sup> )CO(O <sup>-</sup> ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00526	*	*	CO(O <sup>-</sup> )C(OH)(CO(O <sup>-</sup> ))CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH)(CO(O <sup>-</sup> ))CO(O <sup>-</sup> )	7.4 · 10 <sup>+00</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04039	*	*	CO(O <sup>-</sup> )C(OH)(CO(O <sup>-</sup> ))CHO + OH → 0.929 CO(O <sup>-</sup> )C(OH)(CO(O <sup>-</sup> ))CO(OO <sup>·</sup> ) + 0.071 CO(O <sup>-</sup> )C(O <sup>·</sup> )(CO(O <sup>-</sup> ))CHO + H <sub>2</sub> O - 0.929 O <sub>2</sub>	1.3 · 10 <sup>+09</sup>		
R <sub>o</sub> 04040	*		CO(O <sup>-</sup> )C(OH)(CO(O <sup>-</sup> ))CHO + NO <sub>3</sub> → 0.500 CO(O <sup>-</sup> )C(OH)(CHO)CO(O <sup>·</sup> ) + 0.500 CO(O <sup>-</sup> )C(OH)(CHO)CO(O <sup>·</sup> ) + NO <sub>3</sub> <sup>-</sup>	7.8 · 10 <sup>+07</sup>		
R <sub>o</sub> 04041	*	*	CO(O <sup>-</sup> )C(OH)(CO(O <sup>-</sup> ))CO(OO <sup>·</sup> ) → CO(OH)C(OH)(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04042	*	*	CO(O <sup>-</sup> )C(O <sup>·</sup> )(CO(O <sup>-</sup> ))CHO → 0.667 · CO(O <sup>-</sup> ) + 0.667 CO(O <sup>-</sup> )COCHO + 0.333 CO(O <sup>-</sup> )COCO(O <sup>-</sup> ) + 0.333 CH <sup>·</sup> (OH) <sub>2</sub> - 0.333 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04043	*		CO(O <sup>-</sup> )C(OH)(CHO)CO(O <sup>·</sup> ) → CO(O <sup>-</sup> )C(OH)(OO <sup>·</sup> )CHO + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04044			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + OH → 0.916 CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CH(OH)(OO <sup>·</sup> ) + 0.084 CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CH <sub>2</sub> (O <sup>·</sup> ) + H <sub>2</sub> O - 0.916 O <sub>2</sub>	9.9 · 10 <sup>+08</sup>		
R <sub>o</sub> 04045			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + NO <sub>3</sub> → 0.500 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O <sup>·</sup> ) + 0.500 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O <sup>·</sup> ) + NO <sub>3</sub> <sup>-</sup>	7.8 · 10 <sup>+07</sup>		
R <sub>o</sub> 04046			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CH(OH)(OO <sup>·</sup> ) → CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04047			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O <sup>·</sup> ) → CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO <sup>·</sup> )CO(O <sup>-</sup> ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00527			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O <sup>-</sup> )	6.7 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04048			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CHO + OH → CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(OO·) + H <sub>2</sub> O - O <sub>2</sub>	1.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 04049			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CHO + NO <sub>3</sub> → 0.500 CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CHO)CO(O·) + 0.500 CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CHO)CO(O·) + NO <sub>3</sub> <sup>-</sup>	7.8 · 10 <sup>+07</sup>		
R <sub>o</sub> 04050			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(OO·) → CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04051			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CHO)CO(O·) → CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO·)CHO + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00528			CO(OH)C(ONO <sub>2</sub> )(CO(OH))CO(O <sup>-</sup> ) ⇌ CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + H <sup>+</sup>	2.4 · 10 <sup>-03</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04052			CO(OH)C(ONO <sub>2</sub> )(CO(OH))CO(O <sup>-</sup> ) + OH → CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O·) + H <sub>2</sub> O	1.4 · 10 <sup>+06</sup>		
R <sub>o</sub> 04053			CO(OH)C(ONO <sub>2</sub> )(CO(OH))CO(O <sup>-</sup> ) + NO <sub>3</sub> → CO(OH)C(ONO <sub>2</sub> )(CO(OH))CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.5 · 10 <sup>+07</sup>		
R <sub>o</sub> 04054			CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O·) → CO(OH)C(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00529	*	*	CO(OH)C(OH)(CO(OH))CO(O <sup>-</sup> ) ⇌ CO(OH)C(OH)(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + H <sup>+</sup>	5.9 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04055	*	*	CO(OH)C(OH)(CO(OH))CO(O <sup>-</sup> ) + OH → 0.967 CO(OH)C(O·)(CO(OH))CO(O <sup>-</sup> ) + 0.033 CO(OH)C(OH)(CO(O <sup>-</sup> ))CO(O·) + H <sub>2</sub> O	4.3 · 10 <sup>+07</sup>		
R <sub>o</sub> 04056	*		CO(OH)C(OH)(CO(OH))CO(O <sup>-</sup> ) + NO <sub>3</sub> → CO(OH)C(OH)(CO(OH))CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.5 · 10 <sup>+07</sup>		
R <sub>o</sub> 04057	*	*	CO(OH)C(O·)(CO(OH))CO(O <sup>-</sup> ) → 0.667 · CO(OH) + 0.667 CO(OH)COCO(O <sup>-</sup> ) + 0.333 CO(OH)COCO(OH) + 0.333 · CO(O <sup>-</sup> )	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04058	*	*	CO(OH)C(OH)(CO(O <sup>-</sup> ))CO(O·) → CO(OH)C(OH)(OO·)CO(O <sup>-</sup> ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00530			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CO(O <sup>-</sup> ) ⇌ CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + H <sup>+</sup>	2.6 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04059			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CO(O <sup>-</sup> ) + OH → 0.401 CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))C(OH) <sub>2</sub> (OO·) + 0.599 CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CH(OH)(O·) + H <sub>2</sub> O - 0.401 O <sub>2</sub>	6.1 · 10 <sup>+08</sup>		
R <sub>o</sub> 04060			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.5 · 10 <sup>+07</sup>		
R <sub>o</sub> 04061			CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))C(OH) <sub>2</sub> (OO·) → CO(OH)C(ONO <sub>2</sub> )(CO(OH))CO(O <sup>-</sup> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04062			CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(ONO <sub>2</sub> )(CO(OH))CO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04063			CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CH(OH)(O·) → CO(OH)C(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04064			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(OH))CO(O·) → CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CO(OH) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00531	*	*	CH(OH) <sub>2</sub> C(OH)(CO(OH))CO(O <sup>-</sup> ) ⇌ CH(OH) <sub>2</sub> C(OH)(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + H <sup>+</sup>	6.4 · 10 <sup>-05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04065	*	*	CH(OH) <sub>2</sub> C(OH)(CO(OH))CO(O <sup>-</sup> ) + OH → 0.364 CO(OH)C(OH)(CO(O <sup>-</sup> ))C(OH) <sub>2</sub> (OO·) + 0.543 CO(OH)C(OH)(CO(O <sup>-</sup> ))CH(OH)(O·) + 0.093 CH(OH) <sub>2</sub> C(O·)(CO(OH))CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.364 O <sub>2</sub>	6.7 · 10 <sup>+08</sup>		
R <sub>o</sub> 04066	*		CH(OH) <sub>2</sub> C(OH)(CO(OH))CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH(OH) <sub>2</sub> C(OH)(CO(OH))CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.5 · 10 <sup>+07</sup>		
R <sub>o</sub> 04067	*	*	CO(OH)C(OH)(CO(O <sup>-</sup> ))C(OH) <sub>2</sub> (OO·) → CO(OH)C(OH)(CO(OH))CO(O <sup>-</sup> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04068	*	*	CO(OH)C(OH)(CO(O <sup>-</sup> ))CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(OH)(CO(OH))CO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04069	*	*	CO(OH)C(OH)(CO(O <sup>-</sup> ))CH(OH)(O·) → CO(OH)C(OH)(OO·)CO(O <sup>-</sup> ) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04070	*	*	CH(OH) <sub>2</sub> C(O·)(CO(OH))CO(O <sup>-</sup> ) → 0.333 CH · (OH) <sub>2</sub> + 0.333 CO(OH)COCO(O <sup>-</sup> ) + 0.333 CH(OH) <sub>2</sub> COCO(O <sup>-</sup> ) + 0.333 · CO(OH) + 0.333 CH(OH) <sub>2</sub> COCO(OH) + 0.333 · CO(O <sup>-</sup> )	5.0 · 10 <sup>+02</sup>		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04071	*		CH(OH) <sub>2</sub> C(OH)(CO(OH))CO(O·) → CH(OH) <sub>2</sub> C(OH)(OO·)CO(OH) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00532			CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) ⇌ CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + H <sup>+</sup>	1.0 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04072			CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + OH → CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O·) + H <sub>2</sub> O	7.0 · 10 <sup>+05</sup>		
R <sub>o</sub> 04073			CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + NO <sub>3</sub> → 0.500 CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O·) + 0.500 CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O·) + NO <sub>3</sub> <sup>-</sup>	7.8 · 10 <sup>+07</sup>		
R <sub>o</sub> 04074			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O·) → CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04075			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + OH → 0.541 CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))C(OH) <sub>2</sub> (OO·) + 0.459 CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CH(OH)(O·) + H <sub>2</sub> O - 0.541 O <sub>2</sub>	7.9 · 10 <sup>+08</sup>		
R <sub>o</sub> 04076			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + NO <sub>3</sub> → 0.500 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O·) + 0.500 CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O·) + NO <sub>3</sub> <sup>-</sup>	7.8 · 10 <sup>+07</sup>		
R <sub>o</sub> 04077			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))C(OH) <sub>2</sub> (OO·) → CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04078			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04079			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CH(OH)(O·) → CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04080			CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O·) → CH(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00533	*	*	CO(OH)C(OH)(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) ⇌ CO(O <sup>-</sup> )C(OH)(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + H <sup>+</sup>	2.5 · 10 <sup>-05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04081	*	*	CO(OH)C(OH)(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + OH → CO(OH)C(O·)(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + H <sub>2</sub> O	7.3 · 10 <sup>+07</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04082	*		CO(OH)C(OH)(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + NO <sub>3</sub> → 0.500 CO(OH)C(OH)(CO(O <sup>-</sup> ))CO(O <sup>·</sup> ) + 0.500 CO(OH)C(OH)(CO(O <sup>-</sup> ))CO(O <sup>·</sup> ) + NO <sub>3</sub> <sup>-</sup>	7.8 · 10 <sup>+07</sup>		
R <sub>o</sub> 04083	*	*	CO(OH)C(O <sup>·</sup> )(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) → 0.333 · CO(OH) + 0.333 CO(O <sup>-</sup> )COCO(O <sup>-</sup> ) + 0.667 CO(OH)COCO(O <sup>-</sup> ) + 0.667 · CO(O <sup>-</sup> )	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04084	*	*	CH(OH) <sub>2</sub> C(OH)(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + OH → 0.475 CO(O <sup>-</sup> )C(OH)(CO(O <sup>-</sup> ))C(OH) <sub>2</sub> (OO <sup>·</sup> ) + 0.404 CO(O <sup>-</sup> )C(OH)(CO(O <sup>-</sup> ))CH(OH)(O <sup>·</sup> ) + 0.122 CH(OH) <sub>2</sub> C(O <sup>·</sup> )(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.475 O <sub>2</sub>	9.0 · 10 <sup>+08</sup>		
R <sub>o</sub> 04085	*		CH(OH) <sub>2</sub> C(OH)(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + NO <sub>3</sub> → 0.500 CH(OH) <sub>2</sub> C(OH)(CO(O <sup>-</sup> ))CO(O <sup>·</sup> ) + 0.500 CH(OH) <sub>2</sub> C(OH)(CO(O <sup>-</sup> ))CO(O <sup>·</sup> ) + NO <sub>3</sub> <sup>-</sup>	7.8 · 10 <sup>+07</sup>		
R <sub>o</sub> 04086	*	*	CO(O <sup>-</sup> )C(OH)(CO(O <sup>-</sup> ))C(OH) <sub>2</sub> (OO <sup>·</sup> ) → CO(OH)C(OH)(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04087	*	*	CO(O <sup>-</sup> )C(OH)(CO(O <sup>-</sup> ))CH(OH)(O <sup>·</sup> ) $\xrightarrow{O_2}$ CO(OH)C(OH)(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04088	*	*	CO(O <sup>-</sup> )C(OH)(CO(O <sup>-</sup> ))CH(OH)(O <sup>·</sup> ) → CO(O <sup>-</sup> )C(OH)(OO <sup>·</sup> )CO(O <sup>-</sup> ) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04089	*	*	CH(OH) <sub>2</sub> C(O <sup>·</sup> )(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) → 0.333 CH · (OH) <sub>2</sub> + 0.333 CO(O <sup>-</sup> )COCO(O <sup>-</sup> ) + 0.667 CH(OH) <sub>2</sub> COCO(O <sup>-</sup> ) + 0.667 · CO(O <sup>-</sup> )	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04090	*		CH(OH) <sub>2</sub> C(OH)(CO(O <sup>-</sup> ))CO(O <sup>·</sup> ) → CH(OH) <sub>2</sub> C(OH)(OO <sup>·</sup> )CO(O <sup>-</sup> ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04091	*	*	CO(O <sup>-</sup> )C(OH)(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + OH → CO(O <sup>-</sup> )C(O <sup>·</sup> )(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + H <sub>2</sub> O	1.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04092	*		CO(O <sup>-</sup> )C(OH)(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + NO <sub>3</sub> → 0.333 CO(O <sup>-</sup> )C(OH)(CO(O <sup>-</sup> ))CO(O <sup>·</sup> ) + 0.333 CO(O <sup>-</sup> )C(OH)(CO(O <sup>-</sup> ))CO(O <sup>·</sup> ) + 0.333 CO(O <sup>-</sup> )C(OH)(CO(O <sup>-</sup> ))CO(O <sup>·</sup> ) + NO <sub>3</sub> <sup>-</sup>	7.8 · 10 <sup>+07</sup>		
R <sub>o</sub> 04093	*	*	CO(O <sup>-</sup> )C(O <sup>·</sup> )(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) → ·CO(O <sup>-</sup> ) + CO(O <sup>-</sup> )COCO(O <sup>-</sup> )	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04094	*		CO(O <sup>-</sup> )C(OH)(CO(O <sup>-</sup> ))CO(O <sup>·</sup> ) → CO(O <sup>-</sup> )C(OH)(OO <sup>·</sup> )CO(O <sup>-</sup> ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04095			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + NO <sub>3</sub> → 0.333 CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O <sup>·</sup> ) + 0.333 CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O <sup>·</sup> ) + 0.333 CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(CO(O <sup>-</sup> ))CO(O <sup>·</sup> ) + NO <sub>3</sub> <sup>-</sup>	7.8 · 10 <sup>+07</sup>		
E <sub>o</sub> 00534	*	*	CH <sub>3</sub> CH(CO(OH))CHO $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> CH(CH(OH) <sub>2</sub> )CO(OH)	1.4 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00535	*	*	CH <sub>3</sub> CH(CO(OH))CHO $\rightleftharpoons$ CH <sub>3</sub> CH(CO(O <sup>-</sup> ))CHO + H <sup>+</sup>	5.9 · 10 <sup>-05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04096	*	*	CH <sub>3</sub> CH(CO(OH))CHO + OH → 0.126 CO(OH)CH(CHO)CH <sub>2</sub> (OO <sup>·</sup> ) + 0.874 CH <sub>3</sub> CH(CO(OH))CO(OO <sup>·</sup> ) + H <sub>2</sub> O - O <sub>2</sub>	1.9 · 10 <sup>+09</sup>		
R <sub>o</sub> 04097	*		CH <sub>3</sub> CH(CO(OH))CHO + NO <sub>3</sub> → 0.126 CO(OH)CH(CHO)CH <sub>2</sub> (OO <sup>·</sup> ) + 0.874 CH <sub>3</sub> CH(CO(OH))CO(OO <sup>·</sup> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	1.7 · 10 <sup>+07</sup>		
R <sub>o</sub> 04098	*	*	CO(OH)CH(CHO)CH <sub>2</sub> (OO <sup>·</sup> ) $\xrightarrow{RO_2}$ 0.200 CO(OH)CH(CHO)CH <sub>2</sub> (O <sup>·</sup> ) + 0.550 CO(OH)CH(CHO)CHO + 0.250 CH <sub>2</sub> (OH)CH(CO(OH))CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04099	*	*	CH <sub>3</sub> CH(CO(OH))CO(OO <sup>·</sup> ) → CH <sub>3</sub> CH(CO(OH))CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04100	*	*	CO(OH)CH(CHO)CH <sub>2</sub> (O <sup>·</sup> ) $\xrightarrow{O_2}$ CO(OH)CH(CHO)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04101	*	*	CO(OH)CH(CHO)CH <sub>2</sub> (O <sup>·</sup> ) → CO(OH)CH(OO <sup>·</sup> )CHO + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04102	*	*	CO(OH)CH(OO <sup>·</sup> )CHO + CO(OH)CH(OO <sup>·</sup> )CHO → 2.000 CHOCHO + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 04103	*	*	CO(OH)CH(OO <sup>·</sup> )CHO $\xrightarrow{RO_2}$ 0.200 CO(OH)CH(O <sup>·</sup> )CHO + 0.550 CO(OH)COCHO + 0.250 CO(OH)CH(OH)CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
E <sub>o</sub> 00536	*	*	CH <sub>3</sub> CH(CO(O <sup>-</sup> ))CHO $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> CH(CH(OH) <sub>2</sub> )CO(O <sup>-</sup> )	1.2 · 10 <sup>+00</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04104	*	*	CH <sub>3</sub> CH(CO(O <sup>-</sup> ))CHO + OH → 0.126 CO(O <sup>-</sup> )CH(CHO)CH <sub>2</sub> (OO <sup>·</sup> ) + 0.874 CH <sub>3</sub> CH(CO(O <sup>-</sup> ))CO(OO <sup>·</sup> ) + H <sub>2</sub> O - O <sub>2</sub>	3.4 · 10 <sup>+09</sup>		
R <sub>o</sub> 04105	*		CH <sub>3</sub> CH(CO(O <sup>-</sup> ))CHO + NO <sub>3</sub> → CH <sub>3</sub> CH(CHO)CO(O <sup>·</sup> ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 04106	*	*	CO(O <sup>-</sup> )CH(CHO)CH <sub>2</sub> (OO <sup>·</sup> ) $\xrightarrow{RO_2}$ 0.200 CO(O <sup>-</sup> )CH(CHO)CH <sub>2</sub> (O <sup>·</sup> ) + 0.550 CO(O <sup>-</sup> )CH(CHO)CHO + 0.250 CH <sub>2</sub> (OH)CH(CO(O <sup>-</sup> ))CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04107	*	*	CH <sub>3</sub> CH(CO(O <sup>-</sup> ))CO(OO <sup>·</sup> ) → CH <sub>3</sub> CH(CO(OH))CO(O <sup>-</sup> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04108	*		CH <sub>3</sub> CH(CHO)CO(O <sup>·</sup> ) → CH <sub>3</sub> CH(OO <sup>·</sup> )CHO + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04109	*	*	CO(O <sup>-</sup> )CH(CHO)CH <sub>2</sub> (O <sup>·</sup> ) $\xrightarrow{O_2}$ CO(O <sup>-</sup> )CH(CHO)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04110	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{CHO})\text{CH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{CH}(\text{OO}\cdot)\text{CHO} + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04111	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OO}\cdot)\text{CHO} + \text{CO}(\text{O}^-)\text{CH}(\text{OO}\cdot)\text{CHO} \rightarrow$ $2.000 \text{ CHOCHO} + 2.000 \text{ CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{ OH}^- - 2.000 \text{ H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 04112	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{OO}\cdot)\text{CHO} \xrightarrow{\text{RO}_2} 0.200 \text{ CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{CHO} +$ $0.550 \text{ CO}(\text{O}^-)\text{COCHO} + 0.250 \text{ CO}(\text{O}^-)\text{CH}(\text{OH})\text{CHO} + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
E <sub>o</sub> 00537	*	*	$\text{CH}_3\text{CH}(\text{CH}(\text{OH})_2)\text{CO}(\text{OH}) \rightleftharpoons \text{CH}_3\text{CH}(\text{CH}(\text{OH})_2)\text{CO}(\text{O}^-) + \text{H}^+$	$3.4 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04113	*	*	$\text{CH}_3\text{CH}(\text{CH}(\text{OH})_2)\text{CO}(\text{OH}) + \text{OH} \rightarrow$ $0.228 \text{ CH}(\text{OH})_2\text{CH}(\text{CO}(\text{OH}))\text{CH}_2(\text{OO}\cdot) +$ $0.467 \text{ CH}_3\text{CH}(\text{CO}(\text{OH}))\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.305 \text{ CH}_3\text{CH}(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.695 \text{ O}_2$	$1.2 \cdot 10^{+09}$		
R <sub>o</sub> 04114	*		$\text{CH}_3\text{CH}(\text{CH}(\text{OH})_2)\text{CO}(\text{OH}) + \text{NO}_3 \rightarrow$ $0.228 \text{ CH}(\text{OH})_2\text{CH}(\text{CO}(\text{OH}))\text{CH}_2(\text{OO}\cdot) +$ $0.467 \text{ CH}_3\text{CH}(\text{CO}(\text{OH}))\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.305 \text{ CH}_3\text{CH}(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.695 \text{ O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 04115	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{OH}))\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CH}(\text{OH})_2\text{CH}(\text{CO}(\text{OH}))\text{CH}_2(\text{O}\cdot) + 0.550 \text{ CH}(\text{OH})_2\text{CH}(\text{CO}(\text{OH}))\text{CHO} +$ $0.250 \text{ CH}_2(\text{OH})\text{CH}(\text{CH}(\text{OH})_2)\text{CO}(\text{OH}) + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04116	*	*	$\text{CH}_3\text{CH}(\text{CO}(\text{OH}))\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{CO}(\text{OH}))\text{CO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04117	*	*	$\text{CH}_3\text{CH}(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_3\text{CH}(\text{CO}(\text{OH}))\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04118	*	*	$\text{CH}_3\text{CH}(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OO}\cdot)\text{CO}(\text{OH}) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04119	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{OH}))\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{OH}))\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04120	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{OH}))\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CH}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CO}(\text{OH}) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04121	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CO}(\text{OH}) + \text{CH}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CO}(\text{OH}) \rightarrow$ $2.000 \text{ CH}(\text{OH})_2\text{CHO} + 2.000 \text{ CO}_2 + -\text{O}_2-$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 04122	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CO}(\text{OH}) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CO}(\text{OH}) + 0.550 \text{ CH}(\text{OH})_2\text{COCO}(\text{OH}) +$ $0.250 \text{ CH}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{OH}) + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
E <sub>o</sub> 00538	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{CO}(\text{OH}))\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{CH}(\text{CH}(\text{OH})_2)\text{CO}(\text{OH})$	$2.8 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00539	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{CO}(\text{OH}))\text{CHO} \rightleftharpoons \text{CH}_2(\text{OH})\text{CH}(\text{CO}(\text{O}^-))\text{CHO} + \text{H}^+$	$8.5 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04123	*	*	CH <sub>2</sub> (OH)CH(CO(OH))CHO + OH $\rightarrow$ 0.363 CO(OH)CH(CHO)CH(OH)(OO $\cdot$ ) + 0.604 CH <sub>2</sub> (OH)CH(CO(OH))CO(OO $\cdot$ ) + 0.033 CO(OH)CH(CHO)CH <sub>2</sub> (O $\cdot$ ) + H <sub>2</sub> O - 0.967 O <sub>2</sub>	2.6 · 10 <sup>+09</sup>		
R <sub>o</sub> 04124	*		CH <sub>2</sub> (OH)CH(CO(OH))CHO + NO <sub>3</sub> $\rightarrow$ 0.363 CO(OH)CH(CHO)CH(OH)(OO $\cdot$ ) + 0.604 CH <sub>2</sub> (OH)CH(CO(OH))CO(OO $\cdot$ ) + 0.033 CO(OH)CH(CHO)CH <sub>2</sub> (O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.967 O <sub>2</sub>	1.6 · 10 <sup>+07</sup>		
R <sub>o</sub> 04125	*	*	CO(OH)CH(CHO)CH(OH)(OO $\cdot$ ) $\rightarrow$ CO(OH)CH(CHO)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04126	*	*	CH <sub>2</sub> (OH)CH(CO(OH))CO(OO $\cdot$ ) $\rightarrow$ CH <sub>2</sub> (OH)CH(CO(OH))CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
E <sub>o</sub> 00540	*	*	CO(OH)CH(CHO)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CO(OH)	1.2 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00541	*	*	CO(OH)CH(CHO)CHO $\rightleftharpoons$ CO(O <sup>-</sup> )CH(CHO)CHO + H <sup>+</sup>	2.2 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04127	*	*	CO(OH)CH(CHO)CHO + OH $\rightarrow$ CO(OH)CH(CHO)CO(OO $\cdot$ ) + H <sub>2</sub> O - O <sub>2</sub>	2.6 · 10 <sup>+09</sup>		
R <sub>o</sub> 04128	*		CO(OH)CH(CHO)CHO + NO <sub>3</sub> $\rightarrow$ CO(OH)CH(CHO)CO(OO $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	5.5 · 10 <sup>+06</sup>		
R <sub>o</sub> 04129	*	*	CO(OH)CH(CHO)CO(OO $\cdot$ ) $\rightarrow$ CO(OH)CH(CO(OH))CHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
E <sub>o</sub> 00542	*	*	CH <sub>3</sub> CH(CO(OH))CO(OH) $\rightleftharpoons$ CH <sub>3</sub> CH(CO(OH))CO(O <sup>-</sup> ) + H <sup>+</sup>	2.8 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04130	*	*	CH <sub>3</sub> CH(CO(OH))CO(OH) + OH $\rightarrow$ CO(OH)CH(CO(OH))CH <sub>2</sub> (OO $\cdot$ ) + H <sub>2</sub> O - O <sub>2</sub>	1.9 · 10 <sup>+08</sup>		
R <sub>o</sub> 04131	*		CH <sub>3</sub> CH(CO(OH))CO(OH) + NO <sub>3</sub> $\rightarrow$ CO(OH)CH(CO(OH))CH <sub>2</sub> (OO $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	5.1 · 10 <sup>+03</sup>		
R <sub>o</sub> 04132	*	*	CO(OH)CH(CO(OH))CH <sub>2</sub> (OO $\cdot$ ) $\xrightarrow{RO_2}$ 0.200 CO(OH)CH(CO(OH))CH <sub>2</sub> (O $\cdot$ ) + 0.550 CO(OH)CH(CO(OH))CHO + 0.250 CH <sub>2</sub> (OH)CH(CO(OH))CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04133	*	*	CO(OH)CH(CO(OH))CH <sub>2</sub> (O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)CH(CO(OH))CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04134	*	*	CO(OH)CH(CO(OH))CH <sub>2</sub> (O $\cdot$ ) $\rightarrow$ CO(OH)CH(OO $\cdot$ )CO(OH) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04135	*	*	CH <sub>3</sub> CH(CH(OH) <sub>2</sub> )CO(O <sup>-</sup> ) + OH $\rightarrow$ 0.263 CH(OH) <sub>2</sub> CH(CO(O <sup>-</sup> ))CH <sub>2</sub> (OO $\cdot$ ) + 0.537 CH <sub>3</sub> CH(CO(O <sup>-</sup> ))C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.200 CH <sub>3</sub> CH(CO(O <sup>-</sup> ))CH(OH)(O $\cdot$ ) + H <sub>2</sub> O - 0.800 O <sub>2</sub>	1.9 · 10 <sup>+09</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04136	*		$\text{CH}_3\text{CH}(\text{CH}(\text{OH})_2)\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow \text{CH}_3\text{CH}(\text{CH}(\text{OH})_2)\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 04137	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2^\cdot}$ $0.200 \text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) + 0.550 \text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{O}^-))\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{CH}(\text{CH}(\text{OH})_2)\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04138	*	*	$\text{CH}_3\text{CH}(\text{CO}(\text{O}^-))\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04139	*	*	$\text{CH}_3\text{CH}(\text{CO}(\text{O}^-))\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_3\text{CH}(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04140	*	*	$\text{CH}_3\text{CH}(\text{CO}(\text{O}^-))\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04141	*		$\text{CH}_3\text{CH}(\text{CH}(\text{OH})_2)\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OO}\cdot)\text{CH}(\text{OH})_2 + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04142	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{O}^-))\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04143	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04144	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CH}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) \rightarrow$ $2.000 \text{CH}(\text{OH})_2\text{CHO} + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 04145	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) \xrightarrow{\text{RO}_2^\cdot}$ $0.200 \text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) + 0.550 \text{CH}(\text{OH})_2\text{COCO}(\text{O}^-) +$ $0.250 \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
E <sub>o</sub> 00543	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{CO}(\text{O}^-))\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{CH}(\text{CH}(\text{OH})_2)\text{CO}(\text{O}^-)$	$2.5 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04146	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{CO}(\text{O}^-))\text{CHO} + \text{OH} \rightarrow$ $0.375 \text{CO}(\text{O}^-)\text{CH}(\text{CHO})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.625 \text{CH}_2(\text{OH})\text{CH}(\text{CO}(\text{O}^-))\text{CO}(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$4.5 \cdot 10^{+09}$		
R <sub>o</sub> 04147	*		$\text{CH}_2(\text{OH})\text{CH}(\text{CO}(\text{O}^-))\text{CHO} + \text{NO}_3 \rightarrow \text{CH}_2(\text{OH})\text{CH}(\text{CHO})\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 04148	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{CHO})\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{CH}(\text{CHO})\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04149	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{CO}(\text{O}^-))\text{CO}(\text{OO}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04150	*		$\text{CH}_2(\text{OH})\text{CH}(\text{CHO})\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{CHO} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04151	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{CHO} \xrightarrow{\text{RO}_2^\cdot}$ $0.200 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CHO} + 0.550 \text{CH}_2(\text{OH})\text{COCHO} +$ $0.250 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
E <sub>o</sub> 00544	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{CHO})\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{O}^-))\text{CHO}$	$3.0 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00545	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{CHO})\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{CH}(\text{CH}(\text{OH})_2)\text{CO}(\text{O}^-)$	$1.5 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04152	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{CHO})\text{CHO} + \text{OH} \rightarrow \text{CO}(\text{O}^-)\text{CH}(\text{CHO})\text{CO}(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$4.6 \cdot 10^{+09}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04153	*		$\text{CO}(\text{O}^-)\text{CH}(\text{CHO})\text{CHO} + \text{NO}_3 \rightarrow \text{CHOCH}(\text{CHO})\text{CO}(\text{O}^\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 04154	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{CHO})\text{CO}(\text{OO}^\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}(\text{CO}(\text{O}^-))\text{CHO} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04155	*		$\text{CHOCH}(\text{CHO})\text{CO}(\text{O}^\cdot) \rightarrow \text{CHOCH}(\text{OO}^\cdot)\text{CHO} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04156	*	*	$\text{CHOCH}(\text{OO}^\cdot)\text{CHO} \xrightarrow{\text{RO}_2} 0.200 \text{CHOCH}(\text{O}^\cdot)\text{CHO} + 0.550 \text{CHOCOCHO} + 0.250 \text{CHOCH}(\text{OH})\text{CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
E <sub>o</sub> 00546	*	*	$\text{CH}_3\text{CH}(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) \rightleftharpoons \text{CH}_3\text{CH}(\text{CO}(\text{O}^-))\text{CO}(\text{O}^-) + \text{H}^+$	$1.6 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04157	*	*	$\text{CH}_3\text{CH}(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + \text{OH} \rightarrow 0.970 \text{CO}(\text{OH})\text{CH}(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}^\cdot) + 0.030 \text{CH}_3\text{C}(\text{OO}^\cdot)(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + \text{H}_2\text{O} - \text{O}_2$	$3.5 \cdot 10^{+08}$		
R <sub>o</sub> 04158	*		$\text{CH}_3\text{CH}(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow \text{CH}_3\text{CH}(\text{CO}(\text{OH}))\text{CO}(\text{O}^\cdot) + \text{NO}_3^-$	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 04159	*	*	$\text{CO}(\text{OH})\text{CH}(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}^\cdot) \xrightarrow{\text{RO}_2} 0.200 \text{CO}(\text{OH})\text{CH}(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}^\cdot) + 0.550 \text{CO}(\text{OH})\text{CH}(\text{CO}(\text{O}^-))\text{CHO} + 0.250 \text{CH}_2(\text{OH})\text{CH}(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04160	*	*	$\text{CH}_3\text{C}(\text{OO}^\cdot)(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + \text{CH}_3\text{C}(\text{OO}^\cdot)(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) \rightarrow 2.000 \text{CH}_3\text{COCO}(\text{O}^-) + 2.000 \text{CO}_2 + -\text{O}_2-$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 04161	*	*	$\text{CH}_3\text{C}(\text{OO}^\cdot)(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) \xrightarrow{\text{RO}_2} \text{CH}_3\text{C}(\text{O}^\cdot)(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 04162	*		$\text{CH}_3\text{CH}(\text{CO}(\text{OH}))\text{CO}(\text{O}^\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OO}^\cdot)\text{CO}(\text{OH}) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04163	*	*	$\text{CO}(\text{OH})\text{CH}(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}^\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{CH}(\text{CO}(\text{O}^-))\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04164	*	*	$\text{CO}(\text{OH})\text{CH}(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}^\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}(\text{OO}^\cdot)\text{CO}(\text{O}^-) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00547	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{CH}(\text{OH})_2)\text{CO}(\text{OH}) \rightleftharpoons \text{CH}(\text{OH})_2\text{CH}(\text{CH}(\text{OH})_2)\text{CO}(\text{O}^-) + \text{H}^+$	$7.2 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04165	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{CH}(\text{OH})_2)\text{CO}(\text{OH}) + \text{OH} \rightarrow 0.579 \text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{OH}))\text{C}(\text{OH})_2(\text{OO}^\cdot) + 0.421 \text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{O}^\cdot) + \text{H}_2\text{O} - 0.579 \text{O}_2$	$1.8 \cdot 10^{+09}$		
R <sub>o</sub> 04166	*		$\text{CH}(\text{OH})_2\text{CH}(\text{CH}(\text{OH})_2)\text{CO}(\text{OH}) + \text{NO}_3 \rightarrow 0.579 \text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{OH}))\text{C}(\text{OH})_2(\text{OO}^\cdot) + 0.421 \text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{O}^\cdot) + \text{NO}_3^- + \text{H}^+ - 0.579 \text{O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 04167	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{OH}))\text{C}(\text{OH})_2(\text{OO}^\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{OH}))\text{CO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04168	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{O}^\cdot) \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{OH}))\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04169	*	*	CH(OH) <sub>2</sub> CH(CO(OH))CH(OH)(O $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> CH(OO $\cdot$ )CO(OH) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00548	*	*	CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CO(OH) $\rightleftharpoons$ CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CO(O $^-$ ) + H $^+$	$4.9 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04170	*	*	CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CO(OH) + OH $\rightarrow$ 0.523 CH(OH) <sub>2</sub> CH(CO(OH))CH(OH)(OO $\cdot$ ) + 0.257 CH <sub>2</sub> (OH)CH(CO(OH))C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.041 CH(OH) <sub>2</sub> CH(CO(OH))CH <sub>2</sub> (O $\cdot$ ) + 0.179 CH <sub>2</sub> (OH)CH(CO(OH))CH(OH)(O $\cdot$ ) + H <sub>2</sub> O - 0.780 O <sub>2</sub>	$2.1 \cdot 10^{+09}$		
R <sub>o</sub> 04171	*		CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CO(OH) + NO <sub>3</sub> $\rightarrow$ 0.523 CH(OH) <sub>2</sub> CH(CO(OH))CH(OH)(OO $\cdot$ ) + 0.257 CH <sub>2</sub> (OH)CH(CO(OH))C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.041 CH(OH) <sub>2</sub> CH(CO(OH))CH <sub>2</sub> (O $\cdot$ ) + 0.179 CH <sub>2</sub> (OH)CH(CO(OH))CH(OH)(O $\cdot$ ) + NO <sub>3</sub> $^-$ + H $^+$ - 0.780 O <sub>2</sub>	$1.1 \cdot 10^{+07}$		
R <sub>o</sub> 04172	*	*	CH(OH) <sub>2</sub> CH(CO(OH))CH(OH)(OO $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> CH(CO(OH))CHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04173	*	*	CH <sub>2</sub> (OH)CH(CO(OH))C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CH <sub>2</sub> (OH)CH(CO(OH))CO(OH) + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04174	*	*	CH <sub>2</sub> (OH)CH(CO(OH))CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(CO(OH))CO(OH) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04175	*	*	CH <sub>2</sub> (OH)CH(CO(OH))CH(OH)(O $\cdot$ ) $\rightarrow$ CH <sub>2</sub> (OH)CH(OO $\cdot$ )CO(OH) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04176	*	*	CH <sub>2</sub> (OH)CH(OO $\cdot$ )CO(OH) + CH <sub>2</sub> (OH)CH(OO $\cdot$ )CO(OH) $\rightarrow$ 2.000 CH <sub>2</sub> (OH)CHO + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 04177	*	*	CH <sub>2</sub> (OH)CH(OO $\cdot$ )CO(OH) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(O $\cdot$ )CO(OH) + 0.550 CH <sub>2</sub> (OH)COCO(OH) + 0.250 CH <sub>2</sub> (OH)CH(OH)CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
E <sub>o</sub> 00549	*	*	CH(OH) <sub>2</sub> CH(CO(OH))CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CO(OH)	$1.2 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00550	*	*	CH(OH) <sub>2</sub> CH(CO(OH))CHO $\rightleftharpoons$ CH(OH) <sub>2</sub> CH(CO(O $^-$ ))CHO + H $^+$	$1.2 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04178	*	*	CH(OH) <sub>2</sub> CH(CO(OH))CHO + OH $\rightarrow$ 0.191 CO(OH)CH(CHO)C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.646 CH(OH) <sub>2</sub> CH(CO(OH))CO(OO $\cdot$ ) + 0.162 CO(OH)CH(CHO)CH(OH)(O $\cdot$ ) + H <sub>2</sub> O - 0.838 O <sub>2</sub>	2.3 · 10 <sup>+09</sup>		
R <sub>o</sub> 04179	*		CH(OH) <sub>2</sub> CH(CO(OH))CHO + NO <sub>3</sub> $\rightarrow$ 0.191 CO(OH)CH(CHO)C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.646 CH(OH) <sub>2</sub> CH(CO(OH))CO(OO $\cdot$ ) + 0.162 CO(OH)CH(CHO)CH(OH)(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.838 O <sub>2</sub>	8.7 · 10 <sup>+06</sup>		
R <sub>o</sub> 04180	*	*	CO(OH)CH(CHO)C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)CH(CO(OH))CHO + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04181	*	*	CH(OH) <sub>2</sub> CH(CO(OH))CO(OO $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> CH(CO(OH))CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04182	*	*	CO(OH)CH(CHO)CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)CH(CO(OH))CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04183	*	*	CO(OH)CH(CHO)CH(OH)(O $\cdot$ ) $\rightarrow$ CO(OH)CH(OO $\cdot$ )CHO + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00551	*	*	CO(OH)CH(CO(OH))CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(CO(OH))CO(OH)	1.5 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00552	*	*	CO(OH)CH(CO(OH))CHO $\rightleftharpoons$ CO(OH)CH(CO(O <sup>-</sup> ))CHO + H <sup>+</sup>	1.0 · 10 <sup>-03</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04184	*	*	CO(OH)CH(CO(OH))CHO + OH $\rightarrow$ CO(OH)CH(CO(OH))CO(OO $\cdot$ ) + H <sub>2</sub> O - O <sub>2</sub>	1.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 04185	*		CO(OH)CH(CO(OH))CHO + NO <sub>3</sub> $\rightarrow$ CO(OH)CH(CO(OH))CO(OO $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	6.1 · 10 <sup>+06</sup>		
R <sub>o</sub> 04186	*	*	CO(OH)CH(CO(OH))CO(OO $\cdot$ ) $\rightarrow$ CO(OH)CH(CO(OH))CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
E <sub>o</sub> 00553	*	*	CH <sub>2</sub> (OH)CH(CO(OH))CO(OH) $\rightleftharpoons$ CH <sub>2</sub> (OH)CH(CO(OH))CO(O <sup>-</sup> ) + H <sup>+</sup>	4.0 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04187	*	*	CH <sub>2</sub> (OH)CH(CO(OH))CO(OH) + OH $\rightarrow$ 0.894 CO(OH)CH(CO(OH))CH(OH)(OO $\cdot$ ) + 0.106 CO(OH)CH(CO(OH))CH <sub>2</sub> (O $\cdot$ ) + H <sub>2</sub> O - 0.894 O <sub>2</sub>	8.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04188	*		CH <sub>2</sub> (OH)CH(CO(OH))CO(OH) + NO <sub>3</sub> $\rightarrow$ 0.894 CO(OH)CH(CO(OH))CH(OH)(OO $\cdot$ ) + 0.106 CO(OH)CH(CO(OH))CH <sub>2</sub> (O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.894 O <sub>2</sub>	6.2 · 10 <sup>+03</sup>		
R <sub>o</sub> 04189	*	*	CO(OH)CH(CO(OH))CH(OH)(OO $\cdot$ ) $\rightarrow$ CO(OH)CH(CO(OH))CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04190	*	*	CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CO(O <sup>-</sup> ) + OH → 0.707 CH(OH) <sub>2</sub> CH(CO(O <sup>-</sup> ))C(OH) <sub>2</sub> (OO·) + 0.293 CH(OH) <sub>2</sub> CH(CO(O <sup>-</sup> ))CH(OH)(O·) + H <sub>2</sub> O - 0.707 O <sub>2</sub>	2.6 · 10 <sup>+09</sup>		
R <sub>o</sub> 04191	*		CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 04192	*	*	CH(OH) <sub>2</sub> CH(CO(O <sup>-</sup> ))C(OH) <sub>2</sub> (OO·) → CH(OH) <sub>2</sub> CH(CO(OH))CO(O <sup>-</sup> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04193	*	*	CH(OH) <sub>2</sub> CH(CO(O <sup>-</sup> ))CH(OH)(O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(CO(OH))CO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04194	*	*	CH(OH) <sub>2</sub> CH(CO(O <sup>-</sup> ))CH(OH)(O·) → CH(OH) <sub>2</sub> CH(OO·)CO(O <sup>-</sup> ) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04195	*		CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CO(O·) → CH(OH) <sub>2</sub> CH(OO·)CH(OH) <sub>2</sub> + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04196	*	*	CH(OH) <sub>2</sub> CH(OO·)CH(OH) <sub>2</sub> $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH(O·)CH(OH) <sub>2</sub> + 0.550 CH(OH) <sub>2</sub> COCH(OH) <sub>2</sub> + 0.250 CH(OH) <sub>2</sub> CH(OH)CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04197	*	*	CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CO(O <sup>-</sup> ) + OH → 0.593 CH(OH) <sub>2</sub> CH(CO(O <sup>-</sup> ))CH(OH)(OO·) + 0.292 CH <sub>2</sub> (OH)CH(CO(O <sup>-</sup> ))C(OH) <sub>2</sub> (OO·) + 0.115 CH <sub>2</sub> (OH)CH(CO(O <sup>-</sup> ))CH(OH)(O·) + H <sub>2</sub> O - 0.885 O <sub>2</sub>	3.3 · 10 <sup>+09</sup>		
R <sub>o</sub> 04198	*		CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 04199	*	*	CH(OH) <sub>2</sub> CH(CO(O <sup>-</sup> ))CH(OH)(OO·) → CH(OH) <sub>2</sub> CH(CO(O <sup>-</sup> ))CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04200	*	*	CH <sub>2</sub> (OH)CH(CO(O <sup>-</sup> ))C(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)CH(CO(OH))CO(O <sup>-</sup> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04201	*	*	CH <sub>2</sub> (OH)CH(CO(O <sup>-</sup> ))CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(CO(OH))CO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04202	*	*	CH <sub>2</sub> (OH)CH(CO(O <sup>-</sup> ))CH(OH)(O·) → CH <sub>2</sub> (OH)CH(OO·)CO(O <sup>-</sup> ) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04203	*		CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CO(O·) → CH <sub>2</sub> (OH)CH(OO·)CH(OH) <sub>2</sub> + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04204	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{CH}(\text{OH})_2 \xrightarrow{\text{RO}_2}$ 0.200 $\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})_2 + 0.550 \text{CH}_2(\text{OH})\text{COCH}(\text{OH})_2 +$ 0.250 $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})_2 + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04205	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{O}^-))\text{CHO} + \text{OH} \rightarrow$ 0.206 $\text{CO}(\text{O}^-)\text{CH}(\text{CHO})\text{C}(\text{OH})_2(\text{OO}\cdot) +$ 0.695 $\text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{O}^-))\text{CO}(\text{OO}\cdot) +$ 0.099 $\text{CO}(\text{O}^-)\text{CH}(\text{CHO})\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.901 \text{O}_2$	$3.8 \cdot 10^{+09}$		
R <sub>o</sub> 04206	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{O}^-))\text{CHO} + \text{NO}_3 \rightarrow \text{CH}(\text{OH})_2\text{CH}(\text{CHO})\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 04207	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{CHO})\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CO}(\text{OH})\text{CH}(\text{CO}(\text{O}^-))\text{CHO} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04208	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{O}^-))\text{CO}(\text{OO}\cdot) \rightarrow$ $\text{CH}(\text{OH})_2\text{CH}(\text{CO}(\text{OH}))\text{CO}(\text{O}^-) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04209	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{CHO})\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{OH})\text{CH}(\text{CO}(\text{O}^-))\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04210	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{CHO})\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{CH}(\text{OO}\cdot)\text{CHO} + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04211	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{CHO})\text{CO}(\text{O}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CHO} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04212	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CHO} \xrightarrow{\text{RO}_2}$ 0.200 $\text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CHO} + 0.550 \text{CH}(\text{OH})_2\text{COCHO} +$ 0.250 $\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04213	*	*	$\text{CH}_3\text{CH}(\text{CO}(\text{O}^-))\text{CO}(\text{O}^-) + \text{OH} \rightarrow 0.942 \text{CO}(\text{O}^-)\text{CH}(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) +$ 0.058 $\text{CH}_3\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CO}(\text{O}^-) + \text{H}_2\text{O} - \text{O}_2$	$6.2 \cdot 10^{+08}$		
R <sub>o</sub> 04214	*	*	$\text{CH}_3\text{CH}(\text{CO}(\text{O}^-))\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow$ 0.500 $\text{CH}_3\text{CH}(\text{CO}(\text{O}^-))\text{CO}(\text{O}\cdot) + 0.500 \text{CH}_3\text{CH}(\text{CO}(\text{O}^-))\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$7.8 \cdot 10^{+07}$		
R <sub>o</sub> 04215	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ 0.200 $\text{CO}(\text{O}^-)\text{CH}(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) + 0.550 \text{CO}(\text{O}^-)\text{CH}(\text{CO}(\text{O}^-))\text{CHO} +$ 0.250 $\text{CH}_2(\text{OH})\text{CH}(\text{CO}(\text{O}^-))\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04216	*	*	$\text{CH}_3\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CO}(\text{O}^-) + \text{CH}_3\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CO}(\text{O}^-) \rightarrow$ 2.000 $\text{CH}_3\text{COCO}(\text{O}^-) + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 04217	*	*	$\text{CH}_3\text{C}(\text{OO}\cdot)(\text{CO}(\text{O}^-))\text{CO}(\text{O}^-) \xrightarrow{\text{RO}_2} \text{CH}_3\text{C}(\text{O}\cdot)(\text{CO}(\text{O}^-))\text{CO}(\text{O}^-) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 04218	*	*	$\text{CH}_3\text{CH}(\text{CO}(\text{O}^-))\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04219	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{CH}(\text{CO}(\text{O}^-))\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04220	*	*	$\text{CO}(\text{O}^-)\text{CH}(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00554	*	*	$\text{CO(OH)CH(CO(O}^-))\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{CH(CO(OH))CO(O}^-)$	$1.4 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00555	*	*	$\text{CO(OH)CH(CO(O}^-))\text{CHO} \rightleftharpoons \text{CO(O}^-)\text{CH(CO(O}^-))\text{CHO} + \text{H}^+$	$5.9 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04221	*	*	$\text{CO(OH)CH(CO(O}^-))\text{CHO} + \text{OH} \rightarrow$ $\text{CO(OH)CH(CO(O}^-))\text{CO(OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$1.8 \cdot 10^{+09}$		
R <sub>o</sub> 04222	*		$\text{CO(OH)CH(CO(O}^-))\text{CHO} + \text{NO}_3 \rightarrow \text{CO(OH)CH(CHO)CO(O}\cdot) + \text{NO}_3^-$	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 04223	*	*	$\text{CO(OH)CH(CO(O}^-))\text{CO(OO}\cdot) \rightarrow$ $\text{CO(OH)CH(CO(OH))CO(O}^-) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04224	*		$\text{CO(OH)CH(CHO)CO(O}\cdot) \rightarrow \text{CO(OH)CH(OO}\cdot)\text{CHO} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00556	*	*	$\text{CH}_2(\text{OH})\text{CH(CO(OH))CO(O}^-) \rightleftharpoons \text{CH}_2(\text{OH})\text{CH(CO(O}^-))\text{CO(O}^-) + \text{H}^+$	$2.3 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04225	*	*	$\text{CH}_2(\text{OH})\text{CH(CO(OH))CO(O}^-) + \text{OH} \rightarrow$ $0.937 \text{ CO(OH)CH(CO(O}^-))\text{CH(OH)(OO}\cdot) +$ $0.063 \text{ CO(OH)CH(CO(O}^-))\text{CH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.937 \text{ O}_2$	$1.4 \cdot 10^{+09}$		
R <sub>o</sub> 04226	*		$\text{CH}_2(\text{OH})\text{CH(CO(OH))CO(O}^-) + \text{NO}_3 \rightarrow$ $\text{CH}_2(\text{OH})\text{CH(CO(OH))CO(O}\cdot) + \text{NO}_3^-$	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 04227	*	*	$\text{CO(OH)CH(CO(O}^-))\text{CH(OH)(OO}\cdot) \rightarrow \text{CO(OH)CH(CO(O}^-))\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04228	*		$\text{CH}_2(\text{OH})\text{CH(CO(OH))CO(O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH(OO}\cdot)\text{CO(OH)} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00557	*	*	$\text{CO(OH)CH(CO(OH))CO(OH)} \rightleftharpoons \text{CO(OH)CH(CO(OH))CO(O}^-) + \text{H}^+$	$2.5 \cdot 10^{-03}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04229	*	*	$\text{CO(OH)CH(CO(OH))CO(OH)} + \text{OH} \rightarrow$ $0.071 \text{ CO(OH)C(OO}\cdot)(\text{CO(OH)})\text{CO(OH)} +$ $0.929 \text{ CO(OH)CH(CO(OH))CO(O}\cdot) + \text{H}_2\text{O} - 0.071 \text{ O}_2$	$2.3 \cdot 10^{+06}$		
R <sub>o</sub> 04230	*		$\text{CO(OH)CH(CO(OH))CO(OH)} + \text{NO}_3 \rightarrow$ $0.071 \text{ CO(OH)C(OO}\cdot)(\text{CO(OH)})\text{CO(OH)} +$ $0.929 \text{ CO(OH)CH(CO(OH))CO(O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.071 \text{ O}_2$	$1.3 \cdot 10^{+05}$		
R <sub>o</sub> 04231	*	*	$\text{CO(OH)C(OO}\cdot)(\text{CO(OH)})\text{CO(OH)} + \text{CO(OH)C(OO}\cdot)(\text{CO(OH)})\text{CO(OH)} \rightarrow$ $2.000 \text{ CO(OH)COCO(OH)} + 2.000 \text{ CO}_2 + -\text{O}_2-$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 04232	*	*	$\text{CO(OH)C(OO}\cdot)(\text{CO(OH)})\text{CO(OH)} \xrightarrow{\text{RO}_2}$ $\text{CO(OH)C(O}\cdot)(\text{CO(OH)})\text{CO(OH)} + 0.500 \text{ O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 04233	*	*	$\text{CO(OH)CH(CO(OH))CO(O}\cdot) \rightarrow \text{CO(OH)CH(OO}\cdot)\text{CO(OH)} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00558	*	*	$\text{CH(OH)}_2\text{CH(CO(OH))CO(OH)} \rightleftharpoons \text{CH(OH)}_2\text{CH(CO(OH))CO(O}^-) + \text{H}^+$	$5.9 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04234	*	*	CH(OH) <sub>2</sub> CH(CO(OH))CO(OH) + OH $\rightarrow$ 0.478 CO(OH)CH(CO(OH))C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.522 CO(OH)CH(CO(OH))CH(OH)(O $\cdot$ ) + H <sub>2</sub> O - 0.478 O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04235	*		CH(OH) <sub>2</sub> CH(CO(OH))CO(OH) + NO <sub>3</sub> $\rightarrow$ 0.478 CO(OH)CH(CO(OH))C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.522 CO(OH)CH(CO(OH))CH(OH)(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.478 O <sub>2</sub>	$8.8 \cdot 10^{+06}$		
R <sub>o</sub> 04236	*	*	CO(OH)CH(CO(OH))C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)CH(CO(OH))CO(OH) + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04237	*	*	CO(OH)CH(CO(OH))CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)CH(CO(OH))CO(OH) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04238	*	*	CO(OH)CH(CO(OH))CH(OH)(O $\cdot$ ) $\rightarrow$ CO(OH)CH(OO $\cdot$ )CO(OH) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04239	*	*	CH <sub>2</sub> (OH)CH(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + OH $\rightarrow$ 0.963 CO(O <sup>-</sup> )CH(CO(O <sup>-</sup> ))CH(OH)(OO $\cdot$ ) + 0.037 CO(O <sup>-</sup> )CH(CO(O <sup>-</sup> ))CH <sub>2</sub> (O $\cdot$ ) + H <sub>2</sub> O - 0.963 O <sub>2</sub>	$2.4 \cdot 10^{+09}$		
R <sub>o</sub> 04240	*		CH <sub>2</sub> (OH)CH(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + NO <sub>3</sub> $\rightarrow$ 0.500 CH <sub>2</sub> (OH)CH(CO(O <sup>-</sup> ))CO(O $\cdot$ ) + 0.500 CH <sub>2</sub> (OH)CH(CO(O <sup>-</sup> ))CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	$7.8 \cdot 10^{+07}$		
R <sub>o</sub> 04241	*	*	CO(O <sup>-</sup> )CH(CO(O <sup>-</sup> ))CH(OH)(OO $\cdot$ ) $\rightarrow$ CO(O <sup>-</sup> )CH(CO(O <sup>-</sup> ))CHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04242	*		CH <sub>2</sub> (OH)CH(CO(O <sup>-</sup> ))CO(O $\cdot$ ) $\rightarrow$ CH <sub>2</sub> (OH)CH(OO $\cdot$ )CO(O <sup>-</sup> ) + CO <sub>2</sub> - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00559	*	*	CO(O <sup>-</sup> )CH(CO(O <sup>-</sup> ))CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(CO(O <sup>-</sup> ))CO(O <sup>-</sup> )	$1.2 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04243	*	*	CO(O <sup>-</sup> )CH(CO(O <sup>-</sup> ))CHO + OH $\rightarrow$ CO(O <sup>-</sup> )CH(CO(O <sup>-</sup> ))CO(OO $\cdot$ ) + H <sub>2</sub> O - O <sub>2</sub>	$3.1 \cdot 10^{+09}$		
R <sub>o</sub> 04244	*		CO(O <sup>-</sup> )CH(CO(O <sup>-</sup> ))CHO + NO <sub>3</sub> $\rightarrow$ 0.500 CO(O <sup>-</sup> )CH(CHO)CO(O $\cdot$ ) + 0.500 CO(O <sup>-</sup> )CH(CHO)CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	$7.8 \cdot 10^{+07}$		
R <sub>o</sub> 04245	*	*	CO(O <sup>-</sup> )CH(CO(O <sup>-</sup> ))CO(OO $\cdot$ ) $\rightarrow$ CO(OH)CH(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04246	*		CO(O <sup>-</sup> )CH(CHO)CO(O $\cdot$ ) $\rightarrow$ CO(O <sup>-</sup> )CH(OO $\cdot$ )CHO + CO <sub>2</sub> - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00560	*	*	CO(OH)CH(CO(OH))CO(O <sup>-</sup> ) $\rightleftharpoons$ CO(OH)CH(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + H <sup>+</sup>	$2.8 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04247	*	*	CO(OH)CH(CO(OH))CO(O <sup>-</sup> ) + OH $\rightarrow$ 0.283 CO(OH)C(OO $\cdot$ )(CO(OH))CO(O <sup>-</sup> ) + 0.717 CO(OH)CH(CO(O <sup>-</sup> ))CO(O $\cdot$ ) + H <sub>2</sub> O - 0.283 O <sub>2</sub>	$2.0 \cdot 10^{+06}$		
R <sub>o</sub> 04248	*		CO(OH)CH(CO(OH))CO(O <sup>-</sup> ) + NO <sub>3</sub> $\rightarrow$ CO(OH)CH(CO(OH))CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 04249	*	*	CO(OH)C(OO $\cdot$ )(CO(OH))CO(O <sup>-</sup> ) + CO(OH)C(OO $\cdot$ )(CO(OH))CO(O <sup>-</sup> ) $\rightarrow$ 2.000 CO(OH)COCO(O <sup>-</sup> ) + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 04250	*	*	CO(OH)C(OO $\cdot$ )(CO(OH))CO(O <sup>-</sup> ) $\xrightarrow{RO_2}$ CO(OH)C(O $\cdot$ )(CO(OH))CO(O <sup>-</sup> ) + 0.500 O <sub>2</sub>	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 04251	*	*	CO(OH)CH(CO(O <sup>-</sup> ))CO(O $\cdot$ ) $\rightarrow$ CO(OH)CH(OO $\cdot$ )CO(O <sup>-</sup> ) + CO <sub>2</sub> - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
E <sub>o</sub> 00561	*	*	CH(OH) <sub>2</sub> CH(CO(OH))CO(O <sup>-</sup> ) $\rightleftharpoons$ CH(OH) <sub>2</sub> CH(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + H <sup>+</sup>	$3.4 \cdot 10^{-05}$		
R <sub>o</sub> 04252	*	*	CH(OH) <sub>2</sub> CH(CO(OH))CO(O <sup>-</sup> ) + OH $\rightarrow$ 0.617 CO(OH)CH(CO(O <sup>-</sup> ))C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.383 CO(OH)CH(CO(O <sup>-</sup> ))CH(OH)(O $\cdot$ ) + H <sub>2</sub> O - 0.617 O <sub>2</sub>	$9.9 \cdot 10^{+08}$		
R <sub>o</sub> 04253	*		CH(OH) <sub>2</sub> CH(CO(OH))CO(O <sup>-</sup> ) + NO <sub>3</sub> $\rightarrow$ CH(OH) <sub>2</sub> CH(CO(OH))CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 04254	*	*	CO(OH)CH(CO(O <sup>-</sup> ))C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)CH(CO(OH))CO(O <sup>-</sup> ) + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04255	*	*	CO(OH)CH(CO(O <sup>-</sup> ))CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)CH(CO(OH))CO(O <sup>-</sup> ) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04256	*	*	CO(OH)CH(CO(O <sup>-</sup> ))CH(OH)(O $\cdot$ ) $\rightarrow$ CO(OH)CH(OO $\cdot$ )CO(O <sup>-</sup> ) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04257	*		CH(OH) <sub>2</sub> CH(CO(OH))CO(O $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> CH(OO $\cdot$ )CO(OH) + CO <sub>2</sub> - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
E <sub>o</sub> 00562	*	*	CO(OH)CH(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) $\rightleftharpoons$ CO(O <sup>-</sup> )CH(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + H <sup>+</sup>	$1.6 \cdot 10^{-05}$		
R <sub>o</sub> 04258	*	*	CO(OH)CH(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + OH $\rightarrow$ 0.730 CO(OH)C(OO $\cdot$ )(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + 0.270 CO(O <sup>-</sup> )CH(CO(O <sup>-</sup> ))CO(O $\cdot$ ) + H <sub>2</sub> O - 0.730 O <sub>2</sub>	$2.6 \cdot 10^{+06}$		
R <sub>o</sub> 04259	*		CO(OH)CH(CO(O <sup>-</sup> ))CO(O <sup>-</sup> ) + NO <sub>3</sub> $\rightarrow$ 0.500 CO(OH)CH(CO(O <sup>-</sup> ))CO(O $\cdot$ ) + 0.500 CO(OH)CH(CO(O <sup>-</sup> ))CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	$7.8 \cdot 10^{+07}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04260	*	*	$\text{CO(OH)C(OO}\cdot\text{)(CO(O}^-)\text{)CO(O}^-) + CO(OH)C(OO}\cdot\text{)(CO(O}^-)\text{)CO(O}^-) \rightarrow$ $2.000 \text{ CO(O}^-)\text{COCO(O}^-) + 2.000 \text{ CO}_2 + -\text{O}_2-$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 04261	*	*	$\text{CO(OH)C(OO}\cdot\text{)(CO(O}^-)\text{)CO(O}^-) \xrightarrow{RO_2}$ $\text{CO(OH)C(O}\cdot\text{)(CO(O}^-)\text{)CO(O}^-) + 0.500 \text{ O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 04262	*	*	$\text{CO(O}^-)\text{CH(CO(O}^-)\text{)CO(O}\cdot\text{) \rightarrow CO(O}^-)\text{CH(OO}\cdot\text{)CO(O}^-) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04263	*	*	$\text{CH(OH)}_2\text{CH(CO(O}^-)\text{)CO(O}^-) + \text{OH} \rightarrow$ $0.739 \text{ CO(O}^-)\text{CH(CO(O}^-)\text{)C(OH)}_2\text{(OO}\cdot\text{) +}$ $0.261 \text{ CO(O}^-)\text{CH(CO(O}^-)\text{)CH(OH)(O}\cdot\text{) + H}_2\text{O} - 0.739 \text{ O}_2$	$1.5 \cdot 10^{+09}$		
R <sub>o</sub> 04264	*		$\text{CH(OH)}_2\text{CH(CO(O}^-)\text{)CO(O}^-) + \text{NO}_3 \rightarrow$ $0.500 \text{ CH(OH)}_2\text{CH(CO(O}^-)\text{)CO(O}\cdot\text{) +}$ $0.500 \text{ CH(OH)}_2\text{CH(CO(O}^-)\text{)CO(O}\cdot\text{) + NO}_3^-$	$7.8 \cdot 10^{+07}$		
R <sub>o</sub> 04265	*	*	$\text{CO(O}^-)\text{CH(CO(O}^-)\text{)C(OH)}_2\text{(OO}\cdot\text{) \rightarrow}$ $\text{CO(OH)CH(CO(O}^-)\text{)CO(O}^-) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04266	*	*	$\text{CO(O}^-)\text{CH(CO(O}^-)\text{)CH(OH)(O}\cdot\text{) \xrightarrow{O_2}$ $\text{CO(OH)CH(CO(O}^-)\text{)CO(O}^-) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04267	*	*	$\text{CO(O}^-)\text{CH(CO(O}^-)\text{)CH(OH)(O}\cdot\text{) \rightarrow}$ $\text{CO(O}^-)\text{CH(OO}\cdot\text{)CO(O}^-) + \text{CHO(OH) - O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04268	*		$\text{CH(OH)}_2\text{CH(CO(O}^-)\text{)CO(O}\cdot\text{) \rightarrow CH(OH)}_2\text{CH(OO}\cdot\text{)CO(O}^-) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04269	*	*	$\text{CO(O}^-)\text{CH(CO(O}^-)\text{)CO(O}^-) + \text{OH} \rightarrow$ $\text{CO(O}^-)\text{C(OO}\cdot\text{)(CO(O}^-)\text{)CO(O}^-) + \text{H}_2\text{O} - \text{O}_2$	$6.5 \cdot 10^{+06}$		
R <sub>o</sub> 04270	*		$\text{CO(O}^-)\text{CH(CO(O}^-)\text{)CO(O}^-) + \text{NO}_3 \rightarrow$ $0.333 \text{ CO(O}^-)\text{CH(CO(O}^-)\text{)CO(O}\cdot\text{) + 0.333 CO(O}^-)\text{CH(CO(O}^-)\text{)CO(O}\cdot\text{) +}$ $0.333 \text{ CO(O}^-)\text{CH(CO(O}^-)\text{)CO(O}\cdot\text{) + NO}_3^-$	$7.8 \cdot 10^{+07}$		
R <sub>o</sub> 04271	*	*	$\text{CO(O}^-)\text{C(OO}\cdot\text{)(CO(O}^-)\text{)CO(O}^-) + \text{CO(O}^-)\text{C(OO}\cdot\text{)(CO(O}^-)\text{)CO(O}^-) \rightarrow}$ $2.000 \text{ CO(O}^-)\text{COCO(O}^-) + 2.000 \text{ CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{ OH}^- - 2.000 \text{ H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 04272	*	*	$\text{CO(O}^-)\text{C(OO}\cdot\text{)(CO(O}^-)\text{)CO(O}^-) \xrightarrow{RO_2}$ $\text{CO(O}^-)\text{C(O}\cdot\text{)(CO(O}^-)\text{)CO(O}^-) + 0.500 \text{ O}_2$	$1.0 \cdot 10^{+06}$		
E <sub>o</sub> 00563	*	*	$\text{CH}_3\text{CH(CH}_3\text{)CO(OH) \rightleftharpoons CH}_3\text{CH(CH}_3\text{)CO(O}^-) + \text{H}^+$	$1.6 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04273	*	*	$\text{CH}_3\text{CH(CH}_3\text{)CO(OH) + OH \rightarrow 0.916 CH}_3\text{CH(CO(OH))CH}_2\text{(OO}\cdot\text{) +}$ $0.084 \text{ CH}_3\text{C(OO}\cdot\text{)(CH}_3\text{)CO(OH) + H}_2\text{O} - \text{O}_2$	$6.9 \cdot 10^{+08}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04274	*		$\text{CH}_3\text{CH}(\text{CH}_3)\text{CO}(\text{OH}) + \text{NO}_3 \rightarrow 0.916 \text{CH}_3\text{CH}(\text{CO}(\text{OH}))\text{CH}_2(\text{OO}\cdot) + 0.084 \text{CH}_3\text{C}(\text{OO}\cdot)(\text{CH}_3)\text{CO}(\text{OH}) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$2.7 \cdot 10^{+02}$		
R <sub>o</sub> 04275	*	*	$\text{CH}_3\text{CH}(\text{CO}(\text{OH}))\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2} 0.200 \text{CH}_3\text{CH}(\text{CO}(\text{OH}))\text{CH}_2(\text{O}\cdot) + 0.550 \text{CH}_3\text{CH}(\text{CO}(\text{OH}))\text{CHO} + 0.250 \text{CH}_3\text{CH}(\text{CH}_2(\text{OH}))\text{CO}(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04276	*	*	$\text{CH}_3\text{C}(\text{OO}\cdot)(\text{CH}_3)\text{CO}(\text{OH}) + \text{CH}_3\text{C}(\text{OO}\cdot)(\text{CH}_3)\text{CO}(\text{OH}) \rightarrow 2.000 \text{CH}_3\text{COCH}_3 + 2.000 \text{CO}_2 + -\text{O}_2-$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 04277	*	*	$\text{CH}_3\text{C}(\text{OO}\cdot)(\text{CH}_3)\text{CO}(\text{OH}) \xrightarrow{\text{RO}_2} \text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_3)\text{CO}(\text{OH}) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 04278	*	*	$\text{CH}_3\text{CH}(\text{CO}(\text{OH}))\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_3\text{CH}(\text{CO}(\text{OH}))\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04279	*	*	$\text{CH}_3\text{CH}(\text{CO}(\text{OH}))\text{CH}_2(\text{O}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OO}\cdot)\text{CO}(\text{OH}) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04280	*	*	$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_3)\text{CO}(\text{OH}) \rightarrow 0.667 \text{CH}_3(\text{OO}\cdot) + 0.667 \text{CH}_3\text{COCO}(\text{OH}) + 0.333 \text{CH}_3\text{COCH}_3 + 0.333 \cdot \text{CO}(\text{OH}) - 0.667 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04281	*	*	$\text{CH}_3\text{CH}(\text{CH}_3)\text{CO}(\text{O}^-) + \text{OH} \rightarrow 0.849 \text{CH}_3\text{CH}(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) + 0.151 \text{CH}_3\text{C}(\text{OO}\cdot)(\text{CH}_3)\text{CO}(\text{O}^-) + \text{H}_2\text{O} - \text{O}_2$	$1.3 \cdot 10^{+09}$		Anbar et al. (1966a)
R <sub>o</sub> 04282	*		$\text{CH}_3\text{CH}(\text{CH}_3)\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow \text{CH}_3\text{CH}(\text{CH}_3)\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 04283	*	*	$\text{CH}_3\text{CH}(\text{CO}(\text{O}^-))\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2} 0.200 \text{CH}_3\text{CH}(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) + 0.550 \text{CH}_3\text{CH}(\text{CO}(\text{O}^-))\text{CHO} + 0.250 \text{CH}_3\text{CH}(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04284	*	*	$\text{CH}_3\text{C}(\text{OO}\cdot)(\text{CH}_3)\text{CO}(\text{O}^-) + \text{CH}_3\text{C}(\text{OO}\cdot)(\text{CH}_3)\text{CO}(\text{O}^-) \rightarrow 2.000 \text{CH}_3\text{COCH}_3 + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 04285	*	*	$\text{CH}_3\text{C}(\text{OO}\cdot)(\text{CH}_3)\text{CO}(\text{O}^-) \xrightarrow{\text{RO}_2} \text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_3)\text{CO}(\text{O}^-) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 04286	*		$\text{CH}_3\text{CH}(\text{CH}_3)\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OO}\cdot)\text{CH}_3 + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04287	*	*	$\text{CH}_3\text{CH}(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_3\text{CH}(\text{CO}(\text{O}^-))\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04288	*	*	$\text{CH}_3\text{CH}(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OO}\cdot)\text{CO}(\text{O}^-) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04289	*	*	$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_3)\text{CO}(\text{O}^-) \rightarrow 0.667 \text{CH}_3(\text{OO}\cdot) + 0.667 \text{CH}_3\text{COCO}(\text{O}^-) + 0.333 \text{CH}_3\text{COCH}_3 + 0.333 \cdot \text{CO}(\text{O}^-) - 0.667 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04290	*		$\text{CH}_3\text{CH}(\text{OO}\cdot)\text{CH}_3 \xrightarrow{\text{RO}_2} 0.200 \text{CH}_3\text{CH}(\text{O}\cdot)\text{CH}_3 + 0.550 \text{CH}_3\text{COCH}_3 + 0.250 \text{CH}_3\text{CH}(\text{OH})\text{CH}_3 + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
E <sub>o</sub> 00564	*	*	$\text{CH}_3\text{CH}(\text{CH}_2(\text{OH}))\text{CO}(\text{OH}) \rightleftharpoons \text{CH}_3\text{CH}(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) + \text{H}^+$	$2.3 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04291	*	*	CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CO(OH) + OH → 0.184 CH <sub>2</sub> (OH)CH(CO(OH))CH <sub>2</sub> (OO·) + 0.762 CH <sub>3</sub> CH(CO(OH))CH(OH)(OO·) + 0.054 CH <sub>3</sub> CH(CO(OH))CH <sub>2</sub> (O·) + H <sub>2</sub> O – 0.946 O <sub>2</sub>	1.6 · 10 <sup>+09</sup>		
R <sub>o</sub> 04292	*		CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CO(OH) + NO <sub>3</sub> → 0.184 CH <sub>2</sub> (OH)CH(CO(OH))CH <sub>2</sub> (OO·) + 0.762 CH <sub>3</sub> CH(CO(OH))CH(OH)(OO·) + 0.054 CH <sub>3</sub> CH(CO(OH))CH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> – 0.946 O <sub>2</sub>	3.2 · 10 <sup>+02</sup>		
R <sub>o</sub> 04293	*	*	CH <sub>2</sub> (OH)CH(CO(OH))CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(CO(OH))CH <sub>2</sub> (O·) + 0.550 CH <sub>2</sub> (OH)CH(CO(OH))CHO + 0.250 CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04294	*	*	CH <sub>3</sub> CH(CO(OH))CH(OH)(OO·) → CH <sub>3</sub> CH(CO(OH))CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04295	*	*	CH <sub>2</sub> (OH)CH(CO(OH))CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(CO(OH))CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04296	*	*	CH <sub>2</sub> (OH)CH(CO(OH))CH <sub>2</sub> (O·) → CH <sub>2</sub> (OH)CH(OO·)CO(OH) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04297	*	*	CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CO(O <sup>-</sup> ) + OH → 0.188 CH <sub>2</sub> (OH)CH(CO(O <sup>-</sup> ))CH <sub>2</sub> (OO·) + 0.780 CH <sub>3</sub> CH(CO(O <sup>-</sup> ))CH(OH)(OO·) + 0.031 CH <sub>3</sub> CH(CO(O <sup>-</sup> ))CH <sub>2</sub> (O·) + H <sub>2</sub> O – 0.969 O <sub>2</sub>	2.8 · 10 <sup>+09</sup>		
R <sub>o</sub> 04298	*		CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 04299	*	*	CH <sub>2</sub> (OH)CH(CO(O <sup>-</sup> ))CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(CO(O <sup>-</sup> ))CH <sub>2</sub> (O·) + 0.550 CH <sub>2</sub> (OH)CH(CO(O <sup>-</sup> ))CHO + 0.250 CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CO(O <sup>-</sup> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04300	*	*	CH <sub>3</sub> CH(CO(O <sup>-</sup> ))CH(OH)(OO·) → CH <sub>3</sub> CH(CO(O <sup>-</sup> ))CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04301	*		CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CO(O·) → CH <sub>3</sub> CH(OO·)CH <sub>2</sub> (OH) + CO <sub>2</sub> – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04302	*	*	CH <sub>2</sub> (OH)CH(CO(O <sup>-</sup> ))CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(CO(O <sup>-</sup> ))CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04303	*	*	CH <sub>2</sub> (OH)CH(CO(O <sup>-</sup> ))CH <sub>2</sub> (O·) → CH <sub>2</sub> (OH)CH(OO·)CO(O <sup>-</sup> ) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00565	*	*	CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CO(OH) ⇌ CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CO(O <sup>-</sup> ) + H <sup>+</sup>	3.4 · 10 <sup>-05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04304	*	*	CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CO(OH) + OH → 0.930 CH <sub>2</sub> (OH)CH(CO(OH))CH(OH)(OO·) + 0.070 CH <sub>2</sub> (OH)CH(CO(OH))CH <sub>2</sub> (O·) + H <sub>2</sub> O – 0.930 O <sub>2</sub>	2.5 · 10 <sup>+09</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04305	*		$\text{CH}_2(\text{OH})\text{CH}(\text{CH}_2(\text{OH}))\text{CO}(\text{OH}) + \text{NO}_3 \rightarrow$ $0.930 \text{CH}_2(\text{OH})\text{CH}(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.070 \text{CH}_2(\text{OH})\text{CH}(\text{CO}(\text{OH}))\text{CH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.930 \text{O}_2$	$3.7 \cdot 10^{+02}$		
R <sub>o</sub> 04306	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{CO}(\text{OH}))\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{CO}(\text{OH}))\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04307	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) + \text{OH} \rightarrow$ $0.959 \text{CH}_2(\text{OH})\text{CH}(\text{CO}(\text{O}^-))\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.041 \text{CH}_2(\text{OH})\text{CH}(\text{CO}(\text{O}^-))\text{CH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.959 \text{O}_2$	$4.3 \cdot 10^{+09}$		
R <sub>o</sub> 04308	*		$\text{CH}_2(\text{OH})\text{CH}(\text{CH}_2(\text{OH}))\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{CH}_2(\text{OH}))\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 04309	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{CO}(\text{O}^-))\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}(\text{CO}(\text{O}^-))\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04310	*		$\text{CH}_2(\text{OH})\text{CH}(\text{CH}_2(\text{OH}))\text{CO}(\text{O}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{CH}_2(\text{OH}) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04311	*	*	$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2(\text{OH}) + \text{OH} \rightarrow$ $0.284 \text{CH}_3\text{CH}(\text{CH}_2(\text{OH}))\text{CH}_2(\text{OO}\cdot) + 0.126 \text{CH}_3\text{C}(\text{OO}\cdot)(\text{CH}_3)\text{CH}_2(\text{OH}) +$ $0.590 \text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{OH})(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$3.3 \cdot 10^{+09}$		Burton et al. (1988a)
R <sub>o</sub> 04312	*		$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2(\text{OH}) + \text{NO}_3 \rightarrow$ $0.284 \text{CH}_3\text{CH}(\text{CH}_2(\text{OH}))\text{CH}_2(\text{OO}\cdot) + 0.126 \text{CH}_3\text{C}(\text{OO}\cdot)(\text{CH}_3)\text{CH}_2(\text{OH}) +$ $0.590 \text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{OH})(\text{OO}\cdot) + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$1.6 \cdot 10^{+06}$		Shastri and Huie (1990)
R <sub>o</sub> 04313	*	*	$\text{CH}_3\text{CH}(\text{CH}_2(\text{OH}))\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_3\text{CH}(\text{CH}_2(\text{OH}))\text{CH}_2(\text{O}\cdot) + 0.550 \text{CH}_3\text{CH}(\text{CH}_2(\text{OH}))\text{CHO} +$ $0.250 \text{CH}_3\text{CH}(\text{CH}_2(\text{OH}))\text{CH}_2(\text{OH}) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04314	*	*	$\text{CH}_3\text{C}(\text{OO}\cdot)(\text{CH}_3)\text{CH}_2(\text{OH}) \xrightarrow{\text{RO}_2} \text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_3)\text{CH}_2(\text{OH}) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 04315	*	*	$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{CH}_3)\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04316	*	*	$\text{CH}_3\text{CH}(\text{CH}_2(\text{OH}))\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_3\text{CH}(\text{CH}_2(\text{OH}))\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04317	*	*	$\text{CH}_3\text{CH}(\text{CH}_2(\text{OH}))\text{CH}_2(\text{O}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OO}\cdot)\text{CH}_2(\text{OH}) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04318	*	*	$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_3)\text{CH}_2(\text{OH}) \rightarrow 0.667 \text{CH}_3(\text{OO}\cdot) + 0.667 \text{CH}_3\text{COCH}_2(\text{OH}) +$ $0.333 \text{CH}_3\text{COCH}_3 + 0.333 \text{CH}_2(\text{OH})\cdot - 0.667 \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04319	*	*	CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH) + OH → 0.100 CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CH <sub>2</sub> (OO·) + 0.038 CH <sub>3</sub> C(OO·)(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH) + 0.826 CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CH(OH)(OO·) + 0.037 CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CH <sub>2</sub> (O·) + H <sub>2</sub> O – 0.963 O <sub>2</sub>	4.7 · 10 <sup>+09</sup>		
R <sub>o</sub> 04320	*		CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH) + NO <sub>3</sub> → 0.100 CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CH <sub>2</sub> (OO·) + 0.038 CH <sub>3</sub> C(OO·)(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH) + 0.826 CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CH(OH)(OO·) + 0.037 CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.963 O <sub>2</sub>	2.2 · 10 <sup>+06</sup>		
R <sub>o</sub> 04321	*	*	CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CH <sub>2</sub> (O·) + 0.550 CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CHO + 0.250 CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04322	*	*	CH <sub>3</sub> C(OO·)(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH) $\xrightarrow{RO_2}$ CH <sub>3</sub> C(O·)(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04323	*	*	CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CH(OH)(OO·) → CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04324	*	*	CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04325	*	*	CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CH <sub>2</sub> (O·) → CH <sub>2</sub> (OH)CH(OO·)CH <sub>2</sub> (OH) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04326	*	*	CH <sub>3</sub> C(O·)(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH) → 0.333 CH <sub>3</sub> (OO·) + 0.333 CH <sub>2</sub> (OH)COCH <sub>2</sub> (OH) + 0.667 CH <sub>3</sub> COCH <sub>2</sub> (OH) + 0.667 CH <sub>2</sub> (OH)· – 0.333 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00566	*	*	CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CHO $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CH(OH) <sub>2</sub>	2.5 · 10 <sup>+00</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04327	*	*	CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CHO + OH → 0.083 CH <sub>2</sub> (OH)CH(CHO)CH <sub>2</sub> (OO·) + 0.344 CH <sub>3</sub> CH(CHO)CH(OH)(OO·) + 0.573 CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CO(OO·) + H <sub>2</sub> O – O <sub>2</sub>	4.6 · 10 <sup>+09</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04328	*		CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CHO + NO <sub>3</sub> → 0.083 CH <sub>2</sub> (OH)CH(CHO)CH <sub>2</sub> (OO·) + 0.344 CH <sub>3</sub> CH(CHO)CH(OH)(OO·) + 0.573 CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CO(OO·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	3.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 04329	*	*	CH <sub>2</sub> (OH)CH(CHO)CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(CHO)CH <sub>2</sub> (O·) + 0.550 CH <sub>2</sub> (OH)CH(CHO)CHO + 0.250 CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04330	*	*	CH <sub>3</sub> CH(CHO)CH(OH)(OO·) → CH <sub>3</sub> CH(CHO)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04331	*	*	CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CO(OO·) → CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04332	*	*	CH <sub>2</sub> (OH)CH(CHO)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(CHO)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04333	*	*	CH <sub>2</sub> (OH)CH(CHO)CH <sub>2</sub> (O·) → CH <sub>2</sub> (OH)CH(OO·)CHO + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04334	*	*	CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CH(OH) <sub>2</sub> + OH → 0.124 CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CH <sub>2</sub> (OO·) + 0.516 CH <sub>3</sub> CH(CH(OH) <sub>2</sub> )CH(OH)(OO·) + 0.254 CH <sub>3</sub> CH(CH <sub>2</sub> (OH))C(OH) <sub>2</sub> (OO·) + 0.106 CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CH(OH)(O·) + H <sub>2</sub> O - 0.894 O <sub>2</sub>	3.6 · 10 <sup>+09</sup>		
R <sub>o</sub> 04335	*		CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.124 CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CH <sub>2</sub> (OO·) + 0.516 CH <sub>3</sub> CH(CH(OH) <sub>2</sub> )CH(OH)(OO·) + 0.254 CH <sub>3</sub> CH(CH <sub>2</sub> (OH))C(OH) <sub>2</sub> (OO·) + 0.106 CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.894 O <sub>2</sub>	1.3 · 10 <sup>+07</sup>		
R <sub>o</sub> 04336	*	*	CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CH <sub>2</sub> (O·) + 0.550 CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CHO + 0.250 CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04337	*	*	CH <sub>3</sub> CH(CH(OH) <sub>2</sub> )CH(OH)(OO·) → CH <sub>3</sub> CH(CH(OH) <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04338	*	*	CH <sub>3</sub> CH(CH <sub>2</sub> (OH))C(OH) <sub>2</sub> (OO·) → CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04339	*	*	CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04340	*	*	CH <sub>3</sub> CH(CH <sub>2</sub> (OH))CH(OH)(O·) → CH <sub>3</sub> CH(OO·)CH <sub>2</sub> (OH) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04341	*	*	CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04342	*	*	CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CH <sub>2</sub> (O·) → CH <sub>2</sub> (OH)CH(OO·)CH(OH) <sub>2</sub> + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04343	*	*	CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH) + OH $\rightarrow$ 0.954 CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CH(OH)(OO $\cdot$ ) + 0.046 CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CH <sub>2</sub> (O $\cdot$ ) + H <sub>2</sub> O - 0.954 O <sub>2</sub>	$5.8 \cdot 10^{+09}$		
R <sub>o</sub> 04344	*		CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH) + NO <sub>3</sub> $\rightarrow$ 0.954 CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CH(OH)(OO $\cdot$ ) + 0.046 CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CH <sub>2</sub> (O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.954 O <sub>2</sub>	$2.2 \cdot 10^{+06}$		
R <sub>o</sub> 04345	*	*	CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CH(OH)(OO $\cdot$ ) $\rightarrow$ CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
E <sub>o</sub> 00567	*	*	CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CH(OH) <sub>2</sub>	$5.1 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04346	*	*	CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CHO + OH $\rightarrow$ 0.529 CH <sub>2</sub> (OH)CH(CHO)CH(OH)(OO $\cdot$ ) + 0.440 CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CO(OO $\cdot$ ) + 0.031 CH <sub>2</sub> (OH)CH(CHO)CH <sub>2</sub> (O $\cdot$ ) + H <sub>2</sub> O - 0.969 O <sub>2</sub>	$5.7 \cdot 10^{+09}$		
R <sub>o</sub> 04347	*		CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CHO + NO <sub>3</sub> $\rightarrow$ 0.529 CH <sub>2</sub> (OH)CH(CHO)CH(OH)(OO $\cdot$ ) + 0.440 CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CO(OO $\cdot$ ) + 0.031 CH <sub>2</sub> (OH)CH(CHO)CH <sub>2</sub> (O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.969 O <sub>2</sub>	$3.7 \cdot 10^{+07}$		
R <sub>o</sub> 04348	*	*	CH <sub>2</sub> (OH)CH(CHO)CH(OH)(OO $\cdot$ ) $\rightarrow$ CH <sub>2</sub> (OH)CH(CHO)CHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04349	*	*	CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CO(OO $\cdot$ ) $\rightarrow$ CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
E <sub>o</sub> 00568	*	*	CH <sub>3</sub> CH(CHO)CHO $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> CH(CH(OH) <sub>2</sub> )CHO	$3.0 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00569	*	*	CH <sub>3</sub> CH(CHO)CHO $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> CH(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub>	$1.5 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04350	*	*	CH <sub>3</sub> CH(CHO)CHO + OH $\rightarrow$ 0.067 CHOCH(CHO)CH <sub>2</sub> (OO $\cdot$ ) + 0.933 CH <sub>3</sub> CH(CHO)CO(OO $\cdot$ ) + H <sub>2</sub> O - O <sub>2</sub>	$4.7 \cdot 10^{+09}$		
R <sub>o</sub> 04351	*		CH <sub>3</sub> CH(CHO)CHO + NO <sub>3</sub> $\rightarrow$ 0.067 CHOCH(CHO)CH <sub>2</sub> (OO $\cdot$ ) + 0.933 CH <sub>3</sub> CH(CHO)CO(OO $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	$1.5 \cdot 10^{+07}$		
R <sub>o</sub> 04352	*	*	CHOCH(CHO)CH <sub>2</sub> (OO $\cdot$ ) $\xrightarrow{RO_2}$ 0.200 CHOCH(CHO)CH <sub>2</sub> (O $\cdot$ ) + 0.550 CHOCH(CHO)CHO + 0.250 CH <sub>2</sub> (OH)CH(CHO)CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04353	*	*	CH <sub>3</sub> CH(CHO)CO(OO $\cdot$ ) $\rightarrow$ CH <sub>3</sub> CH(CO(OH))CHO + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04354	*	*	$\text{CHOCH(CHO)CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CHOCH(CHO)CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04355	*	*	$\text{CHOCH(CHO)CH}_2(\text{O}\cdot) \rightarrow \text{CHOCH(OO}\cdot\text{)CHO} + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00570	*	*	$\text{CH}_2(\text{OH})\text{CH(CHO)CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{CH(CH(OH)}_2\text{)CHO}$	$6.1 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00571	*	*	$\text{CH}_2(\text{OH})\text{CH(CHO)CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{CH(CH(OH)}_2\text{)CH(OH)}_2$	$6.5 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04356	*	*	$\text{CH}_2(\text{OH})\text{CH(CHO)CHO} + \text{OH} \rightarrow 0.231 \text{ CHOCH(CHO)CH(OH)(OO}\cdot\text{)} +$ $0.769 \text{ CH}_2(\text{OH})\text{CH(CHO)CO(OO}\cdot\text{)} + \text{H}_2\text{O} - \text{O}_2$	$5.3 \cdot 10^{+09}$		
R <sub>o</sub> 04357	*		$\text{CH}_2(\text{OH})\text{CH(CHO)CHO} + \text{NO}_3 \rightarrow 0.231 \text{ CHOCH(CHO)CH(OH)(OO}\cdot\text{)} +$ $0.769 \text{ CH}_2(\text{OH})\text{CH(CHO)CO(OO}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$1.5 \cdot 10^{+07}$		
R <sub>o</sub> 04358	*	*	$\text{CHOCH(CHO)CH(OH)(OO}\cdot\text{)} \rightarrow \text{CHOCH(CHO)CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04359	*	*	$\text{CH}_2(\text{OH})\text{CH(CHO)CO(OO}\cdot\text{)} \rightarrow \text{CH}_2(\text{OH})\text{CH(CO(OH))CHO} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04360	*	*	$\text{CH}_3\text{CH(CH(OH)}_2\text{)CH(OH)}_2 + \text{OH} \rightarrow$ $0.146 \text{ CH(OH)}_2\text{CH(CH(OH)}_2\text{)CH}_2(\text{OO}\cdot\text{)} +$ $0.595 \text{ CH}_3\text{CH(CH(OH)}_2\text{)C(OH)}_2(\text{OO}\cdot\text{)} +$ $0.259 \text{ CH}_3\text{CH(CH(OH)}_2\text{)CH(OH)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.741 \text{ O}_2$	$2.9 \cdot 10^{+09}$		
R <sub>o</sub> 04361	*		$\text{CH}_3\text{CH(CH(OH)}_2\text{)CH(OH)}_2 + \text{NO}_3 \rightarrow$ $0.146 \text{ CH(OH)}_2\text{CH(CH(OH)}_2\text{)CH}_2(\text{OO}\cdot\text{)} +$ $0.595 \text{ CH}_3\text{CH(CH(OH)}_2\text{)C(OH)}_2(\text{OO}\cdot\text{)} +$ $0.259 \text{ CH}_3\text{CH(CH(OH)}_2\text{)CH(OH)(O}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - 0.741 \text{ O}_2$	$1.2 \cdot 10^{+07}$		
R <sub>o</sub> 04362	*	*	$\text{CH(OH)}_2\text{CH(CH(OH)}_2\text{)CH}_2(\text{OO}\cdot\text{)} \xrightarrow{\text{RO}_2}$ $0.200 \text{ CH(OH)}_2\text{CH(CH(OH)}_2\text{)CH}_2(\text{O}\cdot\text{)} + 0.550 \text{ CH(OH)}_2\text{CH(CH(OH)}_2\text{)CHO} +$ $0.250 \text{ CH}_2(\text{OH})\text{CH(CH(OH)}_2\text{)CH(OH)}_2 + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04363	*	*	$\text{CH}_3\text{CH(CH(OH)}_2\text{)C(OH)}_2(\text{OO}\cdot\text{)} \rightarrow \text{CH}_3\text{CH(CH(OH)}_2\text{)CO(OH)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04364	*	*	$\text{CH}_3\text{CH(CH(OH)}_2\text{)CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CH}_3\text{CH(CH(OH)}_2\text{)CO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04365	*	*	$\text{CH}_3\text{CH(CH(OH)}_2\text{)CH(OH)(O}\cdot\text{)} \rightarrow \text{CH}_3\text{CH(OO}\cdot\text{)CH(OH)}_2 + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04366	*	*	$\text{CH(OH)}_2\text{CH(CH(OH)}_2\text{)CH}_2(\text{O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CH(OH)}_2\text{CH(CH(OH)}_2\text{)CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04367	*	*	$\text{CH(OH)}_2\text{CH(CH(OH)}_2\text{)CH}_2(\text{O}\cdot\text{)} \rightarrow$ $\text{CH(OH)}_2\text{CH(OO}\cdot\text{)CH(OH)}_2 + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04368	*	*	CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub> + OH → 0.410 CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CH(OH)(OO·) + 0.403 CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.187 CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CH(OH)(O·) + H <sub>2</sub> O – 0.813 O <sub>2</sub>	4.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 04369	*		CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.410 CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CH(OH)(OO·) + 0.403 CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.187 CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.813 O <sub>2</sub>	1.3 · 10 <sup>+07</sup>		
R <sub>o</sub> 04370	*	*	CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CH(OH)(OO·) → CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04371	*	*	CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04372	*	*	CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04373	*	*	CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CH(OH)(O·) → CH <sub>2</sub> (OH)CH(OO·)CH(OH) <sub>2</sub> + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04374	*	*	CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CH(OH) <sub>2</sub> + OH → 0.712 CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CH(OH)(OO·) + 0.175 CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))C(OH) <sub>2</sub> (OO·) + 0.036 CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CH <sub>2</sub> (O·) + 0.078 CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CH(OH)(O·) + H <sub>2</sub> O – 0.887 O <sub>2</sub>	4.9 · 10 <sup>+09</sup>		
R <sub>o</sub> 04375	*		CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.712 CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CH(OH)(OO·) + 0.175 CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))C(OH) <sub>2</sub> (OO·) + 0.036 CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CH <sub>2</sub> (O·) + 0.078 CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.887 O <sub>2</sub>	1.5 · 10 <sup>+07</sup>		
R <sub>o</sub> 04376	*	*	CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CH(OH)(OO·) → CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04377	*	*	CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))C(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)CH(CH <sub>2</sub> (OH))CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04378	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{CH}_2(\text{OH}))\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CH}_2(\text{OH})\text{CH}(\text{CH}_2(\text{OH}))\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04379	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{CH}_2(\text{OH}))\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{CH}_2(\text{OH}) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04380	*	*	$\text{CH}_3\text{CH}(\text{CH}(\text{OH})_2)\text{CHO} + \text{OH} \rightarrow 0.091 \text{CH}(\text{OH})_2\text{CH}(\text{CHO})\text{CH}_2(\text{OO}\cdot) +$ $0.186 \text{CH}_3\text{CH}(\text{CHO})\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.629 \text{CH}_3\text{CH}(\text{CH}(\text{OH})_2)\text{CO}(\text{OO}\cdot) +$ $0.094 \text{CH}_3\text{CH}(\text{CHO})\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.906 \text{O}_2$	$4.0 \cdot 10^{+09}$		
R <sub>o</sub> 04381	*		$\text{CH}_3\text{CH}(\text{CH}(\text{OH})_2)\text{CHO} + \text{NO}_3 \rightarrow 0.091 \text{CH}(\text{OH})_2\text{CH}(\text{CHO})\text{CH}_2(\text{OO}\cdot) +$ $0.186 \text{CH}_3\text{CH}(\text{CHO})\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.629 \text{CH}_3\text{CH}(\text{CH}(\text{OH})_2)\text{CO}(\text{OO}\cdot) +$ $0.094 \text{CH}_3\text{CH}(\text{CHO})\text{CH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.906 \text{O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 04382	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{CHO})\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}(\text{OH})_2\text{CH}(\text{CHO})\text{CH}_2(\text{O}\cdot) + 0.550 \text{CH}(\text{OH})_2\text{CH}(\text{CHO})\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{CH}(\text{CH}(\text{OH})_2)\text{CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04383	*	*	$\text{CH}_3\text{CH}(\text{CHO})\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{CO}(\text{OH}))\text{CHO} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04384	*	*	$\text{CH}_3\text{CH}(\text{CH}(\text{OH})_2)\text{CO}(\text{OO}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{CH}(\text{OH})_2)\text{CO}(\text{OH}) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04385	*	*	$\text{CH}_3\text{CH}(\text{CHO})\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_3\text{CH}(\text{CO}(\text{OH}))\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04386	*	*	$\text{CH}_3\text{CH}(\text{CHO})\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow \text{CH}_3\text{CH}(\text{OO}\cdot)\text{CHO} + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04387	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{CHO})\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{CH}(\text{CHO})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04388	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{CHO})\text{CH}_2(\text{O}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CH}(\text{OO}\cdot)\text{CHO} + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04389	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{CH}(\text{OH})_2)\text{CHO} + \text{OH} \rightarrow$ $0.292 \text{CH}(\text{OH})_2\text{CH}(\text{CHO})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.144 \text{CH}_2(\text{OH})\text{CH}(\text{CHO})\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.486 \text{CH}_2(\text{OH})\text{CH}(\text{CH}(\text{OH})_2)\text{CO}(\text{OO}\cdot) +$ $0.078 \text{CH}_2(\text{OH})\text{CH}(\text{CHO})\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.922 \text{O}_2$	$4.9 \cdot 10^{+09}$		
R <sub>o</sub> 04390	*		$\text{CH}_2(\text{OH})\text{CH}(\text{CH}(\text{OH})_2)\text{CHO} + \text{NO}_3 \rightarrow$ $0.292 \text{CH}(\text{OH})_2\text{CH}(\text{CHO})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.144 \text{CH}_2(\text{OH})\text{CH}(\text{CHO})\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.486 \text{CH}_2(\text{OH})\text{CH}(\text{CH}(\text{OH})_2)\text{CO}(\text{OO}\cdot) +$ $0.078 \text{CH}_2(\text{OH})\text{CH}(\text{CHO})\text{CH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.922 \text{O}_2$	$1.1 \cdot 10^{+07}$		
R <sub>o</sub> 04391	*	*	$\text{CH}(\text{OH})_2\text{CH}(\text{CHO})\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}(\text{OH})_2\text{CH}(\text{CHO})\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04392	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{CHO})\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}(\text{CO}(\text{OH}))\text{CHO} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04393	*	*	CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CO(OO·) → CH <sub>2</sub> (OH)CH(CH(OH) <sub>2</sub> )CO(OH) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04394	*	*	CH <sub>2</sub> (OH)CH(CHO)CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(CO(OH))CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04395	*	*	CH <sub>2</sub> (OH)CH(CHO)CH(OH)(O·) → CH <sub>2</sub> (OH)CH(OO·)CHO + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00572	*	*	CHOCH(CHO)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub>	4.4 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04396	*	*	CHOCH(CHO)CHO + OH → CHOCH(CHO)CO(OO·) + H <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 04397	*	*	CHOCH(CHO)CHO + NO <sub>3</sub> → CHOCH(CHO)CO(OO·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – O <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04398	*	*	CHOCH(CHO)CO(OO·) → CO(OH)CH(CHO)CHO + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04399	*	*	CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub> + OH → 0.673 CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.327 CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CH(OH)(O·) + H <sub>2</sub> O – 0.673 O <sub>2</sub>	3.5 · 10 <sup>+09</sup>		
R <sub>o</sub> 04400	*		CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.673 CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.327 CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.673 O <sub>2</sub>	1.2 · 10 <sup>+07</sup>		
R <sub>o</sub> 04401	*	*	CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04402	*	*	CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CH(OH)(O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04403	*	*	CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CH(OH)(O·) → CH(OH) <sub>2</sub> CH(OO·)CH(OH) <sub>2</sub> + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00573	*	*	CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub>	4.4 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04404	*	*	CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CHO + OH → 0.307 CH(OH) <sub>2</sub> CH(CHO)C(OH) <sub>2</sub> (OO·) + 0.519 CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CO(OO·) + 0.174 CH(OH) <sub>2</sub> CH(CHO)CH(OH)(O·) + H <sub>2</sub> O – 0.826 O <sub>2</sub>	4.4 · 10 <sup>+09</sup>		
R <sub>o</sub> 04405	*		CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CHO + NO <sub>3</sub> → 0.307 CH(OH) <sub>2</sub> CH(CHO)C(OH) <sub>2</sub> (OO·) + 0.519 CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CO(OO·) + 0.174 CH(OH) <sub>2</sub> CH(CHO)CH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.826 O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 04406	*	*	CH(OH) <sub>2</sub> CH(CHO)C(OH) <sub>2</sub> (OO·) → CH(OH) <sub>2</sub> CH(CO(OH))CHO + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04407	*	*	CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CO(OO·) → CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04408	*	*	CH(OH) <sub>2</sub> CH(CHO)CH(OH)(O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(CO(OH))CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04409	*	*	CH(OH) <sub>2</sub> CH(CHO)CH(OH)(O·) → CH(OH) <sub>2</sub> CH(OO·)CHO + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00574	*	*	CH(OH) <sub>2</sub> CH(CHO)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub>	4.4 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04410	*	*	CH(OH) <sub>2</sub> CH(CHO)CHO + OH → 0.119 CHOCH(CHO)C(OH) <sub>2</sub> (OO·) + 0.803 CH(OH) <sub>2</sub> CH(CHO)CO(OO·) + 0.078 CHOCH(CHO)CH(OH)(O·) + H <sub>2</sub> O - 0.922 O <sub>2</sub>	4.9 · 10 <sup>+09</sup>		
R <sub>o</sub> 04411	*		CH(OH) <sub>2</sub> CH(CHO)CHO + NO <sub>3</sub> → 0.119 CHOCH(CHO)C(OH) <sub>2</sub> (OO·) + 0.803 CH(OH) <sub>2</sub> CH(CHO)CO(OO·) + 0.078 CHOCH(CHO)CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.922 O <sub>2</sub>	8.5 · 10 <sup>+06</sup>		
R <sub>o</sub> 04412	*	*	CHOCH(CHO)C(OH) <sub>2</sub> (OO·) → CO(OH)CH(CHO)CHO + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04413	*	*	CH(OH) <sub>2</sub> CH(CHO)CO(OO·) → CH(OH) <sub>2</sub> CH(CO(OH))CHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04414	*	*	CHOCH(CHO)CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH(CHO)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04415	*	*	CHOCH(CHO)CH(OH)(O·) → CHOCH(OO·)CHO + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00575	*	*	CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CO(OH) $\rightleftharpoons$ CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CO(O <sup>-</sup> ) + H <sup>+</sup>	2.5 · 10 <sup>-05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04416	*	*	CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CO(OH) + OH → 0.792 CH <sub>3</sub> C(OH)(CO(OH))CH <sub>2</sub> (OO·) + 0.208 CH <sub>3</sub> C(O·)(CH <sub>3</sub> )CO(OH) + H <sub>2</sub> O - 0.792 O <sub>2</sub>	3.2 · 10 <sup>+08</sup>		
R <sub>o</sub> 04417	*		CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CO(OH) + NO <sub>3</sub> → 0.792 CH <sub>3</sub> C(OH)(CO(OH))CH <sub>2</sub> (OO·) + 0.208 CH <sub>3</sub> C(O·)(CH <sub>3</sub> )CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.792 O <sub>2</sub>	1.4 · 10 <sup>+03</sup>		
R <sub>o</sub> 04418	*	*	CH <sub>3</sub> C(OH)(CO(OH))CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>3</sub> C(OH)(CO(OH))CH <sub>2</sub> (O·) + 0.550 CH <sub>3</sub> C(OH)(CO(OH))CHO + 0.250 CH <sub>3</sub> C(OH)(CH <sub>2</sub> (OH))CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04419	*	*	CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CO(O <sup>-</sup> ) + OH → 0.792 CH <sub>3</sub> C(OH)(CO(O <sup>-</sup> ))CH <sub>2</sub> (OO·) + 0.208 CH <sub>3</sub> C(O·)(CH <sub>3</sub> )CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.792 O <sub>2</sub>	5.6 · 10 <sup>+08</sup>		
R <sub>o</sub> 04420	*		CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 04421	*		CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CO(O·) → CH <sub>3</sub> C(OH)(OO·)CH <sub>3</sub> + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00576	*	*	CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CHO $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CH(OH) <sub>2</sub>	7.4 · 10 <sup>+00</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04422	*	*	CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CHO + OH $\rightarrow$ 0.212 CH <sub>3</sub> C(OH)(CHO)CH <sub>2</sub> (OO $\cdot$ ) + 0.732 CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CO(OO $\cdot$ ) + 0.056 CH <sub>3</sub> C(O $\cdot$ )(CH <sub>3</sub> )CHO + H <sub>2</sub> O - 0.944 O <sub>2</sub>	3.0 · 10 <sup>+09</sup>		Acero <i>et al.</i> (2001)
R <sub>o</sub> 04423	*		CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CHO + NO <sub>3</sub> $\rightarrow$ 0.212 CH <sub>3</sub> C(OH)(CHO)CH <sub>2</sub> (OO $\cdot$ ) + 0.732 CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CO(OO $\cdot$ ) + 0.056 CH <sub>3</sub> C(O $\cdot$ )(CH <sub>3</sub> )CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.944 O <sub>2</sub>	2.6 · 10 <sup>+07</sup>		
R <sub>o</sub> 04424	*	*	CH <sub>3</sub> C(OH)(CHO)CH <sub>2</sub> (OO $\cdot$ ) $\xrightarrow{RO_2}$ 0.200 CH <sub>3</sub> C(OH)(CHO)CH <sub>2</sub> (O $\cdot$ ) + 0.550 CH <sub>3</sub> C(OH)(CHO)CHO + 0.250 CH <sub>3</sub> C(OH)(CH <sub>2</sub> (OH))CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04425	*	*	CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CO(OO $\cdot$ ) $\rightarrow$ CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04426	*	*	CH <sub>3</sub> C(O $\cdot$ )(CH <sub>3</sub> )CHO $\rightarrow$ 0.667 CH <sub>3</sub> (OO $\cdot$ ) + 0.667 CH <sub>3</sub> COCHO + 0.333 CH <sub>3</sub> COCH <sub>3</sub> + 0.333 CH $\cdot$ (OH) <sub>2</sub> - 0.667 O <sub>2</sub> - 0.333 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04427	*	*	CH <sub>3</sub> C(OH)(CHO)CH <sub>2</sub> (O $\cdot$ ) $\xrightarrow{O_2}$ CH <sub>3</sub> C(OH)(CHO)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04428	*	*	CH <sub>3</sub> C(OH)(CHO)CH <sub>2</sub> (O $\cdot$ ) $\rightarrow$ CH <sub>3</sub> C(OH)(OO $\cdot$ )CHO + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04429	*	*	CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CH(OH) <sub>2</sub> + OH $\rightarrow$ 0.308 CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CH <sub>2</sub> (OO $\cdot$ ) + 0.315 CH <sub>3</sub> C(OH)(CH <sub>3</sub> )C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.081 CH <sub>3</sub> C(O $\cdot$ )(CH <sub>3</sub> )CH(OH) <sub>2</sub> + 0.296 CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CH(OH)(O $\cdot$ ) + H <sub>2</sub> O - 0.623 O <sub>2</sub>	1.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 04430	*		CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CH(OH) <sub>2</sub> + NO <sub>3</sub> $\rightarrow$ 0.308 CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CH <sub>2</sub> (OO $\cdot$ ) + 0.315 CH <sub>3</sub> C(OH)(CH <sub>3</sub> )C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.081 CH <sub>3</sub> C(O $\cdot$ )(CH <sub>3</sub> )CH(OH) <sub>2</sub> + 0.296 CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CH(OH)(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.623 O <sub>2</sub>	1.1 · 10 <sup>+07</sup>		
R <sub>o</sub> 04431	*	*	CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CH <sub>2</sub> (OO $\cdot$ ) $\xrightarrow{RO_2}$ 0.200 CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CH <sub>2</sub> (O $\cdot$ ) + 0.550 CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CHO + 0.250 CH <sub>3</sub> C(OH)(CH <sub>2</sub> (OH))CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04432	*	*	CH <sub>3</sub> C(OH)(CH <sub>3</sub> )C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04433	*	*	CH <sub>3</sub> C(O $\cdot$ )(CH <sub>3</sub> )CH(OH) <sub>2</sub> $\rightarrow$ 0.667 CH <sub>3</sub> (OO $\cdot$ ) + 0.667 CH <sub>3</sub> COCH(OH) <sub>2</sub> + 0.333 CH <sub>3</sub> COCH <sub>3</sub> + 0.333 CH $\cdot$ (OH) <sub>2</sub> - 0.667 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04434	*	*	CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04435	*	*	CH <sub>3</sub> C(OH)(CH <sub>3</sub> )CH(OH)(O $\cdot$ ) $\rightarrow$ CH <sub>3</sub> C(OH)(OO $\cdot$ )CH <sub>3</sub> + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04436	*	*	CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CH <sub>2</sub> (O $\cdot$ ) $\xrightarrow{O_2}$ CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04437	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{CH}_2(\text{O}\cdot) \rightarrow \text{CH}_3\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})_2 + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00577	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CH}(\text{OH})_2$	$1.5 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04438	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CHO} + \text{OH} \rightarrow$ $0.076 \text{ CH}_2(\text{OH})\text{C}(\text{OH})(\text{CHO})\text{CH}_2(\text{OO}\cdot) +$ $0.316 \text{ CH}_3\text{C}(\text{OH})(\text{CHO})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.526 \text{ CH}_3\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CO}(\text{OO}\cdot) + 0.040 \text{ CH}_3\text{C}(\text{O}\cdot)(\text{CH}_2(\text{OH}))\text{CHO} +$ $0.042 \text{ CH}_3\text{C}(\text{OH})(\text{CHO})\text{CH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.918 \text{ O}_2$	$2.0 \cdot 10^{+09}$		
R <sub>o</sub> 04439	*		$\text{CH}_3\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CHO} + \text{NO}_3 \rightarrow$ $0.076 \text{ CH}_2(\text{OH})\text{C}(\text{OH})(\text{CHO})\text{CH}_2(\text{OO}\cdot) +$ $0.316 \text{ CH}_3\text{C}(\text{OH})(\text{CHO})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.526 \text{ CH}_3\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CO}(\text{OO}\cdot) + 0.040 \text{ CH}_3\text{C}(\text{O}\cdot)(\text{CH}_2(\text{OH}))\text{CHO} +$ $0.042 \text{ CH}_3\text{C}(\text{OH})(\text{CHO})\text{CH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.918 \text{ O}_2$	$2.5 \cdot 10^{+07}$		
R <sub>o</sub> 04440	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CHO})\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CH}_2(\text{OH})\text{C}(\text{OH})(\text{CHO})\text{CH}_2(\text{O}\cdot) + 0.550 \text{ CH}_2(\text{OH})\text{C}(\text{OH})(\text{CHO})\text{CHO} +$ $0.250 \text{ CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CHO} + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04441	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{CHO})\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_3\text{C}(\text{OH})(\text{CHO})\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04442	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CO}(\text{OO}\cdot) \rightarrow$ $\text{CH}_3\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CO}(\text{OH}) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04443	*	*	$\text{CH}_3\text{C}(\text{O}\cdot)(\text{CH}_2(\text{OH}))\text{CHO} \rightarrow 0.333 \text{ CH}_3(\text{OO}\cdot) + 0.333 \text{ CH}_2(\text{OH})\text{COCHO} +$ $0.333 \text{ CH}_3\text{COCHO} + 0.333 \text{ CH}_2(\text{OH})\cdot + 0.333 \text{ CH}_3\text{COCH}_2(\text{OH}) +$ $0.333 \text{ CH}\cdot(\text{OH})_2 - 0.333 \text{ O}_2 - 0.333 \text{ H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04444	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CHO})\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CHO})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04445	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CHO})\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CHO} + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00578	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{CHO})\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{CH}(\text{OH})_2$	$6.3 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04446	*	*	$\text{CH}_3\text{C}(\text{OH})(\text{CHO})\text{CHO} + \text{OH} \rightarrow$ $0.065 \text{ CHOC}(\text{OH})(\text{CHO})\text{CH}_2(\text{OO}\cdot) + 0.901 \text{ CH}_3\text{C}(\text{OH})(\text{CHO})\text{CO}(\text{OO}\cdot) +$ $0.034 \text{ CH}_3\text{C}(\text{O}\cdot)(\text{CHO})\text{CHO} + \text{H}_2\text{O} - 0.966 \text{ O}_2$	$1.9 \cdot 10^{+09}$		
R <sub>o</sub> 04447	*		$\text{CH}_3\text{C}(\text{OH})(\text{CHO})\text{CHO} + \text{NO}_3 \rightarrow$ $0.065 \text{ CHOC}(\text{OH})(\text{CHO})\text{CH}_2(\text{OO}\cdot) + 0.901 \text{ CH}_3\text{C}(\text{OH})(\text{CHO})\text{CO}(\text{OO}\cdot) +$ $0.034 \text{ CH}_3\text{C}(\text{O}\cdot)(\text{CHO})\text{CHO} + \text{NO}_3^- + \text{H}^+ - 0.966 \text{ O}_2$	$9.8 \cdot 10^{+06}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04448	*	*	CHOC(OH)(CHO)CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CHOC(OH)(CHO)CH <sub>2</sub> (O·) + 0.550 CHOC(OH)(CHO)CHO + 0.250 CH <sub>2</sub> (OH)C(OH)(CHO)CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04449	*	*	CH <sub>3</sub> C(OH)(CHO)CO(OO·) → CH <sub>3</sub> C(OH)(CO(OH))CHO + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04450	*	*	CH <sub>3</sub> C(O·)(CHO)CHO → 0.333 CH <sub>3</sub> (OO·) + 0.333 CHOCOCHO + 0.667 CH <sub>3</sub> COCHO + 0.667 CH·(OH) <sub>2</sub> – 0.333 O <sub>2</sub> – 0.667 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04451	*	*	CHOC(OH)(CHO)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CHOC(OH)(CHO)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04452	*	*	CHOC(OH)(CHO)CH <sub>2</sub> (O·) → CHOC(OH)(OO·)CHO + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04453	*	*	CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub> + OH → 0.101 CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CH <sub>2</sub> (OO·) + 0.413 CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.053 CH <sub>3</sub> C(O·)(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub> + 0.433 CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CH(OH)(O·) + H <sub>2</sub> O – 0.514 O <sub>2</sub>	1.7 · 10 <sup>+09</sup>		
R <sub>o</sub> 04454	*		CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.101 CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CH <sub>2</sub> (OO·) + 0.413 CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.053 CH <sub>3</sub> C(O·)(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub> + 0.433 CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.514 O <sub>2</sub>	1.1 · 10 <sup>+07</sup>		
R <sub>o</sub> 04455	*	*	CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CH <sub>2</sub> (O·) + 0.550 CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CHO + 0.250 CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04456	*	*	CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04457	*	*	CH <sub>3</sub> C(O·)(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub> → 0.333 CH <sub>3</sub> (OO·) + 0.333 CH(OH) <sub>2</sub> COCH(OH) <sub>2</sub> + 0.667 CH <sub>3</sub> COCH(OH) <sub>2</sub> + 0.667 CH·(OH) <sub>2</sub> – 0.333 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04458	*	*	CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04459	*	*	CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CH(OH)(O·) → CH <sub>3</sub> C(OH)(OO·)CH(OH) <sub>2</sub> + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04460	*	*	$\text{CH(OH)}_2\text{C(OH)(CH(OH)}_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CH(OH)}_2\text{C(OH)(CH(OH)}_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04461	*	*	$\text{CH(OH)}_2\text{C(OH)(CH(OH)}_2\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CH(OH)}_2\text{C(OH)(OO}\cdot\text{)CH(OH)}_2 + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04462	*	*	$\text{CH}_3\text{C(OH)(CH}_2(\text{OH}))\text{CH(OH)}_2 + \text{OH} \rightarrow$ $0.098 \text{CH}_2(\text{OH})\text{C(OH)(CH(OH)}_2\text{CH}_2(\text{OO}\cdot) +$ $0.406 \text{CH}_3\text{C(OH)(CH(OH)}_2\text{CH(OH)(OO}\cdot) +$ $0.200 \text{CH}_3\text{C(OH)(CH}_2(\text{OH}))\text{C(OH)}_2(\text{OO}\cdot) +$ $0.051 \text{CH}_3\text{C(O}\cdot\text{)(CH}_2(\text{OH}))\text{CH(OH)}_2 + 0.046 \text{CH}_3\text{C(OH)(CH(OH)}_2\text{CH}_2(\text{O}\cdot) +$ $0.200 \text{CH}_3\text{C(OH)(CH}_2(\text{OH}))\text{CH(OH)(O}\cdot) + \text{H}_2\text{O} - 0.703 \text{O}_2$	$1.8 \cdot 10^{+09}$		
R <sub>o</sub> 04463	*		$\text{CH}_3\text{C(OH)(CH}_2(\text{OH}))\text{CH(OH)}_2 + \text{NO}_3 \rightarrow$ $0.098 \text{CH}_2(\text{OH})\text{C(OH)(CH(OH)}_2\text{CH}_2(\text{OO}\cdot) +$ $0.406 \text{CH}_3\text{C(OH)(CH(OH)}_2\text{CH(OH)(OO}\cdot) +$ $0.200 \text{CH}_3\text{C(OH)(CH}_2(\text{OH}))\text{C(OH)}_2(\text{OO}\cdot) +$ $0.051 \text{CH}_3\text{C(O}\cdot\text{)(CH}_2(\text{OH}))\text{CH(OH)}_2 + 0.046 \text{CH}_3\text{C(OH)(CH(OH)}_2\text{CH}_2(\text{O}\cdot) +$ $0.200 \text{CH}_3\text{C(OH)(CH}_2(\text{OH}))\text{CH(OH)(O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.703 \text{O}_2$	$1.2 \cdot 10^{+07}$		
R <sub>o</sub> 04464	*	*	$\text{CH}_2(\text{OH})\text{C(OH)(CH(OH)}_2\text{CH}_2(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_2(\text{OH})\text{C(OH)(CH(OH)}_2\text{CH}_2(\text{O}\cdot) +$ $0.550 \text{CH}_2(\text{OH})\text{C(OH)(CH(OH)}_2\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{C(OH)(CH}_2(\text{OH}))\text{CH(OH)}_2 + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04465	*	*	$\text{CH}_3\text{C(OH)(CH(OH)}_2\text{CH(OH)(OO}\cdot) \rightarrow \text{CH}_3\text{C(OH)(CH(OH)}_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04466	*	*	$\text{CH}_3\text{C(OH)(CH}_2(\text{OH}))\text{C(OH)}_2(\text{OO}\cdot) \rightarrow$ $\text{CH}_3\text{C(OH)(CH}_2(\text{OH}))\text{CO(OH)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04467	*	*	$\text{CH}_3\text{C(O}\cdot\text{)(CH}_2(\text{OH}))\text{CH(OH)}_2 \rightarrow$ $0.333 \text{CH}_3(\text{OO}\cdot) + 0.333 \text{CH}_2(\text{OH})\text{COCH(OH)}_2 + 0.333 \text{CH}_3\text{COCH(OH)}_2 +$ $0.333 \text{CH}_2(\text{OH})\cdot + 0.333 \text{CH}_3\text{COCH}_2(\text{OH}) + 0.333 \text{CH}\cdot(\text{OH)}_2 - 0.333 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04468	*	*	$\text{CH}_3\text{C(OH)(CH}_2(\text{OH}))\text{CH(OH)(O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CH}_3\text{C(OH)(CH}_2(\text{OH}))\text{CO(OH)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04469	*	*	CH <sub>3</sub> C(OH)(CH <sub>2</sub> (OH))CH(OH)(O·) → CH <sub>3</sub> C(OH)(OO·)CH <sub>2</sub> (OH) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04470	*	*	CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04471	*	*	CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CH <sub>2</sub> (O·) → CH <sub>2</sub> (OH)C(OH)(OO·)CH(OH) <sub>2</sub> + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00579	*	*	CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CH(OH) <sub>2</sub>	3.1 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04472	*	*	CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CHO + OH → 0.491 CH <sub>2</sub> (OH)C(OH)(CHO)CH(OH)(OO·) + 0.409 CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CO(OO·) + 0.069 CH <sub>2</sub> (OH)C(OH)(CHO)CH <sub>2</sub> (O·) + 0.031 CH <sub>2</sub> (OH)C(O·)(CH <sub>2</sub> (OH))CHO + H <sub>2</sub> O – 0.900 O <sub>2</sub>	2.4 · 10 <sup>+09</sup>		
R <sub>o</sub> 04473	*		CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CHO + NO <sub>3</sub> → 0.491 CH <sub>2</sub> (OH)C(OH)(CHO)CH(OH)(OO·) + 0.409 CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CO(OO·) + 0.069 CH <sub>2</sub> (OH)C(OH)(CHO)CH <sub>2</sub> (O·) + 0.031 CH <sub>2</sub> (OH)C(O·)(CH <sub>2</sub> (OH))CHO + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.900 O <sub>2</sub>	2.4 · 10 <sup>+07</sup>		
R <sub>o</sub> 04474	*	*	CH <sub>2</sub> (OH)C(OH)(CHO)CH(OH)(OO·) → CH <sub>2</sub> (OH)C(OH)(CHO)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04475	*	*	CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CO(OO·) → CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CO(OH) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04476	*	*	CH <sub>2</sub> (OH)C(O·)(CH <sub>2</sub> (OH))CHO → 0.667 CH <sub>2</sub> (OH)· + 0.667 CH <sub>2</sub> (OH)COCHO + 0.333 CH <sub>2</sub> (OH)COCH <sub>2</sub> (OH) + 0.333 CH·(OH) <sub>2</sub> – 0.333 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00580	*	*	CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub>	6.3 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04477	*	*	CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CHO + OH → 0.077 CH(OH) <sub>2</sub> C(OH)(CHO)CH <sub>2</sub> (OO·) + 0.157 CH <sub>3</sub> C(OH)(CHO)C(OH) <sub>2</sub> (OO·) + 0.533 CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CO(OO·) + 0.040 CH <sub>3</sub> C(O·)(CH(OH) <sub>2</sub> )CHO + 0.192 CH <sub>3</sub> C(OH)(CHO)CH(OH)(O·) + H <sub>2</sub> O – 0.767 O <sub>2</sub>	1.9 · 10 <sup>+09</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04478	*		CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CHO + NO <sub>3</sub> → 0.077 CH(OH) <sub>2</sub> C(OH)(CHO)CH <sub>2</sub> (OO·) + 0.157 CH <sub>3</sub> C(OH)(CHO)C(OH) <sub>2</sub> (OO·) + 0.533 CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CO(OO·) + 0.040 CH <sub>3</sub> C(O·)(CH(OH) <sub>2</sub> )CHO + 0.192 CH <sub>3</sub> C(OH)(CHO)CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.767 O <sub>2</sub>	9.4 · 10 <sup>+06</sup>		
R <sub>o</sub> 04479	*	*	CH(OH) <sub>2</sub> C(OH)(CHO)CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> C(OH)(CHO)CH <sub>2</sub> (O·) + 0.550 CH(OH) <sub>2</sub> C(OH)(CHO)CHO + 0.250 CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04480	*	*	CH <sub>3</sub> C(OH)(CHO)C(OH) <sub>2</sub> (OO·) → CH <sub>3</sub> C(OH)(CO(OH))CHO + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04481	*	*	CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CO(OO·) → CH <sub>3</sub> C(OH)(CH(OH) <sub>2</sub> )CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04482	*	*	CH <sub>3</sub> C(O·)(CH(OH) <sub>2</sub> )CHO → 0.333 CH <sub>3</sub> (OO·) + 0.333 CH(OH) <sub>2</sub> COCHO + 0.333 CH <sub>3</sub> COCHO + 0.333 CH·(OH) <sub>2</sub> + 0.333 CH <sub>3</sub> COCH(OH) <sub>2</sub> + 0.333 CH·(OH) <sub>2</sub> - 0.333 O <sub>2</sub> - 0.333 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04483	*	*	CH <sub>3</sub> C(OH)(CHO)CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>3</sub> C(OH)(CO(OH))CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04484	*	*	CH <sub>3</sub> C(OH)(CHO)CH(OH)(O·) → CH <sub>3</sub> C(OH)(OO·)CHO + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04485	*	*	CH(OH) <sub>2</sub> C(OH)(CHO)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> C(OH)(CHO)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04486	*	*	CH(OH) <sub>2</sub> C(OH)(CHO)CH <sub>2</sub> (O·) → CH(OH) <sub>2</sub> C(OH)(OO·)CHO + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00581	*	*	CHOC(OH)(CHO)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub>	2.7 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04487	*	*	CHOC(OH)(CHO)CHO + OH → CHOC(OH)(CHO)CO(OO·) + H <sub>2</sub> O - O <sub>2</sub>	2.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 04488	*		CHOC(OH)(CHO)CHO + NO <sub>3</sub> → CHOC(OH)(CHO)CO(OO·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	3.2 · 10 <sup>+06</sup>		
R <sub>o</sub> 04489	*	*	CHOC(OH)(CHO)CO(OO·) → CO(OH)C(OH)(CHO)CHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
E <sub>o</sub> 00582	*	*	CH <sub>2</sub> (OH)C(OH)(CHO)CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub>	1.3 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04490	*	*	CH <sub>2</sub> (OH)C(OH)(CHO)CHO + OH → 0.222 CHOC(OH)(CHO)CH(OH)(OO·) + 0.740 CH <sub>2</sub> (OH)C(OH)(CHO)CO(OO·) + 0.038 CHOC(OH)(CHO)CH <sub>2</sub> (O·) + H <sub>2</sub> O - 0.962 O <sub>2</sub>	2.2 · 10 <sup>+09</sup>		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04491	*		CH <sub>2</sub> (OH)C(OH)(CHO)CHO + NO <sub>3</sub> → 0.222 CHOC(OH)(CHO)CH(OH)(OO·) + 0.740 CH <sub>2</sub> (OH)C(OH)(CHO)CO(OO·) + 0.038 CHOC(OH)(CHO)CH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.962 O <sub>2</sub>	9.3 · 10 <sup>+06</sup>		
R <sub>o</sub> 04492	*	*	CHOC(OH)(CHO)CH(OH)(OO·) → CHOC(OH)(CHO)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04493	*	*	CH <sub>2</sub> (OH)C(OH)(CHO)CO(OO·) → CH <sub>2</sub> (OH)C(OH)(CO(OH))CHO + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04494	*	*	CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub> + OH → 0.444 CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.518 CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CH(OH)(O·) + 0.038 CH(OH) <sub>2</sub> C(O·)(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub> + H <sub>2</sub> O - 0.444 O <sub>2</sub>	2.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 04495	*		CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.444 CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.518 CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CH(OH)(O·) + 0.038 CH(OH) <sub>2</sub> C(O·)(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub> + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.444 O <sub>2</sub>	1.1 · 10 <sup>+07</sup>		
R <sub>o</sub> 04496	*	*	CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04497	*	*	CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CH(OH)(O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04498	*	*	CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CH(OH)(O·) → CH(OH) <sub>2</sub> C(OH)(OO·)CH(OH) <sub>2</sub> + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04499	*	*	CH(OH) <sub>2</sub> C(O·)(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub> → CH·(OH) <sub>2</sub> + CH(OH) <sub>2</sub> COCH(OH) <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04500	*	*	CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CH(OH) <sub>2</sub> + OH → 0.591 CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CH(OH)(OO·) + 0.146 CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))C(OH) <sub>2</sub> (OO·) + 0.071 CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CH <sub>2</sub> (O·) + 0.037 CH <sub>2</sub> (OH)C(O·)(CH <sub>2</sub> (OH))CH(OH) <sub>2</sub> + 0.155 CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CH(OH)(O·) + H <sub>2</sub> O - 0.737 O <sub>2</sub>	2.3 · 10 <sup>+09</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04501	*		$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CH}(\text{OH})_2 + \text{NO}_3 \rightarrow$ $0.591 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.146 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.071 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{CH}_2(\text{O}\cdot) +$ $0.037 \text{CH}_2(\text{OH})\text{C}(\text{O}\cdot)(\text{CH}_2(\text{OH}))\text{CH}(\text{OH})_2 +$ $0.155 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.737 \text{O}_2$	$1.4 \cdot 10^{+07}$		
R <sub>o</sub> 04502	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04503	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{C}(\text{OH})_2(\text{OO}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CO}(\text{OH}) + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04504	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{O}\cdot)(\text{CH}_2(\text{OH}))\text{CH}(\text{OH})_2 \rightarrow$ $0.667 \text{CH}_2(\text{OH})\cdot + 0.667 \text{CH}_2(\text{OH})\text{COCH}(\text{OH})_2 +$ $0.333 \text{CH}_2(\text{OH})\text{COCH}_2(\text{OH}) + 0.333 \text{CH}\cdot(\text{OH})_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04505	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CO}(\text{OH}) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04506	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}_2(\text{OH}))\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}_2(\text{OH}) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04507	*	*	$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{CH}(\text{OH})_2 + \text{OH} \rightarrow$ $0.300 \text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.295 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.038 \text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{CH}_2(\text{O}\cdot) +$ $0.038 \text{CH}_2(\text{OH})\text{C}(\text{O}\cdot)(\text{CH}(\text{OH})_2)\text{CH}(\text{OH})_2 +$ $0.329 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{CH}(\text{OH})(\text{O}\cdot) + \text{H}_2\text{O} - 0.595 \text{O}_2$	$2.2 \cdot 10^{+09}$		
R <sub>o</sub> 04508	*		$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{CH}(\text{OH})_2 + \text{NO}_3 \rightarrow$ $0.300 \text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.295 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.038 \text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{CH}_2(\text{O}\cdot) +$ $0.038 \text{CH}_2(\text{OH})\text{C}(\text{O}\cdot)(\text{CH}(\text{OH})_2)\text{CH}(\text{OH})_2 +$ $0.329 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{CH}(\text{OH})_2)\text{CH}(\text{OH})(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.595 \text{O}_2$	$1.2 \cdot 10^{+07}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04509	*	*	CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CH(OH)(OO·) → CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04510	*	*	CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CO(OH) + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04511	*	*	CH <sub>2</sub> (OH)C(O·)(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub> → 0.333 CH <sub>2</sub> (OH)· + 0.333 CH(OH) <sub>2</sub> COCH(OH) <sub>2</sub> + 0.667 CH <sub>2</sub> (OH)COCH(OH) <sub>2</sub> + 0.667 CH·(OH) <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04512	*	*	CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CO(OH) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04513	*	*	CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CH(OH)(O·) → CH <sub>2</sub> (OH)C(OH)(OO·)CH(OH) <sub>2</sub> + CHO(OH) – O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00583	*	*	CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub>	$1.3 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04514	*	*	CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CHO + OH → 0.246 CH(OH) <sub>2</sub> C(OH)(CHO)CH(OH)(OO·) + 0.121 CH <sub>2</sub> (OH)C(OH)(CHO)C(OH) <sub>2</sub> (OO·) + 0.409 CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CO(OO·) + 0.036 CH(OH) <sub>2</sub> C(OH)(CHO)CH <sub>2</sub> (O·) + 0.031 CH <sub>2</sub> (OH)C(O·)(CH(OH) <sub>2</sub> )CHO + 0.157 CH <sub>2</sub> (OH)C(OH)(CHO)CH(OH)(O·) + H <sub>2</sub> O – 0.776 O <sub>2</sub>	$2.3 \cdot 10^{+09}$		
R <sub>o</sub> 04515	*		CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CHO + NO <sub>3</sub> → 0.246 CH(OH) <sub>2</sub> C(OH)(CHO)CH(OH)(OO·) + 0.121 CH <sub>2</sub> (OH)C(OH)(CHO)C(OH) <sub>2</sub> (OO·) + 0.409 CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CO(OO·) + 0.036 CH(OH) <sub>2</sub> C(OH)(CHO)CH <sub>2</sub> (O·) + 0.031 CH <sub>2</sub> (OH)C(O·)(CH(OH) <sub>2</sub> )CHO + 0.157 CH <sub>2</sub> (OH)C(OH)(CHO)CH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.776 O <sub>2</sub>	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 04516	*	*	CH(OH) <sub>2</sub> C(OH)(CHO)CH(OH)(OO·) → CH(OH) <sub>2</sub> C(OH)(CHO)CHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04517	*	*	CH <sub>2</sub> (OH)C(OH)(CHO)C(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)C(OH)(CO(OH))CHO + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04518	*	*	CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CO(OO·) → CH <sub>2</sub> (OH)C(OH)(CH(OH) <sub>2</sub> )CO(OH) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04519	*	*	CH <sub>2</sub> (OH)C(O·)(CH(OH) <sub>2</sub> )CHO → 0.333 CH <sub>2</sub> (OH)· + 0.333 CH(OH) <sub>2</sub> COCHO + 0.333 CH <sub>2</sub> (OH)COCHO + 0.333 CH·(OH) <sub>2</sub> + 0.333 CH <sub>2</sub> (OH)COCH(OH) <sub>2</sub> + 0.333 CH·(OH) <sub>2</sub> – 0.333 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04520	*	*	CH <sub>2</sub> (OH)C(OH)(CHO)CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(OH)(CO(OH))CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04521	*	*	CH <sub>2</sub> (OH)C(OH)(CHO)CH(OH)(O·) → CH <sub>2</sub> (OH)C(OH)(OO·)CHO + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00584	*	*	CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CH(OH) <sub>2</sub>	2.7 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04522	*	*	CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CHO + OH → 0.239 CH(OH) <sub>2</sub> C(OH)(CHO)C(OH) <sub>2</sub> (OO·) + 0.405 CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CO(OO·) + 0.326 CH(OH) <sub>2</sub> C(OH)(CHO)CH(OH)(O·) + 0.031 CH(OH) <sub>2</sub> C(O·)(CH(OH) <sub>2</sub> )CHO + H <sub>2</sub> O – 0.644 O <sub>2</sub>	2.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 04523	*		CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CHO + NO <sub>3</sub> → 0.239 CH(OH) <sub>2</sub> C(OH)(CHO)C(OH) <sub>2</sub> (OO·) + 0.405 CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CO(OO·) + 0.326 CH(OH) <sub>2</sub> C(OH)(CHO)CH(OH)(O·) + 0.031 CH(OH) <sub>2</sub> C(O·)(CH(OH) <sub>2</sub> )CHO + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.644 O <sub>2</sub>	9.4 · 10 <sup>+06</sup>		
R <sub>o</sub> 04524	*	*	CH(OH) <sub>2</sub> C(OH)(CHO)C(OH) <sub>2</sub> (OO·) → CH(OH) <sub>2</sub> C(OH)(CO(OH))CHO + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04525	*	*	CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CO(OO·) → CH(OH) <sub>2</sub> C(OH)(CH(OH) <sub>2</sub> )CO(OH) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04526	*	*	CH(OH) <sub>2</sub> C(OH)(CHO)CH(OH)(O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> C(OH)(CO(OH))CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04527	*	*	CH(OH) <sub>2</sub> C(OH)(CHO)CH(OH)(O·) → CH(OH) <sub>2</sub> C(OH)(OO·)CHO + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04528	*	*	CH(OH) <sub>2</sub> C(O·)(CH(OH) <sub>2</sub> )CHO → 0.667 CH·(OH) <sub>2</sub> + 0.667 CH(OH) <sub>2</sub> COCHO + 0.333 CH(OH) <sub>2</sub> COCH(OH) <sub>2</sub> + 0.333 CH·(OH) <sub>2</sub> – 0.333 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00585	*	*	$\text{CH(OH)}_2\text{C(OH)(CHO)CHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)(CH(OH)}_2\text{)CH(OH)}_2$	$2.7 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04529	*	*	$\text{CH(OH)}_2\text{C(OH)(CHO)CHO} + \text{OH} \rightarrow$ $0.107 \text{ CHOC(OH)(CHO)C(OH)}_2(\text{OO}\cdot) +$ $0.723 \text{ CH(OH)}_2\text{C(OH)(CHO)CO(OO}\cdot) +$ $0.170 \text{ CHOC(OH)(CHO)CH(OH)(O}\cdot) + \text{H}_2\text{O} - 0.830 \text{ O}_2$	$2.1 \cdot 10^{+09}$		
R <sub>o</sub> 04530	*		$\text{CH(OH)}_2\text{C(OH)(CHO)CHO} + \text{NO}_3 \rightarrow$ $0.107 \text{ CHOC(OH)(CHO)C(OH)}_2(\text{OO}\cdot) +$ $0.723 \text{ CH(OH)}_2\text{C(OH)(CHO)CO(OO}\cdot) +$ $0.170 \text{ CHOC(OH)(CHO)CH(OH)(O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.830 \text{ O}_2$	$7.9 \cdot 10^{+06}$		
R <sub>o</sub> 04531	*	*	$\text{CHOC(OH)(CHO)C(OH)}_2(\text{OO}\cdot) \rightarrow \text{CO(OH)C(OH)(CHO)CHO} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04532	*	*	$\text{CH(OH)}_2\text{C(OH)(CHO)CO(OO}\cdot) \rightarrow$ $\text{CH(OH)}_2\text{C(OH)(CO(OH))CHO} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04533	*	*	$\text{CHOC(OH)(CHO)CH(OH)(O}\cdot) \xrightarrow{\text{O}_2} \text{CO(OH)C(OH)(CHO)CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04534	*	*	$\text{CHOC(OH)(CHO)CH(OH)(O}\cdot) \rightarrow \text{CHOC(OH)(OO}\cdot\text{)CHO} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04535	*	*	$\text{CH}_3\text{C(OH)(CH}_3\text{)CH}_2\text{(OH)} + \text{OH} \rightarrow$ $0.282 \text{ CH}_3\text{C(OH)(CH}_2\text{(OH))CH}_2\text{(OO}\cdot) +$ $0.585 \text{ CH}_3\text{C(OH)(CH}_3\text{)CH(OH)(OO}\cdot) + 0.074 \text{ CH}_3\text{C(O}\cdot\text{)(CH}_3\text{)CH}_2\text{(OH)} +$ $0.059 \text{ CH}_3\text{C(OH)(CH}_3\text{)CH}_2\text{(O}\cdot) + \text{H}_2\text{O} - 0.867 \text{ O}_2$	$1.4 \cdot 10^{+09}$		
R <sub>o</sub> 04536	*		$\text{CH}_3\text{C(OH)(CH}_3\text{)CH}_2\text{(OH)} + \text{NO}_3 \rightarrow$ $0.282 \text{ CH}_3\text{C(OH)(CH}_2\text{(OH))CH}_2\text{(OO}\cdot) +$ $0.585 \text{ CH}_3\text{C(OH)(CH}_3\text{)CH(OH)(OO}\cdot) + 0.074 \text{ CH}_3\text{C(O}\cdot\text{)(CH}_3\text{)CH}_2\text{(OH)} +$ $0.059 \text{ CH}_3\text{C(OH)(CH}_3\text{)CH}_2\text{(O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.867 \text{ O}_2$	$2.0 \cdot 10^{+06}$		
R <sub>o</sub> 04537	*	*	$\text{CH}_3\text{C(OH)(CH}_2\text{(OH))CH}_2\text{(OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CH}_3\text{C(OH)(CH}_2\text{(OH))CH}_2\text{(O}\cdot) + 0.550 \text{ CH}_3\text{C(OH)(CH}_2\text{(OH))CHO} +$ $0.250 \text{ CH}_3\text{C(OH)(CH}_2\text{(OH))CH}_2\text{(OH)} + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04538	*	*	$\text{CH}_3\text{C(OH)(CH}_3\text{)CH(OH)(OO}\cdot) \rightarrow \text{CH}_3\text{C(OH)(CH}_3\text{)CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04539	*	*	$\text{CH}_3\text{C(OH)(CH}_3\text{)CH}_2\text{(O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_3\text{C(OH)(CH}_3\text{)CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04540	*	*	$\text{CH}_3\text{C(OH)(CH}_3\text{)CH}_2\text{(O}\cdot) \rightarrow \text{CH}_3\text{C(OH)(OO}\cdot\text{)CH}_3 + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04541	*	*	$\text{CH}_3\text{C(OH)(CH}_2\text{(OH))CH}_2\text{(O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_3\text{C(OH)(CH}_2\text{(OH))CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04542	*	*	$\text{CH}_3\text{C(OH)(CH}_2\text{(OH))CH}_2\text{(O}\cdot) \rightarrow \text{CH}_3\text{C(OH)(OO}\cdot\text{)CH}_2\text{(OH)} + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04543	*	*	CH <sub>3</sub> C(OH)(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH) + OH → 0.093 CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CH <sub>2</sub> (OO·) + 0.774 CH <sub>3</sub> C(OH)(CH <sub>2</sub> (OH))CH(OH)(OO·) + 0.049 CH <sub>3</sub> C(O·)(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH) + 0.084 CH <sub>3</sub> C(OH)(CH <sub>2</sub> (OH))CH <sub>2</sub> (O·) + H <sub>2</sub> O – 0.867 O <sub>2</sub>	2.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 04544	*	*	CH <sub>3</sub> C(OH)(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH) + NO <sub>3</sub> → 0.093 CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CH <sub>2</sub> (OO·) + 0.774 CH <sub>3</sub> C(OH)(CH <sub>2</sub> (OH))CH(OH)(OO·) + 0.049 CH <sub>3</sub> C(O·)(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH) + 0.084 CH <sub>3</sub> C(OH)(CH <sub>2</sub> (OH))CH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.867 O <sub>2</sub>	2.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04545	*	*	CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CH <sub>2</sub> (OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CH <sub>2</sub> (O·) + 0.550 CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CHO + 0.250 CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04546	*	*	CH <sub>3</sub> C(OH)(CH <sub>2</sub> (OH))CH(OH)(OO·) → CH <sub>3</sub> C(OH)(CH <sub>2</sub> (OH))CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04547	*	*	CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04548	*	*	CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CH <sub>2</sub> (O·) → CH <sub>2</sub> (OH)C(OH)(OO·)CH <sub>2</sub> (OH) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04549	*	*	CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH) + OH → 0.864 CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CH(OH)(OO·) + 0.099 CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CH <sub>2</sub> (O·) + 0.036 CH <sub>2</sub> (OH)C(O·)(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH) + H <sub>2</sub> O – 0.864 O <sub>2</sub>	2.5 · 10 <sup>+09</sup>		
R <sub>o</sub> 04550	*	*	CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH) + NO <sub>3</sub> → 0.864 CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CH(OH)(OO·) + 0.099 CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CH <sub>2</sub> (O·) + 0.036 CH <sub>2</sub> (OH)C(O·)(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.864 O <sub>2</sub>	2.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04551	*	*	CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CH(OH)(OO·) → CH <sub>2</sub> (OH)C(OH)(CH <sub>2</sub> (OH))CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04552	*	*	CH <sub>2</sub> (OH)C(O·)(CH <sub>2</sub> (OH))CH <sub>2</sub> (OH) → CH <sub>2</sub> (OH)· + CH <sub>2</sub> (OH)COCH <sub>2</sub> (OH)	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00586	*	*	CO(OH)CH=CH <sub>2</sub> ⇌ CO(O <sup>–</sup> )CH=CH <sub>2</sub> + H <sup>+</sup>	7.9 · 10 <sup>–06</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04553	*	*	$\text{CO(OH)CH=CH}_2 + \text{OH} \rightarrow \text{CH}_2(\text{OH})\text{CH(OO}\cdot\text{)CO(OH)} - \text{O}_2$	$1.5 \cdot 10^{+09}$		<i>Walling and El-Taliawi (1973a)</i>
R <sub>o</sub> 04554			$\text{CO(OH)CH=CH}_2 + \text{NO}_3 \rightarrow \text{CO(OH)CH(OO}\cdot\text{)CH}_2(\text{ONO}_2) - \text{O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 04555			$\text{CO(OH)CH(OO}\cdot\text{)CH}_2(\text{ONO}_2) + \text{CO(OH)CH(OO}\cdot\text{)CH}_2(\text{ONO}_2) \rightarrow$ $2.000 \text{CH}_2(\text{ONO}_2)\text{CHO} + 2.000 \text{CO}_2 + -\text{O}_2 -$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 04556			$\text{CO(OH)CH(OO}\cdot\text{)CH}_2(\text{ONO}_2) \xrightarrow{RO_2}$ $0.200 \text{CO(OH)CH(O}\cdot\text{)CH}_2(\text{ONO}_2) + 0.550 \text{CO(OH)COCH}_2(\text{ONO}_2) +$ $0.250 \text{CO(OH)CH(OH)CH}_2(\text{ONO}_2) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04557			$\text{CO(OH)CH(O}\cdot\text{)CH}_2(\text{ONO}_2) \xrightarrow{O_2} \text{CO(OH)COCH}_2(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04558			$\text{CO(OH)CH(O}\cdot\text{)CH}_2(\text{ONO}_2) \rightarrow 0.500 \cdot \text{CO(OH)} + 0.500 \text{CH}_2(\text{ONO}_2)\text{CHO} +$ $0.500 \text{CO(OH)CHO} + 0.500 \text{CH}_2\text{O} + 0.500 \text{NO}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00587			$\text{CH}_2(\text{ONO}_2)\text{CHO} \xrightleftharpoons{H_2O} \text{CH(OH)}_2\text{CH}_2(\text{ONO}_2)$	$6.7 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04559			$\text{CH}_2(\text{ONO}_2)\text{CHO} + \text{OH} \rightarrow$ $0.233 \text{CHOCH(OH)CH}_2(\text{ONO}_2) + 0.767 \text{CH}_2(\text{ONO}_2)\text{CO(OO}\cdot\text{)} + \text{H}_2\text{O} - \text{O}_2$	$1.3 \cdot 10^{+09}$		
R <sub>o</sub> 04560			$\text{CH}_2(\text{ONO}_2)\text{CHO} + \text{NO}_3 \rightarrow$ $0.233 \text{CHOCH(OH)CH}_2(\text{ONO}_2) + 0.767 \text{CH}_2(\text{ONO}_2)\text{CO(OO}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$3.7 \cdot 10^{+06}$		
R <sub>o</sub> 04561	*	*	$\text{CO(O}^-\text{)CH=CH}_2 + \text{OH} \rightarrow \text{CH}_2(\text{OH})\text{CH(OO}\cdot\text{)CO(O}^-\text{)} - \text{O}_2$	$5.7 \cdot 10^{+09}$		Average of <i>Kumar et al. (1988)</i> and <i>Maruthamuthu (1980)</i>
R <sub>o</sub> 04562			$\text{CO(O}^-\text{)CH=CH}_2 + \text{NO}_3 \rightarrow \text{CO(O}^-\text{)CH(OO}\cdot\text{)CH}_2(\text{ONO}_2) - \text{O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 04563			$\text{CO(O}^-\text{)CH(OO}\cdot\text{)CH}_2(\text{ONO}_2) + \text{CO(O}^-\text{)CH(OO}\cdot\text{)CH}_2(\text{ONO}_2) \rightarrow$ $2.000 \text{CH}_2(\text{ONO}_2)\text{CHO} + 2.000 \text{CO}_2 + \text{H}_2\text{O}_2 + 2.000 \text{OH}^- - 2.000 \text{H}_2\text{O}$	$1.9 \cdot 10^{+07}$		
R <sub>o</sub> 04564			$\text{CO(O}^-\text{)CH(OO}\cdot\text{)CH}_2(\text{ONO}_2) \xrightarrow{RO_2}$ $0.200 \text{CO(O}^-\text{)CH(O}\cdot\text{)CH}_2(\text{ONO}_2) + 0.550 \text{CO(O}^-\text{)COCH}_2(\text{ONO}_2) +$ $0.250 \text{CO(O}^-\text{)CH(OH)CH}_2(\text{ONO}_2) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04565			$\text{CO(O}^-\text{)CH(O}\cdot\text{)CH}_2(\text{ONO}_2) \xrightarrow{O_2} \text{CO(O}^-\text{)COCH}_2(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04566			$\text{CO(O}^-\text{)CH(O}\cdot\text{)CH}_2(\text{ONO}_2) \rightarrow 0.500 \cdot \text{CO(O}^-\text{)} + 0.500 \text{CH}_2(\text{ONO}_2)\text{CHO} +$ $0.500 \text{CO(O}^-\text{)CHO} + 0.500 \text{CH}_2\text{O} + 0.500 \text{NO}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00588			$\text{CO(OH)CH(OH)CH}_2(\text{ONO}_2) \rightleftharpoons \text{CO(O}^-\text{)CH(OH)CH}_2(\text{ONO}_2) + \text{H}^+$	$9.4 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04567			$\text{CO(OH)CH(OH)CH}_2(\text{ONO}_2) + \text{OH} \rightarrow$ $0.065 \text{CO(OH)C(OH)(OO}\cdot\text{)CH}_2(\text{ONO}_2) +$ $0.830 \text{CO(OH)CH(OH)CH(OH)CH}_2(\text{ONO}_2) +$ $0.105 \text{CO(OH)CH(O}\cdot\text{)CH}_2(\text{ONO}_2) + \text{H}_2\text{O} - 0.895 \text{O}_2$	$5.6 \cdot 10^{+08}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04568			CO(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.065 CO(OH)C(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.830 CO(OH)CH(OH)CH(ONO <sub>2</sub> )(OO·) + 0.105 CO(OH)CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.895 O <sub>2</sub>	3.3 · 10 <sup>+04</sup>		
R <sub>o</sub> 04569			CO(OH)C(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) → CO(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04570			CH(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + OH → 0.330 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.284 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.386 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)(O·) + H <sub>2</sub> O - 0.614 O <sub>2</sub>	1.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 04571			CH(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.330 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.284 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.386 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.614 O <sub>2</sub>	8.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04572			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04573			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)(O·) → CH <sub>2</sub> O + CHO(OH) + NO <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04574			CO(O <sup>-</sup> )CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + OH → 0.120 CO(O <sup>-</sup> )C(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.781 CO(O <sup>-</sup> )CH(OH)CH(ONO <sub>2</sub> )(OO·) + 0.099 CO(O <sup>-</sup> )CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.901 O <sub>2</sub>	1.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 04575			CO(O <sup>-</sup> )CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 04576			CO(O <sup>-</sup> )C(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) → CO(O <sup>-</sup> )COCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04577			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CO(O·) → CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)(OO·) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04578			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)(OO·) → CH <sub>2</sub> (ONO <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00589	*	*	CHOCOCH=CH <sub>2</sub> $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> COCH=CH <sub>2</sub>	2.4 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04579	*	*	CHOCOCH=CH <sub>2</sub> + OH → CH <sub>2</sub> (OH)CH(OO·)COCHO - O <sub>2</sub>	6.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 04580			CHOCOCH=CH <sub>2</sub> + NO <sub>3</sub> → CH <sub>2</sub> (ONO <sub>2</sub> )CH(OO·)COCHO - O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 04581			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OO·)COCHO $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (ONO <sub>2</sub> )CH(O·)COCHO + 0.550 CH <sub>2</sub> (ONO <sub>2</sub> )COCOCHO + 0.250 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)COCHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04582			CH <sub>2</sub> (ONO <sub>2</sub> )CH(O·)COCHO $\xrightarrow{O_2}$ CH <sub>2</sub> (ONO <sub>2</sub> )COCOCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04583			CH <sub>2</sub> (ONO <sub>2</sub> )CH(O·)COCHO → 0.500 CH <sub>2</sub> O + 0.500 CHOCOCHO + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CHO + 0.500 CHOCO(OO·) + 0.500 NO <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04584	*	*	$\text{CH(OH)}_2\text{COCH=CH}_2 + \text{OH} \rightarrow 0.052 \text{CH}_2=\text{CHCOCH(OH)(O}\cdot\text{)} +$ $0.948 \text{CH}_2(\text{OH})\text{CH(OO}\cdot\text{)COCH(OH)}_2 + 0.052 \text{H}_2\text{O} - 0.948 \text{O}_2$	$6.3 \cdot 10^{+09}$		
R <sub>o</sub> 04585			$\text{CH(OH)}_2\text{COCH=CH}_2 + \text{NO}_3 \rightarrow 0.052 \text{CH}_2=\text{CHCOCH(OH)(O}\cdot\text{)} +$ $0.948 \text{CH(OH)}_2\text{COCH(OO}\cdot\text{)CH}_2(\text{ONO}_2) + 0.052 \text{NO}_3^- + 0.052 \text{H}^+ - 0.948 \text{O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 04586	*	*	$\text{CH}_2=\text{CHCOCH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CO(OH)COCH=CH}_2 + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04587	*	*	$\text{CH}_2=\text{CHCOCH(OH)(O}\cdot\text{)} \rightarrow \text{CH}_2=\text{CHCO(OO}\cdot\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04588			$\text{CH(OH)}_2\text{COCH(OO}\cdot\text{)CH}_2(\text{ONO}_2) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH(OH)}_2\text{COCH(O}\cdot\text{)CH}_2(\text{ONO}_2) + 0.550 \text{CH(OH)}_2\text{COCOCH}_2(\text{ONO}_2) +$ $0.250 \text{CH(OH)}_2\text{COCH(OH)CH}_2(\text{ONO}_2) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04589	*	*	$\text{CH}_2=\text{CHCO(OO}\cdot\text{)} \rightarrow \text{CO(OH)CH=CH}_2 + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04590			$\text{CH(OH)}_2\text{COCH(O}\cdot\text{)CH}_2(\text{ONO}_2) \xrightarrow{\text{O}_2} \text{CH(OH)}_2\text{COCOCH}_2(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04591			$\text{CH(OH)}_2\text{COCH(O}\cdot\text{)CH}_2(\text{ONO}_2) \rightarrow$ $0.500 \text{CH(OH)}_2\text{CO(OO}\cdot\text{)} + 0.500 \text{CH}_2(\text{ONO}_2)\text{CHO} +$ $0.500 \text{CH(OH)}_2\text{COCHO} + 0.500 \text{CH}_2\text{O} + 0.500 \text{NO}_2 - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00590			$\text{CH}_2(\text{ONO}_2)\text{CH(OH)COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{COCH(OH)CH}_2(\text{ONO}_2)$	$4.5 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00591			$\text{CH}_2(\text{ONO}_2)\text{CH(OH)COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)CH}_2(\text{ONO}_2)$	$3.1 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04592			$\text{CH}_2(\text{ONO}_2)\text{CH(OH)COCHO} + \text{OH} \rightarrow$ $0.496 \text{CHOCOCH(OH)CH(ONO}_2\text{)(OO}\cdot\text{)} +$ $0.086 \text{CH}_2(\text{ONO}_2)\text{C(OH)(OO}\cdot\text{)COCHO} +$ $0.355 \text{CH}_2(\text{ONO}_2)\text{CH(OH)COCO(OO}\cdot\text{)} +$ $0.063 \text{CH}_2(\text{ONO}_2)\text{CH(O}\cdot\text{)COCHO} + \text{H}_2\text{O} - 0.937 \text{O}_2$	$1.2 \cdot 10^{+09}$		
R <sub>o</sub> 04593			$\text{CH}_2(\text{ONO}_2)\text{CH(OH)COCHO} + \text{NO}_3 \rightarrow$ $0.496 \text{CHOCOCH(OH)CH(ONO}_2\text{)(OO}\cdot\text{)} +$ $0.086 \text{CH}_2(\text{ONO}_2)\text{C(OH)(OO}\cdot\text{)COCHO} +$ $0.355 \text{CH}_2(\text{ONO}_2)\text{CH(OH)COCO(OO}\cdot\text{)} +$ $0.063 \text{CH}_2(\text{ONO}_2)\text{CH(O}\cdot\text{)COCHO} + \text{NO}_3^- + \text{H}^+ - 0.937 \text{O}_2$	$9.4 \cdot 10^{+06}$		
R <sub>o</sub> 04594			$\text{CHOCOCH(OH)CH(ONO}_2\text{)(OO}\cdot\text{)} \xrightarrow{\text{RO}_2}$ $0.200 \text{CHOCOCH(OH)CH(ONO}_2\text{)(O}\cdot\text{)} + 0.550 \text{CO(ONO}_2\text{)CH(OH)COCHO} +$ $0.250 \text{CH(OH)(ONO}_2\text{)CH(OH)COCHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04595			$\text{CH}_2(\text{ONO}_2)\text{C(OH)(OO}\cdot\text{)COCHO} \rightarrow \text{CH}_2(\text{ONO}_2)\text{COCOCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04596			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)COCO(OO·) → CO(OH)COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04597			CHOCOCH(OH)CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )CH(OH)COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04598			CHOCOCH(OH)CH(ONO <sub>2</sub> )(O·) → CHOCOCH(OH)(OO·) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00592			CH <sub>2</sub> (ONO <sub>2</sub> )COCOCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> )	3.8 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04599			CH <sub>2</sub> (ONO <sub>2</sub> )COCOCHO → 0.250 CH <sub>2</sub> (ONO <sub>2</sub> )CO(OO·) + 0.250 CHOCO(OO·) + 0.250 CH <sub>2</sub> (ONO <sub>2</sub> )COCO(OO·) + 0.250 CHO(OO·)	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 04600			CH <sub>2</sub> (ONO <sub>2</sub> )COCOCHO + OH → 0.423 CHOCOCOCH(ONO <sub>2</sub> )(OO·) + 0.577 CH <sub>2</sub> (ONO <sub>2</sub> )COCOCO(OO·) + H <sub>2</sub> O - O <sub>2</sub>	6.4 · 10 <sup>+08</sup>		
R <sub>o</sub> 04601			CH <sub>2</sub> (ONO <sub>2</sub> )COCOCHO + NO <sub>3</sub> → 0.423 CHOCOCOCH(ONO <sub>2</sub> )(OO·) + 0.577 CH <sub>2</sub> (ONO <sub>2</sub> )COCOCO(OO·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - O <sub>2</sub>	3.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 04602			CHOCOCOCH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CHOCOCOCH(ONO <sub>2</sub> )(O·) + 0.550 CO(ONO <sub>2</sub> )COCOCHO + 0.250 CH(OH)(ONO <sub>2</sub> )COCOCHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04603			CH <sub>2</sub> (ONO <sub>2</sub> )COCOCO(OO·) → CO(OH)COCOCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04604			CHOCOCOCH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )COCOCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04605			CHOCOCOCH(ONO <sub>2</sub> )(O·) → CHOCOCO(OO·) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04606			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.250 CHO(OH) + 0.250 HO <sub>2</sub> + 0.250 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.250 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.250 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·)	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 04607			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + OH → 0.085 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.182 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.250 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) + 0.236 CH(OH) <sub>2</sub> C(OH)(O·)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.247 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.267 O <sub>2</sub>	1.5 · 10 <sup>+09</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04608			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.085 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.182 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.250 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) + 0.236 CH(OH) <sub>2</sub> C(OH)(O·)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.247 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.267 O <sub>2</sub>	8.1 · 10 <sup>+06</sup>		
R <sub>o</sub> 04609			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04610			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + 0.550 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.250 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04611			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04612			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) → CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04613			CH(OH) <sub>2</sub> C(OH)(O·)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CH · (OH) <sub>2</sub> + 0.500 CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04614			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.500 CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04615			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04616			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) → CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04617			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + OH → 0.076 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.062 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.389 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(OO·) + 0.212 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH(OH)(O·) + 0.211 CH(OH) <sub>2</sub> C(OH)(O·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.049 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.528 O <sub>2</sub>	1.7 · 10 <sup>+09</sup>		
R <sub>o</sub> 04618			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.076 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.062 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.389 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(OO·) + 0.212 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH(OH)(O·) + 0.211 CH(OH) <sub>2</sub> C(OH)(O·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.049 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.528 O <sub>2</sub>	1.1 · 10 <sup>+07</sup>		
R <sub>o</sub> 04619			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CO(OH)C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04620			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) → CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04621			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O·) + 0.550 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + 0.250 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04622			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04623			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH(OH)(O·) → CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> (OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04624			CH(OH) <sub>2</sub> C(OH)(O·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CH·(OH) <sub>2</sub> + 0.500 CO(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04625			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04626			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(O $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) $\rightarrow$ 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CHO + 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04627			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O $\cdot$ ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04628			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO $\cdot$ ) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04629			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04630			CH(OH) <sub>2</sub> COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + OH $\rightarrow$ 0.116 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)COC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.095 CH(OH) <sub>2</sub> COC(OH)(OO $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.472 CH(OH) <sub>2</sub> COCH(OH)CH(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.257 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)COCH(OH)(O $\cdot$ ) + 0.060 CH(OH) <sub>2</sub> COCH(O $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.684 O <sub>2</sub>	1.3 · 10 <sup>+09</sup>		
R <sub>o</sub> 04631			CH(OH) <sub>2</sub> COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> $\rightarrow$ 0.116 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)COC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.095 CH(OH) <sub>2</sub> COC(OH)(OO $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.472 CH(OH) <sub>2</sub> COCH(OH)CH(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.257 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)COCH(OH)(O $\cdot$ ) + 0.060 CH(OH) <sub>2</sub> COCH(O $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.684 O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 04632			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)COC(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04633			CH(OH) <sub>2</sub> COC(OH)(OO $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) $\rightarrow$ CH(OH) <sub>2</sub> COCOCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04634			CH(OH) <sub>2</sub> COCH(OH)CH(ONO <sub>2</sub> )(OO $\cdot$ ) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> COCH(OH)CH(ONO <sub>2</sub> )(O $\cdot$ ) + 0.550 CH(OH) <sub>2</sub> COCH(OH)CO(ONO <sub>2</sub> ) + 0.250 CH(OH) <sub>2</sub> COCH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04635			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)COCH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04636			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)COCH(OH)(O $\cdot$ ) $\rightarrow$ CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CO(OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04637			CH(OH) <sub>2</sub> COCH(OH)CH(ONO <sub>2</sub> )(O $\cdot$ ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04638			CH(OH) <sub>2</sub> COCH(OH)CH(ONO <sub>2</sub> )(O $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> COCH(OH)(OO $\cdot$ ) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04639			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CO(OO $\cdot$ ) $\rightarrow$ CO(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
E <sub>o</sub> 00593			CH(OH) <sub>2</sub> COCOCH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> )	$3.8 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04640			CH(OH) <sub>2</sub> COCOCH <sub>2</sub> (ONO <sub>2</sub> ) $\rightarrow$ 0.250 CHO(OH) + 0.250 HO <sub>2</sub> + 0.250 CH <sub>2</sub> (ONO <sub>2</sub> )COCO(OO $\cdot$ ) + 0.250 CH(OH) <sub>2</sub> CO(OO $\cdot$ ) + 0.250 CH <sub>2</sub> (ONO <sub>2</sub> )CO(OO $\cdot$ )	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 04641			CH(OH) <sub>2</sub> COCOCH <sub>2</sub> (ONO <sub>2</sub> ) + OH $\rightarrow$ 0.175 CH <sub>2</sub> (ONO <sub>2</sub> )COCOC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.373 CH(OH) <sub>2</sub> COCOCH(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.451 CH <sub>2</sub> (ONO <sub>2</sub> )COCOCH(OH)(O $\cdot$ ) + H <sub>2</sub> O - 0.549 O <sub>2</sub>	$7.2 \cdot 10^{+08}$		
R <sub>o</sub> 04642			CH(OH) <sub>2</sub> COCOCH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> $\rightarrow$ 0.175 CH <sub>2</sub> (ONO <sub>2</sub> )COCOC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.373 CH(OH) <sub>2</sub> COCOCH(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.451 CH <sub>2</sub> (ONO <sub>2</sub> )COCOCH(OH)(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.549 O <sub>2</sub>	$8.0 \cdot 10^{+06}$		
R <sub>o</sub> 04643			CH <sub>2</sub> (ONO <sub>2</sub> )COCOC(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)COCOCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04644			CH(OH) <sub>2</sub> COCOCH(ONO <sub>2</sub> )(OO $\cdot$ ) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> COCOCH(ONO <sub>2</sub> )(O $\cdot$ ) + 0.550 CH(OH) <sub>2</sub> COCOCO(ONO <sub>2</sub> ) + 0.250 CH(OH) <sub>2</sub> COCOCH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04645			CH <sub>2</sub> (ONO <sub>2</sub> )COCOCH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)COCOCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04646			CH <sub>2</sub> (ONO <sub>2</sub> )COCOCH(OH)(O $\cdot$ ) $\rightarrow$ CH <sub>2</sub> (ONO <sub>2</sub> )COCO(OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04647			CH(OH) <sub>2</sub> COCOCH(ONO <sub>2</sub> )(O $\cdot$ ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCOCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04648			CH(OH) <sub>2</sub> COCOCH(ONO <sub>2</sub> )(O $\cdot$ ) $\rightarrow$ CH(OH) <sub>2</sub> COCO(OO $\cdot$ ) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00594			$\text{CH(OH)(ONO}_2\text{)COCOCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)}_2\text{C(OH)}_2\text{CH(OH)(ONO}_2\text{)}$	$1.0 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04649			$\text{CH(OH)(ONO}_2\text{)COCOCHO} \rightarrow 0.250 \text{ CH(OH)(ONO}_2\text{)CO(OO}\cdot\text{)} +$ $0.250 \text{ CHOCO(OO}\cdot\text{)} + 0.250 \text{ CH(OH)(ONO}_2\text{)COCO(OO}\cdot\text{)} + 0.250 \text{ CHO(OO}\cdot\text{)}$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 04650			$\text{CH(OH)(ONO}_2\text{)COCOCHO} + \text{OH} \rightarrow$ $0.484 \text{ CHOCOCOC(OH)(ONO}_2\text{)(OO}\cdot\text{)} +$ $0.434 \text{ CH(OH)(ONO}_2\text{)COCOCO(OO}\cdot\text{)} + 0.081 \text{ CHOCOCOCH(ONO}_2\text{)(O}\cdot\text{)} +$ $\text{H}_2\text{O} - 0.919 \text{ O}_2$	$8.5 \cdot 10^{+08}$		
R <sub>o</sub> 04651			$\text{CH(OH)(ONO}_2\text{)COCOCHO} + \text{NO}_3 \rightarrow$ $0.484 \text{ CHOCOCOC(OH)(ONO}_2\text{)(OO}\cdot\text{)} +$ $0.434 \text{ CH(OH)(ONO}_2\text{)COCOCO(OO}\cdot\text{)} + 0.081 \text{ CHOCOCOCH(ONO}_2\text{)(O}\cdot\text{)} +$ $\text{NO}_3^- + \text{H}^+ - 0.919 \text{ O}_2$	$3.3 \cdot 10^{+06}$		
R <sub>o</sub> 04652			$\text{CHOCOCOC(OH)(ONO}_2\text{)(OO}\cdot\text{)} \rightarrow \text{CO(ONO}_2\text{)COCOCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04653			$\text{CH(OH)(ONO}_2\text{)COCOCO(OO}\cdot\text{)} \rightarrow$ $\text{CO(OH)COCOCH(OH)(ONO}_2\text{)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
E <sub>o</sub> 00595			$\text{CO(ONO}_2\text{)COCOCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH(OH)}_2\text{C(OH)}_2\text{C(OH)}_2\text{CO(ONO}_2\text{)}$	$3.8 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04654			$\text{CO(ONO}_2\text{)COCOCHO} \rightarrow 0.250 \text{ CO(ONO}_2\text{)CO(OO}\cdot\text{)} +$ $0.250 \text{ CHOCO(OO}\cdot\text{)} + 0.250 \text{ CO(ONO}_2\text{)COCO(OO}\cdot\text{)} + 0.250 \text{ CHO(OO}\cdot\text{)}$	$1.0 \cdot 10^{-01}$		
R <sub>o</sub> 04655			$\text{CO(ONO}_2\text{)COCOCHO} \xrightarrow{\text{H}_2\text{O}} \text{CO(OH)COCOCHO} + \text{H}^+ + \text{NO}_3$	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 04656			$\text{CO(ONO}_2\text{)COCOCHO} + \text{OH} \rightarrow \text{CO(ONO}_2\text{)COCOCO(OO}\cdot\text{)} + \text{H}_2\text{O} - \text{O}_2$	$3.7 \cdot 10^{+08}$		
R <sub>o</sub> 04657			$\text{CO(ONO}_2\text{)COCOCHO} + \text{NO}_3 \rightarrow$ $\text{CO(ONO}_2\text{)COCOCO(OO}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$1.4 \cdot 10^{+06}$		
R <sub>o</sub> 04658			$\text{CO(ONO}_2\text{)COCOCO(OO}\cdot\text{)} \rightarrow \text{CO(OH)COCOCO(ONO}_2\text{)} + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
E <sub>o</sub> 00596			$\text{CH(OH)(ONO}_2\text{)CH(OH)COCHO} \xrightleftharpoons{\text{H}_2\text{O}}$ $\text{CH(OH)}_2\text{COCH(OH)CH(OH)(ONO}_2\text{)}$	$3.0 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00597			$\text{CH(OH)(ONO}_2\text{)CH(OH)COCHO} \xrightleftharpoons{\text{H}_2\text{O}}$ $\text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)CH(OH)(ONO}_2\text{)}$	$4.2 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04659			CH(OH)(ONO <sub>2</sub> )CH(OH)COCHO + OH → 0.610 CHOCOCH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.288 CH(OH)(ONO <sub>2</sub> )CH(OH)COCO(OO·) + 0.054 CHOCOCH(OH)CH(ONO <sub>2</sub> )(O·) + 0.048 CH(OH)(ONO <sub>2</sub> )CH(O·)COCHO + H <sub>2</sub> O – 0.898 O <sub>2</sub>	1.5 · 10 <sup>+09</sup>		
R <sub>o</sub> 04660			CH(OH)(ONO <sub>2</sub> )CH(OH)COCHO + NO <sub>3</sub> → 0.610 CHOCOCH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.288 CH(OH)(ONO <sub>2</sub> )CH(OH)COCO(OO·) + 0.054 CHOCOCH(OH)CH(ONO <sub>2</sub> )(O·) + 0.048 CH(OH)(ONO <sub>2</sub> )CH(O·)COCHO + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.898 O <sub>2</sub>	1.1 · 10 <sup>+07</sup>		
R <sub>o</sub> 04661			CHOCOCH(OH)C(OH)(ONO <sub>2</sub> )(OO·) → CO(ONO <sub>2</sub> )CH(OH)COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04662			CH(OH)(ONO <sub>2</sub> )CH(OH)COCO(OO·) → CO(OH)COCH(OH)CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04663			CH(OH)(ONO <sub>2</sub> )CH(O·)COCHO $\xrightarrow{O_2}$ CH(OH)(ONO <sub>2</sub> )COCOCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04664			CH(OH)(ONO <sub>2</sub> )CH(O·)COCHO → 0.500 CHO(ONO <sub>2</sub> ) + 0.500 CHOCOCHO + 0.500 CH(OH)(ONO <sub>2</sub> )CHO + 0.500 CHOCO(OO·) + 0.500 HO <sub>2</sub> – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00598			CO(ONO <sub>2</sub> )CH(OH)COCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> COCH(OH)CO(ONO <sub>2</sub> )	4.5 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00599			CO(ONO <sub>2</sub> )CH(OH)COCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> )	3.1 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04665			CO(ONO <sub>2</sub> )CH(OH)COCHO $\xrightarrow{H_2O}$ CO(OH)CH(OH)COCHO + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>–06</sup>	6600.0	
R <sub>o</sub> 04666			CO(ONO <sub>2</sub> )CH(OH)COCHO + OH → 0.037 CO(ONO <sub>2</sub> )C(OH)(OO·)COCHO + 0.841 CO(ONO <sub>2</sub> )CH(OH)COCO(OO·) + 0.121 CO(ONO <sub>2</sub> )CH(O·)COCHO + H <sub>2</sub> O – 0.879 O <sub>2</sub>	5.1 · 10 <sup>+08</sup>		
R <sub>o</sub> 04667			CO(ONO <sub>2</sub> )CH(OH)COCHO + NO <sub>3</sub> → 0.037 CO(ONO <sub>2</sub> )C(OH)(OO·)COCHO + 0.841 CO(ONO <sub>2</sub> )CH(OH)COCO(OO·) + 0.121 CO(ONO <sub>2</sub> )CH(O·)COCHO + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.879 O <sub>2</sub>	3.5 · 10 <sup>+06</sup>		
R <sub>o</sub> 04668			CO(ONO <sub>2</sub> )C(OH)(OO·)COCHO → CO(ONO <sub>2</sub> )COCOCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04669			CO(ONO <sub>2</sub> )CH(OH)COCO(OO·) → CO(OH)COCH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04670			CO(ONO <sub>2</sub> )CH(O·)COCHO $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )COCOCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04671			CO(ONO <sub>2</sub> )CH(O·)COCHO → 0.500 CO + 0.500 CHOCOCHO + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CHOCO(OO·) + 0.500 NO <sub>3</sub> – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00600	*	*	CO(OH)COCH=CH <sub>2</sub> ⇌ CO(O <sup>–</sup> )COCH=CH <sub>2</sub> + H <sup>+</sup>	1.9 · 10 <sup>–02</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04672	*	*	CO(OH)COCH=CH <sub>2</sub> + OH → CH <sub>2</sub> (OH)CH(OO·)COCO(OH) – O <sub>2</sub>	6.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 04673			CO(OH)COCH=CH <sub>2</sub> + NO <sub>3</sub> → CO(OH)COCH(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) – O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 04674			CO(OH)COCH(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{RO_2}$ 0.200 CO(OH)COCH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.550 CO(OH)COCOCH <sub>2</sub> (ONO <sub>2</sub> ) + 0.250 CO(OH)COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04675			CO(OH)COCH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CO(OH)COCOCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04676			CO(OH)COCH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CO(OH)CO(OO·) + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CHO + 0.500 CO(OH)COCHO + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub> – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00601			CO(OH)COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CO(OH)C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> )	5.0 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00602			CO(OH)COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) ⇌ CO(O <sup>–</sup> )COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sup>+</sup>	1.1 · 10 <sup>–01</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04677			CO(OH)COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + OH → 0.107 CO(OH)COC(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.793 CO(OH)COCH(OH)CH(ONO <sub>2</sub> )(OO·) + 0.100 CO(OH)COCH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.900 O <sub>2</sub>	7.6 · 10 <sup>+08</sup>		
R <sub>o</sub> 04678			CO(OH)COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.107 CO(OH)COC(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.793 CO(OH)COCH(OH)CH(ONO <sub>2</sub> )(OO·) + 0.100 CO(OH)COCH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.900 O <sub>2</sub>	3.6 · 10 <sup>+04</sup>		
R <sub>o</sub> 04679			CO(OH)COC(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) → CO(OH)COCOCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04680			CO(OH)COCH(OH)CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CO(OH)COCH(OH)CH(ONO <sub>2</sub> )(O·) + 0.550 CO(OH)COCH(OH)CO(ONO <sub>2</sub> ) + 0.250 CO(OH)COCH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04681			$\text{CO(OH)COCH(OH)CH(ONO}_2\text{)(O}\cdot\text{)} \xrightarrow{\text{O}_2}$ $\text{CO(OH)COCH(OH)CO(ONO}_2\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04682			$\text{CO(OH)COCH(OH)CH(ONO}_2\text{)(O}\cdot\text{)} \rightarrow$ $\text{CO(OH)COCH(OH)(OO}\cdot\text{)} + \text{CHO(ONO}_2\text{)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00603			$\text{CO(OH)COCOCH}_2\text{(ONO}_2\text{)} \xrightleftharpoons{\text{H}_2\text{O}} \text{CO(OH)C(OH)}_2\text{C(OH)}_2\text{CH}_2\text{(ONO}_2\text{)}$	$1.4 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00604			$\text{CO(OH)COCOCH}_2\text{(ONO}_2\text{)} \rightleftharpoons \text{CO(O}^-\text{)COCOCH}_2\text{(ONO}_2\text{)} + \text{H}^+$	$6.4 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04683			$\text{CO(OH)COCOCH}_2\text{(ONO}_2\text{)} + \text{OH} \rightarrow$ $\text{CO(OH)COCOCH(ONO}_2\text{)(OO}\cdot\text{)} + \text{H}_2\text{O} - \text{O}_2$	$2.7 \cdot 10^{+08}$		
R <sub>o</sub> 04684			$\text{CO(OH)COCOCH}_2\text{(ONO}_2\text{)} + \text{NO}_3 \rightarrow$ $\text{CO(OH)COCOCH(ONO}_2\text{)(OO}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - \text{O}_2$	$8.2 \cdot 10^{+05}$		
R <sub>o</sub> 04685			$\text{CO(OH)COCOCH(ONO}_2\text{)(OO}\cdot\text{)} \xrightarrow{\text{RO}_2}$ $0.200 \text{ CO(OH)COCOCH(ONO}_2\text{)(O}\cdot\text{)} + 0.550 \text{ CO(OH)COCOCO(ONO}_2\text{)} +$ $0.250 \text{ CO(OH)COCOCH(OH)(ONO}_2\text{)} + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04686			$\text{CO(OH)COCOCH(ONO}_2\text{)(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CO(OH)COCOCO(ONO}_2\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04687			$\text{CO(OH)COCOCH(ONO}_2\text{)(O}\cdot\text{)} \rightarrow$ $\text{CO(OH)COCO(OO}\cdot\text{)} + \text{CHO(ONO}_2\text{)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04688			$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)CH(OH)(ONO}_2\text{)} + \text{OH} \rightarrow$ $0.064 \text{ CH(OH)(ONO}_2\text{)CH(OH)C(OH)}_2\text{C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.499 \text{ CH(OH)}_2\text{C(OH)}_2\text{CH(OH)C(OH)(ONO}_2\text{)(OO}\cdot\text{)} +$ $0.179 \text{ CH(OH)(ONO}_2\text{)CH(OH)C(OH)}_2\text{CH(OH)(O}\cdot\text{)} +$ $0.178 \text{ CH(OH)}_2\text{C(OH)(O}\cdot\text{)CH(OH)CH(OH)(ONO}_2\text{)} +$ $0.040 \text{ CH(OH)}_2\text{C(OH)}_2\text{CH(O}\cdot\text{)CH(OH)(ONO}_2\text{)} +$ $0.040 \text{ CH(OH)}_2\text{C(OH)}_2\text{CH(OH)CH(ONO}_2\text{)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.564 \text{ O}_2$	$2.0 \cdot 10^{+09}$		
R <sub>o</sub> 04689			$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(OH)CH(OH)(ONO}_2\text{)} + \text{NO}_3 \rightarrow$ $0.064 \text{ CH(OH)(ONO}_2\text{)CH(OH)C(OH)}_2\text{C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.499 \text{ CH(OH)}_2\text{C(OH)}_2\text{CH(OH)C(OH)(ONO}_2\text{)(OO}\cdot\text{)} +$ $0.179 \text{ CH(OH)(ONO}_2\text{)CH(OH)C(OH)}_2\text{CH(OH)(O}\cdot\text{)} +$ $0.178 \text{ CH(OH)}_2\text{C(OH)(O}\cdot\text{)CH(OH)CH(OH)(ONO}_2\text{)} +$ $0.040 \text{ CH(OH)}_2\text{C(OH)}_2\text{CH(O}\cdot\text{)CH(OH)(ONO}_2\text{)} +$ $0.040 \text{ CH(OH)}_2\text{C(OH)}_2\text{CH(OH)CH(ONO}_2\text{)(O}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - 0.564 \text{ O}_2$	$1.2 \cdot 10^{+07}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04690			CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CO(OH)C(OH) <sub>2</sub> CH(OH)CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04691			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) → CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04692			CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> CH(OH)CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04693			CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH(OH)(O·) → CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> (OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04694			CH(OH) <sub>2</sub> C(OH)(O·)CH(OH)CH(OH)(ONO <sub>2</sub> ) → 0.500 CH·(OH) <sub>2</sub> + 0.500 CO(OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CH(OH)(ONO <sub>2</sub> )CH(OH)(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04695			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(O·)CH(OH)(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04696			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(O·)CH(OH)(ONO <sub>2</sub> ) → 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.500 CH(OH)(ONO <sub>2</sub> )CHO + 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04697			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) → 0.250 CHO(OH) + 0.250 HO <sub>2</sub> + 0.250 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.250 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.250 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·)	1.0 · 10 <sup>–01</sup>		
R <sub>o</sub> 04698			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + OH → 0.075 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.243 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) + 0.220 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) + 0.208 CH(OH) <sub>2</sub> C(OH)(O·)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.208 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(O·)CH(OH)(ONO <sub>2</sub> ) + 0.046 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O – 0.318 O <sub>2</sub>	1.7 · 10 <sup>+09</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04699			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.075 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.243 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) + 0.220 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) + 0.208 CH(OH) <sub>2</sub> C(OH)(O·)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.208 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(O·)CH(OH)(ONO <sub>2</sub> ) + 0.046 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.318 O <sub>2</sub>	9.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04700			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04701			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) → CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04702			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04703			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) → CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04704			CH(OH) <sub>2</sub> C(OH)(O·)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) → 0.500 CH·(OH) <sub>2</sub> + 0.500 CO(OH)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04705			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(O·)CH(OH)(ONO <sub>2</sub> ) → 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.500 CO(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00605			CH(OH) <sub>2</sub> COCOCH(OH)(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> )	1.0 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04706			CH(OH) <sub>2</sub> COCOCH(OH)(ONO <sub>2</sub> ) → 0.250 CHO(OH) + 0.250 HO <sub>2</sub> + 0.250 CH(OH)(ONO <sub>2</sub> )COCO(OO·) + 0.250 CH(OH) <sub>2</sub> CO(OO·) + 0.250 CH(OH)(ONO <sub>2</sub> )CO(OO·)	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 04707			CH(OH) <sub>2</sub> COCOCH(OH)(ONO <sub>2</sub> ) + OH → 0.136 CH(OH)(ONO <sub>2</sub> )COCOC(OH) <sub>2</sub> (OO·) + 0.440 CH(OH) <sub>2</sub> COCOC(OH)(ONO <sub>2</sub> )(OO·) + 0.350 CH(OH)(ONO <sub>2</sub> )COCOCH(OH)(O·) + 0.074 CH(OH) <sub>2</sub> COCOCH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O - 0.576 O <sub>2</sub>	9.3 · 10 <sup>+08</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04708			CH(OH) <sub>2</sub> COCOCH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.136 CH(OH)(ONO <sub>2</sub> )COCOC(OH) <sub>2</sub> (OO·) + 0.440 CH(OH) <sub>2</sub> COCOC(OH)(ONO <sub>2</sub> )(OO·) + 0.350 CH(OH)(ONO <sub>2</sub> )COCOCH(OH)(O·) + 0.074 CH(OH) <sub>2</sub> COCOCH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.576 O <sub>2</sub>	8.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 04709			CH(OH)(ONO <sub>2</sub> )COCOC(OH) <sub>2</sub> (OO·) → CO(OH)COCOCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04710			CH(OH) <sub>2</sub> COCOC(OH)(ONO <sub>2</sub> )(OO·) → CH(OH) <sub>2</sub> COCOCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04711			CH(OH)(ONO <sub>2</sub> )COCOCH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)COCOCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04712			CH(OH)(ONO <sub>2</sub> )COCOCH(OH)(O·) → CH(OH)(ONO <sub>2</sub> )COCO(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00606			CH(OH) <sub>2</sub> COCOCO(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> )	3.8 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04713			CH(OH) <sub>2</sub> COCOCO(ONO <sub>2</sub> ) → 0.250 CHO(OH) + 0.250 HO <sub>2</sub> + 0.250 CO(ONO <sub>2</sub> )COCO(OO·) + 0.250 CH(OH) <sub>2</sub> CO(OO·) + 0.250 CO(ONO <sub>2</sub> )CO(OO·)	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 04714			CH(OH) <sub>2</sub> COCOCO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CH(OH) <sub>2</sub> COCOCO(OH) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>-06</sup>	6600.0	
R <sub>o</sub> 04715			CH(OH) <sub>2</sub> COCOCO(ONO <sub>2</sub> ) + OH → 0.280 CO(ONO <sub>2</sub> )COCOC(OH) <sub>2</sub> (OO·) + 0.720 CO(ONO <sub>2</sub> )COCOCH(OH)(O·) + H <sub>2</sub> O - 0.280 O <sub>2</sub>	4.5 · 10 <sup>+08</sup>		
R <sub>o</sub> 04716			CH(OH) <sub>2</sub> COCOCO(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.280 CO(ONO <sub>2</sub> )COCOC(OH) <sub>2</sub> (OO·) + 0.720 CO(ONO <sub>2</sub> )COCOCH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.280 O <sub>2</sub>	7.4 · 10 <sup>+06</sup>		
R <sub>o</sub> 04717			CO(ONO <sub>2</sub> )COCOC(OH) <sub>2</sub> (OO·) → CO(OH)COCOCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04718			CO(ONO <sub>2</sub> )COCOCH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)COCOCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04719			CO(ONO <sub>2</sub> )COCOCH(OH)(O·) → CO(ONO <sub>2</sub> )COCO(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04720			CH(OH) <sub>2</sub> COCH(OH)CH(OH)(ONO <sub>2</sub> ) + OH → 0.093 CH(OH)(ONO <sub>2</sub> )CH(OH)COC(OH) <sub>2</sub> (OO·) + 0.031 CH(OH) <sub>2</sub> COC(OH)(OO·)CH(OH)(ONO <sub>2</sub> ) + 0.574 CH(OH) <sub>2</sub> COCH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.206 CH(OH)(ONO <sub>2</sub> )CH(OH)COCH(OH)(O·) + 0.046 CH(OH) <sub>2</sub> COCH(O·)CH(OH)(ONO <sub>2</sub> ) + 0.051 CH(OH) <sub>2</sub> COCH(OH)CH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O – 0.698 O <sub>2</sub>	1.6 · 10 <sup>+09</sup>		
R <sub>o</sub> 04721			CH(OH) <sub>2</sub> COCH(OH)CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.093 CH(OH)(ONO <sub>2</sub> )CH(OH)COC(OH) <sub>2</sub> (OO·) + 0.031 CH(OH) <sub>2</sub> COC(OH)(OO·)CH(OH)(ONO <sub>2</sub> ) + 0.574 CH(OH) <sub>2</sub> COCH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.206 CH(OH)(ONO <sub>2</sub> )CH(OH)COCH(OH)(O·) + 0.046 CH(OH) <sub>2</sub> COCH(O·)CH(OH)(ONO <sub>2</sub> ) + 0.051 CH(OH) <sub>2</sub> COCH(OH)CH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.698 O <sub>2</sub>	1.2 · 10 <sup>+07</sup>		
R <sub>o</sub> 04722			CH(OH)(ONO <sub>2</sub> )CH(OH)COC(OH) <sub>2</sub> (OO·) → CO(OH)COCH(OH)CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04723			CH(OH) <sub>2</sub> COC(OH)(OO·)CH(OH)(ONO <sub>2</sub> ) → CH(OH) <sub>2</sub> COCOCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04724			CH(OH) <sub>2</sub> COCH(OH)C(OH)(ONO <sub>2</sub> )(OO·) → CH(OH) <sub>2</sub> COCH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04725			CH(OH)(ONO <sub>2</sub> )CH(OH)COCH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)COCH(OH)CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04726			CH(OH)(ONO <sub>2</sub> )CH(OH)COCH(OH)(O·) → CH(OH)(ONO <sub>2</sub> )CH(OH)CO(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04727			CH(OH) <sub>2</sub> COCH(O·)CH(OH)(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCOCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04728			CH(OH) <sub>2</sub> COCH(O·)CH(OH)(ONO <sub>2</sub> ) → 0.500 CH(OH) <sub>2</sub> CO(OO·) + 0.500 CH(OH)(ONO <sub>2</sub> )CHO + 0.500 CH(OH) <sub>2</sub> COCHO + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04729			CH(OH) <sub>2</sub> COCH(OH)CO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CH(OH) <sub>2</sub> COCH(OH)CO(OH) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>–06</sup>	6600.0	

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04730			CH(OH) <sub>2</sub> COCH(OH)CO(ONO <sub>2</sub> ) + OH → 0.265 CO(ONO <sub>2</sub> )CH(OH)COC(OH) <sub>2</sub> (OO·) + 0.039 CH(OH) <sub>2</sub> COC(OH)(OO·)CO(ONO <sub>2</sub> ) + 0.584 CO(ONO <sub>2</sub> )CH(OH)COCH(OH)(O·) + 0.111 CH(OH) <sub>2</sub> COCH(O·)CO(ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.305 O <sub>2</sub>	5.6 · 10 <sup>+08</sup>		
R <sub>o</sub> 04731			CH(OH) <sub>2</sub> COCH(OH)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.265 CO(ONO <sub>2</sub> )CH(OH)COC(OH) <sub>2</sub> (OO·) + 0.039 CH(OH) <sub>2</sub> COC(OH)(OO·)CO(ONO <sub>2</sub> ) + 0.584 CO(ONO <sub>2</sub> )CH(OH)COCH(OH)(O·) + 0.111 CH(OH) <sub>2</sub> COCH(O·)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.305 O <sub>2</sub>	9.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 04732			CO(ONO <sub>2</sub> )CH(OH)COC(OH) <sub>2</sub> (OO·) → CO(OH)COCH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04733			CH(OH) <sub>2</sub> COC(OH)(OO·)CO(ONO <sub>2</sub> ) → CH(OH) <sub>2</sub> COCOCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04734			CO(ONO <sub>2</sub> )CH(OH)COCH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)COCH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04735			CO(ONO <sub>2</sub> )CH(OH)COCH(OH)(O·) → CO(ONO <sub>2</sub> )CH(OH)CO(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04736			CH(OH) <sub>2</sub> COCH(O·)CO(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCOCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04737			CH(OH) <sub>2</sub> COCH(O·)CO(ONO <sub>2</sub> ) → 0.500 CH(OH) <sub>2</sub> CO(OO·) + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CH(OH) <sub>2</sub> COCHO + 0.500 CO + 0.500 NO <sub>3</sub> – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04738			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CO(OH) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>–06</sup>	6600.0	
R <sub>o</sub> 04739			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + OH → 0.141 CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.393 CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH(OH)(O·) + 0.391 CH(OH) <sub>2</sub> C(OH)(O·)CH(OH)CO(ONO <sub>2</sub> ) + 0.075 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(O·)CO(ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.141 O <sub>2</sub>	9.2 · 10 <sup>+08</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04740			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.141 CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.393 CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH(OH)(O·) + 0.391 CH(OH) <sub>2</sub> C(OH)(O·)CH(OH)CO(ONO <sub>2</sub> ) + 0.075 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(O·)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.141 O <sub>2</sub>	9.7 · 10 <sup>+06</sup>		
R <sub>o</sub> 04741			CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CO(OH)C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04742			CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04743			CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH(OH)(O·) → CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> (OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04744			CH(OH) <sub>2</sub> C(OH)(O·)CH(OH)CO(ONO <sub>2</sub> ) → 0.500 CH·(OH) <sub>2</sub> + 0.500 CO(OH)CH(OH)CO(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CO(ONO <sub>2</sub> )CH(OH)(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04745			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(O·)CO(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04746			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(O·)CO(ONO <sub>2</sub> ) → 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + 0.500 CO + 0.500 NO <sub>3</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00607			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> )	3.8 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04747			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) → 0.250 CHO(OH) + 0.250 HO <sub>2</sub> + 0.250 CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + 0.250 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.250 CH <sub>2</sub> (ONO <sub>2</sub> )CO(OO·)	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 04748			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) + OH → 0.103 CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.277 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(OO·) + 0.335 CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH(OH)(O·) + 0.285 CH(OH) <sub>2</sub> C(OH)(O·)COCH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.380 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04749			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.103 CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.277 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(OO·) + 0.335 CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH(OH)(O·) + 0.285 CH(OH) <sub>2</sub> C(OH)(O·)COCH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.380 O <sub>2</sub>	8.1 · 10 <sup>+06</sup>		
R <sub>o</sub> 04750			CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CO(OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04751			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O·) + 0.550 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + 0.250 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04752			CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04753			CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH(OH)(O·) → CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04754			CH(OH) <sub>2</sub> C(OH)(O·)COCH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CH·(OH) <sub>2</sub> + 0.500 CO(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CO(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04755			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04756			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O·) → CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OO·) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04757			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) → 0.250 CHO(OH) + 0.250 HO <sub>2</sub> + 0.250 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.250 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.250 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·)	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 04758			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>-06</sup>	6600.0	

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04759			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + OH → 0.110 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.323 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) + 0.305 CH(OH) <sub>2</sub> C(OH)(O·)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.262 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(O·)CO(ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.110 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 04760			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.110 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.323 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) + 0.305 CH(OH) <sub>2</sub> C(OH)(O·)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.262 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(O·)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.110 O <sub>2</sub>	7.4 · 10 <sup>+06</sup>		
R <sub>o</sub> 04761			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04762			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04763			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(O·) → CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04764			CH(OH) <sub>2</sub> C(OH)(O·)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) → 0.500 CH·(OH) <sub>2</sub> + 0.500 CO(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04765			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(O·)CO(ONO <sub>2</sub> ) → 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + 0.500 CO + 0.500 NO <sub>3</sub> – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04766	*	*	CO(O <sup>–</sup> )COCH=CH <sub>2</sub> + OH → CH <sub>2</sub> (OH)CH(OO·)COCO(O <sup>–</sup> ) – O <sub>2</sub>	6.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 04767			CO(O <sup>–</sup> )COCH=CH <sub>2</sub> + NO <sub>3</sub> → CO(O <sup>–</sup> )COCH(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) – O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 04768			CO(O <sup>–</sup> )COCH(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{RO_2}$ 0.200 CO(O <sup>–</sup> )COCH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.550 CO(O <sup>–</sup> )COCOCH <sub>2</sub> (ONO <sub>2</sub> ) + 0.250 CO(O <sup>–</sup> )COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04769			CO(O <sup>–</sup> )COCH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CO(O <sup>–</sup> )COCOCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04770			CO(O <sup>–</sup> )COCH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CO(O <sup>–</sup> )CO(OO·) + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CHO + 0.500 CO(O <sup>–</sup> )COCHO + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub> – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00608			$\text{CO}(\text{O}^-)\text{COCOCH}_2(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}} \text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CH}_2(\text{ONO}_2)$	$1.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00609			$\text{CO}(\text{O}^-)\text{COCOCH}_2(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}} \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2)$	$1.4 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04771			$\text{CO}(\text{O}^-)\text{COCOCH}_2(\text{ONO}_2) + \text{OH} \rightarrow$ $\text{CO}(\text{O}^-)\text{COCOCH}(\text{ONO}_2)(\text{OO}\cdot) + \text{H}_2\text{O} - \text{O}_2$	$2.7 \cdot 10^{+08}$		
R <sub>o</sub> 04772			$\text{CO}(\text{O}^-)\text{COCOCH}_2(\text{ONO}_2) + \text{NO}_3 \rightarrow \text{CH}_2(\text{ONO}_2)\text{COCOCO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 04773			$\text{CO}(\text{O}^-)\text{COCOCH}(\text{ONO}_2)(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CO}(\text{O}^-)\text{COCOCH}(\text{ONO}_2)(\text{O}\cdot) + 0.550 \text{ CO}(\text{O}^-)\text{COCOCO}(\text{ONO}_2) +$ $0.250 \text{ CO}(\text{O}^-)\text{COCOCH}(\text{OH})(\text{ONO}_2) + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04774			$\text{CH}_2(\text{ONO}_2)\text{COCOCO}(\text{O}\cdot) \rightarrow \text{CH}_2(\text{ONO}_2)\text{COCO}(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04775			$\text{CO}(\text{O}^-)\text{COCOCH}(\text{ONO}_2)(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{COCOCO}(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04776			$\text{CO}(\text{O}^-)\text{COCOCH}(\text{ONO}_2)(\text{O}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{COCO}(\text{OO}\cdot) + \text{CHO}(\text{ONO}_2) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00610			$\text{CO}(\text{O}^-)\text{COCH}(\text{OH})\text{CH}_2(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}} \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2(\text{ONO}_2)$	$1.2 \cdot 10^{-01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04777			$\text{CO}(\text{O}^-)\text{COCH}(\text{OH})\text{CH}_2(\text{ONO}_2) + \text{OH} \rightarrow$ $0.174 \text{ CO}(\text{O}^-)\text{COC}(\text{OH})(\text{OO}\cdot)\text{CH}_2(\text{ONO}_2) +$ $0.733 \text{ CO}(\text{O}^-)\text{COCH}(\text{OH})\text{CH}(\text{ONO}_2)(\text{OO}\cdot) +$ $0.093 \text{ CO}(\text{O}^-)\text{COCH}(\text{O}\cdot)\text{CH}_2(\text{ONO}_2) + \text{H}_2\text{O} - 0.907 \text{ O}_2$	$8.2 \cdot 10^{+08}$		
R <sub>o</sub> 04778			$\text{CO}(\text{O}^-)\text{COCH}(\text{OH})\text{CH}_2(\text{ONO}_2) + \text{NO}_3 \rightarrow$ $\text{CH}_2(\text{ONO}_2)\text{CH}(\text{OH})\text{COCO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 04779			$\text{CO}(\text{O}^-)\text{COC}(\text{OH})(\text{OO}\cdot)\text{CH}_2(\text{ONO}_2) \rightarrow \text{CO}(\text{O}^-)\text{COCOCH}_2(\text{ONO}_2) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04780			$\text{CO}(\text{O}^-)\text{COCH}(\text{OH})\text{CH}(\text{ONO}_2)(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CO}(\text{O}^-)\text{COCH}(\text{OH})\text{CH}(\text{ONO}_2)(\text{O}\cdot) +$ $0.550 \text{ CO}(\text{O}^-)\text{COCH}(\text{OH})\text{CO}(\text{ONO}_2) +$ $0.250 \text{ CO}(\text{O}^-)\text{COCH}(\text{OH})\text{CH}(\text{OH})(\text{ONO}_2) + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04781			$\text{CH}_2(\text{ONO}_2)\text{CH}(\text{OH})\text{COCO}(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{ONO}_2)\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04782			$\text{CO}(\text{O}^-)\text{COCH}(\text{OH})\text{CH}(\text{ONO}_2)(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CO}(\text{O}^-)\text{COCH}(\text{OH})\text{CO}(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04783			$\text{CO}(\text{O}^-)\text{COCH}(\text{OH})\text{CH}(\text{ONO}_2)(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{COCH}(\text{OH})(\text{OO}\cdot) + \text{CHO}(\text{ONO}_2) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00611			$\text{CO}(\text{OH})\text{COCH}(\text{OH})\text{CO}(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}} \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{ONO}_2)$	$5.0 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00612			$\text{CO(OH)COCH(OH)CO(ONO}_2\text{)} \rightleftharpoons \text{CO(O}^-\text{)COCH(OH)CO(ONO}_2\text{)} + \text{H}^+$	$1.1 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04784			$\text{CO(OH)COCH(OH)CO(ONO}_2\text{)} \xrightarrow{\text{H}_2\text{O}}$	$7.5 \cdot 10^{-06}$	6600.0	
			$\text{CO(OH)CH(OH)COCO(OH)} + \text{H}^+ + \text{NO}_3$			
R <sub>o</sub> 04785			$\text{CO(OH)COCH(OH)CO(ONO}_2\text{)} + \text{OH} \rightarrow$	$7.7 \cdot 10^{+07}$		
			$0.192 \text{ CO(OH)COC(OH)(OO}\cdot\text{)CO(ONO}_2\text{)} +$			
			$0.808 \text{ CO(OH)COCH(O}\cdot\text{)CO(ONO}_2\text{)} + \text{H}_2\text{O} - 0.192 \text{ O}_2$			
R <sub>o</sub> 04786			$\text{CO(OH)COCH(OH)CO(ONO}_2\text{)} + \text{NO}_3 \rightarrow$	$3.7 \cdot 10^{+05}$		
			$0.192 \text{ CO(OH)COC(OH)(OO}\cdot\text{)CO(ONO}_2\text{)} +$			
			$0.808 \text{ CO(OH)COCH(O}\cdot\text{)CO(ONO}_2\text{)} + \text{NO}_3^- + \text{H}^+ - 0.192 \text{ O}_2$			
R <sub>o</sub> 04787			$\text{CO(OH)COC(OH)(OO}\cdot\text{)CO(ONO}_2\text{)} \rightarrow \text{CO(OH)COCOCO(ONO}_2\text{)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04788			$\text{CO(OH)COCH(O}\cdot\text{)CO(ONO}_2\text{)} \xrightarrow{\text{O}_2} \text{CO(OH)COCOCO(ONO}_2\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04789			$\text{CO(OH)COCH(O}\cdot\text{)CO(ONO}_2\text{)} \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \text{ CO(OH)CO(OO}\cdot\text{)} + 0.500 \text{ CO(ONO}_2\text{)CHO} + 0.500 \text{ CO(OH)COCHO} +$			
			$0.500 \text{ CO} + 0.500 \text{ NO}_3 - 0.500 \text{ O}_2$			
E <sub>o</sub> 00613			$\text{CO(OH)COCH(OH)CH(OH)(ONO}_2\text{)} \xrightleftharpoons{\text{H}_2\text{O}}$	$1.0 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
			$\text{CO(OH)C(OH)}_2\text{CH(OH)CH(OH)(ONO}_2\text{)}$			
E <sub>o</sub> 00614			$\text{CO(OH)COCH(OH)CH(OH)(ONO}_2\text{)} \rightleftharpoons$	$1.6 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
			$\text{CO(O}^-\text{)COCH(OH)CH(OH)(ONO}_2\text{)} + \text{H}^+$			
R <sub>o</sub> 04790			$\text{CO(OH)COCH(OH)CH(OH)(ONO}_2\text{)} + \text{OH} \rightarrow$	$1.1 \cdot 10^{+09}$		
			$0.856 \text{ CO(OH)COCH(OH)C(OH)(ONO}_2\text{)(OO}\cdot\text{)} +$			
			$0.068 \text{ CO(OH)COCH(O}\cdot\text{)CH(OH)(ONO}_2\text{)} +$			
			$0.076 \text{ CO(OH)COCH(OH)CH(ONO}_2\text{)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.856 \text{ O}_2$			
R <sub>o</sub> 04791			$\text{CO(OH)COCH(OH)CH(OH)(ONO}_2\text{)} + \text{NO}_3 \rightarrow$	$2.5 \cdot 10^{+04}$		
			$0.856 \text{ CO(OH)COCH(OH)C(OH)(ONO}_2\text{)(OO}\cdot\text{)} +$			
			$0.068 \text{ CO(OH)COCH(O}\cdot\text{)CH(OH)(ONO}_2\text{)} +$			
			$0.076 \text{ CO(OH)COCH(OH)CH(ONO}_2\text{)(O}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - 0.856 \text{ O}_2$			
R <sub>o</sub> 04792			$\text{CO(OH)COCH(OH)C(OH)(ONO}_2\text{)(OO}\cdot\text{)} \rightarrow$	$2.0 \cdot 10^{+02}$		
			$\text{CO(OH)COCH(OH)CO(ONO}_2\text{)} + \text{HO}_2$			
R <sub>o</sub> 04793			$\text{CO(OH)COCH(O}\cdot\text{)CH(OH)(ONO}_2\text{)} \xrightarrow{\text{O}_2}$	$5.0 \cdot 10^{+06}$		
			$\text{CO(OH)COCOCH(OH)(ONO}_2\text{)} + \text{HO}_2$			

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04794			CO(OH)COCH(O·)CH(OH)(ONO <sub>2</sub> ) → 0.500 CO(OH)CO(OO·) + 0.500 CH(OH)(ONO <sub>2</sub> )CHO + 0.500 CO(OH)COCHO + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00615			CO(OH)COCOCO(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> )	$1.4 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00616			CO(OH)COCOCO(ONO <sub>2</sub> ) $\rightleftharpoons$ CO(O <sup>-</sup> )COCOCO(ONO <sub>2</sub> ) + H <sup>+</sup>	$6.4 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04795			CO(OH)COCOCO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CO(OH)COCOCO(OH) + H <sup>+</sup> + NO <sub>3</sub>	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 04796			CO(OH)COCOCO(ONO <sub>2</sub> ) + OH → CO(ONO <sub>2</sub> )COCOCO(O·) + H <sub>2</sub> O	$7.0 \cdot 10^{+05}$		
R <sub>o</sub> 04797			CO(OH)COCOCO(ONO <sub>2</sub> ) + NO <sub>3</sub> → CO(ONO <sub>2</sub> )COCOCO(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	$8.4 \cdot 10^{+06}$		
R <sub>o</sub> 04798			CO(ONO <sub>2</sub> )COCOCO(O·) → CO(ONO <sub>2</sub> )COCO(OO·) + CO <sub>2</sub> - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00617			CO(OH)COCOCH(OH)(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> )	$5.8 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00618			CO(OH)COCOCH(OH)(ONO <sub>2</sub> ) $\rightleftharpoons$ CO(O <sup>-</sup> )COCOCH(OH)(ONO <sub>2</sub> ) + H <sup>+</sup>	$9.2 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04799			CO(OH)COCOCH(OH)(ONO <sub>2</sub> ) + OH → 0.856 CO(OH)COCOC(OH)(ONO <sub>2</sub> )(OO·) + 0.144 CO(OH)COCOCH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O - 0.856 O <sub>2</sub>	$4.8 \cdot 10^{+08}$		
R <sub>o</sub> 04800			CO(OH)COCOCH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.856 CO(OH)COCOC(OH)(ONO <sub>2</sub> )(OO·) + 0.144 CO(OH)COCOCH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.856 O <sub>2</sub>	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 04801			CO(OH)COCOC(OH)(ONO <sub>2</sub> )(OO·) → CO(OH)COCOCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
E <sub>o</sub> 00619			CO(OH)C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) $\rightleftharpoons$ CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sup>+</sup>	$1.9 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04802			CO(OH)C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + OH → 0.067 CO(OH)C(OH) <sub>2</sub> C(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.627 CO(OH)C(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(OO·) + 0.226 CO(OH)C(OH)(O·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.079 CO(OH)C(OH) <sub>2</sub> CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.694 O <sub>2</sub>	$1.1 \cdot 10^{+09}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04803			CO(OH)C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.067 CO(OH)C(OH) <sub>2</sub> C(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.627 CO(OH)C(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(OO·) + 0.226 CO(OH)C(OH)(O·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.079 CO(OH)C(OH) <sub>2</sub> CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.694 O <sub>2</sub>	8.8 · 10 <sup>+06</sup>		
R <sub>o</sub> 04804			CO(OH)C(OH) <sub>2</sub> C(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) → CO(OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04805			CO(OH)C(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CO(OH)C(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O·) + 0.550 CO(OH)C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + 0.250 CO(OH)C(OH) <sub>2</sub> CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04806			CO(OH)C(OH)(O·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 · CO(OH) + 0.500 CO(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CO(OH)CO(OH) + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04807			CO(OH)C(OH) <sub>2</sub> CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04808			CO(OH)C(OH) <sub>2</sub> CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CO(OH)C(OH) <sub>2</sub> (OO·) + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CHO + 0.500 CO(OH)C(OH) <sub>2</sub> CHO + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04809			CO(OH)C(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04810			CO(OH)C(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O·) → CO(OH)C(OH) <sub>2</sub> CH(OH)(OO·) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00620			CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) ⇌ CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sup>+</sup>	3.1 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04811			CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + OH $\rightarrow$ 0.310 CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.268 CO(OH)C(OH)(O $\cdot$ )C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.422 CO(OH)C(OH) <sub>2</sub> C(OH)(O $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.310 O <sub>2</sub>	8.5 · 10 <sup>+08</sup>		
R <sub>o</sub> 04812			CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> $\rightarrow$ 0.310 CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.268 CO(OH)C(OH)(O $\cdot$ )C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.422 CO(OH)C(OH) <sub>2</sub> C(OH)(O $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.310 O <sub>2</sub>	6.8 · 10 <sup>+06</sup>		
R <sub>o</sub> 04813			CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO $\cdot$ ) $\xrightarrow{RO_2}$ 0.200 CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O $\cdot$ ) + 0.550 CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.250 CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04814			CO(OH)C(OH)(O $\cdot$ )C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) $\rightarrow$ 0.500 · CO(OH) + 0.500 CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CO(OH)CO(OH) + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO $\cdot$ ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04815			CO(OH)C(OH) <sub>2</sub> C(OH)(O $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) $\rightarrow$ 0.500 CO(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.500 CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CO(OH)C(OH) <sub>2</sub> CO(OH) + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04816			CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04817			CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O $\cdot$ ) $\rightarrow$ CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00621			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> )	3.8 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04818			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) $\rightarrow$ 0.250 CHO(OH) + 0.250 HO <sub>2</sub> + 0.250 CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.250 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.250 CO(ONO <sub>2</sub> )CO(OO $\cdot$ )	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 04819			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCO(OH) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>-06</sup>	6600.0	

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04820			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + OH → 0.143 CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.463 CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH(OH)(O·) + 0.394 CH(OH) <sub>2</sub> C(OH)(O·)COCO(ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.143 O <sub>2</sub>	7.8 · 10 <sup>+08</sup>		
R <sub>o</sub> 04821			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.143 CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.463 CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH(OH)(O·) + 0.394 CH(OH) <sub>2</sub> C(OH)(O·)COCO(ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.143 O <sub>2</sub>	7.4 · 10 <sup>+06</sup>		
R <sub>o</sub> 04822			CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CO(OH)C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04823			CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04824			CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH(OH)(O·) → CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04825			CH(OH) <sub>2</sub> C(OH)(O·)COCO(ONO <sub>2</sub> ) → 0.500 CH · (OH) <sub>2</sub> + 0.500 CO(OH)COCO(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CO(ONO <sub>2</sub> )CO(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00622			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> )	1.0 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04826			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) → 0.250 CHO(OH) + 0.250 HO <sub>2</sub> + 0.250 CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + 0.250 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.250 CH(OH)(ONO <sub>2</sub> )CO(OO·)	1.0 · 10 <sup>–01</sup>		
R <sub>o</sub> 04827			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) + OH → 0.085 CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.348 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COC(OH)(ONO <sub>2</sub> )(OO·) + 0.277 CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH(OH)(O·) + 0.236 CH(OH) <sub>2</sub> C(OH)(O·)COCH(OH)(ONO <sub>2</sub> ) + 0.053 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O – 0.434 O <sub>2</sub>	1.3 · 10 <sup>+09</sup>		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04828			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.085 CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.348 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COC(OH)(ONO <sub>2</sub> )(OO·) + 0.277 CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH(OH)(O·) + 0.236 CH(OH) <sub>2</sub> C(OH)(O·)COCH(OH)(ONO <sub>2</sub> ) + 0.053 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.434 O <sub>2</sub>	8.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 04829			CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CO(OH)C(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 04830			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COC(OH)(ONO <sub>2</sub> )(OO·) → CH(OH) <sub>2</sub> C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04831			CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04832			CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH(OH)(O·) → CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04833			CH(OH) <sub>2</sub> C(OH)(O·)COCH(OH)(ONO <sub>2</sub> ) → 0.500 CH · (OH) <sub>2</sub> + 0.500 CO(OH)COCH(OH)(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CH(OH)(ONO <sub>2</sub> )CO(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00623			CO(O <sup>-</sup> )COCH(OH)CH(OH)(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)CH(OH)(ONO <sub>2</sub> )	2.4 · 10 <sup>-01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04834			CO(O <sup>-</sup> )COCH(OH)CH(OH)(ONO <sub>2</sub> ) + OH → 0.051 CO(O <sup>-</sup> )COC(OH)(OO·)CH(OH)(ONO <sub>2</sub> ) + 0.813 CO(O <sup>-</sup> )COCH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.065 CO(O <sup>-</sup> )COCH(O·)CH(OH)(ONO <sub>2</sub> ) + 0.072 CO(O <sup>-</sup> )COCH(OH)CH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O - 0.864 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 04835			CO(O <sup>-</sup> )COCH(OH)CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → CH(OH)(ONO <sub>2</sub> )CH(OH)COCO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 04836			CO(O <sup>-</sup> )COC(OH)(OO·)CH(OH)(ONO <sub>2</sub> ) → CO(O <sup>-</sup> )COCOCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04837			CO(O <sup>-</sup> )COCH(OH)C(OH)(ONO <sub>2</sub> )(OO·) → CO(O <sup>-</sup> )COCH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04838			$\text{CO(O}^-\text{)COCH(O}\cdot\text{)CH(OH)(ONO}_2\text{)} \xrightarrow{\text{O}_2}$	$5.0 \cdot 10^{+06}$		
			$\text{CO(O}^-\text{)COCOCH(OH)(ONO}_2\text{)} + \text{HO}_2$			
R <sub>o</sub> 04839			$\text{CO(O}^-\text{)COCH(O}\cdot\text{)CH(OH)(ONO}_2\text{)} \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \text{CO(O}^-\text{)CO(OO}\cdot\text{)} + 0.500 \text{CH(OH)(ONO}_2\text{)CHO} +$			
			$0.500 \text{CO(O}^-\text{)COCHO} + 0.500 \text{CHO(ONO}_2\text{)} + 0.500 \text{HO}_2 - \text{O}_2$			
R <sub>o</sub> 04840			$\text{CH(OH)(ONO}_2\text{)CH(OH)COCO(O}\cdot\text{)} \rightarrow$	$5.0 \cdot 10^{+02}$		
			$\text{CH(OH)(ONO}_2\text{)CH(OH)CO(OO}\cdot\text{)} + \text{CO}_2 - \text{O}_2$			
E <sub>o</sub> 00624			$\text{CO(O}^-\text{)COCH(OH)CO(ONO}_2\text{)} \xrightleftharpoons{\text{H}_2\text{O}} \text{CO(O}^-\text{)C(OH)}_2\text{CH(OH)CO(ONO}_2\text{)}$	$1.2 \cdot 10^{-01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04841			$\text{CO(O}^-\text{)COCH(OH)CO(ONO}_2\text{)} \xrightarrow{\text{H}_2\text{O}} \text{CO(OH)CH(OH)COCO(O}^-\text{)} + \text{H}^+ + \text{NO}_3$	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 04842			$\text{CO(O}^-\text{)COCH(OH)CO(ONO}_2\text{)} + \text{OH} \rightarrow$	$8.8 \cdot 10^{+07}$		
			$0.294 \text{CO(O}^-\text{)COC(OH)(OO}\cdot\text{)CO(ONO}_2\text{)} +$			
			$0.706 \text{CO(O}^-\text{)COCH(O}\cdot\text{)CO(ONO}_2\text{)} + \text{H}_2\text{O} - 0.294 \text{O}_2$			
R <sub>o</sub> 04843			$\text{CO(O}^-\text{)COCH(OH)CO(ONO}_2\text{)} + \text{NO}_3 \rightarrow$	$2.0 \cdot 10^{+07}$		
			$\text{CO(ONO}_2\text{)CH(OH)COCO(O}\cdot\text{)} + \text{NO}_3^-$			
R <sub>o</sub> 04844			$\text{CO(O}^-\text{)COC(OH)(OO}\cdot\text{)CO(ONO}_2\text{)} \rightarrow \text{CO(O}^-\text{)COCOCO(ONO}_2\text{)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04845			$\text{CO(O}^-\text{)COCH(O}\cdot\text{)CO(ONO}_2\text{)} \xrightarrow{\text{O}_2} \text{CO(O}^-\text{)COCOCO(ONO}_2\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04846			$\text{CO(O}^-\text{)COCH(O}\cdot\text{)CO(ONO}_2\text{)} \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \text{CO(O}^-\text{)CO(OO}\cdot\text{)} + 0.500 \text{CO(ONO}_2\text{)CHO} + 0.500 \text{CO(O}^-\text{)COCHO} +$			
			$0.500 \text{CO} + 0.500 \text{NO}_3 - 0.500 \text{O}_2$			
R <sub>o</sub> 04847			$\text{CO(ONO}_2\text{)CH(OH)COCO(O}\cdot\text{)} \rightarrow \text{CO(ONO}_2\text{)CH(OH)CO(OO}\cdot\text{)} + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04848			$\text{CO(O}^-\text{)C(OH)}_2\text{CH(OH)CH}_2\text{(ONO}_2\text{)} + \text{OH} \rightarrow$	$1.3 \cdot 10^{+09}$		
			$0.096 \text{CO(O}^-\text{)C(OH)}_2\text{C(OH)(OO}\cdot\text{)CH}_2\text{(ONO}_2\text{)} +$			
			$0.513 \text{CO(O}^-\text{)C(OH)}_2\text{CH(OH)CH(ONO}_2\text{)(OO}\cdot\text{)} +$			
			$0.325 \text{CO(O}^-\text{)C(OH)(O}\cdot\text{)CH(OH)CH}_2\text{(ONO}_2\text{)} +$			
			$0.065 \text{CO(O}^-\text{)C(OH)}_2\text{CH(O}\cdot\text{)CH}_2\text{(ONO}_2\text{)} + \text{H}_2\text{O} - 0.610 \text{O}_2$			
R <sub>o</sub> 04849			$\text{CO(O}^-\text{)C(OH)}_2\text{CH(OH)CH}_2\text{(ONO}_2\text{)} + \text{NO}_3 \rightarrow$	$2.0 \cdot 10^{+07}$		
			$\text{CH}_2\text{(ONO}_2\text{)CH(OH)C(OH)}_2\text{CO(O}\cdot\text{)} + \text{NO}_3^-$			
R <sub>o</sub> 04850			$\text{CO(O}^-\text{)C(OH)}_2\text{C(OH)(OO}\cdot\text{)CH}_2\text{(ONO}_2\text{)} \rightarrow$	$2.0 \cdot 10^{+02}$		
			$\text{CO(O}^-\text{)C(OH)}_2\text{COCH}_2\text{(ONO}_2\text{)} + \text{HO}_2$			

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04851			$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ 0.200 $\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)(\text{O}\cdot) +$ 0.550 $\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) +$ 0.250 $\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{ONO}_2) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04852			$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})\text{CH}_2(\text{ONO}_2) \rightarrow$ 0.500 $\cdot\text{CO}(\text{O}^-) + 0.500 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{ONO}_2) +$ 0.500 $\text{CO}(\text{OH})\text{CO}(\text{O}^-) + 0.500 \text{CH}_2(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04853			$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CH}_2(\text{ONO}_2) \xrightarrow{\text{O}_2}$ $\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{COCH}_2(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04854			$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CH}_2(\text{ONO}_2) \rightarrow$ 0.500 $\text{CO}(\text{O}^-)\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.500 \text{CH}_2(\text{ONO}_2)\text{CHO} +$ 0.500 $\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CHO} + 0.500 \text{CH}_2\text{O} + 0.500 \text{NO}_2 - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04855			$\text{CH}_2(\text{ONO}_2)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{ONO}_2)\text{CH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04856			$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04857			$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CHO}(\text{ONO}_2) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00625			$\text{CO}(\text{O}^-)\text{COCOCH}(\text{OH})(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}} \text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2)$	$7.2 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00626			$\text{CO}(\text{O}^-)\text{COCOCH}(\text{OH})(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}}$ $\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2)$	$1.0 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04858			$\text{CO}(\text{O}^-)\text{COCOCH}(\text{OH})(\text{ONO}_2) + \text{OH} \rightarrow$ 0.856 $\text{CO}(\text{O}^-)\text{COCOC}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) +$ 0.144 $\text{CO}(\text{O}^-)\text{COCOCH}(\text{ONO}_2)(\text{O}\cdot) + \text{H}_2\text{O} - 0.856 \text{O}_2$	$4.8 \cdot 10^{+08}$		
R <sub>o</sub> 04859			$\text{CO}(\text{O}^-)\text{COCOCH}(\text{OH})(\text{ONO}_2) + \text{NO}_3 \rightarrow$ $\text{CH}(\text{OH})(\text{ONO}_2)\text{COCOCO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 04860			$\text{CO}(\text{O}^-)\text{COCOC}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{COCOCO}(\text{ONO}_2) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04861			$\text{CH}(\text{OH})(\text{ONO}_2)\text{COCOCO}(\text{O}\cdot) \rightarrow \text{CH}(\text{OH})(\text{ONO}_2)\text{COCO}(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00627			$\text{CO}(\text{O}^-)\text{COCOCO}(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}} \text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CO}(\text{ONO}_2)$	$1.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00628			$\text{CO}(\text{O}^-)\text{COCOCO}(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}} \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2)$	$1.4 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04862			$\text{CO}(\text{O}^-)\text{COCOCO}(\text{ONO}_2) \xrightarrow{\text{H}_2\text{O}} \text{CO}(\text{OH})\text{COCOCO}(\text{O}^-) + \text{H}^+ + \text{NO}_3$	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 04863			$\text{CO}(\text{O}^-)\text{COCOCO}(\text{ONO}_2) + \text{NO}_3 \rightarrow \text{CO}(\text{ONO}_2)\text{COCOCO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 04864			$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2) + \text{OH} \rightarrow$ $0.257 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{OO}\cdot) +$ $0.392 \text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{O}\cdot)\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2) +$ $0.351 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CH}_2(\text{ONO}_2) + \text{H}_2\text{O} - 0.257 \text{O}_2$	$1.0 \cdot 10^{+09}$		
R <sub>o</sub> 04865			$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2) + \text{NO}_3 \rightarrow$ $\text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 04866			$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{O}\cdot) +$ $0.550 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) +$ $0.250 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04867			$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{O}\cdot)\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2) \rightarrow$ $0.500 \cdot \text{CO}(\text{O}^-) + 0.500 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2) +$ $0.500 \text{CO}(\text{OH})\text{CO}(\text{O}^-) + 0.500 \text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04868			$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CH}_2(\text{ONO}_2) \rightarrow$ $0.500 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CH}_2(\text{ONO}_2) +$ $0.500 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + 0.500 \text{CH}_2\text{O} + 0.500 \text{NO}_2 - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04869			$\text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04870			$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04871			$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CHO}(\text{ONO}_2) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00629			$\text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CH}_2(\text{ONO}_2) \rightleftharpoons \text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CH}_2(\text{ONO}_2) + \text{H}^+$	$2.7 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04872			$\text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CH}_2(\text{ONO}_2) + \text{OH} \rightarrow$ $0.423 \text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{OO}\cdot) +$ $0.577 \text{CO}(\text{O}^-)\text{COC}(\text{OH})(\text{O}\cdot)\text{CH}_2(\text{ONO}_2) + \text{H}_2\text{O} - 0.423 \text{O}_2$	$5.6 \cdot 10^{+08}$		
R <sub>o</sub> 04873			$\text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CH}_2(\text{ONO}_2) + \text{NO}_3 \rightarrow$ $\text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{COCO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04874			CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + 0.550 CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.250 CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04875			CO(O <sup>-</sup> )COC(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CO(O <sup>-</sup> )CO(OO·) + 0.500 CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CO(OH)COCO(O <sup>-</sup> ) + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub> - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04876			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COCO(O·) → CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) + CO <sub>2</sub> - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04877			CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04878			CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) → CO(O <sup>-</sup> )COC(OH) <sub>2</sub> (OO·) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00630			CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) ⇌ CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + H <sup>+</sup>	$3.1 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04879			CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + H <sup>+</sup> + NO <sub>3</sub>	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 04880			CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + OH → 0.438 CO(OH)C(OH)(O·)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.562 CO(OH)C(OH) <sub>2</sub> C(OH)(O·)CO(ONO <sub>2</sub> ) + H <sub>2</sub> O	$5.2 \cdot 10^{+08}$		
R <sub>o</sub> 04881			CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.438 CO(OH)C(OH)(O·)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.562 CO(OH)C(OH) <sub>2</sub> C(OH)(O·)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	$5.9 \cdot 10^{+06}$		
R <sub>o</sub> 04882			CO(OH)C(OH)(O·)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) → 0.500 · CO(OH) + 0.500 CO(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 CO(OH)CO(OH) + 0.500 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04883			CO(OH)C(OH) <sub>2</sub> C(OH)(O·)CO(ONO <sub>2</sub> ) → 0.500 CO(OH)C(OH) <sub>2</sub> (OO·) + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CO(OH)C(OH) <sub>2</sub> CO(OH) + 0.500 CO + 0.500 NO <sub>3</sub> - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00631			CO(OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> )	$1.4 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00632			CO(OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) ⇌ CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) + H <sup>+</sup>	$4.7 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04884			CO(OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) + OH → 0.593 CO(OH)C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(OO·) + 0.407 CO(OH)C(OH)(O·)COCH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.593 O <sub>2</sub>	5.1 · 10 <sup>+08</sup>		
R <sub>o</sub> 04885			CO(OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.593 CO(OH)C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(OO·) + 0.407 CO(OH)C(OH)(O·)COCH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.593 O <sub>2</sub>	6.7 · 10 <sup>+06</sup>		
R <sub>o</sub> 04886			CO(OH)C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CO(OH)C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O·) + 0.550 CO(OH)C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + 0.250 CO(OH)C(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04887			CO(OH)C(OH)(O·)COCH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 · CO(OH) + 0.500 CO(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CO(OH)CO(OH) + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CO(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04888			CO(OH)C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04889			CO(OH)C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O·) → CO(OH)C(OH) <sub>2</sub> CO(OO·) + CHO(ONO <sub>2</sub> ) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00633			CO(OH)C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) ⇌ CO(O <sup>–</sup> )C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + H <sup>+</sup>	1.9 · 10 <sup>–04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04890			CO(OH)C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CO(OH)CH(OH)C(OH) <sub>2</sub> CO(OH) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>–06</sup>	6600.0	
R <sub>o</sub> 04891			CO(OH)C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + OH → 0.040 CO(OH)C(OH) <sub>2</sub> C(OH)(OO·)CO(ONO <sub>2</sub> ) + 0.746 CO(OH)C(OH)(O·)CH(OH)CO(ONO <sub>2</sub> ) + 0.214 CO(OH)C(OH) <sub>2</sub> CH(O·)CO(ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.040 O <sub>2</sub>	3.2 · 10 <sup>+08</sup>		
R <sub>o</sub> 04892			CO(OH)C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.040 CO(OH)C(OH) <sub>2</sub> C(OH)(OO·)CO(ONO <sub>2</sub> ) + 0.746 CO(OH)C(OH)(O·)CH(OH)CO(ONO <sub>2</sub> ) + 0.214 CO(OH)C(OH) <sub>2</sub> CH(O·)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.040 O <sub>2</sub>	8.1 · 10 <sup>+06</sup>		
R <sub>o</sub> 04893			CO(OH)C(OH) <sub>2</sub> C(OH)(OO·)CO(ONO <sub>2</sub> ) → CO(OH)C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04894			CO(OH)C(OH)(O·)CH(OH)CO(ONO <sub>2</sub> ) → 0.500 · CO(OH) + 0.500 CO(OH)CH(OH)CO(ONO <sub>2</sub> ) + 0.500 CO(OH)CO(OH) + 0.500 CO(ONO <sub>2</sub> )CH(OH)(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04895			CO(OH)C(OH) <sub>2</sub> CH(O·)CO(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04896			CO(OH)C(OH) <sub>2</sub> CH(O·)CO(ONO <sub>2</sub> ) → 0.500 CO(OH)C(OH) <sub>2</sub> (OO·) + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CO(OH)C(OH) <sub>2</sub> CHO + 0.500 CO + 0.500 NO <sub>3</sub> – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00634			CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) ⇌ CO(O <sup>–</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + H <sup>+</sup>	3.7 · 10 <sup>–04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04897			CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + OH → 0.382 CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) + 0.218 CO(OH)C(OH)(O·)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.327 CO(OH)C(OH) <sub>2</sub> C(OH)(O·)CH(OH)(ONO <sub>2</sub> ) + 0.073 CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O – 0.382 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 04898			CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.382 CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) + 0.218 CO(OH)C(OH)(O·)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.327 CO(OH)C(OH) <sub>2</sub> C(OH)(O·)CH(OH)(ONO <sub>2</sub> ) + 0.073 CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.382 O <sub>2</sub>	7.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 04899			CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) → CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04900			CO(OH)C(OH)(O·)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) → 0.500 · CO(OH) + 0.500 CO(OH)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.500 CO(OH)CO(OH) + 0.500 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04901			CO(OH)C(OH) <sub>2</sub> C(OH)(O·)CH(OH)(ONO <sub>2</sub> ) → 0.500 CO(OH)C(OH) <sub>2</sub> (OO·) + 0.500 CO(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CO(OH)C(OH) <sub>2</sub> CO(OH) + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00635			CO(OH)C(OH) <sub>2</sub> CH(OH)CH(OH)(ONO <sub>2</sub> ) ⇌ CO(O <sup>–</sup> )C(OH) <sub>2</sub> CH(OH)CH(OH)(ONO <sub>2</sub> ) + H <sup>+</sup>	2.3 · 10 <sup>–04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04902			CO(OH)C(OH) <sub>2</sub> CH(OH)CH(OH)(ONO <sub>2</sub> ) + OH → 0.716 CO(OH)C(OH) <sub>2</sub> CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.170 CO(OH)C(OH)(O·)CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.057 CO(OH)C(OH) <sub>2</sub> CH(O·)CH(OH)(ONO <sub>2</sub> ) + 0.057 CO(OH)C(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O – 0.716 O <sub>2</sub>	1.4 · 10 <sup>+09</sup>		
R <sub>o</sub> 04903			CO(OH)C(OH) <sub>2</sub> CH(OH)CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.716 CO(OH)C(OH) <sub>2</sub> CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.170 CO(OH)C(OH)(O·)CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.057 CO(OH)C(OH) <sub>2</sub> CH(O·)CH(OH)(ONO <sub>2</sub> ) + 0.057 CO(OH)C(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.716 O <sub>2</sub>	9.9 · 10 <sup>+06</sup>		
R <sub>o</sub> 04904			CO(OH)C(OH) <sub>2</sub> CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) → CO(OH)C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04905			CO(OH)C(OH)(O·)CH(OH)CH(OH)(ONO <sub>2</sub> ) → 0.500 · CO(OH) + 0.500 CO(OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CO(OH)CO(OH) + 0.500 CH(OH)(ONO <sub>2</sub> )CH(OH)(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04906			CO(OH)C(OH) <sub>2</sub> CH(O·)CH(OH)(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04907			CO(OH)C(OH) <sub>2</sub> CH(O·)CH(OH)(ONO <sub>2</sub> ) → 0.500 CO(OH)C(OH) <sub>2</sub> (OO·) + 0.500 CH(OH)(ONO <sub>2</sub> )CHO + 0.500 CO(OH)C(OH) <sub>2</sub> CHO + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04908			CO(O <sup>–</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O <sup>–</sup> ) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>–06</sup>	6600.0	
R <sub>o</sub> 04909			CO(O <sup>–</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + OH → 0.577 CO(O <sup>–</sup> )C(OH)(O·)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.423 CO(O <sup>–</sup> )C(OH) <sub>2</sub> C(OH)(O·)CO(ONO <sub>2</sub> ) + H <sub>2</sub> O	7.0 · 10 <sup>+08</sup>		
R <sub>o</sub> 04910			CO(O <sup>–</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + NO <sub>3</sub> → CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O·) + NO <sub>3</sub> <sup>–</sup>	2.0 · 10 <sup>+07</sup>		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04911			$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) \rightarrow$ $0.500 \cdot \text{CO}(\text{O}^-) + 0.500 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) +$ $0.500 \text{CO}(\text{OH})\text{CO}(\text{O}^-) + 0.500 \text{CO}(\text{ONO}_2)\text{C}(\text{OH})_2(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04912			$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{ONO}_2) \rightarrow$ $0.500 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CO}(\text{ONO}_2) +$ $0.500 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + 0.500 \text{CO} + 0.500 \text{NO}_3 - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04913			$\text{CO}(\text{ONO}_2)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{ONO}_2)\text{C}(\text{OH})_2\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00636			$\text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CO}(\text{ONO}_2) \rightleftharpoons \text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CO}(\text{ONO}_2) + \text{H}^+$	$2.7 \cdot 10^{-01}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04914			$\text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CO}(\text{ONO}_2) \xrightarrow{\text{H}_2\text{O}}$ $\text{CO}(\text{OH})\text{C}(\text{OH})_2\text{COCO}(\text{O}^-) + \text{H}^+ + \text{NO}_3$	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 04915			$\text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CO}(\text{ONO}_2) + \text{OH} \rightarrow$ $\text{CO}(\text{O}^-)\text{COC}(\text{OH})(\text{O}\cdot)\text{CO}(\text{ONO}_2) + \text{H}_2\text{O}$	$2.6 \cdot 10^{+08}$		
R <sub>o</sub> 04916			$\text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CO}(\text{ONO}_2) + \text{NO}_3 \rightarrow$ $\text{CO}(\text{ONO}_2)\text{C}(\text{OH})_2\text{COCO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 04917			$\text{CO}(\text{O}^-)\text{COC}(\text{OH})(\text{O}\cdot)\text{CO}(\text{ONO}_2) \rightarrow$ $0.500 \text{CO}(\text{O}^-)\text{CO}(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CO}(\text{ONO}_2) +$ $0.500 \text{CO}(\text{OH})\text{COCO}(\text{O}^-) + 0.500 \text{CO} + 0.500 \text{NO}_3 - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04918			$\text{CO}(\text{ONO}_2)\text{C}(\text{OH})_2\text{COCO}(\text{O}\cdot) \rightarrow \text{CO}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04919			$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) + \text{OH} \rightarrow$ $0.328 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) +$ $0.329 \text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{O}\cdot)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) +$ $0.281 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})(\text{ONO}_2) +$ $0.063 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{O}\cdot) + \text{H}_2\text{O} - 0.328 \text{O}_2$	$1.2 \cdot 10^{+09}$		
R <sub>o</sub> 04920			$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) + \text{NO}_3 \rightarrow$ $\text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 04921			$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04922			$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{O}\cdot)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) \rightarrow$ $0.500 \cdot \text{CO}(\text{O}^-) + 0.500 \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) +$ $0.500 \text{CO}(\text{OH})\text{CO}(\text{O}^-) + 0.500 \text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04923			CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH)(O $\cdot$ )CH(OH)(ONO <sub>2</sub> ) $\rightarrow$ 0.500 CO(O <sup>-</sup> )C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.500 CO(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CO(OH)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04924			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(O $\cdot$ ) $\rightarrow$ CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00637			CO(OH)COC(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) $\rightleftharpoons$ CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + H <sup>+</sup>	3.9 · 10 <sup>-01</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04925			CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + OH $\rightarrow$ 0.484 CO(O <sup>-</sup> )COC(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.414 CO(O <sup>-</sup> )COC(OH)(O $\cdot$ )CH(OH)(ONO <sub>2</sub> ) + 0.103 CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O $\cdot$ ) + H <sub>2</sub> O - 0.484 O <sub>2</sub>	7.5 · 10 <sup>+08</sup>		
R <sub>o</sub> 04926			CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> $\rightarrow$ CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 04927			CO(O <sup>-</sup> )COC(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO $\cdot$ ) $\rightarrow$ CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04928			CO(O <sup>-</sup> )COC(OH)(O $\cdot$ )CH(OH)(ONO <sub>2</sub> ) $\rightarrow$ 0.500 CO(O <sup>-</sup> )CO(OO $\cdot$ ) + 0.500 CO(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CO(OH)COCO(O <sup>-</sup> ) + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04929			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCO(O $\cdot$ ) $\rightarrow$ CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00638			CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CO(O <sup>-</sup> )COC(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> )	1.9 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00639			CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> )	1.4 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04930			CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) + OH $\rightarrow$ 0.453 CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.547 CO(O <sup>-</sup> )C(OH)(O $\cdot$ )COCH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.453 O <sub>2</sub>	6.6 · 10 <sup>+08</sup>		
R <sub>o</sub> 04931			CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> $\rightarrow$ CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 04932			CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(OO $\cdot$ ) $\xrightarrow{RO_2}$ 0.200 CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O $\cdot$ ) + 0.550 CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + 0.250 CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04933			CO(O <sup>-</sup> )C(OH)(O <sup>·</sup> )COCH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 · CO(O <sup>-</sup> ) + 0.500 CO(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CO(OH)CO(O <sup>-</sup> ) + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CO(OO <sup>·</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04934			CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> CO(O <sup>·</sup> ) → CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO <sup>·</sup> ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04935			CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O <sup>·</sup> ) $\xrightarrow{O_2}$ CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04936			CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O <sup>·</sup> ) → CO(O <sup>-</sup> )C(OH) <sub>2</sub> CO(OO <sup>·</sup> ) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04937			CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CO(OH)CH(OH)C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>-06</sup>	6600.0	
R <sub>o</sub> 04938			CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + OH → 0.044 CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH)(OO <sup>·</sup> )CO(ONO <sub>2</sub> ) + 0.822 CO(O <sup>-</sup> )C(OH)(O <sup>·</sup> )CH(OH)CO(ONO <sub>2</sub> ) + 0.134 CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(O <sup>·</sup> )CO(ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.044 O <sub>2</sub>	5.1 · 10 <sup>+08</sup>		
R <sub>o</sub> 04939			CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> → CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CO(O <sup>·</sup> ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 04940			CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(OH)(OO <sup>·</sup> )CO(ONO <sub>2</sub> ) → CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04941			CO(O <sup>-</sup> )C(OH)(O <sup>·</sup> )CH(OH)CO(ONO <sub>2</sub> ) → 0.500 · CO(O <sup>-</sup> ) + 0.500 CO(OH)CH(OH)CO(ONO <sub>2</sub> ) + 0.500 CO(OH)CO(O <sup>-</sup> ) + 0.500 CO(ONO <sub>2</sub> )CH(OH)(OO <sup>·</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04942			CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(O <sup>·</sup> )CO(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04943			CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(O <sup>·</sup> )CO(ONO <sub>2</sub> ) → 0.500 CO(O <sup>-</sup> )C(OH) <sub>2</sub> (OO <sup>·</sup> ) + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CO(O <sup>-</sup> )C(OH) <sub>2</sub> CHO + 0.500 CO + 0.500 NO <sub>3</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04944			CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CO(O <sup>·</sup> ) → CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> (OO <sup>·</sup> ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04945			$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{ONO}_2) + \text{OH} \rightarrow$ $0.031 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})(\text{ONO}_2) +$ $0.615 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{C}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) +$ $0.257 \text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{ONO}_2) +$ $0.049 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})(\text{ONO}_2) +$ $0.049 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)(\text{O}\cdot) + \text{H}_2\text{O} - 0.646 \text{O}_2$	$1.6 \cdot 10^{+09}$		
R <sub>o</sub> 04946			$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{ONO}_2) + \text{NO}_3^- \rightarrow$ $\text{CH}(\text{OH})(\text{ONO}_2)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 04947			$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})(\text{ONO}_2) \rightarrow$ $\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{COCH}(\text{OH})(\text{ONO}_2) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04948			$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{C}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04949			$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{ONO}_2) \rightarrow$ $0.500 \cdot \text{CO}(\text{O}^-) + 0.500 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{ONO}_2) +$ $0.500 \text{CO}(\text{OH})\text{CO}(\text{O}^-) + 0.500 \text{CH}(\text{OH})(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04950			$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})(\text{ONO}_2) \xrightarrow{\text{O}_2}$ $\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{COCH}(\text{OH})(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04951			$\text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})(\text{ONO}_2) \rightarrow$ $0.500 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2(\text{OO}\cdot) + 0.500 \text{CH}(\text{OH})(\text{ONO}_2)\text{CHO} +$ $0.500 \text{CO}(\text{O}^-)\text{C}(\text{OH})_2\text{CHO} + 0.500 \text{CHO}(\text{ONO}_2) + 0.500 \text{HO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04952			$\text{CH}(\text{OH})(\text{ONO}_2)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{O}\cdot) \rightarrow$ $\text{CH}(\text{OH})(\text{ONO}_2)\text{CH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00640			$\text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CH}_2(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}} \text{CO}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2)$	$1.4 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04953			$\text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CH}_2(\text{ONO}_2) + \text{OH} \rightarrow$ $0.423 \text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{OO}\cdot) +$ $0.577 \text{CO}(\text{OH})\text{COC}(\text{OH})(\text{O}\cdot)\text{CH}_2(\text{ONO}_2) + \text{H}_2\text{O} - 0.423 \text{O}_2$	$5.6 \cdot 10^{+08}$		
R <sub>o</sub> 04954			$\text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CH}_2(\text{ONO}_2) + \text{NO}_3^- \rightarrow$ $0.423 \text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{OO}\cdot) +$ $0.577 \text{CO}(\text{OH})\text{COC}(\text{OH})(\text{O}\cdot)\text{CH}_2(\text{ONO}_2) + \text{NO}_3^- + \text{H}^+ - 0.423 \text{O}_2$	$6.8 \cdot 10^{+06}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04955			CO(OH)COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CO(OH)COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + 0.550 CO(OH)COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.250 CO(OH)COC(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04956			CO(OH)COC(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) $\rightarrow$ 0.500 CO(OH)CO(OO·) + 0.500 CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CO(OH)COCO(OH) + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub> - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04957			CO(OH)COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CO(OH)COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04958			CO(OH)COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) $\rightarrow$ CO(OH)COC(OH) <sub>2</sub> (OO·) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00641			CO(OH)C(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> )	$5.8 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00642			CO(OH)C(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) $\rightleftharpoons$ CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) + H <sup>+</sup>	$5.6 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 04959			CO(OH)C(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) + OH $\rightarrow$ 0.624 CO(OH)C(OH) <sub>2</sub> COC(OH)(ONO <sub>2</sub> )(OO·) + 0.282 CO(OH)C(OH)(O·)COCH(OH)(ONO <sub>2</sub> ) + 0.094 CO(OH)C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O - 0.624 O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04960			CO(OH)C(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> $\rightarrow$ 0.624 CO(OH)C(OH) <sub>2</sub> COC(OH)(ONO <sub>2</sub> )(OO·) + 0.282 CO(OH)C(OH)(O·)COCH(OH)(ONO <sub>2</sub> ) + 0.094 CO(OH)C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.624 O <sub>2</sub>	$7.2 \cdot 10^{+06}$		
R <sub>o</sub> 04961			CO(OH)C(OH) <sub>2</sub> COC(OH)(ONO <sub>2</sub> )(OO·) $\rightarrow$ CO(OH)C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04962			CO(OH)C(OH)(O·)COCH(OH)(ONO <sub>2</sub> ) $\rightarrow$ 0.500 · CO(OH) + 0.500 CO(OH)COCH(OH)(ONO <sub>2</sub> ) + 0.500 CO(OH)CO(OH) + 0.500 CH(OH)(ONO <sub>2</sub> )CO(OO·) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00643			CO(OH)C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> )	$1.4 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00644			CO(OH)C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) $\rightleftharpoons$ CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + H <sup>+</sup>	$4.7 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04963			$\text{CO(OH)C(OH)}_2\text{COCO(ONO}_2\text{)} \xrightarrow{H_2O}$	$7.5 \cdot 10^{-06}$	6600.0	
			$\text{CO(OH)C(OH)}_2\text{COCO(OH)} + \text{H}^+ + \text{NO}_3$			
R <sub>o</sub> 04964			$\text{CO(OH)C(OH)}_2\text{COCO(ONO}_2\text{)} + \text{OH} \rightarrow$	$2.1 \cdot 10^{+08}$		
			$\text{CO(OH)C(OH)(O}\cdot\text{)COCO(ONO}_2\text{)} + \text{H}_2\text{O}$			
R <sub>o</sub> 04965			$\text{CO(OH)C(OH)}_2\text{COCO(ONO}_2\text{)} + \text{NO}_3 \rightarrow$	$5.9 \cdot 10^{+06}$		
			$\text{CO(OH)C(OH)(O}\cdot\text{)COCO(ONO}_2\text{)} + \text{NO}_3^- + \text{H}^+$			
R <sub>o</sub> 04966			$\text{CO(OH)C(OH)(O}\cdot\text{)COCO(ONO}_2\text{)} \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \cdot \text{CO(OH)} + 0.500 \text{CO(OH)COCO(ONO}_2\text{)} + 0.500 \text{CO(OH)CO(OH)} +$			
			$0.500 \text{CO(ONO}_2\text{)CO(OO}\cdot\text{)} - 0.500 \text{O}_2$			
E <sub>o</sub> 00645			$\text{CO(O}^-\text{)C(OH)}_2\text{COCH(OH)(ONO}_2\text{)} \xrightleftharpoons{H_2O}$	$7.2 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
			$\text{CO(O}^-\text{)COC(OH)}_2\text{CH(OH)(ONO}_2\text{)}$			
E <sub>o</sub> 00646			$\text{CO(O}^-\text{)C(OH)}_2\text{COCH(OH)(ONO}_2\text{)} \xrightleftharpoons{H_2O}$	$1.0 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
			$\text{CO(O}^-\text{)C(OH)}_2\text{C(OH)}_2\text{CH(OH)(ONO}_2\text{)}$			
R <sub>o</sub> 04967			$\text{CO(O}^-\text{)C(OH)}_2\text{COCH(OH)(ONO}_2\text{)} + \text{OH} \rightarrow$	$8.9 \cdot 10^{+08}$		
			$0.514 \text{CO(O}^-\text{)C(OH)}_2\text{COC(OH)(ONO}_2\text{)(OO}\cdot\text{)} +$			
			$0.408 \text{CO(O}^-\text{)C(OH)(O}\cdot\text{)COCH(OH)(ONO}_2\text{)} +$			
			$0.078 \text{CO(O}^-\text{)C(OH)}_2\text{COCH(ONO}_2\text{)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.514 \text{O}_2$			
R <sub>o</sub> 04968			$\text{CO(O}^-\text{)C(OH)}_2\text{COCH(OH)(ONO}_2\text{)} + \text{NO}_3 \rightarrow$	$2.0 \cdot 10^{+07}$		
			$\text{CH(OH)(ONO}_2\text{)COC(OH)}_2\text{CO(O}\cdot\text{)} + \text{NO}_3^-$			
R <sub>o</sub> 04969			$\text{CO(O}^-\text{)C(OH)}_2\text{COC(OH)(ONO}_2\text{)(OO}\cdot\text{)} \rightarrow$	$2.0 \cdot 10^{+02}$		
			$\text{CO(O}^-\text{)C(OH)}_2\text{COCO(ONO}_2\text{)} + \text{HO}_2$			
R <sub>o</sub> 04970			$\text{CO(O}^-\text{)C(OH)(O}\cdot\text{)COCH(OH)(ONO}_2\text{)} \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \cdot \text{CO(O}^-\text{)} + 0.500 \text{CO(OH)COCH(OH)(ONO}_2\text{)} +$			
			$0.500 \text{CO(OH)CO(O}^-\text{)} + 0.500 \text{CH(OH)(ONO}_2\text{)CO(OO}\cdot\text{)} - 0.500 \text{O}_2$			
R <sub>o</sub> 04971			$\text{CH(OH)(ONO}_2\text{)COC(OH)}_2\text{CO(O}\cdot\text{)} \rightarrow$	$5.0 \cdot 10^{+02}$		
			$\text{CH(OH)(ONO}_2\text{)COC(OH)}_2\text{(OO}\cdot\text{)} + \text{CO}_2 - \text{O}_2$			
E <sub>o</sub> 00647			$\text{CO(O}^-\text{)C(OH)}_2\text{COCO(ONO}_2\text{)} \xrightleftharpoons{H_2O} \text{CO(O}^-\text{)COC(OH)}_2\text{CO(ONO}_2\text{)}$	$1.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00648			$\text{CO(O}^-\text{)C(OH)}_2\text{COCO(ONO}_2\text{)} \xrightleftharpoons{H_2O} \text{CO(O}^-\text{)C(OH)}_2\text{C(OH)}_2\text{CO(ONO}_2\text{)}$	$1.4 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04972			$\text{CO(O}^-\text{)C(OH)}_2\text{COCO(ONO}_2\text{)} \xrightarrow{H_2O}$	$7.5 \cdot 10^{-06}$	6600.0	
			$\text{CO(OH)COC(OH)}_2\text{CO(O}^-\text{)} + \text{H}^+ + \text{NO}_3$			

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04973			CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + OH → CO(O <sup>-</sup> )C(OH)(O <sup>·</sup> )COCO(ONO <sub>2</sub> ) + H <sub>2</sub> O	3.6 · 10 <sup>+08</sup>		
R <sub>o</sub> 04974			CO(O <sup>-</sup> )C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + NO <sub>3</sub> → CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CO(O <sup>·</sup> ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 04975			CO(O <sup>-</sup> )C(OH)(O <sup>·</sup> )COCO(ONO <sub>2</sub> ) → 0.500 · CO(O <sup>-</sup> ) + 0.500 CO(OH)COCO(ONO <sub>2</sub> ) + 0.500 CO(OH)CO(O <sup>-</sup> ) + 0.500 CO(ONO <sub>2</sub> )CO(OO <sup>·</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04976			CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CO(O <sup>·</sup> ) → CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO <sup>·</sup> ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00649			CO(OH)COC(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> )	5.8 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04977			CO(OH)COC(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + OH → 0.484 CO(OH)COC(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO <sup>·</sup> ) + 0.414 CO(OH)COC(OH)(O <sup>·</sup> )CH(OH)(ONO <sub>2</sub> ) + 0.103 CO(OH)COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O <sup>·</sup> ) + H <sub>2</sub> O - 0.484 O <sub>2</sub>	7.5 · 10 <sup>+08</sup>		
R <sub>o</sub> 04978			CO(OH)COC(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.484 CO(OH)COC(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO <sup>·</sup> ) + 0.414 CO(OH)COC(OH)(O <sup>·</sup> )CH(OH)(ONO <sub>2</sub> ) + 0.103 CO(OH)COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O <sup>·</sup> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.484 O <sub>2</sub>	7.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 04979			CO(OH)COC(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO <sup>·</sup> ) → CO(OH)COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 04980			CO(OH)COC(OH)(O <sup>·</sup> )CH(OH)(ONO <sub>2</sub> ) → 0.500 CO(OH)CO(OO <sup>·</sup> ) + 0.500 CO(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CO(OH)COCO(OH) + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00650			CO(OH)COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> )	1.4 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04981			CO(OH)COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CO(OH)C(OH) <sub>2</sub> COCO(OH) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>-06</sup>	6600.0	
R <sub>o</sub> 04982			CO(OH)COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + OH → CO(OH)COC(OH)(O <sup>·</sup> )CO(ONO <sub>2</sub> ) + H <sub>2</sub> O	2.6 · 10 <sup>+08</sup>		
R <sub>o</sub> 04983			CO(OH)COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + NO <sub>3</sub> → CO(OH)COC(OH)(O <sup>·</sup> )CO(ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup>	5.9 · 10 <sup>+06</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04984			CO(OH)COC(OH)(O·)CO(ONO <sub>2</sub> ) → 0.500 CO(OH)CO(OO·) + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CO(OH)COCO(OH) + 0.500 CO + 0.500 NO <sub>3</sub> - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00651	*	*	CHOCH(OH)CH=CH <sub>2</sub> $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)CH=CH <sub>2</sub>	$7.4 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04985	*	*	CHOCH(OH)CH=CH <sub>2</sub> + OH → 0.073 CH <sub>2</sub> =CHCH(OH)CO(OO·) + 0.060 CHOC(OH)(OO·)CH=CH <sub>2</sub> + 0.867 CH <sub>2</sub> (OH)CH(OO·)CH(OH)CHO + 0.133 H <sub>2</sub> O - O <sub>2</sub>	$1.2 \cdot 10^{+10}$		
R <sub>o</sub> 04986			CHOCH(OH)CH=CH <sub>2</sub> + NO <sub>3</sub> → 0.073 CH <sub>2</sub> =CHCH(OH)CO(OO·) + 0.060 CHOC(OH)(OO·)CH=CH <sub>2</sub> + 0.867 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OO·)CH(OH)CHO + 0.133 NO <sub>3</sub> <sup>-</sup> + 0.133 H <sup>+</sup> - O <sub>2</sub>	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 04987	*	*	CH <sub>2</sub> =CHCH(OH)CO(OO·) → CO(OH)CH(OH)CH=CH <sub>2</sub> + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04988	*	*	CHOC(OH)(OO·)CH=CH <sub>2</sub> → CHOCOCH=CH <sub>2</sub> + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 04989			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OO·)CH(OH)CHO $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (ONO <sub>2</sub> )CH(O·)CH(OH)CHO + 0.550 CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)CHO + 0.250 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 04990			CH <sub>2</sub> (ONO <sub>2</sub> )CH(O·)CH(OH)CHO $\xrightarrow{O_2}$ CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)CHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 04991			CH <sub>2</sub> (ONO <sub>2</sub> )CH(O·)CH(OH)CHO → 0.500 CH <sub>2</sub> O + 0.500 CHOCH(OH)CHO + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CHO + 0.500 CHOCH(OH)(OO·) + 0.500 NO <sub>2</sub> - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 04992	*	*	CH(OH) <sub>2</sub> CH(OH)CH=CH <sub>2</sub> + OH → 0.064 CH <sub>2</sub> =CHCH(OH)C(OH) <sub>2</sub> (OO·) + 0.111 CH(OH) <sub>2</sub> C(OH)(OO·)CH=CH <sub>2</sub> + 0.824 CH <sub>2</sub> (OH)CH(OO·)CH(OH)CH(OH) <sub>2</sub> + 0.176 H <sub>2</sub> O - O <sub>2</sub>	$1.2 \cdot 10^{+10}$		
R <sub>o</sub> 04993			CH(OH) <sub>2</sub> CH(OH)CH=CH <sub>2</sub> + NO <sub>3</sub> → 0.064 CH <sub>2</sub> =CHCH(OH)C(OH) <sub>2</sub> (OO·) + 0.111 CH(OH) <sub>2</sub> C(OH)(OO·)CH=CH <sub>2</sub> + 0.824 CH(OH) <sub>2</sub> CH(OH)CH(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.176 NO <sub>3</sub> <sup>-</sup> + 0.176 H <sup>+</sup> - O <sub>2</sub>	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 04994	*	*	CH <sub>2</sub> =CHCH(OH)C(OH) <sub>2</sub> (OO·) → CO(OH)CH(OH)CH=CH <sub>2</sub> + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 04995	*	*	CH(OH) <sub>2</sub> C(OH)(OO·)CH=CH <sub>2</sub> → CH(OH) <sub>2</sub> COCH=CH <sub>2</sub> + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 04996			CH(OH) <sub>2</sub> CH(OH)CH(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH(OH)CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.550 CH(OH) <sub>2</sub> CH(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + 0.250 CH(OH) <sub>2</sub> CH(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 04997			CH(OH) <sub>2</sub> CH(OH)CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 04998			CH(OH) <sub>2</sub> CH(OH)CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CH(OH) <sub>2</sub> CH(OH)(OO·) + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CHO + 0.500 CH(OH) <sub>2</sub> CH(OH)CHO + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00652			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> )	2.9 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 04999			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)CHO + OH → 0.324 CHOCH(OH)CH(OH)CH(ONO <sub>2</sub> )(OO·) + 0.107 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH)(OO·)CH(OH)CHO + 0.054 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH)(OO·)CHO + 0.441 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)CO(OO·) + 0.041 CH <sub>2</sub> (ONO <sub>2</sub> )CH(O·)CH(OH)CHO + 0.033 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(O·)CHO + H <sub>2</sub> O - 0.926 O <sub>2</sub>	2.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 05000			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)CHO + NO <sub>3</sub> → 0.324 CHOCH(OH)CH(OH)CH(ONO <sub>2</sub> )(OO·) + 0.107 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH)(OO·)CH(OH)CHO + 0.054 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH)(OO·)CHO + 0.441 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)CO(OO·) + 0.041 CH <sub>2</sub> (ONO <sub>2</sub> )CH(O·)CH(OH)CHO + 0.033 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.926 O <sub>2</sub>	2.4 · 10 <sup>+07</sup>		
R <sub>o</sub> 05001			CHOCH(OH)CH(OH)CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CHOCH(OH)CH(OH)CH(ONO <sub>2</sub> )(O·) + 0.550 CO(ONO <sub>2</sub> )CH(OH)CH(OH)CHO + 0.250 CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05002			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH)(OO·)CH(OH)CHO → CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05003			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH)(OO·)CHO → CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05004			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)CO(OO·) → CO(OH)CH(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05005			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(O·)CHO $\xrightarrow{O_2}$ CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05006			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(O·)CHO → 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)(OO·) + 0.500 CHOCHO + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CHO + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05007			CHOCH(OH)CH(OH)CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )CH(OH)CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05008			CHOCH(OH)CH(OH)CH(ONO <sub>2</sub> )(O·) → CHOCH(OH)CH(OH)(OO·) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00653			CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)COCH <sub>2</sub> (ONO <sub>2</sub> )	1.9 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00654			CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> )	1.2 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05009			CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)CHO + OH → 0.253 CHOCH(OH)COCH(ONO <sub>2</sub> )(OO·) + 0.042 CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH)(OO·)CHO + 0.655 CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)CO(OO·) + 0.050 CH <sub>2</sub> (ONO <sub>2</sub> )COCH(O·)CHO + H <sub>2</sub> O - 0.950 O <sub>2</sub>	1.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 05010			CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)CHO + NO <sub>3</sub> → 0.253 CHOCH(OH)COCH(ONO <sub>2</sub> )(OO·) + 0.042 CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH)(OO·)CHO + 0.655 CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)CO(OO·) + 0.050 CH <sub>2</sub> (ONO <sub>2</sub> )COCH(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.950 O <sub>2</sub>	9.8 · 10 <sup>+06</sup>		
R <sub>o</sub> 05011			CHOCH(OH)COCH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CHOCH(OH)COCH(ONO <sub>2</sub> )(O·) + 0.550 CO(ONO <sub>2</sub> )COCH(OH)CHO + 0.250 CH(OH)(ONO <sub>2</sub> )COCH(OH)CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05012			CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH)(OO·)CHO → CH <sub>2</sub> (ONO <sub>2</sub> )COCOCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05013			CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)CO(OO·) → CO(OH)CH(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05014			$\text{CH}_2(\text{ONO}_2)\text{COCH}(\text{O}\cdot)\text{CHO} \xrightarrow{\text{O}_2} \text{CH}_2(\text{ONO}_2)\text{COCOCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05015			$\text{CH}_2(\text{ONO}_2)\text{COCH}(\text{O}\cdot)\text{CHO} \rightarrow$ $0.500 \text{CH}_2(\text{ONO}_2)\text{CO}(\text{OO}\cdot) + 0.500 \text{CHOCHO} +$ $0.500 \text{CH}_2(\text{ONO}_2)\text{COCHO} + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{O}_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05016			$\text{CHOCH}(\text{OH})\text{COCH}(\text{ONO}_2)(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{ONO}_2)\text{COCH}(\text{OH})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05017			$\text{CHOCH}(\text{OH})\text{COCH}(\text{ONO}_2)(\text{O}\cdot) \rightarrow$ $\text{CHOCH}(\text{OH})\text{CO}(\text{OO}\cdot) + \text{CHO}(\text{ONO}_2) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00655	*	*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}=\text{CH}_2 \rightleftharpoons \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}=\text{CH}_2 + \text{H}^+$	$4.1 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 05018	*	*	$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}=\text{CH}_2 + \text{OH} \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{CH}(\text{OH})\text{CO}(\text{OH}) - \text{O}_2$	$1.0 \cdot 10^{+10}$		
R <sub>o</sub> 05019			$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}=\text{CH}_2 + \text{NO}_3 \rightarrow$ $\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OO}\cdot)\text{CH}_2(\text{ONO}_2) - \text{O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 05020			$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OO}\cdot)\text{CH}_2(\text{ONO}_2) \xrightarrow{\text{RO}_2}$ $0.200 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2(\text{ONO}_2) +$ $0.550 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{COCH}_2(\text{ONO}_2) +$ $0.250 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{ONO}_2) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 05021			$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2(\text{ONO}_2) \xrightarrow{\text{O}_2}$ $\text{CO}(\text{OH})\text{CH}(\text{OH})\text{COCH}_2(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05022			$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}_2(\text{ONO}_2) \rightarrow$ $0.500 \text{CO}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) + 0.500 \text{CH}_2(\text{ONO}_2)\text{CHO} +$ $0.500 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CHO} + 0.500 \text{CH}_2\text{O} + 0.500 \text{NO}_2 - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05023			$\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2) + \text{OH} \rightarrow$ $0.212 \text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.031 \text{CH}(\text{OH})_2\text{C}(\text{OH})(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2) +$ $0.188 \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{OO}\cdot) +$ $0.258 \text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) +$ $0.055 \text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2) +$ $0.256 \text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CH}_2(\text{ONO}_2) + \text{H}_2\text{O} - 0.431 \text{O}_2$	$1.5 \cdot 10^{+09}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05024			CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.212 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO·) + 0.031 CH(OH) <sub>2</sub> C(OH)(OO·)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.188 CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.258 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CH(OH)(O·) + 0.055 CH(OH) <sub>2</sub> CH(O·)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.256 CH(OH) <sub>2</sub> CH(OH)C(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.431 O <sub>2</sub>	1.1 · 10 <sup>+07</sup>		
R <sub>o</sub> 05025			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO·) → CO(OH)CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05026			CH(OH) <sub>2</sub> C(OH)(OO·)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) → CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05027			CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + 0.550 CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.250 CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05028			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05029			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CH(OH)(O·) → CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05030			CH(OH) <sub>2</sub> CH(O·)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05031			CH(OH) <sub>2</sub> CH(O·)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CH·(OH) <sub>2</sub> + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + 0.500 CH(OH) <sub>2</sub> CHO + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05032			CH(OH) <sub>2</sub> CH(OH)C(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CH(OH) <sub>2</sub> CH(OH)(OO·) + 0.500 CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> CH(OH)CO(OH) + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05033			CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05034			CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) → CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO·) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05035			CH(OH) <sub>2</sub> CH(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + OH $\rightarrow$ 0.167 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.058 CH(OH) <sub>2</sub> C(OH)(OO $\cdot$ )CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.137 CH(OH) <sub>2</sub> CH(OH)C(OH)(OO $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.356 CH(OH) <sub>2</sub> CH(OH)CH(OH)CH(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.194 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)CH(OH)(O $\cdot$ ) + 0.043 CH(OH) <sub>2</sub> CH(O $\cdot$ )CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.045 CH(OH) <sub>2</sub> CH(OH)CH(O $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.718 O <sub>2</sub>	2.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 05036			CH(OH) <sub>2</sub> CH(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> $\rightarrow$ 0.167 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.058 CH(OH) <sub>2</sub> C(OH)(OO $\cdot$ )CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.137 CH(OH) <sub>2</sub> CH(OH)C(OH)(OO $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.356 CH(OH) <sub>2</sub> CH(OH)CH(OH)CH(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.194 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)CH(OH)(O $\cdot$ ) + 0.043 CH(OH) <sub>2</sub> CH(O $\cdot$ )CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.045 CH(OH) <sub>2</sub> CH(OH)CH(O $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.718 O <sub>2</sub>	1.4 · 10 <sup>+07</sup>		
R <sub>o</sub> 05037			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)CH(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05038			CH(OH) <sub>2</sub> C(OH)(OO $\cdot$ )CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) $\rightarrow$ CH(OH) <sub>2</sub> COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05039			CH(OH) <sub>2</sub> CH(OH)C(OH)(OO $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) $\rightarrow$ CH(OH) <sub>2</sub> CH(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05040			CH(OH) <sub>2</sub> CH(OH)CH(OH)CH(ONO <sub>2</sub> )(OO $\cdot$ ) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> CH(OH)CH(OH)CH(ONO <sub>2</sub> )(O $\cdot$ ) + 0.550 CH(OH) <sub>2</sub> CH(OH)CH(OH)CO(ONO <sub>2</sub> ) + 0.250 CH(OH) <sub>2</sub> CH(OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05041			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)CH(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05042			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)CH(OH)(O $\cdot$ ) $\rightarrow$ CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)(OO $\cdot$ ) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05043			$\text{CH(OH)}_2\text{CH(O}\cdot\text{)CH(OH)CH}_2\text{(ONO}_2\text{)} \xrightarrow{\text{O}_2}$	$5.0 \cdot 10^{+06}$		
			$\text{CH(OH)}_2\text{COCH(OH)CH}_2\text{(ONO}_2\text{)} + \text{HO}_2$			
R <sub>o</sub> 05044			$\text{CH(OH)}_2\text{CH(O}\cdot\text{)CH(OH)CH}_2\text{(ONO}_2\text{)} \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \text{ CH} \cdot (\text{OH})_2 + 0.500 \text{ CH}_2(\text{ONO}_2)\text{CH(OH)CHO} + 0.500 \text{ CH(OH)}_2\text{CHO} +$			
			$0.500 \text{ CH}_2(\text{ONO}_2)\text{CH(OH)(OO}\cdot\text{)} - 0.500 \text{ O}_2$			
R <sub>o</sub> 05045			$\text{CH(OH)}_2\text{CH(OH)CH(OH)CH(ONO}_2\text{)(O}\cdot\text{)} \xrightarrow{\text{O}_2}$	$5.0 \cdot 10^{+06}$		
			$\text{CH(OH)}_2\text{CH(OH)CH(OH)CO(ONO}_2\text{)} + \text{HO}_2$			
R <sub>o</sub> 05046			$\text{CH(OH)}_2\text{CH(OH)CH(OH)CH(ONO}_2\text{)(O}\cdot\text{)} \rightarrow$	$5.0 \cdot 10^{+02}$		
			$\text{CH(OH)}_2\text{CH(OH)CH(OH)(OO}\cdot\text{)} + \text{CHO(ONO}_2\text{)} - \text{O}_2$			
R <sub>o</sub> 05047			$\text{CH}_2(\text{ONO}_2)\text{CH(OH)CH(OH)(OO}\cdot\text{)} \rightarrow \text{CH}_2(\text{ONO}_2)\text{CH(OH)CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05048			$\text{CH(OH)}_2\text{CH(OH)COCH}_2\text{(ONO}_2\text{)} + \text{OH} \rightarrow$	$1.1 \cdot 10^{+09}$		
			$0.256 \text{ CH}_2(\text{ONO}_2)\text{COCH(OH)C(OH)}_2\text{(OO}\cdot\text{)} +$			
			$0.047 \text{ CH(OH)}_2\text{C(OH)(OO}\cdot\text{)COCH}_2\text{(ONO}_2\text{)} +$			
			$0.286 \text{ CH(OH)}_2\text{CH(OH)COCH(ONO}_2\text{)(OO}\cdot\text{)} +$			
			$0.346 \text{ CH}_2(\text{ONO}_2)\text{COCH(OH)CH(OH)(O}\cdot\text{)} +$			
			$0.066 \text{ CH(OH)}_2\text{CH(O}\cdot\text{)COCH}_2\text{(ONO}_2\text{)} + \text{H}_2\text{O} - 0.588 \text{ O}_2$			
R <sub>o</sub> 05049			$\text{CH(OH)}_2\text{CH(OH)COCH}_2\text{(ONO}_2\text{)} + \text{NO}_3 \rightarrow$	$1.0 \cdot 10^{+07}$		
			$0.256 \text{ CH}_2(\text{ONO}_2)\text{COCH(OH)C(OH)}_2\text{(OO}\cdot\text{)} +$			
			$0.047 \text{ CH(OH)}_2\text{C(OH)(OO}\cdot\text{)COCH}_2\text{(ONO}_2\text{)} +$			
			$0.286 \text{ CH(OH)}_2\text{CH(OH)COCH(ONO}_2\text{)(OO}\cdot\text{)} +$			
			$0.346 \text{ CH}_2(\text{ONO}_2)\text{COCH(OH)CH(OH)(O}\cdot\text{)} +$			
			$0.066 \text{ CH(OH)}_2\text{CH(O}\cdot\text{)COCH}_2\text{(ONO}_2\text{)} + \text{NO}_3^- + \text{H}^+ - 0.588 \text{ O}_2$			
R <sub>o</sub> 05050			$\text{CH}_2(\text{ONO}_2)\text{COCH(OH)C(OH)}_2\text{(OO}\cdot\text{)} \rightarrow$	$1.0 \cdot 10^{+03}$		
			$\text{CO(OH)CH(OH)COCH}_2\text{(ONO}_2\text{)} + \text{HO}_2$			
R <sub>o</sub> 05051			$\text{CH(OH)}_2\text{C(OH)(OO}\cdot\text{)COCH}_2\text{(ONO}_2\text{)} \rightarrow$	$2.0 \cdot 10^{+02}$		
			$\text{CH(OH)}_2\text{COCOCH}_2\text{(ONO}_2\text{)} + \text{HO}_2$			
R <sub>o</sub> 05052			$\text{CH(OH)}_2\text{CH(OH)COCH(ONO}_2\text{)(OO}\cdot\text{)} \xrightarrow{\text{RO}_2}$	$7.3 \cdot 10^{+08}$		
			$0.200 \text{ CH(OH)}_2\text{CH(OH)COCH(ONO}_2\text{)(O}\cdot\text{)} +$			
			$0.550 \text{ CH(OH)}_2\text{CH(OH)COCO(ONO}_2\text{)} +$			
			$0.250 \text{ CH(OH)}_2\text{CH(OH)COCH(OH)(ONO}_2\text{)} + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$			

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05053			$\text{CH}_2(\text{ONO}_2)\text{COCH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CO}(\text{OH})\text{CH}(\text{OH})\text{COCH}_2(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05054			$\text{CH}_2(\text{ONO}_2)\text{COCH}(\text{OH})\text{CH}(\text{OH})(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{ONO}_2)\text{COCH}(\text{OH})(\text{OO}\cdot) + \text{CHO}(\text{OH}) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05055			$\text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{COCH}_2(\text{ONO}_2) \xrightarrow{\text{O}_2} \text{CH}(\text{OH})_2\text{COCOCH}_2(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05056			$\text{CH}(\text{OH})_2\text{CH}(\text{O}\cdot)\text{COCH}_2(\text{ONO}_2) \rightarrow$ $0.500 \text{ CH}\cdot(\text{OH})_2 + 0.500 \text{ CH}_2(\text{ONO}_2)\text{COCHO} + 0.500 \text{ CH}(\text{OH})_2\text{CHO} +$ $0.500 \text{ CH}_2(\text{ONO}_2)\text{CO}(\text{OO}\cdot) - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05057			$\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{COCH}(\text{ONO}_2)(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{COCO}(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05058			$\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{COCH}(\text{ONO}_2)(\text{O}\cdot) \rightarrow$ $\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) + \text{CHO}(\text{ONO}_2) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00656			$\text{CH}(\text{OH})(\text{ONO}_2)\text{COCH}(\text{OH})\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}}$ $\text{CH}(\text{OH})_2\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2)$	$5.1 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05059			$\text{CH}(\text{OH})(\text{ONO}_2)\text{COCH}(\text{OH})\text{CHO} + \text{OH} \rightarrow$ $0.324 \text{ CHOCH}(\text{OH})\text{COC}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) +$ $0.034 \text{ CH}(\text{OH})(\text{ONO}_2)\text{COC}(\text{OH})(\text{OO}\cdot)\text{CHO} +$ $0.553 \text{ CH}(\text{OH})(\text{ONO}_2)\text{COCH}(\text{OH})\text{CO}(\text{OO}\cdot) +$ $0.047 \text{ CHOCH}(\text{OH})\text{COCH}(\text{ONO}_2)(\text{O}\cdot) +$ $0.042 \text{ CH}(\text{OH})(\text{ONO}_2)\text{COCH}(\text{O}\cdot)\text{CHO} + \text{H}_2\text{O} - 0.911 \text{ O}_2$	$1.5 \cdot 10^{+09}$		
R <sub>o</sub> 05060			$\text{CH}(\text{OH})(\text{ONO}_2)\text{COCH}(\text{OH})\text{CHO} + \text{NO}_3 \rightarrow$ $0.324 \text{ CHOCH}(\text{OH})\text{COC}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) +$ $0.034 \text{ CH}(\text{OH})(\text{ONO}_2)\text{COC}(\text{OH})(\text{OO}\cdot)\text{CHO} +$ $0.553 \text{ CH}(\text{OH})(\text{ONO}_2)\text{COCH}(\text{OH})\text{CO}(\text{OO}\cdot) +$ $0.047 \text{ CHOCH}(\text{OH})\text{COCH}(\text{ONO}_2)(\text{O}\cdot) +$ $0.042 \text{ CH}(\text{OH})(\text{ONO}_2)\text{COCH}(\text{O}\cdot)\text{CHO} + \text{NO}_3^- + \text{H}^+ - 0.911 \text{ O}_2$	$9.1 \cdot 10^{+06}$		
R <sub>o</sub> 05061			$\text{CHOCH}(\text{OH})\text{COC}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) \rightarrow$ $\text{CO}(\text{ONO}_2)\text{COCH}(\text{OH})\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05062			$\text{CH}(\text{OH})(\text{ONO}_2)\text{COC}(\text{OH})(\text{OO}\cdot)\text{CHO} \rightarrow$ $\text{CH}(\text{OH})(\text{ONO}_2)\text{COCOCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05063			CH(OH)(ONO <sub>2</sub> )COCH(OH)CO(OO·) → CO(OH)CH(OH)COCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 05064			CH(OH)(ONO <sub>2</sub> )COCH(O·)CHO $\xrightarrow{O_2}$ CH(OH)(ONO <sub>2</sub> )COCOCHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05065			CH(OH)(ONO <sub>2</sub> )COCH(O·)CHO → 0.500 CH(OH)(ONO <sub>2</sub> )CO(OO·) + 0.500 CHOCHO + 0.500 CH(OH)(ONO <sub>2</sub> )COCHO + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00657			CO(ONO <sub>2</sub> )COCH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)COCO(ONO <sub>2</sub> )	$1.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00658			CO(ONO <sub>2</sub> )COCH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> )	$1.2 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05066			CO(ONO <sub>2</sub> )COCH(OH)CHO $\xrightarrow{H_2O}$ CO(OH)COCH(OH)CHO + H <sup>+</sup> + NO <sub>3</sub>	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 05067			CO(ONO <sub>2</sub> )COCH(OH)CHO + OH → 0.047 CO(ONO <sub>2</sub> )COC(OH)(OO·)CHO + 0.886 CO(ONO <sub>2</sub> )COCH(OH)CO(OO·) + 0.067 CO(ONO <sub>2</sub> )COCH(O·)CHO + H <sub>2</sub> O - 0.933 O <sub>2</sub>	$9.2 \cdot 10^{+08}$		
R <sub>o</sub> 05068			CO(ONO <sub>2</sub> )COCH(OH)CHO + NO <sub>3</sub> → 0.047 CO(ONO <sub>2</sub> )COC(OH)(OO·)CHO + 0.886 CO(ONO <sub>2</sub> )COCH(OH)CO(OO·) + 0.067 CO(ONO <sub>2</sub> )COCH(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.933 O <sub>2</sub>	$3.6 \cdot 10^{+06}$		
R <sub>o</sub> 05069			CO(ONO <sub>2</sub> )COC(OH)(OO·)CHO → CO(ONO <sub>2</sub> )COCOCHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05070			CO(ONO <sub>2</sub> )COCH(OH)CO(OO·) → CO(OH)CH(OH)COCO(ONO <sub>2</sub> ) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 05071			CO(ONO <sub>2</sub> )COCH(O·)CHO $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )COCOCHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05072			CO(ONO <sub>2</sub> )COCH(O·)CHO → 0.500 CO(ONO <sub>2</sub> )CO(OO·) + 0.500 CHOCHO + 0.500 CO(ONO <sub>2</sub> )COCHO + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00659			CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)CH(OH)CH(OH)(ONO <sub>2</sub> )	$3.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05073			CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)CHO + OH $\rightarrow$ 0.445 CHOCH(OH)CH(OH)C(OH)(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.039 CH(OH)(ONO <sub>2</sub> )C(OH)(OO $\cdot$ )CH(OH)CHO + 0.047 CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH)(OO $\cdot$ )CHO + 0.400 CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)CO(OO $\cdot$ ) + 0.034 CHOCH(OH)CH(OH)CH(ONO <sub>2</sub> )(O $\cdot$ ) + 0.035 CH(OH)(ONO <sub>2</sub> )CH(O $\cdot$ )CH(OH)CHO + H <sub>2</sub> O - 0.931 O <sub>2</sub>	2.4 · 10 <sup>+09</sup>		
R <sub>o</sub> 05074			CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)CHO + NO <sub>3</sub> $\rightarrow$ 0.445 CHOCH(OH)CH(OH)C(OH)(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.039 CH(OH)(ONO <sub>2</sub> )C(OH)(OO $\cdot$ )CH(OH)CHO + 0.047 CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH)(OO $\cdot$ )CHO + 0.400 CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)CO(OO $\cdot$ ) + 0.034 CHOCH(OH)CH(OH)CH(ONO <sub>2</sub> )(O $\cdot$ ) + 0.035 CH(OH)(ONO <sub>2</sub> )CH(O $\cdot$ )CH(OH)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.931 O <sub>2</sub>	2.7 · 10 <sup>+07</sup>		
R <sub>o</sub> 05075			CHOCH(OH)CH(OH)C(OH)(ONO <sub>2</sub> )(OO $\cdot$ ) $\rightarrow$ CO(ONO <sub>2</sub> )CH(OH)CH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05076			CH(OH)(ONO <sub>2</sub> )C(OH)(OO $\cdot$ )CH(OH)CHO $\rightarrow$ CH(OH)(ONO <sub>2</sub> )COCH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05077			CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH)(OO $\cdot$ )CHO $\rightarrow$ CH(OH)(ONO <sub>2</sub> )CH(OH)COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05078			CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)CO(OO $\cdot$ ) $\rightarrow$ CO(OH)CH(OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05079			CH(OH)(ONO <sub>2</sub> )CH(O $\cdot$ )CH(OH)CHO $\xrightarrow{O_2}$ CH(OH)(ONO <sub>2</sub> )COCH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05080			CH(OH)(ONO <sub>2</sub> )CH(O $\cdot$ )CH(OH)CHO $\rightarrow$ 0.500 CHO(ONO <sub>2</sub> ) + 0.500 CHOCH(OH)CHO + 0.500 CH(OH)(ONO <sub>2</sub> )CHO + 0.500 CHOCH(OH)(OO $\cdot$ ) + 0.500 HO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00660			CO(ONO <sub>2</sub> )CH(OH)CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)CH(OH)CO(ONO <sub>2</sub> )	2.9 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05081			CO(ONO <sub>2</sub> )CH(OH)CH(OH)CHO $\xrightleftharpoons{H_2O}$ CO(OH)CH(OH)CH(OH)CHO + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>-06</sup>	6600.0	

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05082			CO(ONO <sub>2</sub> )CH(OH)CH(OH)CHO + OH $\rightarrow$ 0.034 CO(ONO <sub>2</sub> )C(OH)(OO $\cdot$ )CH(OH)CHO + 0.077 CO(ONO <sub>2</sub> )CH(OH)C(OH)(OO $\cdot$ )CHO + 0.772 CO(ONO <sub>2</sub> )CH(OH)CH(OH)CO(OO $\cdot$ ) + 0.059 CO(ONO <sub>2</sub> )CH(O $\cdot$ )CH(OH)CHO + 0.059 CO(ONO <sub>2</sub> )CH(OH)CH(O $\cdot$ )CHO + H <sub>2</sub> O - 0.883 O <sub>2</sub>	1.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 05083			CO(ONO <sub>2</sub> )CH(OH)CH(OH)CHO + NO <sub>3</sub> $\rightarrow$ 0.034 CO(ONO <sub>2</sub> )C(OH)(OO $\cdot$ )CH(OH)CHO + 0.077 CO(ONO <sub>2</sub> )CH(OH)C(OH)(OO $\cdot$ )CHO + 0.772 CO(ONO <sub>2</sub> )CH(OH)CH(OH)CO(OO $\cdot$ ) + 0.059 CO(ONO <sub>2</sub> )CH(O $\cdot$ )CH(OH)CHO + 0.059 CO(ONO <sub>2</sub> )CH(OH)CH(O $\cdot$ )CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.883 O <sub>2</sub>	9.1 · 10 <sup>+06</sup>		
R <sub>o</sub> 05084			CO(ONO <sub>2</sub> )C(OH)(OO $\cdot$ )CH(OH)CHO $\rightarrow$ CO(ONO <sub>2</sub> )COCH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05085			CO(ONO <sub>2</sub> )CH(OH)C(OH)(OO $\cdot$ )CHO $\rightarrow$ CO(ONO <sub>2</sub> )CH(OH)COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05086			CO(ONO <sub>2</sub> )CH(OH)CH(OH)CO(OO $\cdot$ ) $\rightarrow$ CO(OH)CH(OH)CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05087			CO(ONO <sub>2</sub> )CH(O $\cdot$ )CH(OH)CHO $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )COCH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05088			CO(ONO <sub>2</sub> )CH(O $\cdot$ )CH(OH)CHO $\rightarrow$ 0.500 CO + 0.500 CHOCH(OH)CHO + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CHOCH(OH)(OO $\cdot$ ) + 0.500 NO <sub>3</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05089			CO(ONO <sub>2</sub> )CH(OH)CH(O $\cdot$ )CHO $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )CH(OH)COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05090			CO(ONO <sub>2</sub> )CH(OH)CH(O $\cdot$ )CHO $\rightarrow$ 0.500 CO(ONO <sub>2</sub> )CH(OH)(OO $\cdot$ ) + 0.500 CHOCHO + 0.500 CO(ONO <sub>2</sub> )CH(OH)CHO + 0.500 CH $\cdot$ (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00661			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> )	3.7 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05091			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CHO + OH $\rightarrow$ 0.335 CHOCH(OH)CH(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.065 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH)(OO $\cdot$ )CHO + 0.558 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CO(OO $\cdot$ ) + 0.042 CH <sub>2</sub> (ONO <sub>2</sub> )CH(O $\cdot$ )CHO + H <sub>2</sub> O - 0.958 O <sub>2</sub>	1.8 · 10 <sup>+09</sup>		
R <sub>o</sub> 05092			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CHO + NO <sub>3</sub> $\rightarrow$ 0.335 CHOCH(OH)CH(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.065 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH)(OO $\cdot$ )CHO + 0.558 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CO(OO $\cdot$ ) + 0.042 CH <sub>2</sub> (ONO <sub>2</sub> )CH(O $\cdot$ )CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.958 O <sub>2</sub>	9.5 · 10 <sup>+06</sup>		
R <sub>o</sub> 05093			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH)(OO $\cdot$ )CHO $\rightarrow$ CH <sub>2</sub> (ONO <sub>2</sub> )COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05094			CH <sub>2</sub> (ONO <sub>2</sub> )CH(O $\cdot$ )CHO $\xrightarrow{O_2}$ CH <sub>2</sub> (ONO <sub>2</sub> )COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05095			CH <sub>2</sub> (ONO <sub>2</sub> )CH(O $\cdot$ )CHO $\rightarrow$ 0.500 CH <sub>2</sub> O + 0.500 CHOCHO + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CHO + 0.500 CH $\cdot$ (OH) <sub>2</sub> + 0.500 NO <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05096	*	*	CO(O <sup>-</sup> )CH(OH)CH=CH <sub>2</sub> + OH $\rightarrow$ 0.073 CO(O <sup>-</sup> )C(OH)(OO $\cdot$ )CH=CH <sub>2</sub> + 0.927 CH <sub>2</sub> (OH)CH(OO $\cdot$ )CH(OH)CO(O <sup>-</sup> ) + 0.073 H <sub>2</sub> O - O <sub>2</sub>	1.1 · 10 <sup>+10</sup>		
R <sub>o</sub> 05097			CO(O <sup>-</sup> )CH(OH)CH=CH <sub>2</sub> + NO <sub>3</sub> $\rightarrow$ 0.073 CO(O <sup>-</sup> )C(OH)(OO $\cdot$ )CH=CH <sub>2</sub> + 0.927 CO(O <sup>-</sup> )CH(OH)CH(OO $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.073 NO <sub>3</sub> <sup>-</sup> + 0.073 H <sup>+</sup> - O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 05098	*	*	CO(O <sup>-</sup> )C(OH)(OO $\cdot$ )CH=CH <sub>2</sub> $\rightarrow$ CO(O <sup>-</sup> )COCH=CH <sub>2</sub> + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05099			CO(O <sup>-</sup> )CH(OH)CH(OO $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{RO_2}$ 0.200 CO(O <sup>-</sup> )CH(OH)CH(O $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.550 CO(O <sup>-</sup> )CH(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + 0.250 CO(O <sup>-</sup> )CH(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05100			CO(O <sup>-</sup> )CH(OH)CH(O $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CO(O <sup>-</sup> )CH(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05101			CO(O <sup>-</sup> )CH(OH)CH(O $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) $\rightarrow$ 0.500 CO(O <sup>-</sup> )CH(OH)(OO $\cdot$ ) + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CHO + 0.500 CO(O <sup>-</sup> )CH(OH)CHO + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00662			CO(OH)CH(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CO(OH)CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> )	1.5 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00663			CO(OH)CH(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) $\rightleftharpoons$ CO(O <sup>-</sup> )CH(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + H <sup>+</sup>	1.7 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 05102			CO(OH)CH(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + OH $\rightarrow$ 0.044 CO(OH)C(OH)(OO $\cdot$ )COCH <sub>2</sub> (ONO <sub>2</sub> ) + 0.829 CO(OH)CH(OH)COCH(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.127 CO(OH)CH(O $\cdot$ )COCH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.873 O <sub>2</sub>	3.8 · 10 <sup>+08</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05103			CO(OH)CH(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.044 CO(OH)C(OH)(OO·)COCH <sub>2</sub> (ONO <sub>2</sub> ) + 0.829 CO(OH)CH(OH)COCH(ONO <sub>2</sub> )(OO·) + 0.127 CO(OH)CH(O·)COCH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.873 O <sub>2</sub>	3.1 · 10 <sup>+04</sup>		
R <sub>o</sub> 05104			CO(OH)C(OH)(OO·)COCH <sub>2</sub> (ONO <sub>2</sub> ) → CO(OH)COCOCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05105			CO(OH)CH(OH)COCH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CO(OH)CH(OH)COCH(ONO <sub>2</sub> )(O·) + 0.550 CO(OH)CH(OH)COCO(ONO <sub>2</sub> ) + 0.250 CO(OH)CH(OH)COCH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05106			CO(OH)CH(O·)COCH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CO(OH)COCOCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05107			CO(OH)CH(O·)COCH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 · CO(OH) + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )COCHO + 0.500 CO(OH)CHO + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CO(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05108			CO(OH)CH(OH)COCH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CO(OH)CH(OH)COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05109			CO(OH)CH(OH)COCH(ONO <sub>2</sub> )(O·) → CO(OH)CH(OH)CO(OO·) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00664			CO(OH)CH(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) ⇌ CO(O <sup>-</sup> )CH(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sup>+</sup>	8.3 · 10 <sup>-05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 05110			CO(OH)CH(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + OH → 0.035 CO(OH)C(OH)(OO·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.169 CO(OH)CH(OH)C(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.659 CO(OH)CH(OH)CH(OH)CH(ONO <sub>2</sub> )(OO·) + 0.053 CO(OH)CH(O·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.083 CO(OH)CH(OH)CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.864 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05111			CO(OH)CH(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.035 CO(OH)C(OH)(OO·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.169 CO(OH)CH(OH)C(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.659 CO(OH)CH(OH)CH(OH)CH(ONO <sub>2</sub> )(OO·) + 0.053 CO(OH)CH(O·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.083 CO(OH)CH(OH)CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.864 O <sub>2</sub>	1.6 · 10 <sup>+03</sup>		
R <sub>o</sub> 05112			CO(OH)C(OH)(OO·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) → CO(OH)COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05113			CO(OH)CH(OH)C(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) → CO(OH)CH(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05114			CO(OH)CH(OH)CH(OH)CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CO(OH)CH(OH)CH(OH)CH(ONO <sub>2</sub> )(O·) + 0.550 CO(OH)CH(OH)CH(OH)CO(ONO <sub>2</sub> ) + 0.250 CO(OH)CH(OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05115			CO(OH)CH(O·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CO(OH)COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05116			CO(OH)CH(O·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 · CO(OH) + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CHO + 0.500 CO(OH)CHO + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05117			CO(OH)CH(OH)CH(OH)CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CO(OH)CH(OH)CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05118			CO(OH)CH(OH)CH(OH)CH(ONO <sub>2</sub> )(O·) → CO(OH)CH(OH)CH(OH)(OO·) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05119			CH(OH) <sub>2</sub> CH(OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) + OH → 0.147 CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)C(OH) <sub>2</sub> (OO·) + 0.049 CH(OH) <sub>2</sub> C(OH)(OO·)CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.049 CH(OH) <sub>2</sub> CH(OH)C(OH)(OO·)CH(OH)(ONO <sub>2</sub> ) + 0.475 CH(OH) <sub>2</sub> CH(OH)CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.170 CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)CH(OH)(O·) + 0.038 CH(OH) <sub>2</sub> CH(O·)CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.038 CH(OH) <sub>2</sub> CH(OH)CH(O·)CH(OH)(ONO <sub>2</sub> ) + 0.036 CH(OH) <sub>2</sub> CH(OH)CH(OH)CH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O – 0.719 O <sub>2</sub>	2.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 05120			CH(OH) <sub>2</sub> CH(OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.147 CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)C(OH) <sub>2</sub> (OO·) + 0.049 CH(OH) <sub>2</sub> C(OH)(OO·)CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.049 CH(OH) <sub>2</sub> CH(OH)C(OH)(OO·)CH(OH)(ONO <sub>2</sub> ) + 0.475 CH(OH) <sub>2</sub> CH(OH)CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.170 CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)CH(OH)(O·) + 0.038 CH(OH) <sub>2</sub> CH(O·)CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.038 CH(OH) <sub>2</sub> CH(OH)CH(O·)CH(OH)(ONO <sub>2</sub> ) + 0.036 CH(OH) <sub>2</sub> CH(OH)CH(OH)CH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.719 O <sub>2</sub>	1.5 · 10 <sup>+07</sup>		
R <sub>o</sub> 05121			CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)C(OH) <sub>2</sub> (OO·) → CO(OH)CH(OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05122			CH(OH) <sub>2</sub> C(OH)(OO·)CH(OH)CH(OH)(ONO <sub>2</sub> ) → CH(OH) <sub>2</sub> COCH(OH)CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05123			CH(OH) <sub>2</sub> CH(OH)C(OH)(OO·)CH(OH)(ONO <sub>2</sub> ) → CH(OH) <sub>2</sub> CH(OH)COCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05124			CH(OH) <sub>2</sub> CH(OH)CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) → CH(OH) <sub>2</sub> CH(OH)CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05125			CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH(OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05126			CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)CH(OH)(O·) → CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05127			$\text{CH(OH)}_2\text{CH(O}\cdot\text{)CH(OH)CH(OH)(ONO}_2\text{)} \xrightarrow{\text{O}_2}$	$5.0 \cdot 10^{+06}$		
			$\text{CH(OH)}_2\text{COCH(OH)CH(OH)(ONO}_2\text{)} + \text{HO}_2$			
R <sub>o</sub> 05128			$\text{CH(OH)}_2\text{CH(O}\cdot\text{)CH(OH)CH(OH)(ONO}_2\text{)} \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \text{ CH} \cdot (\text{OH})_2 + 0.500 \text{ CH(OH)(ONO}_2\text{)CH(OH)CHO} +$			
			$0.500 \text{ CH(OH)}_2\text{CHO} + 0.500 \text{ CH(OH)(ONO}_2\text{)CH(OH)(OO}\cdot\text{)} - 0.500 \text{ O}_2$			
R <sub>o</sub> 05129			$\text{CH(OH)}_2\text{CH(OH)CH(O}\cdot\text{)CH(OH)(ONO}_2\text{)} \xrightarrow{\text{O}_2}$	$5.0 \cdot 10^{+06}$		
			$\text{CH(OH)}_2\text{CH(OH)COCH(OH)(ONO}_2\text{)} + \text{HO}_2$			
R <sub>o</sub> 05130			$\text{CH(OH)}_2\text{CH(OH)CH(O}\cdot\text{)CH(OH)(ONO}_2\text{)} \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \text{ CH(OH)}_2\text{CH(OH)(OO}\cdot\text{)} + 0.500 \text{ CH(OH)(ONO}_2\text{)CHO} +$			
			$0.500 \text{ CH(OH)}_2\text{CH(OH)CHO} + 0.500 \text{ CHO(ONO}_2\text{)} + 0.500 \text{ HO}_2 - \text{O}_2$			
R <sub>o</sub> 05131			$\text{CH(OH)(ONO}_2\text{)CH(OH)CH(OH)(OO}\cdot\text{)} \rightarrow$	$2.0 \cdot 10^{+02}$		
			$\text{CH(OH)(ONO}_2\text{)CH(OH)CHO} + \text{HO}_2$			
R <sub>o</sub> 05132			$\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CH(OH)(ONO}_2\text{)} + \text{OH} \rightarrow$	$1.6 \cdot 10^{+09}$		
			$0.192 \text{ CH(OH)(ONO}_2\text{)C(OH)}_2\text{CH(OH)C(OH)}_2\text{(OO}\cdot\text{)} +$			
			$0.258 \text{ CH(OH)}_2\text{CH(OH)C(OH)}_2\text{C(OH)(ONO}_2\text{)(OO}\cdot\text{)} +$			
			$0.233 \text{ CH(OH)(ONO}_2\text{)C(OH)}_2\text{CH(OH)CH(OH)(O}\cdot\text{)} +$			
			$0.049 \text{ CH(OH)}_2\text{CH(O}\cdot\text{)C(OH)}_2\text{CH(OH)(ONO}_2\text{)} +$			
			$0.221 \text{ CH(OH)}_2\text{CH(OH)C(OH)(O}\cdot\text{)CH(OH)(ONO}_2\text{)} +$			
			$0.047 \text{ CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CH(ONO}_2\text{)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.450 \text{ O}_2$			
R <sub>o</sub> 05133			$\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CH(OH)(ONO}_2\text{)} + \text{NO}_3 \rightarrow$	$1.2 \cdot 10^{+07}$		
			$0.192 \text{ CH(OH)(ONO}_2\text{)C(OH)}_2\text{CH(OH)C(OH)}_2\text{(OO}\cdot\text{)} +$			
			$0.258 \text{ CH(OH)}_2\text{CH(OH)C(OH)}_2\text{C(OH)(ONO}_2\text{)(OO}\cdot\text{)} +$			
			$0.233 \text{ CH(OH)(ONO}_2\text{)C(OH)}_2\text{CH(OH)CH(OH)(O}\cdot\text{)} +$			
			$0.049 \text{ CH(OH)}_2\text{CH(O}\cdot\text{)C(OH)}_2\text{CH(OH)(ONO}_2\text{)} +$			
			$0.221 \text{ CH(OH)}_2\text{CH(OH)C(OH)(O}\cdot\text{)CH(OH)(ONO}_2\text{)} +$			
			$0.047 \text{ CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CH(ONO}_2\text{)(O}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - 0.450 \text{ O}_2$			
R <sub>o</sub> 05134			$\text{CH(OH)(ONO}_2\text{)C(OH)}_2\text{CH(OH)C(OH)}_2\text{(OO}\cdot\text{)} \rightarrow$	$1.0 \cdot 10^{+03}$		
			$\text{CO(OH)CH(OH)C(OH)}_2\text{CH(OH)(ONO}_2\text{)} + \text{HO}_2$			
R <sub>o</sub> 05135			$\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{C(OH)(ONO}_2\text{)(OO}\cdot\text{)} \rightarrow$	$2.0 \cdot 10^{+02}$		
			$\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CO(ONO}_2\text{)} + \text{HO}_2$			

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05136			$\text{CH(OH)(ONO}_2\text{)C(OH)}_2\text{CH(OH)CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2}$ $\text{CO(OH)CH(OH)C(OH)}_2\text{CH(OH)(ONO}_2\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05137			$\text{CH(OH)(ONO}_2\text{)C(OH)}_2\text{CH(OH)CH(OH)(O}\cdot\text{)} \rightarrow$ $\text{CH(OH)(ONO}_2\text{)C(OH)}_2\text{CH(OH)(OO}\cdot\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05138			$\text{CH(OH)}_2\text{CH(O}\cdot\text{)C(OH)}_2\text{CH(OH)(ONO}_2\text{)} \xrightarrow{\text{O}_2}$ $\text{CH(OH)}_2\text{COC(OH)}_2\text{CH(OH)(ONO}_2\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05139			$\text{CH(OH)}_2\text{CH(O}\cdot\text{)C(OH)}_2\text{CH(OH)(ONO}_2\text{)} \rightarrow$ $0.500 \text{ CH}\cdot\text{(OH)}_2 + 0.500 \text{ CH(OH)(ONO}_2\text{)C(OH)}_2\text{CHO} +$ $0.500 \text{ CH(OH)}_2\text{CHO} + 0.500 \text{ CH(OH)(ONO}_2\text{)C(OH)}_2\text{(OO}\cdot\text{)} - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05140			$\text{CH(OH)}_2\text{CH(OH)C(OH)(O}\cdot\text{)CH(OH)(ONO}_2\text{)} \rightarrow$ $0.500 \text{ CH(OH)}_2\text{CH(OH)(OO}\cdot\text{)} + 0.500 \text{ CO(OH)CH(OH)(ONO}_2\text{)} +$ $0.500 \text{ CH(OH)}_2\text{CH(OH)CO(OH)} + 0.500 \text{ CHO(ONO}_2\text{)} + 0.500 \text{ HO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05141			$\text{CH(OH)}_2\text{CH(OH)CH}_2\text{(ONO}_2\text{)} + \text{OH} \rightarrow$ $0.212 \text{ CH}_2\text{(ONO}_2\text{)CH(OH)C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.069 \text{ CH(OH)}_2\text{C(OH)(OO}\cdot\text{)CH}_2\text{(ONO}_2\text{)} +$ $0.430 \text{ CH(OH)}_2\text{CH(OH)CH(ONO}_2\text{)(OO}\cdot\text{)} +$ $0.234 \text{ CH}_2\text{(ONO}_2\text{)CH(OH)CH(OH)(O}\cdot\text{)} +$ $0.054 \text{ CH(OH)}_2\text{CH(O}\cdot\text{)CH}_2\text{(ONO}_2\text{)} + \text{H}_2\text{O} - 0.711 \text{ O}_2$	$1.6 \cdot 10^{+09}$		
R <sub>o</sub> 05142			$\text{CH(OH)}_2\text{CH(OH)CH}_2\text{(ONO}_2\text{)} + \text{NO}_3 \rightarrow$ $0.212 \text{ CH}_2\text{(ONO}_2\text{)CH(OH)C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.069 \text{ CH(OH)}_2\text{C(OH)(OO}\cdot\text{)CH}_2\text{(ONO}_2\text{)} +$ $0.430 \text{ CH(OH)}_2\text{CH(OH)CH(ONO}_2\text{)(OO}\cdot\text{)} +$ $0.234 \text{ CH}_2\text{(ONO}_2\text{)CH(OH)CH(OH)(O}\cdot\text{)} +$ $0.054 \text{ CH(OH)}_2\text{CH(O}\cdot\text{)CH}_2\text{(ONO}_2\text{)} + \text{NO}_3^- + \text{H}^+ - 0.711 \text{ O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 05143			$\text{CH(OH)}_2\text{C(OH)(OO}\cdot\text{)CH}_2\text{(ONO}_2\text{)} \rightarrow \text{CH(OH)}_2\text{COCH}_2\text{(ONO}_2\text{)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05144			$\text{CH}_2\text{(ONO}_2\text{)CH(OH)CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CO(OH)CH(OH)CH}_2\text{(ONO}_2\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05145			$\text{CH}_2\text{(ONO}_2\text{)CH(OH)CH(OH)(O}\cdot\text{)} \rightarrow$ $\text{CH}_2\text{(ONO}_2\text{)CH(OH)(OO}\cdot\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05146			$\text{CH(OH)}_2\text{CH(O}\cdot\text{)CH}_2\text{(ONO}_2\text{)} \xrightarrow{\text{O}_2} \text{CH(OH)}_2\text{COCH}_2\text{(ONO}_2\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05147			$\text{CH(OH)}_2\text{CH(O}\cdot\text{)CH}_2\text{(ONO}_2\text{)} \rightarrow 0.500 \text{ CH}\cdot\text{(OH)}_2 +$ $0.500 \text{ CH}_2\text{(ONO}_2\text{)CHO} + 0.500 \text{ CH(OH)}_2\text{CHO} + 0.500 \text{ CH}_2\text{O} + 0.500 \text{ NO}_2$	$5.0 \cdot 10^{+02}$		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00665			$\text{CH(OH)}_2\text{CH(OH)COCH(OH)(ONO}_2\text{)} \xrightleftharpoons{\text{H}_2\text{O}}$	$5.1 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05148			$\text{CH(OH)}_2\text{CH(OH)C(OH)}_2\text{CH(OH)(ONO}_2\text{)}$ $\text{CH(OH)}_2\text{CH(OH)COCH(OH)(ONO}_2\text{)} + \text{OH} \rightarrow$ $0.212 \text{ CH(OH)(ONO}_2\text{)COCH(OH)C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.037 \text{ CH(OH)}_2\text{C(OH)(OO}\cdot\text{)COCH(OH)(ONO}_2\text{)} +$ $0.359 \text{ CH(OH)}_2\text{CH(OH)COC(OH)(ONO}_2\text{)(OO}\cdot\text{)} +$ $0.286 \text{ CH(OH)(ONO}_2\text{)COCH(OH)CH(OH)(O}\cdot\text{)} +$ $0.054 \text{ CH(OH)}_2\text{CH(O}\cdot\text{)COCH(OH)(ONO}_2\text{)} +$ $0.052 \text{ CH(OH)}_2\text{CH(OH)COCH(ONO}_2\text{)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.608 \text{ O}_2$	$1.3 \cdot 10^{+09}$		
R <sub>o</sub> 05149			$\text{CH(OH)}_2\text{CH(OH)COCH(OH)(ONO}_2\text{)} + \text{NO}_3 \rightarrow$ $0.212 \text{ CH(OH)(ONO}_2\text{)COCH(OH)C(OH)}_2\text{(OO}\cdot\text{)} +$ $0.037 \text{ CH(OH)}_2\text{C(OH)(OO}\cdot\text{)COCH(OH)(ONO}_2\text{)} +$ $0.359 \text{ CH(OH)}_2\text{CH(OH)COC(OH)(ONO}_2\text{)(OO}\cdot\text{)} +$ $0.286 \text{ CH(OH)(ONO}_2\text{)COCH(OH)CH(OH)(O}\cdot\text{)} +$ $0.054 \text{ CH(OH)}_2\text{CH(O}\cdot\text{)COCH(OH)(ONO}_2\text{)} +$ $0.052 \text{ CH(OH)}_2\text{CH(OH)COCH(ONO}_2\text{)(O}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - 0.608 \text{ O}_2$	$1.1 \cdot 10^{+07}$		
R <sub>o</sub> 05150			$\text{CH(OH)(ONO}_2\text{)COCH(OH)C(OH)}_2\text{(OO}\cdot\text{)} \rightarrow$ $\text{CO(OH)CH(OH)COCH(OH)(ONO}_2\text{)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 05151			$\text{CH(OH)}_2\text{C(OH)(OO}\cdot\text{)COCH(OH)(ONO}_2\text{)} \rightarrow$ $\text{CH(OH)}_2\text{COCOCH(OH)(ONO}_2\text{)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05152			$\text{CH(OH)}_2\text{CH(OH)COC(OH)(ONO}_2\text{)(OO}\cdot\text{)} \rightarrow$ $\text{CH(OH)}_2\text{CH(OH)COCO(ONO}_2\text{)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05153			$\text{CH(OH)(ONO}_2\text{)COCH(OH)CH(OH)(O}\cdot\text{)} \xrightarrow{\text{O}_2}$ $\text{CO(OH)CH(OH)COCH(OH)(ONO}_2\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05154			$\text{CH(OH)(ONO}_2\text{)COCH(OH)CH(OH)(O}\cdot\text{)} \rightarrow$ $\text{CH(OH)(ONO}_2\text{)COCH(OH)(OO}\cdot\text{)} + \text{CHO(OH)} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05155			$\text{CH(OH)}_2\text{CH(O}\cdot\text{)COCH(OH)(ONO}_2\text{)} \xrightarrow{\text{O}_2}$ $\text{CH(OH)}_2\text{COCOCH(OH)(ONO}_2\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05156			$\text{CH(OH)}_2\text{CH(O}\cdot\text{)COCH(OH)(ONO}_2\text{)} \rightarrow$ $0.500 \text{ CH}\cdot\text{(OH)}_2 + 0.500 \text{ CH(OH)(ONO}_2\text{)COCHO} + 0.500 \text{ CH(OH)}_2\text{CHO} +$ $0.500 \text{ CH(OH)(ONO}_2\text{)CO(OO}\cdot\text{)} - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05157			$\text{CH(OH)}_2\text{CH(OH)COCO(ONO}_2\text{)} \xrightarrow{H_2O}$	$7.5 \cdot 10^{-06}$	6600.0	
			$\text{CH(OH)}_2\text{CH(OH)COCO(OH)} + \text{H}^+ + \text{NO}_3$			
R <sub>o</sub> 05158			$\text{CH(OH)}_2\text{CH(OH)COCO(ONO}_2\text{)} + \text{OH} \rightarrow$	$7.8 \cdot 10^{+08}$		
			$0.363 \text{ CO(ONO}_2\text{)COCH(OH)C(OH)}_2\text{(OO}\cdot\text{)} +$			
			$0.054 \text{ CH(OH)}_2\text{C(OH)(OO}\cdot\text{)COCO(ONO}_2\text{)} +$			
			$0.490 \text{ CO(ONO}_2\text{)COCH(OH)CH(OH)(O}\cdot\text{)} +$			
			$0.093 \text{ CH(OH)}_2\text{CH(O}\cdot\text{)COCO(ONO}_2\text{)} + \text{H}_2\text{O} - 0.417 \text{ O}_2$			
R <sub>o</sub> 05159			$\text{CH(OH)}_2\text{CH(OH)COCO(ONO}_2\text{)} + \text{NO}_3 \rightarrow$	$9.6 \cdot 10^{+06}$		
			$0.363 \text{ CO(ONO}_2\text{)COCH(OH)C(OH)}_2\text{(OO}\cdot\text{)} +$			
			$0.054 \text{ CH(OH)}_2\text{C(OH)(OO}\cdot\text{)COCO(ONO}_2\text{)} +$			
			$0.490 \text{ CO(ONO}_2\text{)COCH(OH)CH(OH)(O}\cdot\text{)} +$			
			$0.093 \text{ CH(OH)}_2\text{CH(O}\cdot\text{)COCO(ONO}_2\text{)} + \text{NO}_3^- + \text{H}^+ - 0.417 \text{ O}_2$			
R <sub>o</sub> 05160			$\text{CO(ONO}_2\text{)COCH(OH)C(OH)}_2\text{(OO}\cdot\text{)} \rightarrow$	$1.0 \cdot 10^{+03}$		
			$\text{CO(OH)CH(OH)COCO(ONO}_2\text{)} + \text{HO}_2$			
R <sub>o</sub> 05161			$\text{CH(OH)}_2\text{C(OH)(OO}\cdot\text{)COCO(ONO}_2\text{)} \rightarrow \text{CH(OH)}_2\text{COCOCO(ONO}_2\text{)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05162			$\text{CO(ONO}_2\text{)COCH(OH)CH(OH)(O}\cdot\text{)} \xrightarrow{O_2}$	$5.0 \cdot 10^{+06}$		
			$\text{CO(OH)CH(OH)COCO(ONO}_2\text{)} + \text{HO}_2$			
R <sub>o</sub> 05163			$\text{CO(ONO}_2\text{)COCH(OH)CH(OH)(O}\cdot\text{)} \rightarrow$	$5.0 \cdot 10^{+02}$		
			$\text{CO(ONO}_2\text{)COCH(OH)(OO}\cdot\text{)} + \text{CHO(OH)} - \text{O}_2$			
R <sub>o</sub> 05164			$\text{CH(OH)}_2\text{CH(O}\cdot\text{)COCO(ONO}_2\text{)} \xrightarrow{O_2} \text{CH(OH)}_2\text{COCOCO(ONO}_2\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05165			$\text{CH(OH)}_2\text{CH(O}\cdot\text{)COCO(ONO}_2\text{)} \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \text{ CH}\cdot\text{(OH)}_2 + 0.500 \text{ CO(ONO}_2\text{)COCHO} + 0.500 \text{ CH(OH)}_2\text{CHO} +$			
			$0.500 \text{ CO(ONO}_2\text{)CO(OO}\cdot\text{)} - 0.500 \text{ O}_2$			
R <sub>o</sub> 05166			$\text{CH(OH)}_2\text{CH(OH)CH(OH)CO(ONO}_2\text{)} \xrightarrow{H_2O}$	$7.5 \cdot 10^{-06}$	6600.0	
			$\text{CH(OH)}_2\text{CH(OH)CH(OH)CO(OH)} + \text{H}^+ + \text{NO}_3$			

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05167			CH(OH) <sub>2</sub> CH(OH)CH(OH)CO(ONO <sub>2</sub> ) + OH → 0.326 CO(ONO <sub>2</sub> )CH(OH)CH(OH)C(OH) <sub>2</sub> (OO·) + 0.092 CH(OH) <sub>2</sub> C(OH)(OO·)CH(OH)CO(ONO <sub>2</sub> ) + 0.049 CH(OH) <sub>2</sub> CH(OH)C(OH)(OO·)CO(ONO <sub>2</sub> ) + 0.378 CO(ONO <sub>2</sub> )CH(OH)CH(OH)CH(OH)(O·) + 0.084 CH(OH) <sub>2</sub> CH(O·)CH(OH)CO(ONO <sub>2</sub> ) + 0.072 CH(OH) <sub>2</sub> CH(OH)CH(O·)CO(ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.467 O <sub>2</sub>	1.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 05168			CH(OH) <sub>2</sub> CH(OH)CH(OH)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.326 CO(ONO <sub>2</sub> )CH(OH)CH(OH)C(OH) <sub>2</sub> (OO·) + 0.092 CH(OH) <sub>2</sub> C(OH)(OO·)CH(OH)CO(ONO <sub>2</sub> ) + 0.049 CH(OH) <sub>2</sub> CH(OH)C(OH)(OO·)CO(ONO <sub>2</sub> ) + 0.378 CO(ONO <sub>2</sub> )CH(OH)CH(OH)CH(OH)(O·) + 0.084 CH(OH) <sub>2</sub> CH(O·)CH(OH)CO(ONO <sub>2</sub> ) + 0.072 CH(OH) <sub>2</sub> CH(OH)CH(O·)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.467 O <sub>2</sub>	1.2 · 10 <sup>+07</sup>		
R <sub>o</sub> 05169			CO(ONO <sub>2</sub> )CH(OH)CH(OH)C(OH) <sub>2</sub> (OO·) → CO(OH)CH(OH)CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05170			CH(OH) <sub>2</sub> C(OH)(OO·)CH(OH)CO(ONO <sub>2</sub> ) → CH(OH) <sub>2</sub> COCH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05171			CH(OH) <sub>2</sub> CH(OH)C(OH)(OO·)CO(ONO <sub>2</sub> ) → CH(OH) <sub>2</sub> CH(OH)COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05172			CO(ONO <sub>2</sub> )CH(OH)CH(OH)CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH(OH)CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05173			CO(ONO <sub>2</sub> )CH(OH)CH(OH)CH(OH)(O·) → CO(ONO <sub>2</sub> )CH(OH)CH(OH)(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05174			CH(OH) <sub>2</sub> CH(O·)CH(OH)CO(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05175			CH(OH) <sub>2</sub> CH(O·)CH(OH)CO(ONO <sub>2</sub> ) → 0.500 CH·(OH) <sub>2</sub> + 0.500 CO(ONO <sub>2</sub> )CH(OH)CHO + 0.500 CH(OH) <sub>2</sub> CHO + 0.500 CO(ONO <sub>2</sub> )CH(OH)(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05176			CH(OH) <sub>2</sub> CH(OH)CH(O·)CO(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(OH)COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05177			CH(OH) <sub>2</sub> CH(OH)CH(O $\cdot$ )CO(ONO <sub>2</sub> ) $\rightarrow$ 0.500 CH(OH) <sub>2</sub> CH(OH)(OO $\cdot$ ) + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CH(OH) <sub>2</sub> CH(OH)CHO + 0.500 CO + 0.500 NO <sub>3</sub> - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05178			CO(ONO <sub>2</sub> )CH(OH)CH(OH)(OO $\cdot$ ) $\rightarrow$ CO(ONO <sub>2</sub> )CH(OH)CHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05179			CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CO(OH) + H <sup>+</sup> + NO <sub>3</sub>	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 05180			CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + OH $\rightarrow$ 0.280 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.033 CH(OH) <sub>2</sub> C(OH)(OO $\cdot$ )C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.340 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CH(OH)(O $\cdot$ ) + 0.072 CH(OH) <sub>2</sub> CH(O $\cdot$ )C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.276 CH(OH) <sub>2</sub> CH(OH)C(OH)(O $\cdot$ )CO(ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.312 O <sub>2</sub>	$1.1 \cdot 10^{+09}$		
R <sub>o</sub> 05181			CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + NO <sub>3</sub> $\rightarrow$ 0.280 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.033 CH(OH) <sub>2</sub> C(OH)(OO $\cdot$ )C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.340 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CH(OH)(O $\cdot$ ) + 0.072 CH(OH) <sub>2</sub> CH(O $\cdot$ )C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.276 CH(OH) <sub>2</sub> CH(OH)C(OH)(O $\cdot$ )CO(ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.312 O <sub>2</sub>	$9.6 \cdot 10^{+06}$		
R <sub>o</sub> 05182			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)CH(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 05183			CH(OH) <sub>2</sub> C(OH)(OO $\cdot$ )C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) $\rightarrow$ CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05184			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)CH(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05185			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CH(OH)(O $\cdot$ ) $\rightarrow$ CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05186			CH(OH) <sub>2</sub> CH(O $\cdot$ )C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05187			CH(OH) <sub>2</sub> CH(O $\cdot$ )C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) $\rightarrow$ 0.500 CH $\cdot$ (OH) <sub>2</sub> + 0.500 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + 0.500 CH(OH) <sub>2</sub> CHO + 0.500 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO $\cdot$ ) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05188			CH(OH) <sub>2</sub> CH(OH)C(OH)(O $\cdot$ )CO(ONO <sub>2</sub> ) $\rightarrow$ 0.500 CH(OH) <sub>2</sub> CH(OH)(OO $\cdot$ ) + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> CH(OH)CO(OH) + 0.500 CO + 0.500 NO <sub>3</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00666			CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> )	3.8 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05189			CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) $\rightarrow$ 0.250 CHO(OH) + 0.250 HO <sub>2</sub> + 0.250 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO $\cdot$ ) + 0.250 CH(OH) <sub>2</sub> CO(OO $\cdot$ ) + 0.250 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO $\cdot$ )	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 05190			CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + OH $\rightarrow$ 0.137 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.231 CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.317 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COCH(OH)(O $\cdot$ ) + 0.315 CH(OH) <sub>2</sub> COC(OH)(O $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.368 O <sub>2</sub>	1.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 05191			CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> $\rightarrow$ 0.137 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COC(OH) <sub>2</sub> (OO $\cdot$ ) + 0.231 CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.317 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COCH(OH)(O $\cdot$ ) + 0.315 CH(OH) <sub>2</sub> COC(OH)(O $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.368 O <sub>2</sub>	8.1 · 10 <sup>+06</sup>		
R <sub>o</sub> 05192			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COC(OH) <sub>2</sub> (OO $\cdot$ ) $\rightarrow$ CO(OH)COC(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05193			CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO $\cdot$ ) $\xrightarrow{RO_2}$ 0.200 CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O $\cdot$ ) + 0.550 CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.250 CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05194			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COCH(OH)(O $\cdot$ ) $\xrightarrow{O_2}$ CO(OH)COC(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05195			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COCH(OH)(O $\cdot$ ) $\rightarrow$ CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO $\cdot$ ) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05196			CH(OH) <sub>2</sub> COC(OH)(O $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) $\rightarrow$ 0.500 CH(OH) <sub>2</sub> CO(OO $\cdot$ ) + 0.500 CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> COCO(OH) + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05197			$\text{CH(OH)}_2\text{COC(OH)}_2\text{CH(ONO}_2\text{)(O}\cdot\text{)} \xrightarrow{\text{O}_2}$	$5.0 \cdot 10^{+06}$		
			$\text{CH(OH)}_2\text{COC(OH)}_2\text{CO(ONO}_2\text{)} + \text{HO}_2$			
R <sub>o</sub> 05198			$\text{CH(OH)}_2\text{COC(OH)}_2\text{CH(ONO}_2\text{)(O}\cdot\text{)} \rightarrow$	$5.0 \cdot 10^{+02}$		
			$\text{CH(OH)}_2\text{COC(OH)}_2\text{(OO}\cdot\text{)} + \text{CHO(ONO}_2\text{)} - \text{O}_2$			
R <sub>o</sub> 05199			$\text{CO(O}^-\text{)CH(OH)CH(OH)CH}_2\text{(ONO}_2\text{)} + \text{OH} \rightarrow$	$1.3 \cdot 10^{+09}$		
			$0.096 \text{CO(O}^-\text{)C(OH)(OO}\cdot\text{)CH(OH)CH}_2\text{(ONO}_2\text{)} +$			
			$0.237 \text{CO(O}^-\text{)CH(OH)C(OH)(OO}\cdot\text{)CH}_2\text{(ONO}_2\text{)} +$			
			$0.526 \text{CO(O}^-\text{)CH(OH)CH(OH)CH(ONO}_2\text{)(OO}\cdot\text{)} +$			
			$0.074 \text{CO(O}^-\text{)CH(O}\cdot\text{)CH(OH)CH}_2\text{(ONO}_2\text{)} +$			
			$0.066 \text{CO(O}^-\text{)CH(OH)CH(O}\cdot\text{)CH}_2\text{(ONO}_2\text{)} + \text{H}_2\text{O} - 0.859 \text{O}_2$			
R <sub>o</sub> 05200			$\text{CO(O}^-\text{)CH(OH)CH(OH)CH}_2\text{(ONO}_2\text{)} + \text{NO}_3 \rightarrow$	$2.0 \cdot 10^{+07}$		
			$\text{CH}_2\text{(ONO}_2\text{)CH(OH)CH(OH)CO(O}\cdot\text{)} + \text{NO}_3^-$			
R <sub>o</sub> 05201			$\text{CO(O}^-\text{)C(OH)(OO}\cdot\text{)CH(OH)CH}_2\text{(ONO}_2\text{)} \rightarrow$	$2.0 \cdot 10^{+02}$		
			$\text{CO(O}^-\text{)COCH(OH)CH}_2\text{(ONO}_2\text{)} + \text{HO}_2$			
R <sub>o</sub> 05202			$\text{CO(O}^-\text{)CH(OH)C(OH)(OO}\cdot\text{)CH}_2\text{(ONO}_2\text{)} \rightarrow$	$2.0 \cdot 10^{+02}$		
			$\text{CO(O}^-\text{)CH(OH)COCH}_2\text{(ONO}_2\text{)} + \text{HO}_2$			
R <sub>o</sub> 05203			$\text{CO(O}^-\text{)CH(OH)CH(OH)CH(ONO}_2\text{)(OO}\cdot\text{)} \xrightarrow{\text{RO}_2}$	$7.3 \cdot 10^{+08}$		
			$0.200 \text{CO(O}^-\text{)CH(OH)CH(OH)CH(ONO}_2\text{)(O}\cdot\text{)} +$			
			$0.550 \text{CO(O}^-\text{)CH(OH)CH(OH)CO(ONO}_2\text{)} +$			
			$0.250 \text{CO(O}^-\text{)CH(OH)CH(OH)CH(OH)(ONO}_2\text{)} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$			
R <sub>o</sub> 05204			$\text{CO(O}^-\text{)CH(O}\cdot\text{)CH(OH)CH}_2\text{(ONO}_2\text{)} \xrightarrow{\text{O}_2}$	$5.0 \cdot 10^{+06}$		
			$\text{CO(O}^-\text{)COCH(OH)CH}_2\text{(ONO}_2\text{)} + \text{HO}_2$			
R <sub>o</sub> 05205			$\text{CO(O}^-\text{)CH(O}\cdot\text{)CH(OH)CH}_2\text{(ONO}_2\text{)} \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \cdot \text{CO(O}^-\text{)} + 0.500 \text{CH}_2\text{(ONO}_2\text{)CH(OH)CHO} + 0.500 \text{CO(O}^-\text{)CHO} +$			
			$0.500 \text{CH}_2\text{(ONO}_2\text{)CH(OH)(OO}\cdot\text{)} - 0.500 \text{O}_2$			
R <sub>o</sub> 05206			$\text{CH}_2\text{(ONO}_2\text{)CH(OH)CH(OH)CO(O}\cdot\text{)} \rightarrow$	$5.0 \cdot 10^{+02}$		
			$\text{CH}_2\text{(ONO}_2\text{)CH(OH)CH(OH)(OO}\cdot\text{)} + \text{CO}_2 - \text{O}_2$			
R <sub>o</sub> 05207			$\text{CO(O}^-\text{)CH(OH)CH(OH)CH(ONO}_2\text{)(O}\cdot\text{)} \xrightarrow{\text{O}_2}$	$5.0 \cdot 10^{+06}$		
			$\text{CO(O}^-\text{)CH(OH)CH(OH)CO(ONO}_2\text{)} + \text{HO}_2$			
R <sub>o</sub> 05208			$\text{CO(O}^-\text{)CH(OH)CH(OH)CH(ONO}_2\text{)(O}\cdot\text{)} \rightarrow$	$5.0 \cdot 10^{+02}$		
			$\text{CO(O}^-\text{)CH(OH)CH(OH)(OO}\cdot\text{)} + \text{CHO(ONO}_2\text{)} - \text{O}_2$			

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00667			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCH}_2(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}} \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2)$	$1.3 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05209			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCH}_2(\text{ONO}_2) + \text{OH} \rightarrow$ $0.125 \text{ CO}(\text{O}^-)\text{C}(\text{OH})(\text{OO}\cdot)\text{COCH}_2(\text{ONO}_2) +$ $0.689 \text{ CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCH}(\text{ONO}_2)(\text{OO}\cdot) +$ $0.185 \text{ CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{COCH}_2(\text{ONO}_2) + \text{H}_2\text{O} - 0.815 \text{ O}_2$	$4.6 \cdot 10^{+08}$		
R <sub>o</sub> 05210			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCH}_2(\text{ONO}_2) + \text{NO}_3 \rightarrow$ $\text{CH}_2(\text{ONO}_2)\text{COCH}(\text{OH})\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 05211			$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{OO}\cdot)\text{COCH}_2(\text{ONO}_2) \rightarrow \text{CO}(\text{O}^-)\text{COCOCH}_2(\text{ONO}_2) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05212			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCH}(\text{ONO}_2)(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCH}(\text{ONO}_2)(\text{O}\cdot) +$ $0.550 \text{ CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCO}(\text{ONO}_2) +$ $0.250 \text{ CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCH}(\text{OH})(\text{ONO}_2) + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 05213			$\text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{COCH}_2(\text{ONO}_2) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{COCOCH}_2(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05214			$\text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{COCH}_2(\text{ONO}_2) \rightarrow$ $0.500 \cdot \text{CO}(\text{O}^-) + 0.500 \text{ CH}_2(\text{ONO}_2)\text{COCHO} + 0.500 \text{ CO}(\text{O}^-)\text{CHO} +$ $0.500 \text{ CH}_2(\text{ONO}_2)\text{CO}(\text{OO}\cdot) - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05215			$\text{CH}_2(\text{ONO}_2)\text{COCH}(\text{OH})\text{CO}(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{ONO}_2)\text{COCH}(\text{OH})(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05216			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCH}(\text{ONO}_2)(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCO}(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05217			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCH}(\text{ONO}_2)(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) + \text{CHO}(\text{ONO}_2) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00668			$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) \rightleftharpoons$ $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) + \text{H}^+$	$8.3 \cdot 10^{-05}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 05218			$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) \xrightarrow{\text{H}_2\text{O}}$ $\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{OH}) + \text{H}^+ + \text{NO}_3$	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 05219			$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) + \text{OH} \rightarrow$ $0.158 \text{ CO}(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) +$ $0.170 \text{ CO}(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{ONO}_2) +$ $0.294 \text{ CO}(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) +$ $0.378 \text{ CO}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{ONO}_2) + \text{H}_2\text{O} - 0.329 \text{ O}_2$	$1.9 \cdot 10^{+08}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05220			CO(OH)CH(OH)CH(OH)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.158 CO(OH)C(OH)(OO·)CH(OH)CO(ONO <sub>2</sub> ) + 0.170 CO(OH)CH(OH)C(OH)(OO·)CO(ONO <sub>2</sub> ) + 0.294 CO(OH)CH(O·)CH(OH)CO(ONO <sub>2</sub> ) + 0.378 CO(OH)CH(OH)CH(O·)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.329 O <sub>2</sub>	1.6 · 10 <sup>+04</sup>		
R <sub>o</sub> 05221			CO(OH)C(OH)(OO·)CH(OH)CO(ONO <sub>2</sub> ) → CO(OH)COCH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05222			CO(OH)CH(OH)C(OH)(OO·)CO(ONO <sub>2</sub> ) → CO(OH)CH(OH)COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05223			CO(OH)CH(O·)CH(OH)CO(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CO(OH)COCH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05224			CO(OH)CH(O·)CH(OH)CO(ONO <sub>2</sub> ) → 0.500 · CO(OH) + 0.500 CO(ONO <sub>2</sub> )CH(OH)CHO + 0.500 CO(OH)CHO + 0.500 CO(ONO <sub>2</sub> )CH(OH)(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05225			CO(OH)CH(OH)CH(O·)CO(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CO(OH)CH(OH)COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05226			CO(OH)CH(OH)CH(O·)CO(ONO <sub>2</sub> ) → 0.500 CO(OH)CH(OH)(OO·) + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CO(OH)CH(OH)CHO + 0.500 CO + 0.500 NO <sub>3</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00669			CO(OH)CH(OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) ⇌ CO(O <sup>-</sup> )CH(OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) + H <sup>+</sup>	9.6 · 10 <sup>-05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 05227			CO(OH)CH(OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) + OH → 0.053 CO(OH)CH(OH)C(OH)(OO·)CH(OH)(ONO <sub>2</sub> ) + 0.784 CO(OH)CH(OH)CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.041 CO(OH)CH(O·)CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.062 CO(OH)CH(OH)CH(O·)CH(OH)(ONO <sub>2</sub> ) + 0.059 CO(OH)CH(OH)CH(OH)CH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O - 0.837 O <sub>2</sub>	1.4 · 10 <sup>+09</sup>		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05228			CO(OH)CH(OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.053 CO(OH)CH(OH)C(OH)(OO·)CH(OH)(ONO <sub>2</sub> ) + 0.784 CO(OH)CH(OH)CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.041 CO(OH)CH(O·)CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.062 CO(OH)CH(OH)CH(O·)CH(OH)(ONO <sub>2</sub> ) + 0.059 CO(OH)CH(OH)CH(OH)CH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.837 O <sub>2</sub>	1.1 · 10 <sup>+03</sup>		
R <sub>o</sub> 05229			CO(OH)CH(OH)C(OH)(OO·)CH(OH)(ONO <sub>2</sub> ) → CO(OH)CH(OH)COCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05230			CO(OH)CH(OH)CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) → CO(OH)CH(OH)CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05231			CO(OH)CH(O·)CH(OH)CH(OH)(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CO(OH)COCH(OH)CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05232			CO(OH)CH(O·)CH(OH)CH(OH)(ONO <sub>2</sub> ) → 0.500 · CO(OH) + 0.500 CH(OH)(ONO <sub>2</sub> )CH(OH)CHO + 0.500 CO(OH)CHO + 0.500 CH(OH)(ONO <sub>2</sub> )CH(OH)(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05233			CO(OH)CH(OH)CH(O·)CH(OH)(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CO(OH)CH(OH)COCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05234			CO(OH)CH(OH)CH(O·)CH(OH)(ONO <sub>2</sub> ) → 0.500 CO(OH)CH(OH)(OO·) + 0.500 CH(OH)(ONO <sub>2</sub> )CHO + 0.500 CO(OH)CH(OH)CHO + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00670			CO(OH)CH(OH)COCO(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CO(OH)CH(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> )	1.5 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00671			CO(OH)CH(OH)COCO(ONO <sub>2</sub> ) $\rightleftharpoons$ CO(O <sup>-</sup> )CH(OH)COCO(ONO <sub>2</sub> ) + H <sup>+</sup>	1.7 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 05235			CO(OH)CH(OH)COCO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CO(OH)CH(OH)COCO(OH) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>-06</sup>	6600.0	
R <sub>o</sub> 05236			CO(OH)CH(OH)COCO(ONO <sub>2</sub> ) + OH → 0.221 CO(OH)C(OH)(OO·)COCO(ONO <sub>2</sub> ) + 0.779 CO(OH)CH(O·)COCO(ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.221 O <sub>2</sub>	6.2 · 10 <sup>+07</sup>		
R <sub>o</sub> 05237			CO(OH)CH(OH)COCO(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.221 CO(OH)C(OH)(OO·)COCO(ONO <sub>2</sub> ) + 0.779 CO(OH)CH(O·)COCO(ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.221 O <sub>2</sub>	3.5 · 10 <sup>+05</sup>		
R <sub>o</sub> 05238			CO(OH)C(OH)(OO·)COCO(ONO <sub>2</sub> ) → CO(OH)COCOCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05239			$\text{CO(OH)CH(O}\cdot\text{)COCO(ONO}_2\text{)} \xrightarrow{\text{O}_2} \text{CO(OH)COCOCO(ONO}_2\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05240			$\text{CO(OH)CH(O}\cdot\text{)COCO(ONO}_2\text{)} \rightarrow$ $0.500 \cdot \text{CO(OH)} + 0.500 \text{CO(ONO}_2\text{)COCHO} + 0.500 \text{CO(OH)CHO} +$ $0.500 \text{CO(ONO}_2\text{)CO(OO}\cdot\text{)} - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00672			$\text{CO(OH)CH(OH)COCH(OH)(ONO}_2\text{)} \xrightleftharpoons{\text{H}_2\text{O}}$ $\text{CO(OH)CH(OH)C(OH)}_2\text{CH(OH)(ONO}_2\text{)}$	$8.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00673			$\text{CO(OH)CH(OH)COCH(OH)(ONO}_2\text{)} \rightleftharpoons$ $\text{CO(O}^-\text{)CH(OH)COCH(OH)(ONO}_2\text{)} + \text{H}^+$	$2.0 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 05241			$\text{CO(OH)CH(OH)COCH(OH)(ONO}_2\text{)} + \text{OH} \rightarrow$ $0.803 \text{CO(OH)CH(OH)COC(OH)(ONO}_2\text{)(OO}\cdot\text{)} +$ $0.081 \text{CO(OH)CH(O}\cdot\text{)COCH(OH)(ONO}_2\text{)} +$ $0.116 \text{CO(OH)CH(OH)COCH(ONO}_2\text{)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.803 \text{O}_2$	$6.0 \cdot 10^{+08}$		
R <sub>o</sub> 05242			$\text{CO(OH)CH(OH)COCH(OH)(ONO}_2\text{)} + \text{NO}_3 \rightarrow$ $0.803 \text{CO(OH)CH(OH)COC(OH)(ONO}_2\text{)(OO}\cdot\text{)} +$ $0.081 \text{CO(OH)CH(O}\cdot\text{)COCH(OH)(ONO}_2\text{)} +$ $0.116 \text{CO(OH)CH(OH)COCH(ONO}_2\text{)(O}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - 0.803 \text{O}_2$	$4.0 \cdot 10^{+04}$		
R <sub>o</sub> 05243			$\text{CO(OH)CH(OH)COC(OH)(ONO}_2\text{)(OO}\cdot\text{)} \rightarrow$ $\text{CO(OH)CH(OH)COCO(ONO}_2\text{)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05244			$\text{CO(OH)CH(O}\cdot\text{)COCH(OH)(ONO}_2\text{)} \xrightarrow{\text{O}_2}$ $\text{CO(OH)COCOCH(OH)(ONO}_2\text{)} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05245			$\text{CO(OH)CH(O}\cdot\text{)COCH(OH)(ONO}_2\text{)} \rightarrow$ $0.500 \cdot \text{CO(OH)} + 0.500 \text{CH(OH)(ONO}_2\text{)COCHO} + 0.500 \text{CO(OH)CHO} +$ $0.500 \text{CH(OH)(ONO}_2\text{)CO(OO}\cdot\text{)} - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00674			$\text{CO(OH)CH(OH)C(OH)}_2\text{CH}_2\text{(ONO}_2\text{)} \rightleftharpoons$ $\text{CO(O}^-\text{)CH(OH)C(OH)}_2\text{CH}_2\text{(ONO}_2\text{)} + \text{H}^+$	$1.2 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 05246			$\text{CO(OH)CH(OH)C(OH)}_2\text{CH}_2\text{(ONO}_2\text{)} + \text{OH} \rightarrow$ $0.391 \text{CO(OH)CH(OH)C(OH)}_2\text{CH(ONO}_2\text{)(OO}\cdot\text{)} +$ $0.076 \text{CO(OH)CH(O}\cdot\text{)C(OH)}_2\text{CH}_2\text{(ONO}_2\text{)} +$ $0.533 \text{CO(OH)CH(OH)C(OH)(O}\cdot\text{)CH}_2\text{(ONO}_2\text{)} + \text{H}_2\text{O} - 0.391 \text{O}_2$	$7.1 \cdot 10^{+08}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05247			CO(OH)CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.391 CO(OH)CH(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.076 CO(OH)CH(O·)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.533 CO(OH)CH(OH)C(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.391 O <sub>2</sub>	8.9 · 10 <sup>+06</sup>		
R <sub>o</sub> 05248			CO(OH)CH(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CO(OH)CH(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + 0.550 CO(OH)CH(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.250 CO(OH)CH(OH)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05249			CO(OH)CH(O·)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CO(OH)COC(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05250			CO(OH)CH(O·)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 · CO(OH) + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + 0.500 CO(OH)CHO + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05251			CO(OH)CH(OH)C(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CO(OH)CH(OH)(OO·) + 0.500 CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CO(OH)CH(OH)CO(OH) + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05252			CO(OH)CH(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CO(OH)CH(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05253			CO(OH)CH(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) → CO(OH)CH(OH)C(OH) <sub>2</sub> (OO·) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00675			CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> )	3.8 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05254			CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) → 0.250 CHO(OH) + 0.250 HO <sub>2</sub> + 0.250 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) + 0.250 CH(OH) <sub>2</sub> CO(OO·) + 0.250 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·)	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 05255			CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CO(OH) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>-06</sup>	6600.0	
R <sub>o</sub> 05256			CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + OH → 0.193 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> COC(OH) <sub>2</sub> (OO·) + 0.446 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCH(OH)(O·) + 0.362 CH(OH) <sub>2</sub> COC(OH)(O·)CO(ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.193 O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05257			CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.193 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> COC(OH) <sub>2</sub> (OO·) + 0.446 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCH(OH)(O·) + 0.362 CH(OH) <sub>2</sub> COC(OH)(O·)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.193 O <sub>2</sub>	7.4 · 10 <sup>+06</sup>		
R <sub>o</sub> 05258			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> COC(OH) <sub>2</sub> (OO·) → CO(OH)COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05259			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05260			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCH(OH)(O·) → CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05261			CH(OH) <sub>2</sub> COC(OH)(O·)CO(ONO <sub>2</sub> ) → 0.500 CH(OH) <sub>2</sub> CO(OO·) + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> COCO(OH) + 0.500 CO + 0.500 NO <sub>3</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00676			CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> )	1.0 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05262			CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) → 0.250 CHO(OH) + 0.250 HO <sub>2</sub> + 0.250 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) + 0.250 CH(OH) <sub>2</sub> CO(OO·) + 0.250 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·)	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 05263			CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + OH → 0.116 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> COC(OH) <sub>2</sub> (OO·) + 0.297 CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) + 0.269 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCH(OH)(O·) + 0.254 CH(OH) <sub>2</sub> COC(OH)(O·)CH(OH)(ONO <sub>2</sub> ) + 0.063 CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O - 0.414 O <sub>2</sub>	1.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 05264			CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.116 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> COC(OH) <sub>2</sub> (OO·) + 0.297 CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) + 0.269 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCH(OH)(O·) + 0.254 CH(OH) <sub>2</sub> COC(OH)(O·)CH(OH)(ONO <sub>2</sub> ) + 0.063 CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.414 O <sub>2</sub>	9.0 · 10 <sup>+06</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05265			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> COC(OH) <sub>2</sub> (OO·) → CO(OH)COC(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 05266			CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) → CH(OH) <sub>2</sub> COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05267			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)COC(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05268			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCH(OH)(O·) → CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) + CHO(OH) – O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05269			CH(OH) <sub>2</sub> COC(OH)(O·)CH(OH)(ONO <sub>2</sub> ) → 0.500 CH(OH) <sub>2</sub> CO(OO·) + 0.500 CO(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> COCO(OH) + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> – O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00677			CO(O <sup>–</sup> )CH(OH)COCH(OH)(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CO(O <sup>–</sup> )CH(OH)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> )	$7.9 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05270			CO(O <sup>–</sup> )CH(OH)COCH(OH)(ONO <sub>2</sub> ) + OH → 0.080 CO(O <sup>–</sup> )C(OH)(OO·)COCH(OH)(ONO <sub>2</sub> ) + 0.697 CO(O <sup>–</sup> )CH(OH)COC(OH)(ONO <sub>2</sub> )(OO·) + 0.123 CO(O <sup>–</sup> )CH(O·)COCH(OH)(ONO <sub>2</sub> ) + 0.100 CO(O <sup>–</sup> )CH(OH)COCH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O – 0.776 O <sub>2</sub>	$6.9 \cdot 10^{+08}$		
R <sub>o</sub> 05271			CO(O <sup>–</sup> )CH(OH)COCH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → CH(OH)(ONO <sub>2</sub> )COCH(OH)CO(O·) + NO <sub>3</sub> <sup>–</sup>	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 05272			CO(O <sup>–</sup> )C(OH)(OO·)COCH(OH)(ONO <sub>2</sub> ) → CO(O <sup>–</sup> )COCOCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05273			CO(O <sup>–</sup> )CH(OH)COC(OH)(ONO <sub>2</sub> )(OO·) → CO(O <sup>–</sup> )CH(OH)COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05274			CO(O <sup>–</sup> )CH(O·)COCH(OH)(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CO(O <sup>–</sup> )COCOCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05275			CO(O <sup>–</sup> )CH(O·)COCH(OH)(ONO <sub>2</sub> ) → 0.500 · CO(O <sup>–</sup> ) + 0.500 CH(OH)(ONO <sub>2</sub> )COCHO + 0.500 CO(O <sup>–</sup> )CHO + 0.500 CH(OH)(ONO <sub>2</sub> )CO(OO·) – 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05276			CH(OH)(ONO <sub>2</sub> )COCH(OH)CO(O·) → CH(OH)(ONO <sub>2</sub> )COCH(OH)(OO·) + CO <sub>2</sub> – O <sub>2</sub>	$5.0 \cdot 10^{+02}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00678			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCO}(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}} \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2)$	$1.3 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05277			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCO}(\text{ONO}_2) \xrightarrow{\text{H}_2\text{O}}$	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 05278			$\text{CO}(\text{OH})\text{COCH}(\text{OH})\text{CO}(\text{O}^-) + \text{H}^+ + \text{NO}_3$ $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCO}(\text{ONO}_2) + \text{OH} \rightarrow$ $0.356 \text{ CO}(\text{O}^-)\text{C}(\text{OH})(\text{OO}\cdot)\text{COCO}(\text{ONO}_2) +$ $0.644 \text{ CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{COCO}(\text{ONO}_2) + \text{H}_2\text{O} - 0.356 \text{ O}_2$	$1.3 \cdot 10^{+08}$		
R <sub>o</sub> 05279			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCO}(\text{ONO}_2) + \text{NO}_3 \rightarrow$ $\text{CO}(\text{ONO}_2)\text{COCH}(\text{OH})\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 05280			$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{OO}\cdot)\text{COCO}(\text{ONO}_2) \rightarrow \text{CO}(\text{O}^-)\text{COCOCO}(\text{ONO}_2) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05281			$\text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{COCO}(\text{ONO}_2) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{COCOCO}(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05282			$\text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{COCO}(\text{ONO}_2) \rightarrow$ $0.500 \cdot \text{CO}(\text{O}^-) + 0.500 \text{ CO}(\text{ONO}_2)\text{COCHO} + 0.500 \text{ CO}(\text{O}^-)\text{CHO} +$ $0.500 \text{ CO}(\text{ONO}_2)\text{CO}(\text{OO}\cdot) - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05283			$\text{CO}(\text{ONO}_2)\text{COCH}(\text{OH})\text{CO}(\text{O}\cdot) \rightarrow \text{CO}(\text{ONO}_2)\text{COCH}(\text{OH})(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05284			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2) + \text{OH} \rightarrow$ $0.063 \text{ CO}(\text{O}^-)\text{C}(\text{OH})(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2) +$ $0.347 \text{ CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{OO}\cdot) +$ $0.118 \text{ CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2) +$ $0.472 \text{ CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CH}_2(\text{ONO}_2) + \text{H}_2\text{O} - 0.410 \text{ O}_2$	$8.0 \cdot 10^{+08}$		
R <sub>o</sub> 05285			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2) + \text{NO}_3 \rightarrow$ $\text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 05286			$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2) \rightarrow$ $\text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CH}_2(\text{ONO}_2) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05287			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{O}\cdot) +$ $0.550 \text{ CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) +$ $0.250 \text{ CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 05288			$\text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2) \xrightarrow{\text{O}_2}$ $\text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CH}_2(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05289			$\text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2) \rightarrow$ $0.500 \cdot \text{CO}(\text{O}^-) + 0.500 \text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CHO} + 0.500 \text{CO}(\text{O}^-)\text{CHO} +$ $0.500 \text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05290			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CH}_2(\text{ONO}_2) \rightarrow$ $0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CH}_2(\text{ONO}_2) +$ $0.500 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^-) + 0.500 \text{CH}_2\text{O} + 0.500 \text{NO}_2 - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05291			$\text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05292			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05293			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CHO}(\text{ONO}_2) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05294			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{ONO}_2) + \text{OH} \rightarrow$ $0.077 \text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{ONO}_2) +$ $0.081 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})(\text{ONO}_2) +$ $0.675 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) +$ $0.063 \text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{ONO}_2) +$ $0.054 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})(\text{ONO}_2) +$ $0.051 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)(\text{O}\cdot) + \text{H}_2\text{O} - 0.833 \text{O}_2$	$1.6 \cdot 10^{+09}$		
R <sub>o</sub> 05295			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{ONO}_2) + \text{NO}_3 \rightarrow$ $\text{CH}(\text{OH})(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 05296			$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{ONO}_2) \rightarrow$ $\text{CO}(\text{O}^-)\text{COCH}(\text{OH})\text{CH}(\text{OH})(\text{ONO}_2) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05297			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})(\text{ONO}_2) \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCH}(\text{OH})(\text{ONO}_2) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05298			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05299			$\text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{ONO}_2) \xrightarrow{\text{O}_2}$ $\text{CO}(\text{O}^-)\text{COCH}(\text{OH})\text{CH}(\text{OH})(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05300			CO(O <sup>-</sup> )CH(O $\cdot$ )CH(OH)CH(OH)(ONO <sub>2</sub> ) $\rightarrow$ 0.500 $\cdot$ CO(O <sup>-</sup> ) + 0.500 CH(OH)(ONO <sub>2</sub> )CH(OH)CHO + 0.500 CO(O <sup>-</sup> )CHO + 0.500 CH(OH)(ONO <sub>2</sub> )CH(OH)(OO $\cdot$ ) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05301			CO(O <sup>-</sup> )CH(OH)CH(O $\cdot$ )CH(OH)(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CO(O <sup>-</sup> )CH(OH)COCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05302			CO(O <sup>-</sup> )CH(OH)CH(O $\cdot$ )CH(OH)(ONO <sub>2</sub> ) $\rightarrow$ 0.500 CO(O <sup>-</sup> )CH(OH)(OO $\cdot$ ) + 0.500 CH(OH)(ONO <sub>2</sub> )CHO + 0.500 CO(O <sup>-</sup> )CH(OH)CHO + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05303			CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)CO(O $\cdot$ ) $\rightarrow$ CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)(OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05304			CO(O <sup>-</sup> )CH(OH)CH(OH)CO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CO(OH)CH(OH)CH(OH)CO(O <sup>-</sup> ) + H <sup>+</sup> + NO <sub>3</sub>	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 05305			CO(O <sup>-</sup> )CH(OH)CH(OH)CO(ONO <sub>2</sub> ) + OH $\rightarrow$ 0.313 CO(O <sup>-</sup> )C(OH)(OO $\cdot$ )CH(OH)CO(ONO <sub>2</sub> ) + 0.172 CO(O <sup>-</sup> )CH(OH)C(OH)(OO $\cdot$ )CO(ONO <sub>2</sub> ) + 0.297 CO(O <sup>-</sup> )CH(O $\cdot$ )CH(OH)CO(ONO <sub>2</sub> ) + 0.217 CO(O <sup>-</sup> )CH(OH)CH(O $\cdot$ )CO(ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.485 O <sub>2</sub>	$3.3 \cdot 10^{+08}$		
R <sub>o</sub> 05306			CO(O <sup>-</sup> )CH(OH)CH(OH)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> $\rightarrow$ CO(ONO <sub>2</sub> )CH(OH)CH(OH)CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 05307			CO(O <sup>-</sup> )C(OH)(OO $\cdot$ )CH(OH)CO(ONO <sub>2</sub> ) $\rightarrow$ CO(O <sup>-</sup> )COCH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05308			CO(O <sup>-</sup> )CH(OH)C(OH)(OO $\cdot$ )CO(ONO <sub>2</sub> ) $\rightarrow$ CO(O <sup>-</sup> )CH(OH)COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05309			CO(O <sup>-</sup> )CH(O $\cdot$ )CH(OH)CO(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CO(O <sup>-</sup> )COCH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05310			CO(O <sup>-</sup> )CH(O $\cdot$ )CH(OH)CO(ONO <sub>2</sub> ) $\rightarrow$ 0.500 $\cdot$ CO(O <sup>-</sup> ) + 0.500 CO(ONO <sub>2</sub> )CH(OH)CHO + 0.500 CO(O <sup>-</sup> )CHO + 0.500 CO(ONO <sub>2</sub> )CH(OH)(OO $\cdot$ ) - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05311			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{ONO}_2) \xrightarrow{\text{O}_2}$	$5.0 \cdot 10^{+06}$		
			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{COCO}(\text{ONO}_2) + \text{HO}_2$			
R <sub>o</sub> 05312			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{ONO}_2) \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \text{ CO}(\text{O}^-)\text{CH}(\text{OH})(\text{OO}\cdot) + 0.500 \text{ CO}(\text{ONO}_2)\text{CHO} +$			
			$0.500 \text{ CO}(\text{O}^-)\text{CH}(\text{OH})\text{CHO} + 0.500 \text{ CO} + 0.500 \text{ NO}_3 - 0.500 \text{ O}_2$			
R <sub>o</sub> 05313			$\text{CO}(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) \rightarrow$	$5.0 \cdot 10^{+02}$		
			$\text{CO}(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$			
E <sub>o</sub> 00679			$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) \rightleftharpoons$	$1.2 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) + \text{H}^+$			
R <sub>o</sub> 05314			$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) \xrightarrow{\text{H}_2\text{O}}$	$7.5 \cdot 10^{-06}$	6600.0	
			$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{H}^+ + \text{NO}_3$			
R <sub>o</sub> 05315			$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) + \text{OH} \rightarrow$	$3.7 \cdot 10^{+08}$		
			$0.032 \text{ CO}(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) +$			
			$0.143 \text{ CO}(\text{OH})\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) +$			
			$0.825 \text{ CO}(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{ONO}_2) + \text{H}_2\text{O} - 0.032 \text{ O}_2$			
R <sub>o</sub> 05316			$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) + \text{NO}_3 \rightarrow$	$8.1 \cdot 10^{+06}$		
			$0.032 \text{ CO}(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) +$			
			$0.143 \text{ CO}(\text{OH})\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) +$			
			$0.825 \text{ CO}(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{ONO}_2) + \text{NO}_3^- + \text{H}^+ - 0.032 \text{ O}_2$			
R <sub>o</sub> 05317			$\text{CO}(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) \rightarrow$	$2.0 \cdot 10^{+02}$		
			$\text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CO}(\text{ONO}_2) + \text{HO}_2$			
R <sub>o</sub> 05318			$\text{CO}(\text{OH})\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) \xrightarrow{\text{O}_2}$	$5.0 \cdot 10^{+06}$		
			$\text{CO}(\text{OH})\text{COC}(\text{OH})_2\text{CO}(\text{ONO}_2) + \text{HO}_2$			
R <sub>o</sub> 05319			$\text{CO}(\text{OH})\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \cdot \text{CO}(\text{OH}) + 0.500 \text{ CO}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CHO} + 0.500 \text{ CO}(\text{OH})\text{CHO} +$			
			$0.500 \text{ CO}(\text{ONO}_2)\text{C}(\text{OH})_2(\text{OO}\cdot) - 0.500 \text{ O}_2$			
R <sub>o</sub> 05320			$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{ONO}_2) \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \text{ CO}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) + 0.500 \text{ CO}(\text{OH})\text{CO}(\text{ONO}_2) +$			
			$0.500 \text{ CO}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{OH}) + 0.500 \text{ CO} + 0.500 \text{ NO}_3 - 0.500 \text{ O}_2$			
E <sub>o</sub> 00680			$\text{CO}(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) \rightleftharpoons$	$1.4 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) + \text{H}^+$			

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05321			CO(OH)CH(OH)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + OH → 0.462 CO(OH)CH(OH)C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) + 0.059 CO(OH)CH(O·)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.395 CO(OH)CH(OH)C(OH)(O·)CH(OH)(ONO <sub>2</sub> ) + 0.084 CO(OH)CH(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O – 0.462 O <sub>2</sub>	9.1 · 10 <sup>+08</sup>		
R <sub>o</sub> 05322			CO(OH)CH(OH)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.462 CO(OH)CH(OH)C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) + 0.059 CO(OH)CH(O·)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.395 CO(OH)CH(OH)C(OH)(O·)CH(OH)(ONO <sub>2</sub> ) + 0.084 CO(OH)CH(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.462 O <sub>2</sub>	9.9 · 10 <sup>+06</sup>		
R <sub>o</sub> 05323			CO(OH)CH(OH)C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) → CO(OH)CH(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05324			CO(OH)CH(O·)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CO(OH)COC(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05325			CO(OH)CH(O·)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) → 0.500 · CO(OH) + 0.500 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + 0.500 CO(OH)CHO + 0.500 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05326			CO(OH)CH(OH)C(OH)(O·)CH(OH)(ONO <sub>2</sub> ) → 0.500 CO(OH)CH(OH)(OO·) + 0.500 CO(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CO(OH)CH(OH)CO(OH) + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05327			CO(O <sup>–</sup> )CH(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CO(OH)C(OH) <sub>2</sub> CH(OH)CO(O <sup>–</sup> ) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>–06</sup>	6600.0	
R <sub>o</sub> 05328			CO(O <sup>–</sup> )CH(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + OH → 0.093 CO(O <sup>–</sup> )C(OH)(OO·)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.212 CO(O <sup>–</sup> )CH(O·)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.695 CO(O <sup>–</sup> )CH(OH)C(OH)(O·)CO(ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.093 O <sub>2</sub>	4.4 · 10 <sup>+08</sup>		
R <sub>o</sub> 05329			CO(O <sup>–</sup> )CH(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + NO <sub>3</sub> → CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CO(O·) + NO <sub>3</sub> <sup>–</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 05330			CO(O <sup>–</sup> )C(OH)(OO·)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) → CO(O <sup>–</sup> )COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05331			$\text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) \xrightarrow{\text{O}_2}$	$5.0 \cdot 10^{+06}$		
			$\text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CO}(\text{ONO}_2) + \text{HO}_2$			
R <sub>o</sub> 05332			$\text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \cdot \text{CO}(\text{O}^-) + 0.500 \text{CO}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CHO} + 0.500 \text{CO}(\text{O}^-)\text{CHO} +$			
			$0.500 \text{CO}(\text{ONO}_2)\text{C}(\text{OH})_2(\text{OO}\cdot) - 0.500 \text{O}_2$			
R <sub>o</sub> 05333			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{ONO}_2) \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CO}(\text{ONO}_2) +$			
			$0.500 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^-) + 0.500 \text{CO} + 0.500 \text{NO}_3 - 0.500 \text{O}_2$			
R <sub>o</sub> 05334			$\text{CO}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) \rightarrow$	$5.0 \cdot 10^{+02}$		
			$\text{CO}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$			
R <sub>o</sub> 05335			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) + \text{OH} \rightarrow$	$1.0 \cdot 10^{+09}$		
			$0.048 \text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) +$			
			$0.421 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) +$			
			$0.094 \text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) +$			
			$0.360 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})(\text{ONO}_2) +$			
			$0.077 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{O}\cdot) + \text{H}_2\text{O} - 0.469 \text{O}_2$			
R <sub>o</sub> 05336			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) + \text{NO}_3 \rightarrow$	$2.0 \cdot 10^{+07}$		
			$\text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) + \text{NO}_3^-$			
R <sub>o</sub> 05337			$\text{CO}(\text{O}^-)\text{C}(\text{OH})(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) \rightarrow$	$2.0 \cdot 10^{+02}$		
			$\text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) + \text{HO}_2$			
R <sub>o</sub> 05338			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) \rightarrow$	$2.0 \cdot 10^{+02}$		
			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) + \text{HO}_2$			
R <sub>o</sub> 05339			$\text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) \xrightarrow{\text{O}_2}$	$5.0 \cdot 10^{+06}$		
			$\text{CO}(\text{O}^-)\text{COC}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) + \text{HO}_2$			
R <sub>o</sub> 05340			$\text{CO}(\text{O}^-)\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \cdot \text{CO}(\text{O}^-) + 0.500 \text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2\text{CHO} +$			
			$0.500 \text{CO}(\text{O}^-)\text{CHO} + 0.500 \text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2(\text{OO}\cdot) - 0.500 \text{O}_2$			
R <sub>o</sub> 05341			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})(\text{ONO}_2) \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CH}(\text{OH})(\text{ONO}_2) +$			
			$0.500 \text{CO}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{O}^-) + 0.500 \text{CHO}(\text{ONO}_2) + 0.500 \text{HO}_2 - \text{O}_2$			

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05342			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CO(O·) → CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO·) + CO <sub>2</sub> - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05343	*	*	CH(OH)=CH <sub>2</sub> + OH → CH <sub>2</sub> (OH)CH(OH)(OO·) - O <sub>2</sub>	$1.0 \cdot 10^{+10}$		
R <sub>o</sub> 05344			CH(OH)=CH <sub>2</sub> + NO <sub>3</sub> → CH <sub>2</sub> (OH)CH(OH)(OO·) - O <sub>2</sub>	$1.5 \cdot 10^{+09}$		
R <sub>o</sub> 05345	*	*	CH <sub>2</sub> (OH)COCH=CH <sub>2</sub> + OH → CH <sub>2</sub> (OH)COCH(OO·)CH <sub>2</sub> (OH) - O <sub>2</sub>	$6.0 \cdot 10^{+09}$		
R <sub>o</sub> 05346			CH <sub>2</sub> (OH)COCH=CH <sub>2</sub> + NO <sub>3</sub> → CH <sub>2</sub> (OH)COCH(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) - O <sub>2</sub>	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 05347			CH <sub>2</sub> (OH)COCH(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)COCH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.550 CH <sub>2</sub> (OH)COCOCH <sub>2</sub> (ONO <sub>2</sub> ) + 0.250 CH <sub>2</sub> (OH)COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 05348			CH <sub>2</sub> (OH)COCH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCOCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05349			CH <sub>2</sub> (OH)COCH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)CO(OO·) + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CHO + 0.500 CH <sub>2</sub> (OH)COCHO + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub> - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00681			CH <sub>2</sub> (OH)COCOCH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> )	$1.1 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00682			CH <sub>2</sub> (OH)COCOCH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> )	$4.4 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05350			CH <sub>2</sub> (OH)COCOCH <sub>2</sub> (ONO <sub>2</sub> ) + OH → 0.439 CH <sub>2</sub> (ONO <sub>2</sub> )COCOCH(OH)(OO·) + 0.439 CH <sub>2</sub> (OH)COCOCH(ONO <sub>2</sub> )(OO·) + 0.122 CH <sub>2</sub> (ONO <sub>2</sub> )COCOCH <sub>2</sub> (O·) + H <sub>2</sub> O - 0.878 O <sub>2</sub>	$6.2 \cdot 10^{+08}$		
R <sub>o</sub> 05351			CH <sub>2</sub> (OH)COCOCH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.439 CH <sub>2</sub> (ONO <sub>2</sub> )COCOCH(OH)(OO·) + 0.439 CH <sub>2</sub> (OH)COCOCH(ONO <sub>2</sub> )(OO·) + 0.122 CH <sub>2</sub> (ONO <sub>2</sub> )COCOCH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.878 O <sub>2</sub>	$1.3 \cdot 10^{+06}$		
R <sub>o</sub> 05352			CH <sub>2</sub> (ONO <sub>2</sub> )COCOCH(OH)(OO·) → CH <sub>2</sub> (ONO <sub>2</sub> )COCOCHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05353			CH <sub>2</sub> (OH)COCOCH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)COCOCH(ONO <sub>2</sub> )(O·) + 0.550 CH <sub>2</sub> (OH)COCOCO(ONO <sub>2</sub> ) + 0.250 CH <sub>2</sub> (OH)COCOCH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 05354			CH <sub>2</sub> (ONO <sub>2</sub> )COCOCH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (ONO <sub>2</sub> )COCOCHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05355			CH <sub>2</sub> (ONO <sub>2</sub> )COCOCH <sub>2</sub> (O·) → CH <sub>2</sub> (ONO <sub>2</sub> )COCO(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05356			CH <sub>2</sub> (OH)COCOCH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCOCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05357			CH <sub>2</sub> (OH)COCOCH(ONO <sub>2</sub> )(O·) → CH <sub>2</sub> (OH)COCO(OO·) + CHO(ONO <sub>2</sub> ) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00683			CH <sub>2</sub> (OH)COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> )	7.0 · 10 <sup>-01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05358			CH <sub>2</sub> (OH)COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + OH → 0.264 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)COCH(OH)(OO·) + 0.107 CH <sub>2</sub> (OH)COC(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.503 CH <sub>2</sub> (OH)COCH(OH)CH(ONO <sub>2</sub> )(OO·) + 0.063 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)COCH <sub>2</sub> (O·) + 0.064 CH <sub>2</sub> (OH)COCH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.874 O <sub>2</sub>	1.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 05359			CH <sub>2</sub> (OH)COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.264 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)COCH(OH)(OO·) + 0.107 CH <sub>2</sub> (OH)COC(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.503 CH <sub>2</sub> (OH)COCH(OH)CH(ONO <sub>2</sub> )(OO·) + 0.063 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)COCH <sub>2</sub> (O·) + 0.064 CH <sub>2</sub> (OH)COCH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> – 0.874 O <sub>2</sub>	1.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 05360			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)COCH(OH)(OO·) → CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05361			CH <sub>2</sub> (OH)COC(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) → CH <sub>2</sub> (OH)COCOCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05362			CH <sub>2</sub> (OH)COCH(OH)CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)COCH(OH)CH(ONO <sub>2</sub> )(O·) + 0.550 CH <sub>2</sub> (OH)COCH(OH)CO(ONO <sub>2</sub> ) + 0.250 CH <sub>2</sub> (OH)COCH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05363			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)COCH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05364			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)COCH <sub>2</sub> (O·) → CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CO(OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05365			CH <sub>2</sub> (OH)COCH(OH)CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05366			CH <sub>2</sub> (OH)COCH(OH)CH(ONO <sub>2</sub> )(O·) → CH <sub>2</sub> (OH)COCH(OH)(OO·) + CHO(ONO <sub>2</sub> ) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05367			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + OH → 0.173 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH(OH)(OO·) + 0.070 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.416 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(OO·) + 0.052 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.236 CH <sub>2</sub> (OH)C(OH)(O·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.053 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.659 O <sub>2</sub>	1.6 · 10 <sup>+09</sup>		
R <sub>o</sub> 05368			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.173 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH(OH)(OO·) + 0.070 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.416 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(OO·) + 0.052 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.236 CH <sub>2</sub> (OH)C(OH)(O·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.053 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.659 O <sub>2</sub>	1.2 · 10 <sup>+07</sup>		
R <sub>o</sub> 05369			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH(OH)(OO·) → CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05370			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05371			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O·) + 0.550 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + 0.250 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05372			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05373			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) → CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> (OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05374			CH <sub>2</sub> (OH)C(OH)(O·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05375			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05376			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) $\rightarrow$ 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CHO + 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CHO + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05377			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O $\cdot$ ) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05378			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O $\cdot$ ) $\rightarrow$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)(OO $\cdot$ ) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05379			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + OH $\rightarrow$ 0.198 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO $\cdot$ ) + 0.198 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.063 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) + 0.270 CH <sub>2</sub> (OH)C(OH)(O $\cdot$ )C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.270 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(O $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.397 O <sub>2</sub>	1.3 · 10 <sup>+09</sup>		
R <sub>o</sub> 05380			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> $\rightarrow$ 0.198 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO $\cdot$ ) + 0.198 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.063 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) + 0.270 CH <sub>2</sub> (OH)C(OH)(O $\cdot$ )C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.270 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(O $\cdot$ )CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.397 O <sub>2</sub>	8.9 · 10 <sup>+06</sup>		
R <sub>o</sub> 05381			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO $\cdot$ ) $\rightarrow$ CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05382			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO $\cdot$ ) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O $\cdot$ ) + 0.550 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.250 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05383			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) $\xrightarrow{O_2}$ CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05384			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) $\rightarrow$ CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO $\cdot$ ) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05385			CH <sub>2</sub> (OH)C(OH)(O·)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05386			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO·) + 0.500 CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CO(OH) + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub> – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05387			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05388			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CHO(ONO <sub>2</sub> ) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00684			CH <sub>2</sub> (OH)COCH(OH)CH(OH)(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH(OH)(ONO <sub>2</sub> )	1.4 · 10 <sup>+00</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05389			CH <sub>2</sub> (OH)COCH(OH)CH(OH)(ONO <sub>2</sub> ) + OH → 0.209 CH(OH)(ONO <sub>2</sub> )CH(OH)COCH(OH)(OO·) + 0.034 CH <sub>2</sub> (OH)COC(OH)(OO·)CH(OH)(ONO <sub>2</sub> ) + 0.605 CH <sub>2</sub> (OH)COCH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.050 CH(OH)(ONO <sub>2</sub> )CH(OH)COCH <sub>2</sub> (O·) + 0.048 CH <sub>2</sub> (OH)COCH(O·)CH(OH)(ONO <sub>2</sub> ) + 0.053 CH <sub>2</sub> (OH)COCH(OH)CH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O – 0.849 O <sub>2</sub>	1.5 · 10 <sup>+09</sup>		
R <sub>o</sub> 05390			CH <sub>2</sub> (OH)COCH(OH)CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.209 CH(OH)(ONO <sub>2</sub> )CH(OH)COCH(OH)(OO·) + 0.034 CH <sub>2</sub> (OH)COC(OH)(OO·)CH(OH)(ONO <sub>2</sub> ) + 0.605 CH <sub>2</sub> (OH)COCH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.050 CH(OH)(ONO <sub>2</sub> )CH(OH)COCH <sub>2</sub> (O·) + 0.048 CH <sub>2</sub> (OH)COCH(O·)CH(OH)(ONO <sub>2</sub> ) + 0.053 CH <sub>2</sub> (OH)COCH(OH)CH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.849 O <sub>2</sub>	1.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 05391			CH(OH)(ONO <sub>2</sub> )CH(OH)COCH(OH)(OO·) → CH(OH)(ONO <sub>2</sub> )CH(OH)COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05392			CH <sub>2</sub> (OH)COC(OH)(OO·)CH(OH)(ONO <sub>2</sub> ) → CH <sub>2</sub> (OH)COCOCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05393			CH <sub>2</sub> (OH)COCH(OH)C(OH)(ONO <sub>2</sub> )(OO·) → CH <sub>2</sub> (OH)COCH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05394			CH(OH)(ONO <sub>2</sub> )CH(OH)COCH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH)(ONO <sub>2</sub> )CH(OH)COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05395			CH(OH)(ONO <sub>2</sub> )CH(OH)COCH <sub>2</sub> (O·) → CH(OH)(ONO <sub>2</sub> )CH(OH)CO(OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05396			CH <sub>2</sub> (OH)COCH(O·)CH(OH)(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCOCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05397			CH <sub>2</sub> (OH)COCH(O·)CH(OH)(ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)CO(OO·) + 0.500 CH(OH)(ONO <sub>2</sub> )CHO + 0.500 CH <sub>2</sub> (OH)COCHO + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00685			CH <sub>2</sub> (OH)COCH(OH)CO(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> )	7.0 · 10 <sup>-01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05398			CH <sub>2</sub> (OH)COCH(OH)CO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CH <sub>2</sub> (OH)COCH(OH)CO(OH) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>-06</sup>	6600.0	
R <sub>o</sub> 05399			CH <sub>2</sub> (OH)COCH(OH)CO(ONO <sub>2</sub> ) + OH → 0.663 CO(ONO <sub>2</sub> )CH(OH)COCH(OH)(OO·) + 0.049 CH <sub>2</sub> (OH)COC(OH)(OO·)CO(ONO <sub>2</sub> ) + 0.158 CO(ONO <sub>2</sub> )CH(OH)COCH <sub>2</sub> (O·) + 0.130 CH <sub>2</sub> (OH)COCH(O·)CO(ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.712 O <sub>2</sub>	4.8 · 10 <sup>+08</sup>		
R <sub>o</sub> 05400			CH <sub>2</sub> (OH)COCH(OH)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.663 CO(ONO <sub>2</sub> )CH(OH)COCH(OH)(OO·) + 0.049 CH <sub>2</sub> (OH)COC(OH)(OO·)CO(ONO <sub>2</sub> ) + 0.158 CO(ONO <sub>2</sub> )CH(OH)COCH <sub>2</sub> (O·) + 0.130 CH <sub>2</sub> (OH)COCH(O·)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> – 0.712 O <sub>2</sub>	1.3 · 10 <sup>+06</sup>		
R <sub>o</sub> 05401			CO(ONO <sub>2</sub> )CH(OH)COCH(OH)(OO·) → CO(ONO <sub>2</sub> )CH(OH)COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05402			CH <sub>2</sub> (OH)COC(OH)(OO·)CO(ONO <sub>2</sub> ) → CH <sub>2</sub> (OH)COCOCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05403			CO(ONO <sub>2</sub> )CH(OH)COCH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )CH(OH)COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05404			CO(ONO <sub>2</sub> )CH(OH)COCH <sub>2</sub> (O·) → CO(ONO <sub>2</sub> )CH(OH)CO(OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05405			$\text{CH}_2(\text{OH})\text{COCH}(\text{O}\cdot)\text{CO}(\text{ONO}_2) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCOCO}(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05406			$\text{CH}_2(\text{OH})\text{COCH}(\text{O}\cdot)\text{CO}(\text{ONO}_2) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\text{CO}(\text{OO}\cdot) + 0.500 \text{CO}(\text{ONO}_2)\text{CHO} +$ $0.500 \text{CH}_2(\text{OH})\text{COCHO} + 0.500 \text{CO} + 0.500 \text{NO}_3 - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00686			$\text{CH}_2(\text{OH})\text{COCOCH}(\text{OH})(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2)$	$3.2 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00687			$\text{CH}_2(\text{OH})\text{COCOCH}(\text{OH})(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}}$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2)$	$2.8 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05407			$\text{CH}_2(\text{OH})\text{COCOCH}(\text{OH})(\text{ONO}_2) + \text{OH} \rightarrow$ $0.328 \text{CH}(\text{OH})(\text{ONO}_2)\text{COCOCH}(\text{OH})(\text{OO}\cdot) +$ $0.498 \text{CH}_2(\text{OH})\text{COCOC}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) +$ $0.091 \text{CH}(\text{OH})(\text{ONO}_2)\text{COCOCH}_2(\text{O}\cdot) +$ $0.084 \text{CH}_2(\text{OH})\text{COCOCH}(\text{ONO}_2)(\text{O}\cdot) + \text{H}_2\text{O} - 0.825 \text{O}_2$	$8.2 \cdot 10^{+08}$		
R <sub>o</sub> 05408			$\text{CH}_2(\text{OH})\text{COCOCH}(\text{OH})(\text{ONO}_2) + \text{NO}_3 \rightarrow$ $0.328 \text{CH}(\text{OH})(\text{ONO}_2)\text{COCOCH}(\text{OH})(\text{OO}\cdot) +$ $0.498 \text{CH}_2(\text{OH})\text{COCOC}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) +$ $0.091 \text{CH}(\text{OH})(\text{ONO}_2)\text{COCOCH}_2(\text{O}\cdot) +$ $0.084 \text{CH}_2(\text{OH})\text{COCOCH}(\text{ONO}_2)(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.825 \text{O}_2$	$1.2 \cdot 10^{+06}$		
R <sub>o</sub> 05409			$\text{CH}(\text{OH})(\text{ONO}_2)\text{COCOCH}(\text{OH})(\text{OO}\cdot) \rightarrow$ $\text{CH}(\text{OH})(\text{ONO}_2)\text{COCOCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05410			$\text{CH}_2(\text{OH})\text{COCOC}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{COCOCO}(\text{ONO}_2) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05411			$\text{CH}(\text{OH})(\text{ONO}_2)\text{COCOCH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}(\text{OH})(\text{ONO}_2)\text{COCOCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05412			$\text{CH}(\text{OH})(\text{ONO}_2)\text{COCOCH}_2(\text{O}\cdot) \rightarrow$ $\text{CH}(\text{OH})(\text{ONO}_2)\text{COCO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00688			$\text{CH}_2(\text{OH})\text{COCOCO}(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CO}(\text{ONO}_2)$	$1.1 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00689			$\text{CH}_2(\text{OH})\text{COCOCO}(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2)$	$4.4 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05413			$\text{CH}_2(\text{OH})\text{COCOCO}(\text{ONO}_2) \xrightarrow{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{COCOCO}(\text{OH}) + \text{H}^+ + \text{NO}_3$	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 05414			$\text{CH}_2(\text{OH})\text{COCOCO}(\text{ONO}_2) + \text{OH} \rightarrow$ $0.782 \text{CO}(\text{ONO}_2)\text{COCOCH}(\text{OH})(\text{OO}\cdot) + 0.218 \text{CO}(\text{ONO}_2)\text{COCOCH}_2(\text{O}\cdot) +$ $\text{H}_2\text{O} - 0.782 \text{O}_2$	$3.5 \cdot 10^{+08}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05415			CH <sub>2</sub> (OH)COCOCO(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.782 CO(ONO <sub>2</sub> )COCOCH(OH)(OO·) + 0.218 CO(ONO <sub>2</sub> )COCOCH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.782 O <sub>2</sub>	1.1 · 10 <sup>+06</sup>		
R <sub>o</sub> 05416			CO(ONO <sub>2</sub> )COCOCH(OH)(OO·) → CO(ONO <sub>2</sub> )COCOCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05417			CO(ONO <sub>2</sub> )COCOCH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )COCOCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05418			CO(ONO <sub>2</sub> )COCOCH <sub>2</sub> (O·) → CO(ONO <sub>2</sub> )COCO(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05419			CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + OH → 0.320 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COCH(OH)(OO·) + 0.254 CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.080 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COCH <sub>2</sub> (O·) + 0.346 CH <sub>2</sub> (OH)COC(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.574 O <sub>2</sub>	9.4 · 10 <sup>+08</sup>		
R <sub>o</sub> 05420			CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.320 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COCH(OH)(OO·) + 0.254 CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.080 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COCH <sub>2</sub> (O·) + 0.346 CH <sub>2</sub> (OH)COC(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.574 O <sub>2</sub>	8.8 · 10 <sup>+06</sup>		
R <sub>o</sub> 05421			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COCH(OH)(OO·) → CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05422			CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + 0.550 CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.250 CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05423			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COCH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05424			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COCH <sub>2</sub> (O·) → CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05425			CH <sub>2</sub> (OH)COC(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)CO(OO·) + 0.500 CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)COCO(OH) + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05426			CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05427			CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) → CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> (OO·) + CHO(ONO <sub>2</sub> ) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05428			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + OH → 0.173 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) + 0.262 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) + 0.055 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.235 CH <sub>2</sub> (OH)C(OH)(O·)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.225 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(O·)CH(OH)(ONO <sub>2</sub> ) + 0.050 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O – 0.435 O <sub>2</sub>	1.5 · 10 <sup>+09</sup>		
R <sub>o</sub> 05429			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.173 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) + 0.262 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) + 0.055 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.235 CH <sub>2</sub> (OH)C(OH)(O·)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.225 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(O·)CH(OH)(ONO <sub>2</sub> ) + 0.050 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.435 O <sub>2</sub>	9.9 · 10 <sup>+06</sup>		
R <sub>o</sub> 05430			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) → CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05431			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05432			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05433			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) → CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05434			CH <sub>2</sub> (OH)C(OH)(O·)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05435			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(O·)CH(OH)(ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO·) + 0.500 CO(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CO(OH) + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05436			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH(OH)(ONO <sub>2</sub> ) + OH → 0.145 CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH(OH)(OO·) + 0.529 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.044 CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.198 CH <sub>2</sub> (OH)C(OH)(O·)CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.042 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O·)CH(OH)(ONO <sub>2</sub> ) + 0.042 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O – 0.675 O <sub>2</sub>	1.9 · 10 <sup>+09</sup>		
R <sub>o</sub> 05437			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.145 CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH(OH)(OO·) + 0.529 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.044 CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.198 CH <sub>2</sub> (OH)C(OH)(O·)CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.042 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O·)CH(OH)(ONO <sub>2</sub> ) + 0.042 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.675 O <sub>2</sub>	1.3 · 10 <sup>+07</sup>		
R <sub>o</sub> 05438			CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH(OH)(OO·) → CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05439			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05440			CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05441			CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O·) → CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> (OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05442			CH <sub>2</sub> (OH)C(OH)(O·)CH(OH)CH(OH)(ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CH(OH)(ONO <sub>2</sub> )CH(OH)(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05443			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O·)CH(OH)(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05444			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O·)CH(OH)(ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO·) + 0.500 CH(OH)(ONO <sub>2</sub> )CHO + 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CHO + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05445			$\text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CO}(\text{ONO}_2) \xrightarrow{H_2O}$	$7.5 \cdot 10^{-06}$	6600.0	
			$\text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CO}(\text{OH}) + \text{H}^+ + \text{NO}_3$			
R <sub>o</sub> 05446			$\text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CO}(\text{ONO}_2) + \text{OH} \rightarrow$	$6.4 \cdot 10^{+08}$		
			$0.469 \text{CO}(\text{ONO}_2)\text{C}(\text{OH})_2\text{COCH}(\text{OH})(\text{OO}\cdot) +$			
			$0.117 \text{CO}(\text{ONO}_2)\text{C}(\text{OH})_2\text{COCH}_2(\text{O}\cdot) +$			
			$0.414 \text{CH}_2(\text{OH})\text{COC}(\text{OH})(\text{O}\cdot)\text{CO}(\text{ONO}_2) + \text{H}_2\text{O} - 0.469 \text{O}_2$			
R <sub>o</sub> 05447			$\text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CO}(\text{ONO}_2) + \text{NO}_3 \rightarrow$	$8.0 \cdot 10^{+06}$		
			$0.469 \text{CO}(\text{ONO}_2)\text{C}(\text{OH})_2\text{COCH}(\text{OH})(\text{OO}\cdot) +$			
			$0.117 \text{CO}(\text{ONO}_2)\text{C}(\text{OH})_2\text{COCH}_2(\text{O}\cdot) +$			
			$0.414 \text{CH}_2(\text{OH})\text{COC}(\text{OH})(\text{O}\cdot)\text{CO}(\text{ONO}_2) + \text{NO}_3^- + \text{H}^+ - 0.469 \text{O}_2$			
R <sub>o</sub> 05448			$\text{CO}(\text{ONO}_2)\text{C}(\text{OH})_2\text{COCH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CO}(\text{ONO}_2)\text{C}(\text{OH})_2\text{COCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05449			$\text{CO}(\text{ONO}_2)\text{C}(\text{OH})_2\text{COCH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{ONO}_2)\text{C}(\text{OH})_2\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05450			$\text{CO}(\text{ONO}_2)\text{C}(\text{OH})_2\text{COCH}_2(\text{O}\cdot) \rightarrow$	$5.0 \cdot 10^{+02}$		
			$\text{CO}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$			
R <sub>o</sub> 05451			$\text{CH}_2(\text{OH})\text{COC}(\text{OH})(\text{O}\cdot)\text{CO}(\text{ONO}_2) \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \text{CH}_2(\text{OH})\text{CO}(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CO}(\text{ONO}_2) +$			
			$0.500 \text{CH}_2(\text{OH})\text{COCO}(\text{OH}) + 0.500 \text{CO} + 0.500 \text{NO}_3 - 0.500 \text{O}_2$			
R <sub>o</sub> 05452			$\text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) + \text{OH} \rightarrow$	$1.1 \cdot 10^{+09}$		
			$0.268 \text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2\text{COCH}(\text{OH})(\text{OO}\cdot) +$			
			$0.322 \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{C}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) +$			
			$0.067 \text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2\text{COCH}_2(\text{O}\cdot) +$			
			$0.275 \text{CH}_2(\text{OH})\text{COC}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})(\text{ONO}_2) +$			
			$0.068 \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{O}\cdot) + \text{H}_2\text{O} - 0.589 \text{O}_2$			
R <sub>o</sub> 05453			$\text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) + \text{NO}_3 \rightarrow$	$9.8 \cdot 10^{+06}$		
			$0.268 \text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2\text{COCH}(\text{OH})(\text{OO}\cdot) +$			
			$0.322 \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{C}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) +$			
			$0.067 \text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2\text{COCH}_2(\text{O}\cdot) +$			
			$0.275 \text{CH}_2(\text{OH})\text{COC}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})(\text{ONO}_2) +$			
			$0.068 \text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.589 \text{O}_2$			
R <sub>o</sub> 05454			$\text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2\text{COCH}(\text{OH})(\text{OO}\cdot) \rightarrow$	$2.0 \cdot 10^{+02}$		
			$\text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2\text{COCHO} + \text{HO}_2$			

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05455			CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) → CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05456			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05457			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCH <sub>2</sub> (O·) → CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05458			CH <sub>2</sub> (OH)COC(OH)(O·)CH(OH)(ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)CO(OO·) + 0.500 CO(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)COCO(OH) + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05459			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OH) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>–06</sup>	6600.0	
R <sub>o</sub> 05460			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + OH → 0.264 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) + 0.083 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.359 CH <sub>2</sub> (OH)C(OH)(O·)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.294 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(O·)CO(ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.264 O <sub>2</sub>	1.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 05461			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.264 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) + 0.083 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.359 CH <sub>2</sub> (OH)C(OH)(O·)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.294 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(O·)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.264 O <sub>2</sub>	8.1 · 10 <sup>+06</sup>		
R <sub>o</sub> 05462			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(OO·) → CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05463			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05464			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (O·) → CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05465			CH <sub>2</sub> (OH)C(OH)(O·)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05466			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH)(O $\cdot$ )CO(ONO <sub>2</sub> ) $\rightarrow$ 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CO(OH) + 0.500 CO + 0.500 NO <sub>3</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05467			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CO(OH) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>-06</sup>	6600.0	
R <sub>o</sub> 05468			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + OH $\rightarrow$ 0.344 CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH(OH)(OO $\cdot$ ) + 0.103 CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) + 0.468 CH <sub>2</sub> (OH)C(OH)(O $\cdot$ )CH(OH)CO(ONO <sub>2</sub> ) + 0.085 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O $\cdot$ )CO(ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.344 O <sub>2</sub>	8.1 · 10 <sup>+08</sup>		
R <sub>o</sub> 05469			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> $\rightarrow$ 0.344 CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH(OH)(OO $\cdot$ ) + 0.103 CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) + 0.468 CH <sub>2</sub> (OH)C(OH)(O $\cdot$ )CH(OH)CO(ONO <sub>2</sub> ) + 0.085 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O $\cdot$ )CO(ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.344 O <sub>2</sub>	1.1 · 10 <sup>+07</sup>		
R <sub>o</sub> 05470			CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH(OH)(OO $\cdot$ ) $\rightarrow$ CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05471			CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05472			CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) $\rightarrow$ CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05473			CH <sub>2</sub> (OH)C(OH)(O $\cdot$ )CH(OH)CO(ONO <sub>2</sub> ) $\rightarrow$ 0.500 CH <sub>2</sub> (OH) $\cdot$ + 0.500 CO(OH)CH(OH)CO(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CO(ONO <sub>2</sub> )CH(OH)(OO $\cdot$ ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05474			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O $\cdot$ )CO(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05475			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(O $\cdot$ )CO(ONO <sub>2</sub> ) $\rightarrow$ 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CHO + 0.500 CO + 0.500 NO <sub>3</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00690			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> )	1.1 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
E <sub>o</sub> 00691			$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}_2(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2)$	$4.4 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05476			$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}_2(\text{ONO}_2) + \text{OH} \rightarrow$ $0.252 \text{ CH}_2(\text{ONO}_2)\text{COC}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.318 \text{ CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}(\text{ONO}_2)(\text{OO}\cdot) +$ $0.088 \text{ CH}_2(\text{ONO}_2)\text{COC}(\text{OH})_2\text{CH}_2(\text{O}\cdot) +$ $0.342 \text{ CH}_2(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{COCH}_2(\text{ONO}_2) + \text{H}_2\text{O} - 0.569 \text{ O}_2$	$9.5 \cdot 10^{+08}$		
R <sub>o</sub> 05477			$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}_2(\text{ONO}_2) + \text{NO}_3 \rightarrow$ $0.252 \text{ CH}_2(\text{ONO}_2)\text{COC}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.318 \text{ CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}(\text{ONO}_2)(\text{OO}\cdot) +$ $0.088 \text{ CH}_2(\text{ONO}_2)\text{COC}(\text{OH})_2\text{CH}_2(\text{O}\cdot) +$ $0.342 \text{ CH}_2(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{COCH}_2(\text{ONO}_2) + \text{NO}_3^- + \text{H}^+ - 0.569 \text{ O}_2$	$8.8 \cdot 10^{+06}$		
R <sub>o</sub> 05478			$\text{CH}_2(\text{ONO}_2)\text{COC}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow$ $\text{CH}_2(\text{ONO}_2)\text{COC}(\text{OH})_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05479			$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}(\text{ONO}_2)(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{ CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}(\text{ONO}_2)(\text{O}\cdot) +$ $0.550 \text{ CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCO}(\text{ONO}_2) +$ $0.250 \text{ CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}(\text{OH})(\text{ONO}_2) + 0.350 \text{ O}_2 + 0.150 \text{ H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 05480			$\text{CH}_2(\text{ONO}_2)\text{COC}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_2(\text{ONO}_2)\text{COC}(\text{OH})_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05481			$\text{CH}_2(\text{ONO}_2)\text{COC}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{ONO}_2)\text{COC}(\text{OH})_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05482			$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{COCH}_2(\text{ONO}_2) \rightarrow$ $0.500 \text{ CH}_2(\text{OH})\cdot + 0.500 \text{ CO}(\text{OH})\text{COCH}_2(\text{ONO}_2) +$ $0.500 \text{ CH}_2(\text{OH})\text{CO}(\text{OH}) + 0.500 \text{ CH}_2(\text{ONO}_2)\text{CO}(\text{OO}\cdot) - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05483			$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}(\text{ONO}_2)(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCO}(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05484			$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{COCH}(\text{ONO}_2)(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) + \text{CHO}(\text{ONO}_2) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00692			$\text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{COCHO} \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}(\text{OH})_2\text{C}(\text{OH})_2\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2)$	$3.8 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05485			$\text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{COCHO} \rightarrow 0.250 \text{ CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2(\text{OO}\cdot) +$ $0.250 \text{ CHOCO}(\text{OO}\cdot) + 0.250 \text{ CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CO}(\text{OO}\cdot) + 0.250 \text{ CHO}(\text{OO}\cdot)$	$1.0 \cdot 10^{-01}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05486			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COCHO + OH → 0.245 CHOCOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.421 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COCO(OO·) + 0.334 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH)(O·)COCHO + H <sub>2</sub> O – 0.666 O <sub>2</sub>	9.7 · 10 <sup>+08</sup>		
R <sub>o</sub> 05487			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COCHO + NO <sub>3</sub> → 0.245 CHOCOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.421 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COCO(OO·) + 0.334 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH)(O·)COCHO + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.666 O <sub>2</sub>	6.7 · 10 <sup>+06</sup>		
R <sub>o</sub> 05488			CHOCOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CHOCOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + 0.550 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCHO + 0.250 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05489			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COCO(OO·) → CO(OH)COC(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05490			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH)(O·)COCHO → 0.500 CH <sub>2</sub> O + 0.500 CO(OH)COCHO + 0.500 CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CHOCO(OO·) + 0.500 NO <sub>2</sub> – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05491			CHOCOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05492			CHOCOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) → CHOCOC(OH) <sub>2</sub> (OO·) + CHO(ONO <sub>2</sub> ) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00693			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> )	3.8 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05493			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO → 0.250 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.250 CHOC(OH) <sub>2</sub> (OO·) + 0.250 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.250 CHO(OO·)	1.0 · 10 <sup>–01</sup>		
R <sub>o</sub> 05494			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + OH → 0.207 CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.282 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OO·) + 0.281 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH)(O·)C(OH) <sub>2</sub> CHO + 0.230 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH)(O·)CHO + H <sub>2</sub> O – 0.488 O <sub>2</sub>	1.3 · 10 <sup>+09</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05495			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + NO <sub>3</sub> → 0.207 CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.282 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OO·) + 0.281 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH)(O·)C(OH) <sub>2</sub> CHO + 0.230 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH)(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.488 O <sub>2</sub>	6.7 · 10 <sup>+06</sup>		
R <sub>o</sub> 05496			CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + 0.550 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + 0.250 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05497			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OO·) → CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05498			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH)(O·)C(OH) <sub>2</sub> CHO → 0.500 CH <sub>2</sub> O + 0.500 CO(OH)C(OH) <sub>2</sub> CHO + 0.500 CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CHOC(OH) <sub>2</sub> (OO·) + 0.500 NO <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05499			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH)(O·)CHO → 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.500 CO(OH)CHO + 0.500 CO(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CH · (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05500			CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05501			CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) → CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00694			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> )	4.5 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00695			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> )	3.1 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05502			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO + OH → 0.436 CHOC(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(OO·) + 0.060 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH)(OO·)C(OH) <sub>2</sub> CHO + 0.247 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CO(OO·) + 0.055 CH <sub>2</sub> (ONO <sub>2</sub> )CH(O·)C(OH) <sub>2</sub> CHO + 0.202 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH)(O·)CHO + H <sub>2</sub> O - 0.743 O <sub>2</sub>	1.5 · 10 <sup>+09</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05503			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO + NO <sub>3</sub> → 0.436 CHOC(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(OO·) + 0.060 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH)(OO·)C(OH) <sub>2</sub> CHO + 0.247 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CO(OO·) + 0.055 CH <sub>2</sub> (ONO <sub>2</sub> )CH(O·)C(OH) <sub>2</sub> CHO + 0.202 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH)(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.743 O <sub>2</sub>	8.7 · 10 <sup>+06</sup>		
R <sub>o</sub> 05504			CHOC(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CHOC(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O·) + 0.550 CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO + 0.250 CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05505			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH)(OO·)C(OH) <sub>2</sub> CHO → CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05506			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CO(OO·) → CO(OH)C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05507			CH <sub>2</sub> (ONO <sub>2</sub> )CH(O·)C(OH) <sub>2</sub> CHO $\xrightarrow{O_2}$ CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05508			CH <sub>2</sub> (ONO <sub>2</sub> )CH(O·)C(OH) <sub>2</sub> CHO → 0.500 CH <sub>2</sub> O + 0.500 CHOC(OH) <sub>2</sub> CHO + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CHO + 0.500 CHOC(OH) <sub>2</sub> (OO·) + 0.500 NO <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05509			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)C(OH)(O·)CHO → 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)(OO·) + 0.500 CO(OH)CHO + 0.500 CO(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05510			CHOC(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05511			CHOC(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O·) → CHOC(OH) <sub>2</sub> CH(OH)(OO·) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00696			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> )	1.1 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00697			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> )	4.4 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05512			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCO(OH) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>-06</sup>	6600.0	

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05513			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + OH → 0.369 CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH(OH)(OO·) + 0.129 CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.502 CH <sub>2</sub> (OH)C(OH)(O·)COCO(ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.369 O <sub>2</sub>	6.5 · 10 <sup>+08</sup>		
R <sub>o</sub> 05514			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.369 CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH(OH)(OO·) + 0.129 CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.502 CH <sub>2</sub> (OH)C(OH)(O·)COCO(ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.369 O <sub>2</sub>	8.1 · 10 <sup>+06</sup>		
R <sub>o</sub> 05515			CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH(OH)(OO·) → CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05516			CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05517			CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH <sub>2</sub> (O·) → CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05518			CH <sub>2</sub> (OH)C(OH)(O·)COCO(ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)COCO(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CO(ONO <sub>2</sub> )CO(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00698			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> )	3.2 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00699			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> )	2.8 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05519			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) + OH → 0.203 CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH(OH)(OO·) + 0.390 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COC(OH)(ONO <sub>2</sub> )(OO·) + 0.071 CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.277 CH <sub>2</sub> (OH)C(OH)(O·)COCH(OH)(ONO <sub>2</sub> ) + 0.059 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O – 0.593 O <sub>2</sub>	1.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 05520			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.203 CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH(OH)(OO·) + 0.390 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COC(OH)(ONO <sub>2</sub> )(OO·) + 0.071 CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.277 CH <sub>2</sub> (OH)C(OH)(O·)COCH(OH)(ONO <sub>2</sub> ) + 0.059 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.593 O <sub>2</sub>	9.4 · 10 <sup>+06</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05521			CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH(OH)(OO·) → CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05522			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COC(OH)(ONO <sub>2</sub> )(OO·) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05523			CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05524			CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CH <sub>2</sub> (O·) → CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05525			CH <sub>2</sub> (OH)C(OH)(O·)COCH(OH)(ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)COCH(OH)(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CH(OH)(ONO <sub>2</sub> )CO(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00700			CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> )	3.8 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05526			CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO → 0.250 CH <sub>2</sub> (ONO <sub>2</sub> )CO(OO·) + 0.250 CHOC(OH) <sub>2</sub> (OO·) + 0.250 CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + 0.250 CHO(OO·)	1.0 · 10 <sup>−01</sup>		
R <sub>o</sub> 05527			CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO + OH → 0.338 CHOC(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(OO·) + 0.364 CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> CO(OO·) + 0.298 CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH)(O·)CHO + H <sub>2</sub> O – 0.702 O <sub>2</sub>	8.9 · 10 <sup>+08</sup>		
R <sub>o</sub> 05528			CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO + NO <sub>3</sub> → 0.338 CHOC(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(OO·) + 0.364 CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> CO(OO·) + 0.298 CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH)(O·)CHO + NO <sub>3</sub> <sup>−</sup> + H <sup>+</sup> – 0.702 O <sub>2</sub>	6.7 · 10 <sup>+06</sup>		
R <sub>o</sub> 05529			CHOC(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2^{\cdot}}$ 0.200 CHOC(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O·) + 0.550 CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO + 0.250 CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05530			CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH) <sub>2</sub> CO(OO·) → CO(OH)C(OH) <sub>2</sub> COCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05531			CH <sub>2</sub> (ONO <sub>2</sub> )COC(OH)(O·)CHO → 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CO(OO·) + 0.500 CO(OH)CHO + 0.500 CO(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CH·(OH) <sub>2</sub> – 0.500 O <sub>2</sub> – 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05532			CHOC(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05533			CHOC(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O·) → CHOC(OH) <sub>2</sub> CO(OO·) + CHO(ONO <sub>2</sub> ) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00701			CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> COCH(OH)CO(ONO <sub>2</sub> )	4.5 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00702			CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> )	3.1 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05534			CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO $\xrightarrow{H_2O}$ CO(OH)CH(OH)C(OH) <sub>2</sub> CHO + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>–06</sup>	6600.0	
R <sub>o</sub> 05535			CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO + OH → 0.500 CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CO(OO·) + 0.091 CO(ONO <sub>2</sub> )CH(O·)C(OH) <sub>2</sub> CHO + 0.409 CO(ONO <sub>2</sub> )CH(OH)C(OH)(O·)CHO + H <sub>2</sub> O – 0.500 O <sub>2</sub>	7.6 · 10 <sup>+08</sup>		
R <sub>o</sub> 05536			CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO + NO <sub>3</sub> → 0.500 CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CO(OO·) + 0.091 CO(ONO <sub>2</sub> )CH(O·)C(OH) <sub>2</sub> CHO + 0.409 CO(ONO <sub>2</sub> )CH(OH)C(OH)(O·)CHO + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.500 O <sub>2</sub>	7.3 · 10 <sup>+06</sup>		
R <sub>o</sub> 05537			CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CO(OO·) → CO(OH)C(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05538			CO(ONO <sub>2</sub> )CH(O·)C(OH) <sub>2</sub> CHO $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05539			CO(ONO <sub>2</sub> )CH(O·)C(OH) <sub>2</sub> CHO → 0.500 CO + 0.500 CHOC(OH) <sub>2</sub> CHO + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CHOC(OH) <sub>2</sub> (OO·) + 0.500 NO <sub>3</sub> – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05540			CO(ONO <sub>2</sub> )CH(OH)C(OH)(O·)CHO → 0.500 CO(ONO <sub>2</sub> )CH(OH)(OO·) + 0.500 CO(OH)CHO + 0.500 CO(OH)CH(OH)CO(ONO <sub>2</sub> ) + 0.500 CH·(OH) <sub>2</sub> – 0.500 O <sub>2</sub> – 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00703			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> )	3.8 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05541			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO → 0.250 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.250 CHOC(OH) <sub>2</sub> (OO·) + 0.250 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.250 CHO(OO·)	1.0 · 10 <sup>–01</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05542			$\text{CO(ONO}_2\text{)C(OH)}_2\text{C(OH)}_2\text{CHO} \xrightarrow{H_2O}$	$7.5 \cdot 10^{-06}$	6600.0	
			$\text{CO(OH)C(OH)}_2\text{C(OH)}_2\text{CHO} + \text{H}^+ + \text{NO}_3$			
R <sub>o</sub> 05543			$\text{CO(ONO}_2\text{)C(OH)}_2\text{C(OH)}_2\text{CHO} + \text{OH} \rightarrow$	$9.5 \cdot 10^{+08}$		
			$0.380 \text{ CO(ONO}_2\text{)C(OH)}_2\text{C(OH)}_2\text{CO(OO}\cdot\text{)} +$			
			$0.310 \text{ CO(ONO}_2\text{)C(OH)(O}\cdot\text{)C(OH)}_2\text{CHO} +$			
			$0.310 \text{ CO(ONO}_2\text{)C(OH)}_2\text{C(OH)(O}\cdot\text{)CHO} + \text{H}_2\text{O} - 0.380 \text{ O}_2$			
R <sub>o</sub> 05544			$\text{CO(ONO}_2\text{)C(OH)}_2\text{C(OH)}_2\text{CHO} + \text{NO}_3 \rightarrow$	$5.5 \cdot 10^{+06}$		
			$0.380 \text{ CO(ONO}_2\text{)C(OH)}_2\text{C(OH)}_2\text{CO(OO}\cdot\text{)} +$			
			$0.310 \text{ CO(ONO}_2\text{)C(OH)(O}\cdot\text{)C(OH)}_2\text{CHO} +$			
			$0.310 \text{ CO(ONO}_2\text{)C(OH)}_2\text{C(OH)(O}\cdot\text{)CHO} + \text{NO}_3^- + \text{H}^+ - 0.380 \text{ O}_2$			
R <sub>o</sub> 05545			$\text{CO(ONO}_2\text{)C(OH)}_2\text{C(OH)}_2\text{CO(OO}\cdot\text{)} \rightarrow$	$1.0 \cdot 10^{+03}$		
			$\text{CO(OH)C(OH)}_2\text{C(OH)}_2\text{CO(ONO}_2\text{)} + \text{HO}_2 - \text{H}_2\text{O}$			
R <sub>o</sub> 05546			$\text{CO(ONO}_2\text{)C(OH)(O}\cdot\text{)C(OH)}_2\text{CHO} \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \text{ CO} + 0.500 \text{ CO(OH)C(OH)}_2\text{CHO} + 0.500 \text{ CO(OH)CO(ONO}_2\text{)} +$			
			$0.500 \text{ CHOC(OH)}_2\text{(OO}\cdot\text{)} + 0.500 \text{ NO}_3 - 0.500 \text{ O}_2$			
R <sub>o</sub> 05547			$\text{CO(ONO}_2\text{)C(OH)}_2\text{C(OH)(O}\cdot\text{)CHO} \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \text{ CO(ONO}_2\text{)C(OH)}_2\text{(OO}\cdot\text{)} + 0.500 \text{ CO(OH)CHO} +$			
			$0.500 \text{ CO(OH)C(OH)}_2\text{CO(ONO}_2\text{)} + 0.500 \text{ CH} \cdot \text{(OH)}_2 - 0.500 \text{ O}_2 - 0.500 \text{ H}_2\text{O}$			
E <sub>o</sub> 00704			$\text{CH(OH)(ONO}_2\text{)C(OH)}_2\text{COCHO} \xrightleftharpoons{H_2O}$	$1.0 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
			$\text{CH(OH)}_2\text{C(OH)}_2\text{C(OH)}_2\text{CH(OH)(ONO}_2\text{)}$			
R <sub>o</sub> 05548			$\text{CH(OH)(ONO}_2\text{)C(OH)}_2\text{COCHO} \rightarrow$	$1.0 \cdot 10^{-01}$		
			$0.250 \text{ CH(OH)(ONO}_2\text{)C(OH)}_2\text{(OO}\cdot\text{)} + 0.250 \text{ CHOCO(OO}\cdot\text{)} +$			
			$0.250 \text{ CH(OH)(ONO}_2\text{)C(OH)}_2\text{CO(OO}\cdot\text{)} + 0.250 \text{ CHO(OO}\cdot\text{)}$			
R <sub>o</sub> 05549			$\text{CH(OH)(ONO}_2\text{)C(OH)}_2\text{COCHO} + \text{OH} \rightarrow$	$1.2 \cdot 10^{+09}$		
			$0.312 \text{ CHOCOC(OH)}_2\text{C(OH)(ONO}_2\text{)(OO}\cdot\text{)} +$			
			$0.354 \text{ CH(OH)(ONO}_2\text{)C(OH)}_2\text{COCO(OO}\cdot\text{)} +$			
			$0.066 \text{ CHOCOC(OH)}_2\text{CH(ONO}_2\text{)(O}\cdot\text{)} +$			
			$0.267 \text{ CH(OH)(ONO}_2\text{)C(OH)(O}\cdot\text{)COCHO} + \text{H}_2\text{O} - 0.666 \text{ O}_2$			



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05550			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCHO + NO <sub>3</sub> → 0.312 CHOCOC(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) + 0.354 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCO(OO·) + 0.066 CHOCOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + 0.267 CH(OH)(ONO <sub>2</sub> )C(OH)(O·)COCHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.666 O <sub>2</sub>	7.4 · 10 <sup>+06</sup>		
R <sub>o</sub> 05551			CHOCOC(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) → CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05552			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCO(OO·) → CO(OH)COC(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05553			CH(OH)(ONO <sub>2</sub> )C(OH)(O·)COCHO → 0.500 CHO(ONO <sub>2</sub> ) + 0.500 CO(OH)COCHO + 0.500 CO(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CHOCO(OO·) + 0.500 HO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00705			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> )	3.8 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05554			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCHO → 0.250 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.250 CHOCO(OO·) + 0.250 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) + 0.250 CHO(OO·)	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 05555			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCHO $\xrightleftharpoons{H_2O}$ CO(OH)C(OH) <sub>2</sub> COCHO + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>-06</sup>	6600.0	
R <sub>o</sub> 05556			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCHO + OH → 0.607 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCO(OO·) + 0.393 CO(ONO <sub>2</sub> )C(OH)(O·)COCHO + H <sub>2</sub> O - 0.607 O <sub>2</sub>	6.7 · 10 <sup>+08</sup>		
R <sub>o</sub> 05557			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCHO + NO <sub>3</sub> → 0.607 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCO(OO·) + 0.393 CO(ONO <sub>2</sub> )C(OH)(O·)COCHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.607 O <sub>2</sub>	5.5 · 10 <sup>+06</sup>		
R <sub>o</sub> 05558			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCO(OO·) → CO(OH)COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05559			CO(ONO <sub>2</sub> )C(OH)(O·)COCHO → 0.500 CO + 0.500 CO(OH)COCHO + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CHOCO(OO·) + 0.500 NO <sub>3</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00706			CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> COCH(OH)CH(OH)(ONO <sub>2</sub> )	3.0 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00707			CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)CH(OH)(ONO <sub>2</sub> )	4.2 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05560			CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO + OH → 0.544 CHOC(OH) <sub>2</sub> CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.203 CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CO(OO·) + 0.043 CHOC(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O·) + 0.043 CH(OH)(ONO <sub>2</sub> )CH(O·)C(OH) <sub>2</sub> CHO + 0.166 CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH)(O·)CHO + H <sub>2</sub> O – 0.747 O <sub>2</sub>	1.9 · 10 <sup>+09</sup>		
R <sub>o</sub> 05561			CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO + NO <sub>3</sub> → 0.544 CHOC(OH) <sub>2</sub> CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.203 CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CO(OO·) + 0.043 CHOC(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(O·) + 0.043 CH(OH)(ONO <sub>2</sub> )CH(O·)C(OH) <sub>2</sub> CHO + 0.166 CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH)(O·)CHO + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.747 O <sub>2</sub>	9.7 · 10 <sup>+06</sup>		
R <sub>o</sub> 05562			CHOC(OH) <sub>2</sub> CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) → CO(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05563			CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> CO(OO·) → CO(OH)C(OH) <sub>2</sub> CH(OH)CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05564			CH(OH)(ONO <sub>2</sub> )CH(O·)C(OH) <sub>2</sub> CHO $\xrightarrow{O_2}$ CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05565			CH(OH)(ONO <sub>2</sub> )CH(O·)C(OH) <sub>2</sub> CHO → 0.500 CHO(ONO <sub>2</sub> ) + 0.500 CHOC(OH) <sub>2</sub> CHO + 0.500 CH(OH)(ONO <sub>2</sub> )CHO + 0.500 CHOC(OH) <sub>2</sub> (OO·) + 0.500 HO <sub>2</sub> – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05566			CH(OH)(ONO <sub>2</sub> )CH(OH)C(OH)(O·)CHO → 0.500 CH(OH)(ONO <sub>2</sub> )CH(OH)(OO·) + 0.500 CO(OH)CHO + 0.500 CO(OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CH · (OH) <sub>2</sub> – 0.500 O <sub>2</sub> – 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00708			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> )	1.0 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05567			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO → 0.250 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.250 CHOC(OH) <sub>2</sub> (OO·) + 0.250 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.250 CHO(OO·)	1.0 · 10 <sup>–01</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05568			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + OH → 0.272 CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) + 0.244 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OO·) + 0.052 CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + 0.233 CH(OH)(ONO <sub>2</sub> )C(OH)(O·)C(OH) <sub>2</sub> CHO + 0.199 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH)(O·)CHO + H <sub>2</sub> O – 0.516 O <sub>2</sub>	1.5 · 10 <sup>+09</sup>		
R <sub>o</sub> 05569			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + NO <sub>3</sub> → 0.272 CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) + 0.244 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OO·) + 0.052 CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + 0.233 CH(OH)(ONO <sub>2</sub> )C(OH)(O·)C(OH) <sub>2</sub> CHO + 0.199 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH)(O·)CHO + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.516 O <sub>2</sub>	7.4 · 10 <sup>+06</sup>		
R <sub>o</sub> 05570			CHOC(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) → CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05571			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(OO·) → CO(OH)C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05572			CH(OH)(ONO <sub>2</sub> )C(OH)(O·)C(OH) <sub>2</sub> CHO → 0.500 CHO(ONO <sub>2</sub> ) + 0.500 CO(OH)C(OH) <sub>2</sub> CHO + 0.500 CO(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CHOC(OH) <sub>2</sub> (OO·) + 0.500 HO <sub>2</sub> – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05573			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH)(O·)CHO → 0.500 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.500 CO(OH)CHO + 0.500 CO(OH)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + 0.500 CH · (OH) <sub>2</sub> – 0.500 O <sub>2</sub> – 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00709			CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> )	1.0 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05574			CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO → 0.250 CH(OH)(ONO <sub>2</sub> )CO(OO·) + 0.250 CHOC(OH) <sub>2</sub> (OO·) + 0.250 CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + 0.250 CHO(OO·)	1.0 · 10 <sup>–01</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05575			CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO + OH → 0.409 CHOC(OH) <sub>2</sub> COC(OH)(ONO <sub>2</sub> )(OO·) + 0.291 CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CO(OO·) + 0.062 CHOC(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O·) + 0.238 CH(OH)(ONO <sub>2</sub> )COC(OH)(O·)CHO + H <sub>2</sub> O - 0.700 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 05576			CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO + NO <sub>3</sub> → 0.409 CHOC(OH) <sub>2</sub> COC(OH)(ONO <sub>2</sub> )(OO·) + 0.291 CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CO(OO·) + 0.062 CHOC(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(O·) + 0.238 CH(OH)(ONO <sub>2</sub> )COC(OH)(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.700 O <sub>2</sub>	7.2 · 10 <sup>+06</sup>		
R <sub>o</sub> 05577			CHOC(OH) <sub>2</sub> COC(OH)(ONO <sub>2</sub> )(OO·) → CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05578			CH(OH)(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CO(OO·) → CO(OH)C(OH) <sub>2</sub> COCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05579			CH(OH)(ONO <sub>2</sub> )COC(OH)(O·)CHO → 0.500 CH(OH)(ONO <sub>2</sub> )CO(OO·) + 0.500 CO(OH)CHO + 0.500 CO(OH)COCH(OH)(ONO <sub>2</sub> ) + 0.500 CH · (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00710			CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> )	3.8 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05580			CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO → 0.250 CO(ONO <sub>2</sub> )CO(OO·) + 0.250 CHOC(OH) <sub>2</sub> (OO·) + 0.250 CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + 0.250 CHO(OO·)	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 05581			CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO $\xrightarrow{H_2O}$ CO(OH)COC(OH) <sub>2</sub> CHO + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>-06</sup>	6600.0	
R <sub>o</sub> 05582			CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO + OH → 0.550 CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CO(OO·) + 0.450 CO(ONO <sub>2</sub> )COC(OH)(O·)CHO + H <sub>2</sub> O - 0.550 O <sub>2</sub>	5.9 · 10 <sup>+08</sup>		
R <sub>o</sub> 05583			CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CHO + NO <sub>3</sub> → 0.550 CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CO(OO·) + 0.450 CO(ONO <sub>2</sub> )COC(OH)(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.550 O <sub>2</sub>	5.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 05584			CO(ONO <sub>2</sub> )COC(OH) <sub>2</sub> CO(OO·) → CO(OH)C(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05585			CO(ONO <sub>2</sub> )COC(OH)(O·)CHO → 0.500 CO(ONO <sub>2</sub> )CO(OO·) + 0.500 CO(OH)CHO + 0.500 CO(OH)COCO(ONO <sub>2</sub> ) + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05586	*	*	CH <sub>2</sub> (OH)CH(OH)CH=CH <sub>2</sub> + OH → 0.058 CH <sub>2</sub> =CHCH(OH)CH(OH)(OO·) + 0.112 CH <sub>2</sub> (OH)C(OH)(OO·)CH=CH <sub>2</sub> + 0.830 CH <sub>2</sub> (OH)CH(OH)CH(OO·)CH <sub>2</sub> (OH) + 0.170 H <sub>2</sub> O - O <sub>2</sub>	1.2 · 10 <sup>+10</sup>		
R <sub>o</sub> 05587			CH <sub>2</sub> (OH)CH(OH)CH=CH <sub>2</sub> + NO <sub>3</sub> → 0.058 CH <sub>2</sub> =CHCH(OH)CH(OH)(OO·) + 0.112 CH <sub>2</sub> (OH)C(OH)(OO·)CH=CH <sub>2</sub> + 0.830 CH <sub>2</sub> (OH)CH(OH)CH(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.170 NO <sub>3</sub> <sup>-</sup> + 0.170 H <sup>+</sup> - O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 05588	*	*	CH <sub>2</sub> =CHCH(OH)CH(OH)(OO·) → CHOCH(OH)CH=CH <sub>2</sub> + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05589	*	*	CH <sub>2</sub> (OH)C(OH)(OO·)CH=CH <sub>2</sub> → CH <sub>2</sub> (OH)COCH=CH <sub>2</sub> + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05590			CH <sub>2</sub> (OH)CH(OH)CH(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(OH)CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.550 CH <sub>2</sub> (OH)CH(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + 0.250 CH <sub>2</sub> (OH)CH(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05591			CH <sub>2</sub> (OH)CH(OH)CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05592			CH <sub>2</sub> (OH)CH(OH)CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)CH(OH)(OO·) + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CHO + 0.500 CH <sub>2</sub> (OH)CH(OH)CHO + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00711			CH <sub>2</sub> (OH)CH(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> )	2.7 · 10 <sup>+00</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05593			CH <sub>2</sub> (OH)CH(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + OH → 0.498 CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)CH(OH)(OO·) + 0.105 CH <sub>2</sub> (OH)C(OH)(OO·)COCH <sub>2</sub> (ONO <sub>2</sub> ) + 0.261 CH <sub>2</sub> (OH)CH(OH)COCH(ONO <sub>2</sub> )(OO·) + 0.073 CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)CH <sub>2</sub> (O·) + 0.063 CH <sub>2</sub> (OH)CH(O·)COCH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.864 O <sub>2</sub>	1.2 · 10 <sup>+09</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05594			CH <sub>2</sub> (OH)CH(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.498 CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)CH(OH)(OO·) + 0.105 CH <sub>2</sub> (OH)C(OH)(OO·)COCH <sub>2</sub> (ONO <sub>2</sub> ) + 0.261 CH <sub>2</sub> (OH)CH(OH)COCH(ONO <sub>2</sub> )(OO·) + 0.073 CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)CH <sub>2</sub> (O·) + 0.063 CH <sub>2</sub> (OH)CH(O·)COCH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.864 O <sub>2</sub>	1.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 05595			CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)CH(OH)(OO·) → CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05596			CH <sub>2</sub> (OH)C(OH)(OO·)COCH <sub>2</sub> (ONO <sub>2</sub> ) → CH <sub>2</sub> (OH)COCOCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05597			CH <sub>2</sub> (OH)CH(OH)COCH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(OH)COCH(ONO <sub>2</sub> )(O·) + 0.550 CH <sub>2</sub> (OH)CH(OH)COCO(ONO <sub>2</sub> ) + 0.250 CH <sub>2</sub> (OH)CH(OH)COCH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05598			CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05599			CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)CH <sub>2</sub> (O·) → CH <sub>2</sub> (ONO <sub>2</sub> )COCH(OH)(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05600			CH <sub>2</sub> (OH)CH(O·)COCH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCOCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05601			CH <sub>2</sub> (OH)CH(O·)COCH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )COCHO + 0.500 CH <sub>2</sub> (OH)CHO + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CO(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05602			CH <sub>2</sub> (OH)CH(OH)COCH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(OH)COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05603			CH <sub>2</sub> (OH)CH(OH)COCH(ONO <sub>2</sub> )(O·) → CH <sub>2</sub> (OH)CH(OH)CO(OO·) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05604			CH <sub>2</sub> (OH)CH(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + OH → 0.314 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)CH(OH)(OO·) + 0.127 CH <sub>2</sub> (OH)C(OH)(OO·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.127 CH <sub>2</sub> (OH)CH(OH)C(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.314 CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(ONO <sub>2</sub> )(OO·) + 0.039 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)CH <sub>2</sub> (O·) + 0.040 CH <sub>2</sub> (OH)CH(O·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.040 CH <sub>2</sub> (OH)CH(OH)CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.881 O <sub>2</sub>	2.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 05605			CH <sub>2</sub> (OH)CH(OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.314 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)CH(OH)(OO·) + 0.127 CH <sub>2</sub> (OH)C(OH)(OO·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.127 CH <sub>2</sub> (OH)CH(OH)C(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.314 CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(ONO <sub>2</sub> )(OO·) + 0.039 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)CH <sub>2</sub> (O·) + 0.040 CH <sub>2</sub> (OH)CH(O·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.040 CH <sub>2</sub> (OH)CH(OH)CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.881 O <sub>2</sub>	2.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05606			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)CH(OH)(OO·) → CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05607			CH <sub>2</sub> (OH)C(OH)(OO·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) → CH <sub>2</sub> (OH)COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05608			CH <sub>2</sub> (OH)CH(OH)C(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) → CH <sub>2</sub> (OH)CH(OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05609			CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(ONO <sub>2</sub> )(O·) + 0.550 CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(ONO <sub>2</sub> ) + 0.250 CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05610			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05611			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)CH <sub>2</sub> (O·) → CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)(OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05612			CH <sub>2</sub> (OH)CH(O·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05613			CH <sub>2</sub> (OH)CH(O·)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CHO + 0.500 CH <sub>2</sub> (OH)CHO + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05614			CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05615			CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(ONO <sub>2</sub> )(O·) → CH <sub>2</sub> (OH)CH(OH)CH(OH)(OO·) + CHO(ONO <sub>2</sub> ) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05616			CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) + OH → 0.281 CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)CH(OH)(OO·) + 0.108 CH <sub>2</sub> (OH)C(OH)(OO·)CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.046 CH <sub>2</sub> (OH)CH(OH)C(OH)(OO·)CH(OH)(ONO <sub>2</sub> ) + 0.427 CH <sub>2</sub> (OH)CH(OH)CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.035 CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)CH <sub>2</sub> (O·) + 0.036 CH <sub>2</sub> (OH)CH(O·)CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.034 CH <sub>2</sub> (OH)CH(OH)CH(O·)CH(OH)(ONO <sub>2</sub> ) + 0.032 CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O – 0.863 O <sub>2</sub>	2.5 · 10 <sup>+09</sup>		
R <sub>o</sub> 05617			CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.281 CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)CH(OH)(OO·) + 0.108 CH <sub>2</sub> (OH)C(OH)(OO·)CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.046 CH <sub>2</sub> (OH)CH(OH)C(OH)(OO·)CH(OH)(ONO <sub>2</sub> ) + 0.427 CH <sub>2</sub> (OH)CH(OH)CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.035 CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)CH <sub>2</sub> (O·) + 0.036 CH <sub>2</sub> (OH)CH(O·)CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.034 CH <sub>2</sub> (OH)CH(OH)CH(O·)CH(OH)(ONO <sub>2</sub> ) + 0.032 CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.863 O <sub>2</sub>	2.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05618			CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)CH(OH)(OO·) → CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05619			CH <sub>2</sub> (OH)C(OH)(OO·)CH(OH)CH(OH)(ONO <sub>2</sub> ) → CH <sub>2</sub> (OH)COCH(OH)CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05620			CH <sub>2</sub> (OH)CH(OH)C(OH)(OO·)CH(OH)(ONO <sub>2</sub> ) → CH <sub>2</sub> (OH)CH(OH)COCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05621			CH <sub>2</sub> (OH)CH(OH)CH(OH)C(OH)(ONO <sub>2</sub> )(OO·) → CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05622			CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05623			CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)CH <sub>2</sub> (O·) → CH(OH)(ONO <sub>2</sub> )CH(OH)CH(OH)(OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05624			CH <sub>2</sub> (OH)CH(O·)CH(OH)CH(OH)(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCH(OH)CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05625			CH <sub>2</sub> (OH)CH(O·)CH(OH)CH(OH)(ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CH(OH)(ONO <sub>2</sub> )CH(OH)CHO + 0.500 CH <sub>2</sub> (OH)CHO + 0.500 CH(OH)(ONO <sub>2</sub> )CH(OH)(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05626			CH <sub>2</sub> (OH)CH(OH)CH(O·)CH(OH)(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(OH)COCH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05627			CH <sub>2</sub> (OH)CH(OH)CH(O·)CH(OH)(ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)CH(OH)(OO·) + 0.500 CH(OH)(ONO <sub>2</sub> )CHO + 0.500 CH <sub>2</sub> (OH)CH(OH)CHO + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05628			CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + OH → 0.415 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CH(OH)(OO·) + 0.070 CH <sub>2</sub> (OH)C(OH)(OO·)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.173 CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.055 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) + 0.052 CH <sub>2</sub> (OH)CH(O·)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.235 CH <sub>2</sub> (OH)CH(OH)C(OH)(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.658 O <sub>2</sub>	1.6 · 10 <sup>+09</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05629			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2) + \text{NO}_3 \rightarrow$ $0.415 \text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.070 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2) +$ $0.173 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{OO}\cdot) +$ $0.055 \text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) +$ $0.052 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2) +$ $0.235 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CH}_2(\text{ONO}_2) + \text{NO}_3^- + \text{H}^+ - 0.658 \text{O}_2$	$1.2 \cdot 10^{+07}$		
R <sub>o</sub> 05630			$\text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow$ $\text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05631			$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2) \rightarrow$ $\text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CH}_2(\text{ONO}_2) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05632			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{OO}\cdot) \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{O}\cdot) +$ $0.550 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) +$ $0.250 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 05633			$\text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05634			$\text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05635			$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2) \xrightarrow{\text{O}_2}$ $\text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CH}_2(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05636			$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CH}_2(\text{ONO}_2) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2\text{CHO} + 0.500 \text{CH}_2(\text{OH})\text{CHO} +$ $0.500 \text{CH}_2(\text{ONO}_2)\text{C}(\text{OH})_2(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05637			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CH}_2(\text{ONO}_2) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) + 0.500 \text{CO}(\text{OH})\text{CH}_2(\text{ONO}_2) +$ $0.500 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{OH}) + 0.500 \text{CH}_2\text{O} + 0.500 \text{NO}_2 - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05638			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05639			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CHO}(\text{ONO}_2) - \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05640			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) \xrightarrow{\text{H}_2\text{O}}$	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 05641			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{OH}) + \text{H}^+ + \text{NO}_3$ $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) + \text{OH} \rightarrow$ $0.569 \text{CO}(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.188 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) +$ $0.042 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{ONO}_2) +$ $0.071 \text{CO}(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) +$ $0.072 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) +$ $0.059 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{ONO}_2) + \text{H}_2\text{O} - 0.798 \text{O}_2$	$1.2 \cdot 10^{+09}$		
R <sub>o</sub> 05642			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) + \text{NO}_3 \rightarrow$ $0.569 \text{CO}(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.188 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) +$ $0.042 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{ONO}_2) +$ $0.071 \text{CO}(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) +$ $0.072 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) +$ $0.059 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{ONO}_2) + \text{NO}_3^- + \text{H}^+ - 0.798 \text{O}_2$	$1.7 \cdot 10^{+06}$		
R <sub>o</sub> 05643			$\text{CO}(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow$ $\text{CO}(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05644			$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) \rightarrow$ $\text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{CO}(\text{ONO}_2) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05645			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{ONO}_2) \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{ONO}_2) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05646			$\text{CO}(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CO}(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05647			$\text{CO}(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05648			$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) \xrightarrow{\text{O}_2}$ $\text{CH}_2(\text{OH})\text{COCH}(\text{OH})\text{CO}(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05649			$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CO}(\text{ONO}_2)\text{CH}(\text{OH})\text{CHO} + 0.500 \text{CH}_2(\text{OH})\text{CHO} +$ $0.500 \text{CO}(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05650			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{ONO}_2) \xrightarrow{\text{O}_2}$	$5.0 \cdot 10^{+06}$		
			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{ONO}_2) + \text{HO}_2$			
R <sub>o</sub> 05651			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CO}(\text{ONO}_2) \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \text{CH}_2(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) + 0.500 \text{CO}(\text{ONO}_2)\text{CHO} +$			
			$0.500 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CHO} + 0.500 \text{CO} + 0.500 \text{NO}_3 - 0.500 \text{O}_2$			
E <sub>o</sub> 00712			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCH}(\text{OH})(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}}$	$1.6 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2)$			
R <sub>o</sub> 05652			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCH}(\text{OH})(\text{ONO}_2) + \text{OH} \rightarrow$	$1.4 \cdot 10^{+09}$		
			$0.419 \text{CH}(\text{OH})(\text{ONO}_2)\text{COCH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$			
			$0.085 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{COCH}(\text{OH})(\text{ONO}_2) +$			
			$0.334 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COC}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) +$			
			$0.061 \text{CH}(\text{OH})(\text{ONO}_2)\text{COCH}(\text{OH})\text{CH}_2(\text{O}\cdot) +$			
			$0.053 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{COCH}(\text{OH})(\text{ONO}_2) +$			
			$0.048 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCH}(\text{ONO}_2)(\text{O}\cdot) + \text{H}_2\text{O} - 0.838 \text{O}_2$			
R <sub>o</sub> 05653			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCH}(\text{OH})(\text{ONO}_2) + \text{NO}_3 \rightarrow$	$1.6 \cdot 10^{+06}$		
			$0.419 \text{CH}(\text{OH})(\text{ONO}_2)\text{COCH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$			
			$0.085 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{COCH}(\text{OH})(\text{ONO}_2) +$			
			$0.334 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COC}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) +$			
			$0.061 \text{CH}(\text{OH})(\text{ONO}_2)\text{COCH}(\text{OH})\text{CH}_2(\text{O}\cdot) +$			
			$0.053 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{COCH}(\text{OH})(\text{ONO}_2) +$			
			$0.048 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCH}(\text{ONO}_2)(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.838 \text{O}_2$			
R <sub>o</sub> 05654			$\text{CH}(\text{OH})(\text{ONO}_2)\text{COCH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow$	$2.0 \cdot 10^{+02}$		
			$\text{CH}(\text{OH})(\text{ONO}_2)\text{COCH}(\text{OH})\text{CHO} + \text{HO}_2$			
R <sub>o</sub> 05655			$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{COCH}(\text{OH})(\text{ONO}_2) \rightarrow$	$2.0 \cdot 10^{+02}$		
			$\text{CH}_2(\text{OH})\text{COCOCH}(\text{OH})(\text{ONO}_2) + \text{HO}_2$			
R <sub>o</sub> 05656			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COC}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) \rightarrow$	$2.0 \cdot 10^{+02}$		
			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{ONO}_2) + \text{HO}_2$			
R <sub>o</sub> 05657			$\text{CH}(\text{OH})(\text{ONO}_2)\text{COCH}(\text{OH})\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2}$	$5.0 \cdot 10^{+06}$		
			$\text{CH}(\text{OH})(\text{ONO}_2)\text{COCH}(\text{OH})\text{CHO} + \text{HO}_2$			
R <sub>o</sub> 05658			$\text{CH}(\text{OH})(\text{ONO}_2)\text{COCH}(\text{OH})\text{CH}_2(\text{O}\cdot) \rightarrow$	$5.0 \cdot 10^{+02}$		
			$\text{CH}(\text{OH})(\text{ONO}_2)\text{COCH}(\text{OH})(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$			

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05659			$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{COCH}(\text{OH})(\text{ONO}_2) \xrightarrow{\text{O}_2}$	$5.0 \cdot 10^{+06}$		
			$\text{CH}_2(\text{OH})\text{COCOCH}(\text{OH})(\text{ONO}_2) + \text{HO}_2$			
R <sub>o</sub> 05660			$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{COCH}(\text{OH})(\text{ONO}_2) \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CH}(\text{OH})(\text{ONO}_2)\text{COCHO} + 0.500 \text{CH}_2(\text{OH})\text{CHO} +$			
			$0.500 \text{CH}(\text{OH})(\text{ONO}_2)\text{CO}(\text{OO}\cdot) - 0.500 \text{O}_2$			
E <sub>o</sub> 00713			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{ONO}_2) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2)$	$2.7 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05661			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{ONO}_2) \xrightarrow{\text{H}_2\text{O}}$	$7.5 \cdot 10^{-06}$	6600.0	
			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{OH}) + \text{H}^+ + \text{NO}_3$			
R <sub>o</sub> 05662			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{ONO}_2) + \text{OH} \rightarrow$	$8.7 \cdot 10^{+08}$		
			$0.692 \text{CO}(\text{ONO}_2)\text{COCH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$			
			$0.120 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{COCO}(\text{ONO}_2) +$			
			$0.101 \text{CO}(\text{ONO}_2)\text{COCH}(\text{OH})\text{CH}_2(\text{O}\cdot) +$			
			$0.087 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{COCO}(\text{ONO}_2) + \text{H}_2\text{O} - 0.812 \text{O}_2$			
R <sub>o</sub> 05663			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCO}(\text{ONO}_2) + \text{NO}_3 \rightarrow$	$1.3 \cdot 10^{+06}$		
			$0.692 \text{CO}(\text{ONO}_2)\text{COCH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$			
			$0.120 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{COCO}(\text{ONO}_2) +$			
			$0.101 \text{CO}(\text{ONO}_2)\text{COCH}(\text{OH})\text{CH}_2(\text{O}\cdot) +$			
			$0.087 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{COCO}(\text{ONO}_2) + \text{NO}_3^- + \text{H}^+ - 0.812 \text{O}_2$			
R <sub>o</sub> 05664			$\text{CO}(\text{ONO}_2)\text{COCH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow$	$2.0 \cdot 10^{+02}$		
			$\text{CO}(\text{ONO}_2)\text{COCH}(\text{OH})\text{CHO} + \text{HO}_2$			
R <sub>o</sub> 05665			$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{COCO}(\text{ONO}_2) \rightarrow \text{CH}_2(\text{OH})\text{COCOCO}(\text{ONO}_2) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05666			$\text{CO}(\text{ONO}_2)\text{COCH}(\text{OH})\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{ONO}_2)\text{COCH}(\text{OH})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05667			$\text{CO}(\text{ONO}_2)\text{COCH}(\text{OH})\text{CH}_2(\text{O}\cdot) \rightarrow$	$5.0 \cdot 10^{+02}$		
			$\text{CO}(\text{ONO}_2)\text{COCH}(\text{OH})(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$			
R <sub>o</sub> 05668			$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{COCO}(\text{ONO}_2) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCOCO}(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05669			$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{COCO}(\text{ONO}_2) \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CO}(\text{ONO}_2)\text{COCHO} + 0.500 \text{CH}_2(\text{OH})\text{CHO} +$			
			$0.500 \text{CO}(\text{ONO}_2)\text{CO}(\text{OO}\cdot) - 0.500 \text{O}_2$			

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05670			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) + \text{OH} \rightarrow$ $0.370 \text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.059 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) +$ $0.234 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) +$ $0.049 \text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) +$ $0.047 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) +$ $0.200 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})(\text{ONO}_2) +$ $0.042 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{O}\cdot) + \text{H}_2\text{O} - 0.662 \text{O}_2$	$1.8 \cdot 10^{+09}$		
R <sub>o</sub> 05671			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) + \text{NO}_3 \rightarrow$ $0.370 \text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.059 \text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) +$ $0.234 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) +$ $0.049 \text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) +$ $0.047 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) +$ $0.200 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})(\text{O}\cdot)\text{CH}(\text{OH})(\text{ONO}_2) +$ $0.042 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.662 \text{O}_2$	$1.3 \cdot 10^{+07}$		
R <sub>o</sub> 05672			$\text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow$ $\text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05673			$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) \rightarrow$ $\text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05674			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})_2\text{CO}(\text{ONO}_2) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05675			$\text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05676			$\text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05677			$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) \xrightarrow{\text{O}_2}$ $\text{CH}_2(\text{OH})\text{COC}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05678			$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{ONO}_2) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2\text{CHO} +$ $0.500 \text{CH}_2(\text{OH})\text{CHO} + 0.500 \text{CH}(\text{OH})(\text{ONO}_2)\text{C}(\text{OH})_2(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05679			CH <sub>2</sub> (OH)CH(OH)C(OH)(O·)CH(OH)(ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)CH(OH)(OO·) + 0.500 CO(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CH(OH)CO(OH) + 0.500 CHO(ONO <sub>2</sub> ) + 0.500 HO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05680			CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) $\xrightarrow{H_2O}$ CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CO(OH) + H <sup>+</sup> + NO <sub>3</sub>	7.5 · 10 <sup>-06</sup>	6600.0	
R <sub>o</sub> 05681			CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + OH → 0.538 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CH(OH)(OO·) + 0.074 CH <sub>2</sub> (OH)C(OH)(OO·)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.071 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) + 0.068 CH <sub>2</sub> (OH)CH(O·)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.249 CH <sub>2</sub> (OH)CH(OH)C(OH)(O·)CO(ONO <sub>2</sub> ) + H <sub>2</sub> O - 0.612 O <sub>2</sub>	1.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 05682			CH <sub>2</sub> (OH)CH(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.538 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CH(OH)(OO·) + 0.074 CH <sub>2</sub> (OH)C(OH)(OO·)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.071 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) + 0.068 CH <sub>2</sub> (OH)CH(O·)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.249 CH <sub>2</sub> (OH)CH(OH)C(OH)(O·)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.612 O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 05683			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CH(OH)(OO·) → CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05684			CH <sub>2</sub> (OH)C(OH)(OO·)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) → CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05685			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05686			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CH <sub>2</sub> (O·) → CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05687			CH <sub>2</sub> (OH)CH(O·)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COC(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05688			CH <sub>2</sub> (OH)CH(O·)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + 0.500 CH <sub>2</sub> (OH)CHO + 0.500 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05689			CH <sub>2</sub> (OH)CH(OH)C(OH)(O·)CO(ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)CH(OH)(OO·) + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CH(OH)CO(OH) + 0.500 CO + 0.500 NO <sub>3</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00714			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)COCH <sub>2</sub> (ONO <sub>2</sub> )	1.9 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00715			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> )	1.2 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05690			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CHO + OH → 0.170 CHOCH(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.556 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CO(OO·) + 0.231 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH)(O·)CH(OH)CHO + 0.042 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(O·)CHO + H <sub>2</sub> O - 0.726 O <sub>2</sub>	1.6 · 10 <sup>+09</sup>		
R <sub>o</sub> 05691			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CHO + NO <sub>3</sub> → 0.170 CHOCH(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.556 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CO(OO·) + 0.231 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH)(O·)CH(OH)CHO + 0.042 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.726 O <sub>2</sub>	8.8 · 10 <sup>+06</sup>		
R <sub>o</sub> 05692			CHOCH(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CHOCH(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + 0.550 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CHO + 0.250 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05693			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CO(OO·) → CO(OH)CH(OH)C(OH) <sub>2</sub> CH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05694			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH)(O·)CH(OH)CHO → 0.500 CH <sub>2</sub> O + 0.500 CO(OH)CH(OH)CHO + 0.500 CO(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.500 CHOCH(OH)(OO·) + 0.500 NO <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05695			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(O·)CHO $\xrightarrow{O_2}$ CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05696			CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(O·)CHO → 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.500 CHOCHO + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05697			CHOCH(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05698			CHOCH(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) $\rightarrow$ CHOCH(OH)C(OH) <sub>2</sub> (OO·) + CHO(ONO <sub>2</sub> ) - O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00716			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)COCO(ONO <sub>2</sub> )	$1.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00717			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> )	$1.2 \cdot 10^{+02}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05699			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CHO $\xrightarrow{H_2O}$ CO(OH)C(OH) <sub>2</sub> CH(OH)CHO + H <sup>+</sup> + NO <sub>3</sub>	$7.5 \cdot 10^{-06}$	6600.0	
R <sub>o</sub> 05700			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CHO + OH $\rightarrow$ 0.706 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CO(OO·) + 0.240 CO(ONO <sub>2</sub> )C(OH)(O·)CH(OH)CHO + 0.054 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(O·)CHO + H <sub>2</sub> O - 0.706 O <sub>2</sub>	$1.3 \cdot 10^{+09}$		
R <sub>o</sub> 05701			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CHO + NO <sub>3</sub> $\rightarrow$ 0.706 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CO(OO·) + 0.240 CO(ONO <sub>2</sub> )C(OH)(O·)CH(OH)CHO + 0.054 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.706 O <sub>2</sub>	$7.3 \cdot 10^{+06}$		
R <sub>o</sub> 05702			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CO(OO·) $\rightarrow$ CO(OH)CH(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + HO <sub>2</sub> - H <sub>2</sub> O	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 05703			CO(ONO <sub>2</sub> )C(OH)(O·)CH(OH)CHO $\rightarrow$ 0.500 CO + 0.500 CO(OH)CH(OH)CHO + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CHOCH(OH)(OO·) + 0.500 NO <sub>3</sub> - 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05704			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(O·)CHO $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05705			CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(O·)CHO $\rightarrow$ 0.500 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.500 CHOCHO + 0.500 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00718			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(OH)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> )	$5.1 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05706			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CHO + OH → 0.230 CHOCH(OH)C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) + 0.495 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CO(OO·) + 0.042 CHOCH(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + 0.196 CH(OH)(ONO <sub>2</sub> )C(OH)(O·)CH(OH)CHO + 0.038 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(O·)CHO + H <sub>2</sub> O - 0.724 O <sub>2</sub>	1.8 · 10 <sup>+09</sup>		
R <sub>o</sub> 05707			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CHO + NO <sub>3</sub> → 0.230 CHOCH(OH)C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) + 0.495 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CO(OO·) + 0.042 CHOCH(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(O·) + 0.196 CH(OH)(ONO <sub>2</sub> )C(OH)(O·)CH(OH)CHO + 0.038 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.724 O <sub>2</sub>	9.8 · 10 <sup>+06</sup>		
R <sub>o</sub> 05708			CHOCH(OH)C(OH) <sub>2</sub> C(OH)(ONO <sub>2</sub> )(OO·) → CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05709			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)CO(OO·) → CO(OH)CH(OH)C(OH) <sub>2</sub> CH(OH)(ONO <sub>2</sub> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05710			CH(OH)(ONO <sub>2</sub> )C(OH)(O·)CH(OH)CHO → 0.500 CHO(ONO <sub>2</sub> ) + 0.500 CO(OH)CH(OH)CHO + 0.500 CO(OH)CH(OH)(ONO <sub>2</sub> ) + 0.500 CHOCH(OH)(OO·) + 0.500 HO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05711			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(O·)CHO $\xrightarrow{O_2}$ CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05712			CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(O·)CHO → 0.500 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.500 CHOCHO + 0.500 CH(OH)(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05713	*	*	CH <sub>2</sub> (OH)CH=CH <sub>2</sub> + OH → 0.132 CH <sub>2</sub> =CHCH(OH)(OO·) + 0.868 CH <sub>2</sub> (OH)CH(OO·)CH <sub>2</sub> (OH) + 0.132 H <sub>2</sub> O - O <sub>2</sub>	5.9 · 10 <sup>+09</sup>		Maruthamuthu (1980)
R <sub>o</sub> 05714			CH <sub>2</sub> (OH)CH=CH <sub>2</sub> + NO <sub>3</sub> → 0.132 CH <sub>2</sub> =CHCH(OH)(OO·) + 0.868 CH <sub>2</sub> (OH)CH(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.132 NO <sub>3</sub> <sup>-</sup> + 0.132 H <sup>+</sup> - O <sub>2</sub>	2.2 · 10 <sup>+08</sup>		Average of Alfassi <i>et al.</i> (1993) and Ito <i>et al.</i> (1989b)
R <sub>o</sub> 05715	*	*	CH <sub>2</sub> =CHCH(OH)(OO·) → CHOCH=CH <sub>2</sub> + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05716			CH <sub>2</sub> (OH)CH(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{RO_2^{\cdot}}$ 0.200 CH <sub>2</sub> (OH)CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.550 CH <sub>2</sub> (OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + 0.250 CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05717			CH <sub>2</sub> (OH)CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05718			CH <sub>2</sub> (OH)CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CH <sub>2</sub> (ONO <sub>2</sub> )CHO + 0.500 CH <sub>2</sub> (OH)CHO + 0.500 CH <sub>2</sub> O + 0.500 NO <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05719	*	*	CHOCH=CH <sub>2</sub> + OH → 0.107 CH <sub>2</sub> =CHCO(OO·) + 0.893 CH <sub>2</sub> (OH)CH(OO·)CHO + 0.107 H <sub>2</sub> O – O <sub>2</sub>	7.0 · 10 <sup>+09</sup>		<i>Lilie and Henglein (1970)</i>
R <sub>o</sub> 05720			CHOCH=CH <sub>2</sub> + NO <sub>3</sub> → 0.107 CH <sub>2</sub> =CHCO(OO·) + 0.893 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OO·)CHO + 0.107 NO <sub>3</sub> <sup>–</sup> + 0.107 H <sup>+</sup> – O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 05721			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OO·)CHO $\xrightarrow{RO_2^{\cdot}}$ 0.200 CH <sub>2</sub> (ONO <sub>2</sub> )CH(O·)CHO + 0.550 CH <sub>2</sub> (ONO <sub>2</sub> )COCHO + 0.250 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CHO + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05722			CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + OH → 0.381 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)(OO·) + 0.145 CH <sub>2</sub> (OH)C(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.381 CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )(OO·) + 0.045 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) + 0.048 CH <sub>2</sub> (OH)CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.906 O <sub>2</sub>	1.9 · 10 <sup>+09</sup>		
R <sub>o</sub> 05723			CH <sub>2</sub> (OH)CH(OH)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.381 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH(OH)(OO·) + 0.145 CH <sub>2</sub> (OH)C(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) + 0.381 CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )(OO·) + 0.045 CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) + 0.048 CH <sub>2</sub> (OH)CH(O·)CH <sub>2</sub> (ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.906 O <sub>2</sub>	1.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 05724			CH <sub>2</sub> (OH)C(OH)(OO·)CH <sub>2</sub> (ONO <sub>2</sub> ) → CH <sub>2</sub> (OH)COCH <sub>2</sub> (ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05725			CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2^{\cdot}}$ 0.200 CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )(O·) + 0.550 CH <sub>2</sub> (OH)CH(OH)CO(ONO <sub>2</sub> ) + 0.250 CH <sub>2</sub> (OH)CH(OH)CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05726			CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (ONO <sub>2</sub> )CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05727			$\text{CH}_2(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \rightarrow \text{CH}_2(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05728			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05729			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CHO}(\text{ONO}_2) - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05730			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{ONO}_2) + \text{OH} \rightarrow$ $0.321 \text{ CH}(\text{OH})(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.052 \text{ CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})(\text{ONO}_2) +$ $0.510 \text{ CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) +$ $0.040 \text{ CH}(\text{OH})(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) +$ $0.041 \text{ CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})(\text{ONO}_2) +$ $0.037 \text{ CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)(\text{O}\cdot) + \text{H}_2\text{O} - 0.882 \text{ O}_2$	$2.2 \cdot 10^{+09}$		
R <sub>o</sub> 05731			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{ONO}_2) + \text{NO}_3 \rightarrow$ $0.321 \text{ CH}(\text{OH})(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.052 \text{ CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})(\text{ONO}_2) +$ $0.510 \text{ CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) +$ $0.040 \text{ CH}(\text{OH})(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) +$ $0.041 \text{ CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})(\text{ONO}_2) +$ $0.037 \text{ CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.882 \text{ O}_2$	$1.6 \cdot 10^{+06}$		
R <sub>o</sub> 05732			$\text{CH}_2(\text{OH})\text{C}(\text{OH})(\text{OO}\cdot)\text{CH}(\text{OH})(\text{ONO}_2) \rightarrow$ $\text{CH}_2(\text{OH})\text{COCH}(\text{OH})(\text{ONO}_2) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05733			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{OH})(\text{ONO}_2)(\text{OO}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05734			$\text{CH}(\text{OH})(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}(\text{OH})(\text{ONO}_2)\text{CH}(\text{OH})\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05735			$\text{CH}(\text{OH})(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CH}(\text{OH})(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05736			$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})(\text{ONO}_2) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCH}(\text{OH})(\text{ONO}_2) + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05737			$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}(\text{OH})(\text{ONO}_2) \rightarrow$ $0.500 \text{ CH}_2(\text{OH})\cdot + 0.500 \text{ CH}(\text{OH})(\text{ONO}_2)\text{CHO} + 0.500 \text{ CH}_2(\text{OH})\text{CHO} +$ $0.500 \text{ CHO}(\text{ONO}_2) + 0.500 \text{ HO}_2 - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05738			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) \xrightarrow{\text{H}_2\text{O}_2} \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{OH}) + \text{H}^+ + \text{NO}_3$	$7.5 \cdot 10^{-06}$	6600.0	

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05739			CH <sub>2</sub> (OH)CH(OH)CO(ONO <sub>2</sub> ) + OH → 0.737 CO(ONO <sub>2</sub> )CH(OH)CH(OH)(OO·) + 0.062 CH <sub>2</sub> (OH)C(OH)(OO·)CO(ONO <sub>2</sub> ) + 0.108 CO(ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) + 0.093 CH <sub>2</sub> (OH)CH(O·)CO(ONO <sub>2</sub> ) + H <sub>2</sub> O – 0.799 O <sub>2</sub>	8.1 · 10 <sup>+08</sup>		
R <sub>o</sub> 05740			CH <sub>2</sub> (OH)CH(OH)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.737 CO(ONO <sub>2</sub> )CH(OH)CH(OH)(OO·) + 0.062 CH <sub>2</sub> (OH)C(OH)(OO·)CO(ONO <sub>2</sub> ) + 0.108 CO(ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) + 0.093 CH <sub>2</sub> (OH)CH(O·)CO(ONO <sub>2</sub> ) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.799 O <sub>2</sub>	1.3 · 10 <sup>+06</sup>		
R <sub>o</sub> 05741			CH <sub>2</sub> (OH)C(OH)(OO·)CO(ONO <sub>2</sub> ) → CH <sub>2</sub> (OH)COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05742			CO(ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(ONO <sub>2</sub> )CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05743			CO(ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) → CO(ONO <sub>2</sub> )CH(OH)(OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05744			CH <sub>2</sub> (OH)CH(O·)CO(ONO <sub>2</sub> ) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05745			CH <sub>2</sub> (OH)CH(O·)CO(ONO <sub>2</sub> ) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CH <sub>2</sub> (OH)CHO + 0.500 CO + 0.500 NO <sub>3</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00719	*	*	CH <sub>2</sub> (OH)CH=CHCO(OH) ⇌ CH <sub>2</sub> (OH)CH=CHCO(O <sup>–</sup> ) + H <sup>+</sup>	2.5 · 10 <sup>–05</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 05746	*	*	CH <sub>2</sub> (OH)CH=CHCO(OH) + OH → 0.098 CO(OH)CH=CHCH(OH)(OO·) + 0.451 CH <sub>2</sub> (OH)CH(OH)CH(OO·)CO(OH) + 0.451 CH <sub>2</sub> (OH)CH(OO·)CH(OH)CO(OH) + 0.098 H <sub>2</sub> O – O <sub>2</sub>	6.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 05747			CH <sub>2</sub> (OH)CH=CHCO(OH) + NO <sub>3</sub> → 0.098 CO(OH)CH=CHCH(OH)(OO·) + 0.451 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OO·)CO(OH) + 0.451 CH <sub>2</sub> (OH)CH(OO·)CH(ONO <sub>2</sub> )CO(OH) + 0.098 NO <sub>3</sub> <sup>–</sup> + 0.098 H <sup>+</sup> – O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 05748	*	*	CO(OH)CH=CHCH(OH)(OO·) → CO(OH)CH=CHCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05749	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OO·)CO(OH) + CH <sub>2</sub> (OH)CH(OH)CH(OO·)CO(OH) → 2.000 CH <sub>2</sub> (OH)CH(OH)CHO + 2.000 CO <sub>2</sub> + –O <sub>2</sub> –	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 05750	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OO·)CO(OH) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(OH)CH(O·)CO(OH) + 0.550 CH <sub>2</sub> (OH)CH(OH)COCO(OH) + 0.250 CH <sub>2</sub> (OH)CH(OH)CH(OH)CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05751			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OO·)CO(OH) + CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OO·)CO(OH) → 2.000 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CHO + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 05752			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OO·)CO(OH) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(O·)CO(OH) + 0.550 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCO(OH) + 0.250 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05753			CH <sub>2</sub> (OH)CH(OO·)CH(ONO <sub>2</sub> )CO(OH) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(O·)CH(ONO <sub>2</sub> )CO(OH) + 0.550 CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CO(OH) + 0.250 CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CO(OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05754			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(O·)CO(OH) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05755			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(O·)CO(OH) → 0.500 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )(OO·) + 0.500 CO(OH)CHO + 0.500 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CHO + 0.500 ·CO(OH) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05756			CH <sub>2</sub> (OH)CH(O·)CH(ONO <sub>2</sub> )CO(OH) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05757			CH <sub>2</sub> (OH)CH(O·)CH(ONO <sub>2</sub> )CO(OH) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)CH(ONO <sub>2</sub> )CHO + 0.500 CH <sub>2</sub> (OH)CHO + 0.500 CO(OH)CH(ONO <sub>2</sub> )(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05758			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )(OO·) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )(O·) + 0.550 CH <sub>2</sub> (OH)CO(ONO <sub>2</sub> ) + 0.250 CH <sub>2</sub> (OH)CH(OH)(ONO <sub>2</sub> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05759			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05760			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )(O·) → CH <sub>2</sub> (OH)· + CHO(ONO <sub>2</sub> )	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05761			CH <sub>2</sub> (OH)CH(OH)(ONO <sub>2</sub> ) + OH → 0.187 CH(OH)(ONO <sub>2</sub> )CH(OH)(OO·) + 0.703 CH <sub>2</sub> (OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.056 CH(OH)(ONO <sub>2</sub> )CH <sub>2</sub> (O·) + 0.054 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )(O·) + H <sub>2</sub> O - 0.890 O <sub>2</sub>	1.6 · 10 <sup>+09</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05762			CH <sub>2</sub> (OH)CH(OH)(ONO <sub>2</sub> ) + NO <sub>3</sub> → 0.187 CH(OH)(ONO <sub>2</sub> )CH(OH)(OO·) + 0.703 CH <sub>2</sub> (OH)C(OH)(ONO <sub>2</sub> )(OO·) + 0.056 CH(OH)(ONO <sub>2</sub> )CH <sub>2</sub> (O·) + 0.054 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.890 O <sub>2</sub>	1.3 · 10 <sup>+06</sup>		
R <sub>o</sub> 05763			CH <sub>2</sub> (OH)C(OH)(ONO <sub>2</sub> )(OO·) → CH <sub>2</sub> (OH)CO(ONO <sub>2</sub> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05764			CH(OH)(ONO <sub>2</sub> )CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH)(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05765			CH(OH)(ONO <sub>2</sub> )CH <sub>2</sub> (O·) → CHO(ONO <sub>2</sub> ) + CH <sub>2</sub> O + HO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00720			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub>	1.4 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05766			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CHO + OH → 0.333 CHOCH(ONO <sub>2</sub> )CH(OH)(OO·) + 0.064 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)CHO + 0.554 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CO(OO·) + 0.049 CHOCH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) + H <sub>2</sub> O - 0.951 O <sub>2</sub>	1.8 · 10 <sup>+09</sup>		
R <sub>o</sub> 05767			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CHO + NO <sub>3</sub> → 0.333 CHOCH(ONO <sub>2</sub> )CH(OH)(OO·) + 0.064 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)CHO + 0.554 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CO(OO·) + 0.049 CHOCH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.951 O <sub>2</sub>	9.5 · 10 <sup>+06</sup>		
R <sub>o</sub> 05768			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CO(OO·) → CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05769			CHOCH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CHOCH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05770			CHOCH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) → CHOCH(ONO <sub>2</sub> )(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05771	*	*	CH <sub>2</sub> (OH)CH=CHCO(O <sup>-</sup> ) + OH → 0.500 CH <sub>2</sub> (OH)CH(OH)CH(OO·)CO(O <sup>-</sup> ) + 0.500 CH <sub>2</sub> (OH)CH(OO·)CH(OH)CO(O <sup>-</sup> ) - O <sub>2</sub>	2.3 · 10 <sup>+10</sup>		
R <sub>o</sub> 05772			CH <sub>2</sub> (OH)CH=CHCO(O <sup>-</sup> ) + NO <sub>3</sub> → 0.500 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OO·)CO(O <sup>-</sup> ) + 0.500 CH <sub>2</sub> (OH)CH(OO·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) - O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 05773			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OO·)CO(O <sup>-</sup> ) + CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OO·)CO(O <sup>-</sup> ) → 2.000 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CHO + 2.000 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2.000 OH <sup>-</sup> - 2.000 H <sub>2</sub> O	1.9 · 10 <sup>+07</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05774			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OO·)CO(O <sup>-</sup> ) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(O·)CO(O <sup>-</sup> ) + 0.550 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCO(O <sup>-</sup> ) + 0.250 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CO(O <sup>-</sup> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05775			CH <sub>2</sub> (OH)CH(OO·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(O·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + 0.550 CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + 0.250 CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05776			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(O·)CO(O <sup>-</sup> ) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05777			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(O·)CO(O <sup>-</sup> ) → 0.500 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )(OO·) + 0.500 CO(O <sup>-</sup> )CHO + 0.500 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CHO + 0.500 · CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05778			CH <sub>2</sub> (OH)CH(O·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05779			CH <sub>2</sub> (OH)CH(O·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CHO + 0.500 CH <sub>2</sub> (OH)CHO + 0.500 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00721			CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CO(OH) ⇌ CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + H <sup>+</sup>	2.2 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 05780			CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CO(OH) + OH → 0.641 CO(OH)CH(ONO <sub>2</sub> )CH(OH)CH(OH)(OO·) + 0.164 CH <sub>2</sub> (OH)C(OH)(OO·)CH(ONO <sub>2</sub> )CO(OH) + 0.034 CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(OO·)CO(OH) + 0.080 CO(OH)CH(ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) + 0.081 CH <sub>2</sub> (OH)CH(O·)CH(ONO <sub>2</sub> )CO(OH) + H <sub>2</sub> O - 0.839 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05781			CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CO(OH) + NO <sub>3</sub> → 0.641 CO(OH)CH(ONO <sub>2</sub> )CH(OH)CH(OH)(OO·) + 0.164 CH <sub>2</sub> (OH)C(OH)(OO·)CH(ONO <sub>2</sub> )CO(OH) + 0.034 CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(OO·)CO(OH) + 0.080 CO(OH)CH(ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) + 0.081 CH <sub>2</sub> (OH)CH(O·)CH(ONO <sub>2</sub> )CO(OH) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.839 O <sub>2</sub>	1.6 · 10 <sup>+03</sup>		
R <sub>o</sub> 05782			CO(OH)CH(ONO <sub>2</sub> )CH(OH)CH(OH)(OO·) → CO(OH)CH(ONO <sub>2</sub> )CH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05783			CH <sub>2</sub> (OH)C(OH)(OO·)CH(ONO <sub>2</sub> )CO(OH) → CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05784			CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(OO·)CO(OH) + CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(OO·)CO(OH) → 2.000 CH <sub>2</sub> (OH)CH(OH)CO(ONO <sub>2</sub> ) + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 05785			CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(OO·)CO(OH) $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(O·)CO(OH) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05786			CO(OH)CH(ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(OH)CH(ONO <sub>2</sub> )CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05787			CO(OH)CH(ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) → CO(OH)CH(ONO <sub>2</sub> )CH(OH)(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05788			CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(O·)CO(OH) → 0.500 CH <sub>2</sub> (OH)CH(OH)(OO·) + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CH(OH)CO(ONO <sub>2</sub> ) + 0.500 · CO(OH) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00722			CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CO(OH) $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH)	1.5 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00723			CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CO(OH) $\rightleftharpoons$ CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + H <sup>+</sup>	4.5 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 05789			CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CO(OH) + OH → 0.774 CO(OH)CH(ONO <sub>2</sub> )COCH(OH)(OO·) + 0.041 CH <sub>2</sub> (OH)COC(ONO <sub>2</sub> )(OO·)CO(OH) + 0.185 CO(OH)CH(ONO <sub>2</sub> )COCH <sub>2</sub> (O·) + H <sub>2</sub> O - 0.815 O <sub>2</sub>	4.1 · 10 <sup>+08</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05790			CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CO(OH) + NO <sub>3</sub> → 0.774 CO(OH)CH(ONO <sub>2</sub> )COCH(OH)(OO·) + 0.041 CH <sub>2</sub> (OH)COC(ONO <sub>2</sub> )(OO·)CO(OH) + 0.185 CO(OH)CH(ONO <sub>2</sub> )COCH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.815 O <sub>2</sub>	3.2 · 10 <sup>+04</sup>		
R <sub>o</sub> 05791			CO(OH)CH(ONO <sub>2</sub> )COCH(OH)(OO·) → CO(OH)CH(ONO <sub>2</sub> )COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05792			CH <sub>2</sub> (OH)COC(ONO <sub>2</sub> )(OO·)CO(OH) + CH <sub>2</sub> (OH)COC(ONO <sub>2</sub> )(OO·)CO(OH) → 2.000 CH <sub>2</sub> (OH)COCO(ONO <sub>2</sub> ) + 2.000 CO <sub>2</sub> + -O <sub>2</sub> -	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 05793			CH <sub>2</sub> (OH)COC(ONO <sub>2</sub> )(OO·)CO(OH) $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)COC(ONO <sub>2</sub> )(O·)CO(OH) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05794			CO(OH)CH(ONO <sub>2</sub> )COCH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(OH)CH(ONO <sub>2</sub> )COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05795			CO(OH)CH(ONO <sub>2</sub> )COCH <sub>2</sub> (O·) → CO(OH)CH(ONO <sub>2</sub> )CO(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05796			CH <sub>2</sub> (OH)COC(ONO <sub>2</sub> )(O·)CO(OH) → 0.500 CH <sub>2</sub> (OH)CO(OO·) + 0.500 CO(OH)CO(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)COCO(ONO <sub>2</sub> ) + 0.500 · CO(OH) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00724			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCO(OH) $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OH)	1.9 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00725			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCO(OH) $\rightleftharpoons$ CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCO(O <sup>-</sup> ) + H <sup>+</sup>	2.1 · 10 <sup>-01</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 05797			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCO(OH) + OH → 0.781 CO(OH)COCH(ONO <sub>2</sub> )CH(OH)(OO·) + 0.105 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)COCO(OH) + 0.114 CO(OH)COCH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) + H <sub>2</sub> O - 0.886 O <sub>2</sub>	7.7 · 10 <sup>+08</sup>		
R <sub>o</sub> 05798			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCO(OH) + NO <sub>3</sub> → 0.781 CO(OH)COCH(ONO <sub>2</sub> )CH(OH)(OO·) + 0.105 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)COCO(OH) + 0.114 CO(OH)COCH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.886 O <sub>2</sub>	3.6 · 10 <sup>+04</sup>		
R <sub>o</sub> 05799			CO(OH)COCH(ONO <sub>2</sub> )CH(OH)(OO·) → CO(OH)COCH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05800			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)COCO(OH) $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(O·)COCO(OH) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05801			$\text{CO(OH)COCH(ONO}_2\text{)CH}_2\text{(O}\cdot\text{)} \xrightarrow{\text{O}_2} \text{CO(OH)COCH(ONO}_2\text{)CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05802			$\text{CO(OH)COCH(ONO}_2\text{)CH}_2\text{(O}\cdot\text{)} \rightarrow$ $\text{CO(OH)COCH(ONO}_2\text{)(OO}\cdot\text{)} + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05803			$\text{CH}_2\text{(OH)C(ONO}_2\text{)(O}\cdot\text{)COCO(OH)} \rightarrow$ $0.500 \text{CH}_2\text{(OH)}\cdot + 0.500 \text{CO(OH)COCO(ONO}_2\text{)} +$ $0.500 \text{CH}_2\text{(OH)CO(ONO}_2\text{)} + 0.500 \text{CO(OH)CO(OO}\cdot\text{)} - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00726			$\text{CH}_2\text{(OH)CH(ONO}_2\text{)CH(OH)CO(OH)} \rightleftharpoons$ $\text{CH}_2\text{(OH)CH(ONO}_2\text{)CH(OH)CO(O}^-\text{)} + \text{H}^+$	$1.1 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 05804			$\text{CH}_2\text{(OH)CH(ONO}_2\text{)CH(OH)CO(OH)} + \text{OH} \rightarrow$ $0.660 \text{CO(OH)CH(OH)CH(ONO}_2\text{)CH(OH)(OO}\cdot\text{)} +$ $0.169 \text{CH}_2\text{(OH)C(ONO}_2\text{)(OO}\cdot\text{)CH(OH)CO(OH)} +$ $0.035 \text{CH}_2\text{(OH)CH(ONO}_2\text{)C(OH)(OO}\cdot\text{)CO(OH)} +$ $0.083 \text{CO(OH)CH(OH)CH(ONO}_2\text{)CH}_2\text{(O}\cdot\text{)} +$ $0.053 \text{CH}_2\text{(OH)CH(ONO}_2\text{)CH(O}\cdot\text{)CO(OH)} + \text{H}_2\text{O} - 0.864 \text{O}_2$	$1.1 \cdot 10^{+09}$		
R <sub>o</sub> 05805			$\text{CH}_2\text{(OH)CH(ONO}_2\text{)CH(OH)CO(OH)} + \text{NO}_3^- \rightarrow$ $0.660 \text{CO(OH)CH(OH)CH(ONO}_2\text{)CH(OH)(OO}\cdot\text{)} +$ $0.169 \text{CH}_2\text{(OH)C(ONO}_2\text{)(OO}\cdot\text{)CH(OH)CO(OH)} +$ $0.035 \text{CH}_2\text{(OH)CH(ONO}_2\text{)C(OH)(OO}\cdot\text{)CO(OH)} +$ $0.083 \text{CO(OH)CH(OH)CH(ONO}_2\text{)CH}_2\text{(O}\cdot\text{)} +$ $0.053 \text{CH}_2\text{(OH)CH(ONO}_2\text{)CH(O}\cdot\text{)CO(OH)} + \text{NO}_3^- + \text{H}^+ - 0.864 \text{O}_2$	$1.8 \cdot 10^{+03}$		
R <sub>o</sub> 05806			$\text{CO(OH)CH(OH)CH(ONO}_2\text{)CH(OH)(OO}\cdot\text{)} \rightarrow$ $\text{CO(OH)CH(OH)CH(ONO}_2\text{)CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05807			$\text{CH}_2\text{(OH)C(ONO}_2\text{)(OO}\cdot\text{)CH(OH)CO(OH)} \xrightarrow{\text{RO}_2}$ $\text{CH}_2\text{(OH)C(ONO}_2\text{)(O}\cdot\text{)CH(OH)CO(OH)} + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 05808			$\text{CH}_2\text{(OH)CH(ONO}_2\text{)C(OH)(OO}\cdot\text{)CO(OH)} \rightarrow$ $\text{CH}_2\text{(OH)CH(ONO}_2\text{)COCO(OH)} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05809			$\text{CO(OH)CH(OH)CH(ONO}_2\text{)CH}_2\text{(O}\cdot\text{)} \xrightarrow{\text{O}_2}$ $\text{CO(OH)CH(OH)CH(ONO}_2\text{)CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05810			$\text{CO(OH)CH(OH)CH(ONO}_2\text{)CH}_2\text{(O}\cdot\text{)} \rightarrow$ $\text{CO(OH)CH(OH)CH(ONO}_2\text{)(OO}\cdot\text{)} + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05811			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(O·)CH(OH)CO(OH) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)CH(OH)CO(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CO(ONO <sub>2</sub> ) + 0.500 CO(OH)CH(OH)(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05812			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> + OH → 0.430 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(OO·) + 0.069 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)CH(OH) <sub>2</sub> + 0.212 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.054 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) + 0.234 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)(O·) + H <sub>2</sub> O - 0.712 O <sub>2</sub>	1.6 · 10 <sup>+09</sup>		
R <sub>o</sub> 05813			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.430 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(OO·) + 0.069 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)CH(OH) <sub>2</sub> + 0.212 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.054 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) + 0.234 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.712 O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 05814			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05815			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05816			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) → CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05817			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05818			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)(O·) → CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05819			CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + OH → 0.531 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH(OH)CH(OH)(OO·) + 0.239 CH <sub>2</sub> (OH)C(OH)(OO·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + 0.096 CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) + 0.066 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) + 0.067 CH <sub>2</sub> (OH)CH(O·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.866 O <sub>2</sub>	1.3 · 10 <sup>+09</sup>		
R <sub>o</sub> 05820			CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 05821			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH(OH)CH(OH)(OO·) → CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05822			CH <sub>2</sub> (OH)C(OH)(OO·)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) → CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05823			CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) + CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) → 2.000 CH <sub>2</sub> (OH)CH(OH)CO(ONO <sub>2</sub> ) + 2.000 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2.000 OH <sup>-</sup> - 2.000 H <sub>2</sub> O	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 05824			CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(O·)CO(O <sup>-</sup> ) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05825			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05826			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) → CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH(OH)(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05827			CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CO(O·) → CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )(OO·) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05828			CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(O·)CO(O <sup>-</sup> ) → 0.500 CH <sub>2</sub> (OH)CH(OH)(OO·) + 0.500 CO(O <sup>-</sup> )CO(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CH(OH)CO(ONO <sub>2</sub> ) + 0.500 · CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00727			CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O <sup>-</sup> )	1.3 · 10 <sup>+00</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05829			CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + OH → 0.704 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )COCH(OH)(OO·) + 0.128 CH <sub>2</sub> (OH)COC(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) + 0.168 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )COCH <sub>2</sub> (O·) + H <sub>2</sub> O - 0.832 O <sub>2</sub>	4.5 · 10 <sup>+08</sup>		
R <sub>o</sub> 05830			CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + NO <sub>3</sub> → CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 05831			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )COCH(OH)(OO·) → CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05832			CH <sub>2</sub> (OH)COC(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) + CH <sub>2</sub> (OH)COC(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) → 2.000 CH <sub>2</sub> (OH)COCO(ONO <sub>2</sub> ) + 2.000 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2.000 OH <sup>-</sup> - 2.000 H <sub>2</sub> O	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 05833			CH <sub>2</sub> (OH)COC(ONO <sub>2</sub> )(OO·)CO(O <sup>-</sup> ) $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)COC(ONO <sub>2</sub> )(O·)CO(O <sup>-</sup> ) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05834			$\text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{COCH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05835			$\text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{COCH}_2(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}(\text{ONO}_2)\text{CO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05836			$\text{CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)\text{CO}(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05837			$\text{CH}_2(\text{OH})\text{COC}(\text{ONO}_2)(\text{O}\cdot)\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\text{CO}(\text{OO}\cdot) + 0.500 \text{CO}(\text{O}^-)\text{CO}(\text{ONO}_2) +$ $0.500 \text{CH}_2(\text{OH})\text{COCO}(\text{ONO}_2) + 0.500 \cdot \text{CO}(\text{O}^-) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05838			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{OH} \rightarrow$ $0.527 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.237 \text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) +$ $0.096 \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{O}^-) +$ $0.066 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}_2(\text{O}\cdot) +$ $0.074 \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{O}\cdot)\text{CO}(\text{O}^-) + \text{H}_2\text{O} - 0.860 \text{O}_2$	$1.3 \cdot 10^{+09}$		
R <sub>o</sub> 05839			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})\text{CO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 05840			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05841			$\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) \xrightarrow{\text{RO}_2}$ $\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 05842			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})(\text{OO}\cdot)\text{CO}(\text{O}^-) \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{COCO}(\text{O}^-) + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05843			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05844			$\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05845			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})\text{CO}(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05846			$\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{CH}(\text{OH})\text{CO}(\text{O}^-) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) +$ $0.500 \text{CH}_2(\text{OH})\text{CO}(\text{ONO}_2) + 0.500 \text{CO}(\text{O}^-)\text{CH}(\text{OH})(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05847			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
E <sub>o</sub> 00728			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{COCO}(\text{O}^-) \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CO}(\text{O}^-)$	$4.4 \cdot 10^{-01}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05848			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{COCO}(\text{O}^-) + \text{OH} \rightarrow$ $0.723 \text{ CO}(\text{O}^-)\text{COCH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.171 \text{ CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{COCO}(\text{O}^-) +$ $0.106 \text{ CO}(\text{O}^-)\text{COCH}(\text{ONO}_2)\text{CH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.894 \text{ O}_2$	$8.3 \cdot 10^{+08}$		
R <sub>o</sub> 05849			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{COCO}(\text{O}^-) + \text{NO}_3 \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{COCO}(\text{O}\cdot) + \text{NO}_3^-$	$2.0 \cdot 10^{+07}$		
R <sub>o</sub> 05850			$\text{CO}(\text{O}^-)\text{COCH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CO}(\text{O}^-)\text{COCH}(\text{ONO}_2)\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05851			$\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{COCO}(\text{O}^-) \xrightarrow{\text{RO}_2\cdot}$ $\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{COCO}(\text{O}^-) + 0.500 \text{ O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 05852			$\text{CO}(\text{O}^-)\text{COCH}(\text{ONO}_2)\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CO}(\text{O}^-)\text{COCH}(\text{ONO}_2)\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05853			$\text{CO}(\text{O}^-)\text{COCH}(\text{ONO}_2)\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CO}(\text{O}^-)\text{COCH}(\text{ONO}_2)(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05854			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{COCO}(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{CO}(\text{OO}\cdot) + \text{CO}_2 - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05855			$\text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{COCO}(\text{O}^-) \rightarrow$ $0.500 \text{ CH}_2(\text{OH})\cdot + 0.500 \text{ CO}(\text{O}^-)\text{COCO}(\text{ONO}_2) +$ $0.500 \text{ CH}_2(\text{OH})\text{CO}(\text{ONO}_2) + 0.500 \text{ CO}(\text{O}^-)\text{CO}(\text{OO}\cdot) - 0.500 \text{ O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00729			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CO}(\text{OH}) \rightleftharpoons$ $\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CO}(\text{O}^-) + \text{H}^+$	$2.7 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 05856			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{OH} \rightarrow$ $0.625 \text{ CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.067 \text{ CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{OH}) +$ $0.082 \text{ CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CH}_2(\text{O}\cdot) +$ $0.226 \text{ CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) + \text{H}_2\text{O} - 0.692 \text{ O}_2$	$1.1 \cdot 10^{+09}$		
R <sub>o</sub> 05857			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CO}(\text{OH}) + \text{NO}_3 \rightarrow$ $0.625 \text{ CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.067 \text{ CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{C}(\text{OH})_2\text{CO}(\text{OH}) +$ $0.082 \text{ CO}(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CH}_2(\text{O}\cdot) +$ $0.226 \text{ CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})(\text{O}\cdot)\text{CO}(\text{OH}) + \text{NO}_3^- + \text{H}^+ - 0.692 \text{ O}_2$	$8.8 \cdot 10^{+06}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05858			CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(OO·) → CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05859			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)C(OH) <sub>2</sub> CO(OH) $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(O·)C(OH) <sub>2</sub> CO(OH) + 0.500 O <sub>2</sub>	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 05860			CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05861			CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) → CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + CH <sub>2</sub> O – O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05862			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH)(O·)CO(OH) → 0.500 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )(OO·) + 0.500 CO(OH)CO(OH) + 0.500 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CO(OH) + 0.500 ·CO(OH) – 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05863			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(O·)C(OH) <sub>2</sub> CO(OH) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CO(ONO <sub>2</sub> ) + 0.500 CO(OH)C(OH) <sub>2</sub> (OO·) – 0.500 O <sub>2</sub>	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00730			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH) ⇌ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O <sup>–</sup> ) + H <sup>+</sup>	$3.2 \cdot 10^{-04}$		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 05864			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH) + OH → 0.376 CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO·) + 0.113 CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.511 CH <sub>2</sub> (OH)C(OH)(O·)CH(ONO <sub>2</sub> )CO(OH) + H <sub>2</sub> O – 0.376 O <sub>2</sub>	$7.4 \cdot 10^{+08}$		
R <sub>o</sub> 05865			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH) + NO <sub>3</sub> → 0.376 CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO·) + 0.113 CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.511 CH <sub>2</sub> (OH)C(OH)(O·)CH(ONO <sub>2</sub> )CO(OH) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.376 O <sub>2</sub>	$8.9 \cdot 10^{+06}$		
R <sub>o</sub> 05866			CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO·) → CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05867			CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05868			CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O·) → CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + CH <sub>2</sub> O – O <sub>2</sub>	$5.0 \cdot 10^{+02}$		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05869			CH <sub>2</sub> (OH)C(OH)(O·)CH(ONO <sub>2</sub> )CO(OH) → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)CH(ONO <sub>2</sub> )CO(OH) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CO(OH)CH(ONO <sub>2</sub> )(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00731			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CO(OH) ⇌ CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CO(O <sup>–</sup> ) + H <sup>+</sup>	1.9 · 10 <sup>–04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 05870			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CO(OH) + OH → 0.789 CO(OH)CH(ONO <sub>2</sub> )CH(OH)(OO·) + 0.062 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)CO(OH) + 0.148 CO(OH)CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) + H <sub>2</sub> O – 0.852 O <sub>2</sub>	5.9 · 10 <sup>+08</sup>		
R <sub>o</sub> 05871			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CO(OH) + NO <sub>3</sub> → 0.789 CO(OH)CH(ONO <sub>2</sub> )CH(OH)(OO·) + 0.062 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)CO(OH) + 0.148 CO(OH)CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.852 O <sub>2</sub>	3.3 · 10 <sup>+04</sup>		
R <sub>o</sub> 05872			CO(OH)CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(OH)CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05873			CO(OH)CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) → CO(OH)CH(ONO <sub>2</sub> )(OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05874			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O <sup>–</sup> ) + OH → 0.512 CO(O <sup>–</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(OO·) + 0.096 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)C(OH) <sub>2</sub> CO(O <sup>–</sup> ) + 0.067 CO(O <sup>–</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) + 0.324 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH)(O·)CO(O <sup>–</sup> ) + H <sub>2</sub> O – 0.608 O <sub>2</sub>	1.3 · 10 <sup>+09</sup>		
R <sub>o</sub> 05875			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O <sup>–</sup> ) + NO <sub>3</sub> → CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O·) + NO <sub>3</sub> <sup>–</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 05876			CO(O <sup>–</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(OO·) → CO(O <sup>–</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05877			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)C(OH) <sub>2</sub> CO(O <sup>–</sup> ) $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(O·)C(OH) <sub>2</sub> CO(O <sup>–</sup> ) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05878			CO(O <sup>–</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CO(O <sup>–</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05879			CO(O <sup>–</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) → CO(O <sup>–</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05880			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH)(O $\cdot$ )CO(O <sup>-</sup> ) $\rightarrow$ 0.500 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.500 CO(OH)CO(O <sup>-</sup> ) + 0.500 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CO(OH) + 0.500 $\cdot$ CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	5.0 $\cdot$ 10 <sup>+02</sup>		
R <sub>o</sub> 05881			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O $\cdot$ ) $\rightarrow$ CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 $\cdot$ 10 <sup>+02</sup>		
R <sub>o</sub> 05882			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(O $\cdot$ )C(OH) <sub>2</sub> CO(O <sup>-</sup> ) $\rightarrow$ 0.500 CH <sub>2</sub> (OH) $\cdot$ + 0.500 CO(O <sup>-</sup> )C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CO(ONO <sub>2</sub> ) + 0.500 CO(O <sup>-</sup> )C(OH) <sub>2</sub> (OO $\cdot$ ) - 0.500 O <sub>2</sub>	5.0 $\cdot$ 10 <sup>+02</sup>		
R <sub>o</sub> 05883			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + OH $\rightarrow$ 0.352 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO $\cdot$ ) + 0.064 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO $\cdot$ )CO(O <sup>-</sup> ) + 0.106 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) + 0.479 CH <sub>2</sub> (OH)C(OH)(O $\cdot$ )CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + H <sub>2</sub> O - 0.416 O <sub>2</sub>	7.9 $\cdot$ 10 <sup>+08</sup>		
R <sub>o</sub> 05884			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + NO <sub>3</sub> $\rightarrow$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	2.0 $\cdot$ 10 <sup>+07</sup>		
R <sub>o</sub> 05885			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO $\cdot$ ) $\rightarrow$ CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 $\cdot$ 10 <sup>+02</sup>		
R <sub>o</sub> 05886			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO $\cdot$ )CO(O <sup>-</sup> ) + CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO $\cdot$ )CO(O <sup>-</sup> ) $\rightarrow$ 2.000 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 2.000 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2.000 OH <sup>-</sup> - 2.000 H <sub>2</sub> O	1.9 $\cdot$ 10 <sup>+07</sup>		
R <sub>o</sub> 05887			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO $\cdot$ )CO(O <sup>-</sup> ) $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O $\cdot$ )CO(O <sup>-</sup> ) + 0.500 O <sub>2</sub>	1.0 $\cdot$ 10 <sup>+06</sup>		
R <sub>o</sub> 05888			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) $\xrightarrow{O_2}$ CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 $\cdot$ 10 <sup>+06</sup>		
R <sub>o</sub> 05889			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O $\cdot$ ) $\rightarrow$ CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO $\cdot$ ) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 $\cdot$ 10 <sup>+02</sup>		
R <sub>o</sub> 05890			CH <sub>2</sub> (OH)C(OH)(O $\cdot$ )CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) $\rightarrow$ 0.500 CH <sub>2</sub> (OH) $\cdot$ + 0.500 CO(OH)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )(OO $\cdot$ ) - 0.500 O <sub>2</sub>	5.0 $\cdot$ 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05891			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O $\cdot$ ) $\rightarrow$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05892			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O $\cdot$ )CO(O <sup>-</sup> ) $\rightarrow$ 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.500 CO(O <sup>-</sup> )CO(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 · CO(O <sup>-</sup> ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05893			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + OH $\rightarrow$ 0.793 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH(OH)(OO $\cdot$ ) + 0.122 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO $\cdot$ )CO(O <sup>-</sup> ) + 0.085 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH <sub>2</sub> (O $\cdot$ ) + H <sub>2</sub> O - 0.915 O <sub>2</sub>	1.0 · 10 <sup>+09</sup>		
R <sub>o</sub> 05894			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + NO <sub>3</sub> $\rightarrow$ CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 05895			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH <sub>2</sub> (O $\cdot$ ) $\xrightarrow{O_2}$ CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05896			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )CH <sub>2</sub> (O $\cdot$ ) $\rightarrow$ CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )(OO $\cdot$ ) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05897			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CO(O $\cdot$ ) $\rightarrow$ CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )(OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00732			CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH)	2.1 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00733			CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO $\rightleftharpoons$ CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + H <sup>+</sup>	4.6 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated
R <sub>o</sub> 05898			CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + OH $\rightarrow$ 0.550 CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO $\cdot$ ) + 0.450 CO(OH)CH(ONO <sub>2</sub> )C(OH)(O $\cdot$ )CHO + H <sub>2</sub> O - 0.550 O <sub>2</sub>	6.9 · 10 <sup>+08</sup>		
R <sub>o</sub> 05899			CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + NO <sub>3</sub> $\rightarrow$ 0.550 CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO $\cdot$ ) + 0.450 CO(OH)CH(ONO <sub>2</sub> )C(OH)(O $\cdot$ )CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.550 O <sub>2</sub>	6.7 · 10 <sup>+06</sup>		
R <sub>o</sub> 05900			CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO $\cdot$ ) $\rightarrow$ CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05901			CO(OH)CH(ONO <sub>2</sub> )C(OH)(O $\cdot$ )CHO $\rightarrow$ 0.500 CO(OH)CH(ONO <sub>2</sub> )(OO $\cdot$ ) + 0.500 CO(OH)CHO + 0.500 CO(OH)CH(ONO <sub>2</sub> )CO(OH) + 0.500 CH · (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00734			CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OH)	5.4 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00735			CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO $\rightleftharpoons$ CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + H <sup>+</sup>	4.3 · 10 <sup>-04</sup>		$k_b = 5 \cdot 10^{10} \text{ M}^{-1} \cdot \text{s}^{-1}$ estimated

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05902			CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + OH → 0.791 CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OO·) + 0.209 CO(OH)C(OH)(O·)CH(ONO <sub>2</sub> )CHO + H <sub>2</sub> O - 0.791 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 05903			CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + NO <sub>3</sub> → 0.791 CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OO·) + 0.209 CO(OH)C(OH)(O·)CH(ONO <sub>2</sub> )CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.791 O <sub>2</sub>	6.7 · 10 <sup>+06</sup>		
R <sub>o</sub> 05904			CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OO·) → CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05905			CO(OH)C(OH)(O·)CH(ONO <sub>2</sub> )CHO → 0.500 · CO(OH) + 0.500 CO(OH)CH(ONO <sub>2</sub> )CHO + 0.500 CO(OH)CO(OH) + 0.500 CHOCH(ONO <sub>2</sub> )(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00736			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CO(O <sup>-</sup> )	3.2 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00737			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O <sup>-</sup> )	4.0 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05906			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + OH → 0.057 CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO·)C(OH) <sub>2</sub> CHO + 0.519 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) + 0.424 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH)(O·)CHO + H <sub>2</sub> O - 0.576 O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05907			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + NO <sub>3</sub> → CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O·) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 05908			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO·)C(OH) <sub>2</sub> CHO + CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO·)C(OH) <sub>2</sub> CHO → 2.000 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + 2.000 CO <sub>2</sub> + H <sub>2</sub> O <sub>2</sub> + 2.000 OH <sup>-</sup> - 2.000 H <sub>2</sub> O	1.9 · 10 <sup>+07</sup>		
R <sub>o</sub> 05909			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(OO·)C(OH) <sub>2</sub> CHO $\xrightarrow{RO_2}$ CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(O·)C(OH) <sub>2</sub> CHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05910			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) → CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05911			CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )C(OH)(O·)CHO → 0.500 CO(O <sup>-</sup> )CH(ONO <sub>2</sub> )(OO·) + 0.500 CO(OH)CHO + 0.500 CO(OH)CH(ONO <sub>2</sub> )CO(O <sup>-</sup> ) + 0.500 CH · (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05912			CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(O·) → CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05913			CO(O <sup>-</sup> )C(ONO <sub>2</sub> )(O $\cdot$ )C(OH) <sub>2</sub> CHO $\rightarrow$ 0.500 · CO(O <sup>-</sup> ) + 0.500 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + 0.500 CO(O <sup>-</sup> )CO(ONO <sub>2</sub> ) + 0.500 CHOC(OH) <sub>2</sub> (OO $\cdot$ ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00738			CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCO(O <sup>-</sup> )	3.0 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00739			CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O <sup>-</sup> )	3.3 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05914			CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + OH $\rightarrow$ 0.037 CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO $\cdot$ )CHO + 0.657 CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OO $\cdot$ ) + 0.306 CO(O <sup>-</sup> )C(OH)(O $\cdot$ )CH(ONO <sub>2</sub> )CHO + H <sub>2</sub> O - 0.694 O <sub>2</sub>	1.4 · 10 <sup>+09</sup>		
R <sub>o</sub> 05915			CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + NO <sub>3</sub> $\rightarrow$ CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O $\cdot$ ) + NO <sub>3</sub> <sup>-</sup>	2.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 05916			CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO $\cdot$ )CHO $\xrightarrow{RO_2}$ CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O $\cdot$ )CHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05917			CO(O <sup>-</sup> )C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OO $\cdot$ ) $\rightarrow$ CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O <sup>-</sup> ) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05918			CO(O <sup>-</sup> )C(OH)(O $\cdot$ )CH(ONO <sub>2</sub> )CHO $\rightarrow$ 0.500 · CO(O <sup>-</sup> ) + 0.500 CO(OH)CH(ONO <sub>2</sub> )CHO + 0.500 CO(OH)CO(O <sup>-</sup> ) + 0.500 CHOCH(ONO <sub>2</sub> )(OO $\cdot$ ) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05919			CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(O $\cdot$ ) $\rightarrow$ CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO $\cdot$ ) + CO <sub>2</sub> - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05920			CO(O <sup>-</sup> )C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O $\cdot$ )CHO $\rightarrow$ 0.500 CO(O <sup>-</sup> )C(OH) <sub>2</sub> (OO $\cdot$ ) + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CO(O <sup>-</sup> )C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 CH · (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00740	*	*	CH <sub>2</sub> (OH)CH=CHCHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)CH=CHCH(OH) <sub>2</sub>	1.9 · 10 <sup>-01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05921	*	*	CH <sub>2</sub> (OH)CH=CHCHO + OH $\rightarrow$ 0.039 CHOCH=CHCH(OH)(OO $\cdot$ ) + 0.047 CH <sub>2</sub> (OH)CH=CHCO(OO $\cdot$ ) + 0.457 CH <sub>2</sub> (OH)CH(OH)CH(OO $\cdot$ )CHO + 0.457 CH <sub>2</sub> (OH)CH(OO $\cdot$ )CH(OH)CHO + 0.085 H <sub>2</sub> O - O <sub>2</sub>	1.5 · 10 <sup>+10</sup>		
R <sub>o</sub> 05922			CH <sub>2</sub> (OH)CH=CHCHO + NO <sub>3</sub> $\rightarrow$ 0.039 CHOCH=CHCH(OH)(OO $\cdot$ ) + 0.047 CH <sub>2</sub> (OH)CH=CHCO(OO $\cdot$ ) + 0.457 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OO $\cdot$ )CHO + 0.457 CH <sub>2</sub> (OH)CH(OO $\cdot$ )CH(ONO <sub>2</sub> )CHO + 0.085 NO <sub>3</sub> <sup>-</sup> + 0.085 H <sup>+</sup> - O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05923	*	*	$\text{CHOCH}=\text{CHCH}(\text{OH})(\text{OO}\cdot) \rightarrow \text{CHOCH}=\text{CHCHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05924	*	*	$\text{CH}_2(\text{OH})\text{CH}=\text{CHCO}(\text{OO}\cdot) \rightarrow \text{CH}_2(\text{OH})\text{CH}=\text{CHCO}(\text{OH}) + \text{HO}_2 - \text{H}_2\text{O}$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 05925	*	*	$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OO}\cdot)\text{CHO} \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{O}\cdot)\text{CHO} + 0.550 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{COCHO} +$ $0.250 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{OH})\text{CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 05926			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{OO}\cdot)\text{CHO} \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{O}\cdot)\text{CHO} +$ $0.550 \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{COCHO} +$ $0.250 \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})\text{CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 05927			$\text{CH}_2(\text{OH})\text{CH}(\text{OO}\cdot)\text{CH}(\text{ONO}_2)\text{CHO} \xrightarrow{\text{RO}_2}$ $0.200 \text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}(\text{ONO}_2)\text{CHO} +$ $0.550 \text{CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)\text{CHO} +$ $0.250 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CHO} + 0.350 \text{O}_2 + 0.150 \text{H}_2\text{O}_2$	$7.3 \cdot 10^{+08}$		
R <sub>o</sub> 05928			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{O}\cdot)\text{CHO} \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05929			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{O}\cdot)\text{CHO} \rightarrow$ $0.500 \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)(\text{OO}\cdot) + 0.500 \text{CHOCHO} +$ $0.500 \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{CHO} + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{O}_2 - 0.500 \text{H}_2\text{O}$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05930			$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}(\text{ONO}_2)\text{CHO} \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05931			$\text{CH}_2(\text{OH})\text{CH}(\text{O}\cdot)\text{CH}(\text{ONO}_2)\text{CHO} \rightarrow$ $0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CHOCH}(\text{ONO}_2)\text{CHO} + 0.500 \text{CH}_2(\text{OH})\text{CHO} +$ $0.500 \text{CHOCH}(\text{ONO}_2)(\text{OO}\cdot) - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
E <sub>o</sub> 00741			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})\text{CHO} \xrightleftharpoons{\text{H}_2\text{O}}$ $\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}(\text{OH})_2$	$4.9 \cdot 10^{+01}$		$k_b = 5.69 \cdot 10^{-3} \text{s}^{-1}$ estimated
R <sub>o</sub> 05932			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})\text{CHO} + \text{OH} \rightarrow$ $0.324 \text{CHOCH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.107 \text{CH}_2(\text{OH})\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CH}(\text{OH})\text{CHO} +$ $0.054 \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})(\text{OO}\cdot)\text{CHO} +$ $0.441 \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})\text{CO}(\text{OO}\cdot) +$ $0.041 \text{CHOCH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}_2(\text{O}\cdot) +$ $0.033 \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}(\text{O}\cdot)\text{CHO} + \text{H}_2\text{O} - 0.926 \text{O}_2$	$2.2 \cdot 10^{+09}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05933			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CHO + NO <sub>3</sub> → 0.324 CHOCH(OH)CH(ONO <sub>2</sub> )CH(OH)(OO·) + 0.107 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)CH(OH)CHO + 0.054 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH)(OO·)CHO + 0.441 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CO(OO·) + 0.041 CHOCH(OH)CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) + 0.033 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.926 O <sub>2</sub>	2.3 · 10 <sup>+07</sup>		
R <sub>o</sub> 05934			CHOCH(OH)CH(ONO <sub>2</sub> )CH(OH)(OO·) → CHOCH(OH)CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05935			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)CH(OH)CHO $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(O·)CH(OH)CHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05936			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH)(OO·)CHO → CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05937			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CO(OO·) → CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05938			CHOCH(OH)CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CHOCH(OH)CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05939			CHOCH(OH)CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) → CHOCH(OH)CH(ONO <sub>2</sub> )(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05940			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(O·)CH(OH)CHO → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(ONO <sub>2</sub> )CH(OH)CHO + 0.500 CH <sub>2</sub> (OH)CO(ONO <sub>2</sub> ) + 0.500 CHOCH(OH)(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05941	*	*	CH <sub>2</sub> (OH)CH=CHCH(OH) <sub>2</sub> + OH → 0.500 CH <sub>2</sub> (OH)CH(OH)CH(OO·)CH(OH) <sub>2</sub> + 0.500 CH <sub>2</sub> (OH)CH(OO·)CH(OH)CH(OH) <sub>2</sub> - O <sub>2</sub>	2.3 · 10 <sup>+10</sup>		
R <sub>o</sub> 05942			CH <sub>2</sub> (OH)CH=CHCH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.500 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OO·)CH(OH) <sub>2</sub> + 0.500 CH <sub>2</sub> (OH)CH(OO·)CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> - O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 05943	*	*	CH <sub>2</sub> (OH)CH(OH)CH(OO·)CH(OH) <sub>2</sub> $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(OH)CH(O·)CH(OH) <sub>2</sub> + 0.550 CH <sub>2</sub> (OH)CH(OH)COCH(OH) <sub>2</sub> + 0.250 CH <sub>2</sub> (OH)CH(OH)CH(OH)CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05944			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OO·)CH(OH) <sub>2</sub> $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(O·)CH(OH) <sub>2</sub> + 0.550 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCH(OH) <sub>2</sub> + 0.250 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05945			CH <sub>2</sub> (OH)CH(OO·)CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(O·)CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> + 0.550 CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> + 0.250 CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 05946			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(O·)CH(OH) <sub>2</sub> $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCH(OH) <sub>2</sub> + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05947			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(O·)CH(OH) <sub>2</sub> → 0.500 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )(OO·) + 0.500 CH(OH) <sub>2</sub> CHO + 0.500 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CHO + 0.500 CH·(OH) <sub>2</sub> – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05948			CH <sub>2</sub> (OH)CH(O·)CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05949			CH <sub>2</sub> (OH)CH(O·)CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> → 0.500 CH <sub>2</sub> (OH)· + 0.500 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + 0.500 CH <sub>2</sub> (OH)CHO + 0.500 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00742			CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub>	1.9 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05950			CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CHO + OH → 0.321 CHOCH(ONO <sub>2</sub> )CH(OH)CH(OH)(OO·) + 0.106 CH <sub>2</sub> (OH)C(OH)(OO·)CH(ONO <sub>2</sub> )CHO + 0.054 CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(OO·)CHO + 0.438 CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CO(OO·) + 0.040 CHOCH(ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) + 0.041 CH <sub>2</sub> (OH)CH(O·)CH(ONO <sub>2</sub> )CHO + H <sub>2</sub> O – 0.919 O <sub>2</sub>	2.2 · 10 <sup>+09</sup>		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05951			CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CHO + NO <sub>3</sub> → 0.321 CHOCH(ONO <sub>2</sub> )CH(OH)CH(OH)(OO·) + 0.106 CH <sub>2</sub> (OH)C(OH)(OO·)CH(ONO <sub>2</sub> )CHO + 0.054 CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(OO·)CHO + 0.438 CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CO(OO·) + 0.040 CHOCH(ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) + 0.041 CH <sub>2</sub> (OH)CH(O·)CH(ONO <sub>2</sub> )CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.919 O <sub>2</sub>	2.4 · 10 <sup>+07</sup>		
R <sub>o</sub> 05952			CHOCH(ONO <sub>2</sub> )CH(OH)CH(OH)(OO·) → CHOCH(OH)CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05953			CH <sub>2</sub> (OH)C(OH)(OO·)CH(ONO <sub>2</sub> )CHO → CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05954			CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(OO·)CHO $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(O·)CHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05955			CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CO(OO·) → CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05956			CHOCH(ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CHOCH(OH)CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05957			CHOCH(ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) → CHOCH(ONO <sub>2</sub> )CH(OH)(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05958			CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(O·)CHO → 0.500 CH <sub>2</sub> (OH)CH(OH)(OO·) + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CH <sub>2</sub> (OH)CH(OH)CO(ONO <sub>2</sub> ) + 0.500 CH · (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00743			CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CH(OH) <sub>2</sub>	1.2 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00744			CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub>	7.9 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05959			CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CHO + OH → 0.250 CHOCH(ONO <sub>2</sub> )COCH(OH)(OO·) + 0.042 CH <sub>2</sub> (OH)COC(ONO <sub>2</sub> )(OO·)CHO + 0.649 CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CO(OO·) + 0.060 CHOCH(ONO <sub>2</sub> )COCH <sub>2</sub> (O·) + H <sub>2</sub> O - 0.940 O <sub>2</sub>	1.3 · 10 <sup>+09</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05960			CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CHO + NO <sub>3</sub> → 0.250 CHOCH(ONO <sub>2</sub> )COCH(OH)(OO·) + 0.042 CH <sub>2</sub> (OH)COC(ONO <sub>2</sub> )(OO·)CHO + 0.649 CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CO(OO·) + 0.060 CHOCH(ONO <sub>2</sub> )COCH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.940 O <sub>2</sub>	9.8 · 10 <sup>+06</sup>		
R <sub>o</sub> 05961			CHOCH(ONO <sub>2</sub> )COCH(OH)(OO·) → CHOCOCH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05962			CH <sub>2</sub> (OH)COC(ONO <sub>2</sub> )(OO·)CHO $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)COC(ONO <sub>2</sub> )(O·)CHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05963			CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CO(OO·) → CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 05964			CHOCH(ONO <sub>2</sub> )COCH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CHOCOCH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05965			CHOCH(ONO <sub>2</sub> )COCH <sub>2</sub> (O·) → CHOCH(ONO <sub>2</sub> )CO(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05966			CH <sub>2</sub> (OH)COC(ONO <sub>2</sub> )(O·)CHO → 0.500 CH <sub>2</sub> (OH)CO(OO·) + 0.500 CO(ONO <sub>2</sub> )CHO + 0.500 CH <sub>2</sub> (OH)COCO(ONO <sub>2</sub> ) + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00745			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	4.7 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 05967			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCHO + OH → 0.491 CHOCOCH(ONO <sub>2</sub> )CH(OH)(OO·) + 0.085 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)COCHO + 0.352 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCO(OO·) + 0.072 CHOCOCH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) + H <sub>2</sub> O - 0.928 O <sub>2</sub>	1.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 05968			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCHO + NO <sub>3</sub> → 0.491 CHOCOCH(ONO <sub>2</sub> )CH(OH)(OO·) + 0.085 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)COCHO + 0.352 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCO(OO·) + 0.072 CHOCOCH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.928 O <sub>2</sub>	9.4 · 10 <sup>+06</sup>		
R <sub>o</sub> 05969			CHOCOCH(ONO <sub>2</sub> )CH(OH)(OO·) → CHOCOCH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05970			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)COCHO $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(O·)COCHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05971			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCO(OO·) → CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05972			$\text{CHOCOCH(ONO}_2\text{)CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CHOCOCH(ONO}_2\text{)CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05973			$\text{CHOCOCH(ONO}_2\text{)CH}_2(\text{O}\cdot) \rightarrow \text{CHOCOCH(ONO}_2\text{)(OO}\cdot\text{)} + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05974			$\text{CH}_2(\text{OH})\text{C(ONO}_2\text{)(O}\cdot\text{)COCHO} \rightarrow$ $0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CO(ONO}_2\text{)COCHO} + 0.500 \text{CH}_2(\text{OH})\text{CO(ONO}_2\text{)} +$ $0.500 \text{CHOCO(OO}\cdot\text{)} - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 05975			$\text{CH}_2(\text{OH})\text{CH(ONO}_2\text{)C(OH)}_2\text{CH(OH)}_2 + \text{OH} \rightarrow$ $0.389 \text{CH(OH)}_2\text{C(OH)}_2\text{CH(ONO}_2\text{)CH(OH)(OO}\cdot\text{)} +$ $0.062 \text{CH}_2(\text{OH})\text{C(ONO}_2\text{)(OO}\cdot\text{)C(OH)}_2\text{CH(OH)}_2 +$ $0.076 \text{CH}_2(\text{OH})\text{CH(ONO}_2\text{)C(OH)}_2\text{C(OH)}_2(\text{OO}\cdot\text{)} +$ $0.051 \text{CH(OH)}_2\text{C(OH)}_2\text{CH(ONO}_2\text{)CH}_2(\text{O}\cdot\text{)} +$ $0.210 \text{CH}_2(\text{OH})\text{CH(ONO}_2\text{)C(OH)(O}\cdot\text{)CH(OH)}_2 +$ $0.212 \text{CH}_2(\text{OH})\text{CH(ONO}_2\text{)C(OH)}_2\text{CH(OH)(O}\cdot\text{)} + \text{H}_2\text{O} - 0.527 \text{O}_2$	$1.7 \cdot 10^{+09}$		
R <sub>o</sub> 05976			$\text{CH}_2(\text{OH})\text{CH(ONO}_2\text{)C(OH)}_2\text{CH(OH)}_2 + \text{NO}_3 \rightarrow$ $0.389 \text{CH(OH)}_2\text{C(OH)}_2\text{CH(ONO}_2\text{)CH(OH)(OO}\cdot\text{)} +$ $0.062 \text{CH}_2(\text{OH})\text{C(ONO}_2\text{)(OO}\cdot\text{)C(OH)}_2\text{CH(OH)}_2 +$ $0.076 \text{CH}_2(\text{OH})\text{CH(ONO}_2\text{)C(OH)}_2\text{C(OH)}_2(\text{OO}\cdot\text{)} +$ $0.051 \text{CH(OH)}_2\text{C(OH)}_2\text{CH(ONO}_2\text{)CH}_2(\text{O}\cdot\text{)} +$ $0.210 \text{CH}_2(\text{OH})\text{CH(ONO}_2\text{)C(OH)(O}\cdot\text{)CH(OH)}_2 +$ $0.212 \text{CH}_2(\text{OH})\text{CH(ONO}_2\text{)C(OH)}_2\text{CH(OH)(O}\cdot\text{)} + \text{NO}_3^- + \text{H}^+ - 0.527 \text{O}_2$	$1.0 \cdot 10^{+07}$		
R <sub>o</sub> 05977			$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(ONO}_2\text{)CH(OH)(OO}\cdot\text{)} \rightarrow$ $\text{CH(OH)}_2\text{C(OH)}_2\text{CH(ONO}_2\text{)CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 05978			$\text{CH}_2(\text{OH})\text{C(ONO}_2\text{)(OO}\cdot\text{)C(OH)}_2\text{CH(OH)}_2 \xrightarrow{\text{RO}_2}$ $\text{CH}_2(\text{OH})\text{C(ONO}_2\text{)(O}\cdot\text{)C(OH)}_2\text{CH(OH)}_2 + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 05979			$\text{CH}_2(\text{OH})\text{CH(ONO}_2\text{)C(OH)}_2\text{C(OH)}_2(\text{OO}\cdot\text{)} \rightarrow$ $\text{CH}_2(\text{OH})\text{CH(ONO}_2\text{)C(OH)}_2\text{CO(OH)} + \text{HO}_2$	$1.0 \cdot 10^{+03}$		
R <sub>o</sub> 05980			$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(ONO}_2\text{)CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CH(OH)}_2\text{C(OH)}_2\text{CH(ONO}_2\text{)CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 05981			$\text{CH(OH)}_2\text{C(OH)}_2\text{CH(ONO}_2\text{)CH}_2(\text{O}\cdot) \rightarrow$ $\text{CH(OH)}_2\text{C(OH)}_2\text{CH(ONO}_2\text{)(OO}\cdot\text{)} + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05982			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH)(O·)CH(OH) <sub>2</sub> → 0.500 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )(OO·) + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CO(OH) + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05983			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05984			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(O·) → CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05985			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(O·)C(OH) <sub>2</sub> CH(OH) <sub>2</sub> → 0.500 CH <sub>2</sub> (OH)· + 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CO(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05986			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> + OH → 0.188 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO·) + 0.031 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CH(OH) <sub>2</sub> + 0.212 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.056 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.256 CH <sub>2</sub> (OH)C(OH)(O·)CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> + 0.258 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(O·) + H <sub>2</sub> O - 0.430 O <sub>2</sub>	1.5 · 10 <sup>+09</sup>		
R <sub>o</sub> 05987			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.188 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO·) + 0.031 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CH(OH) <sub>2</sub> + 0.212 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.056 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.256 CH <sub>2</sub> (OH)C(OH)(O·)CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> + 0.258 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.430 O <sub>2</sub>	1.1 · 10 <sup>+07</sup>		
R <sub>o</sub> 05988			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO·) → CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 05989			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(OO·)CH(OH) <sub>2</sub> $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O·)CH(OH) <sub>2</sub> + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 05990			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05991			$\text{CH(OH)}_2\text{CH(ONO}_2\text{)C(OH)}_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2}$	$5.0 \cdot 10^{+06}$		
			$\text{CH(OH)}_2\text{CH(ONO}_2\text{)C(OH)}_2\text{CHO} + \text{HO}_2$			
R <sub>o</sub> 05992			$\text{CH(OH)}_2\text{CH(ONO}_2\text{)C(OH)}_2\text{CH}_2(\text{O}\cdot) \rightarrow$	$5.0 \cdot 10^{+02}$		
			$\text{CH(OH)}_2\text{CH(ONO}_2\text{)C(OH)}_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$			
R <sub>o</sub> 05993			$\text{CH}_2(\text{OH})\text{C(OH)}(\text{O}\cdot)\text{CH(ONO}_2\text{)CH(OH)}_2 \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \text{CH}_2(\text{OH})\cdot + 0.500 \text{CH(OH)}_2\text{CH(ONO}_2\text{)CO(OH)} +$			
			$0.500 \text{CH}_2(\text{OH})\text{CO(OH)} + 0.500 \text{CH(OH)}_2\text{CH(ONO}_2\text{)(OO}\cdot) - 0.500 \text{O}_2$			
R <sub>o</sub> 05994			$\text{CH}_2(\text{OH})\text{C(OH)}_2\text{CH(ONO}_2\text{)CH(OH)}(\text{O}\cdot) \xrightarrow{\text{O}_2}$	$5.0 \cdot 10^{+06}$		
			$\text{CH}_2(\text{OH})\text{C(OH)}_2\text{CH(ONO}_2\text{)CO(OH)} + \text{HO}_2$			
R <sub>o</sub> 05995			$\text{CH}_2(\text{OH})\text{C(OH)}_2\text{CH(ONO}_2\text{)CH(OH)}(\text{O}\cdot) \rightarrow$	$5.0 \cdot 10^{+02}$		
			$\text{CH}_2(\text{OH})\text{C(OH)}_2\text{CH(ONO}_2\text{)(OO}\cdot) + \text{CHO(OH)} - \text{O}_2$			
R <sub>o</sub> 05996			$\text{CH}_2(\text{OH})\text{C(OH)}_2\text{C(ONO}_2\text{)(O}\cdot)\text{CH(OH)}_2 \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \text{CH}_2(\text{OH})\text{C(OH)}_2(\text{OO}\cdot) + 0.500 \text{CH(OH)}_2\text{CO(ONO}_2) +$			
			$0.500 \text{CH}_2(\text{OH})\text{C(OH)}_2\text{CO(ONO}_2) + 0.500 \text{CH}\cdot(\text{OH})_2 - 0.500 \text{O}_2$			
R <sub>o</sub> 05997			$\text{CH}_2(\text{OH})\text{CH(OH)CH(ONO}_2\text{)CH(OH)}_2 + \text{OH} \rightarrow$	$2.0 \cdot 10^{+09}$		
			$0.355 \text{CH(OH)}_2\text{CH(ONO}_2\text{)CH(OH)CH(OH)(OO}\cdot) +$			
			$0.137 \text{CH}_2(\text{OH})\text{C(OH)}(\text{OO}\cdot)\text{CH(ONO}_2\text{)CH(OH)}_2 +$			
			$0.058 \text{CH}_2(\text{OH})\text{CH(OH)C(ONO}_2\text{)(OO}\cdot)\text{CH(OH)}_2 +$			
			$0.167 \text{CH}_2(\text{OH})\text{CH(OH)CH(ONO}_2\text{)C(OH)}_2(\text{OO}\cdot) +$			
			$0.045 \text{CH(OH)}_2\text{CH(ONO}_2\text{)CH(OH)CH}_2(\text{O}\cdot) +$			
			$0.045 \text{CH}_2(\text{OH})\text{CH(O}\cdot)\text{CH(ONO}_2\text{)CH(OH)}_2 +$			
			$0.194 \text{CH}_2(\text{OH})\text{CH(OH)CH(ONO}_2\text{)CH(OH)}(\text{O}\cdot) + \text{H}_2\text{O} - 0.717 \text{O}_2$			
R <sub>o</sub> 05998			$\text{CH}_2(\text{OH})\text{CH(OH)CH(ONO}_2\text{)CH(OH)}_2 + \text{NO}_3 \rightarrow$	$1.3 \cdot 10^{+07}$		
			$0.355 \text{CH(OH)}_2\text{CH(ONO}_2\text{)CH(OH)CH(OH)(OO}\cdot) +$			
			$0.137 \text{CH}_2(\text{OH})\text{C(OH)}(\text{OO}\cdot)\text{CH(ONO}_2\text{)CH(OH)}_2 +$			
			$0.058 \text{CH}_2(\text{OH})\text{CH(OH)C(ONO}_2\text{)(OO}\cdot)\text{CH(OH)}_2 +$			
			$0.167 \text{CH}_2(\text{OH})\text{CH(OH)CH(ONO}_2\text{)C(OH)}_2(\text{OO}\cdot) +$			
			$0.045 \text{CH(OH)}_2\text{CH(ONO}_2\text{)CH(OH)CH}_2(\text{O}\cdot) +$			
			$0.045 \text{CH}_2(\text{OH})\text{CH(O}\cdot)\text{CH(ONO}_2\text{)CH(OH)}_2 +$			
			$0.194 \text{CH}_2(\text{OH})\text{CH(OH)CH(ONO}_2\text{)CH(OH)}(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.717 \text{O}_2$			

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 05999			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CH(OH)(OO·) → CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06000			CH <sub>2</sub> (OH)C(OH)(OO·)CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> → CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06001			CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(OO·)CH(OH) <sub>2</sub> $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(O·)CH(OH) <sub>2</sub> + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 06002			CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 06003			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 06004			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) → CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06005			CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 06006			CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CH(OH)(O·) → CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06007			CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(O·)CH(OH) <sub>2</sub> → 0.500 CH <sub>2</sub> (OH)CH(OH)(OO·) + 0.500 CH(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CH(OH)CO(ONO <sub>2</sub> ) + 0.500 CH·(OH) <sub>2</sub> – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06008			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CH(OH) <sub>2</sub> + OH → 0.356 CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CH(OH)(OO·) + 0.137 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)CH(OH)CH(OH) <sub>2</sub> + 0.058 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH)(OO·)CH(OH) <sub>2</sub> + 0.167 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> (OO·) + 0.045 CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) + 0.043 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(O·)CH(OH) <sub>2</sub> + 0.194 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CH(OH)(O·) + H <sub>2</sub> O – 0.719 O <sub>2</sub>	2.0 · 10 <sup>+09</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 06009			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.356 CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CH(OH)(OO·) + 0.137 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)CH(OH)CH(OH) <sub>2</sub> + 0.058 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH)(OO·)CH(OH) <sub>2</sub> + 0.167 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> (OO·) + 0.045 CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) + 0.043 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(O·)CH(OH) <sub>2</sub> + 0.194 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.719 O <sub>2</sub>	1.3 · 10 <sup>+07</sup>		
R <sub>o</sub> 06010			CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CH(OH)(OO·) → CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06011			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)CH(OH)CH(OH) <sub>2</sub> $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(O·)CH(OH)CH(OH) <sub>2</sub> + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 06012			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH)(OO·)CH(OH) <sub>2</sub> → CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCH(OH) <sub>2</sub> + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06013			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)C(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 06014			CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 06015			CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) → CH(OH) <sub>2</sub> CH(OH)CH(ONO <sub>2</sub> )(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06016			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 06017			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CH(OH)(O·) → CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06018			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(O·)CH(OH)CH(OH) <sub>2</sub> → 0.500 CH <sub>2</sub> (OH)· + 0.500 CH(OH) <sub>2</sub> CH(OH)CO(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CO(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> CH(OH)(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 06019			CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> + OH → 0.285 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCH(OH)(OO·) + 0.046 CH <sub>2</sub> (OH)COC(ONO <sub>2</sub> )(OO·)CH(OH) <sub>2</sub> + 0.255 CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.068 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCH <sub>2</sub> (O·) + 0.345 CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CH(OH)(O·) + H <sub>2</sub> O - 0.587 O <sub>2</sub>	1.1 · 10 <sup>+09</sup>		
R <sub>o</sub> 06020			CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.285 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCH(OH)(OO·) + 0.046 CH <sub>2</sub> (OH)COC(ONO <sub>2</sub> )(OO·)CH(OH) <sub>2</sub> + 0.255 CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.068 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCH <sub>2</sub> (O·) + 0.345 CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CH(OH)(O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.587 O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 06021			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCH(OH)(OO·) → CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06022			CH <sub>2</sub> (OH)COC(ONO <sub>2</sub> )(OO·)CH(OH) <sub>2</sub> $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)COC(ONO <sub>2</sub> )(O·)CH(OH) <sub>2</sub> + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 06023			CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 06024			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 06025			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )COCH <sub>2</sub> (O·) → CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06026			CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 06027			CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CH(OH)(O·) → CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06028			CH <sub>2</sub> (OH)COC(ONO <sub>2</sub> )(O·)CH(OH) <sub>2</sub> → 0.500 CH <sub>2</sub> (OH)CO(OO·) + 0.500 CH(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)COCO(ONO <sub>2</sub> ) + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00746			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCH(OH) <sub>2</sub> $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	4.7 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 06029			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCH(OH) <sub>2</sub> + OH → 0.467 CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CH(OH)(OO·) + 0.095 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)COCH(OH) <sub>2</sub> + 0.115 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + 0.068 CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) + 0.254 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCH(OH)(O·) + H <sub>2</sub> O – 0.677 O <sub>2</sub>	1.3 · 10 <sup>+09</sup>		
R <sub>o</sub> 06030			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCH(OH) <sub>2</sub> + NO <sub>3</sub> → 0.467 CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CH(OH)(OO·) + 0.095 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)COCH(OH) <sub>2</sub> + 0.115 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) + 0.068 CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) + 0.254 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCH(OH)(O·) + NO <sub>3</sub> <sup>–</sup> + H <sup>+</sup> – 0.677 O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 06031			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CH(OH)(OO·) → CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06032			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)COCH(OH) <sub>2</sub> $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(O·)COCH(OH) <sub>2</sub> + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 06033			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COC(OH) <sub>2</sub> (OO·) → CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCO(OH) + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 06034			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 06035			CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) → CH(OH) <sub>2</sub> COCH(ONO <sub>2</sub> )(OO·) + CH <sub>2</sub> O – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06036			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCH(OH)(O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCO(OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 06037			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )COCH(OH)(O·) → CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CO(OO·) + CHO(OH) – O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06038			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(O·)COCH(OH) <sub>2</sub> → 0.500 CH <sub>2</sub> (OH)· + 0.500 CH(OH) <sub>2</sub> COCO(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)CO(ONO <sub>2</sub> ) + 0.500 CH(OH) <sub>2</sub> CO(OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00747			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub>	9.4 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 06039			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO → 0.500 + 0.500	1.0 · 10 <sup>–01</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 06040			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + OH → 0.227 CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.274 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) + 0.276 CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(O·) + 0.224 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH)(O·)CHO + H <sub>2</sub> O - 0.500 O <sub>2</sub>	1.4 · 10 <sup>+09</sup>		
R <sub>o</sub> 06041			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + NO <sub>3</sub> → 0.227 CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + 0.274 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) + 0.276 CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(O·) + 0.224 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH)(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.500 O <sub>2</sub>	7.9 · 10 <sup>+06</sup>		
R <sub>o</sub> 06042			CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) → CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 06043			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) → CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 06044			CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 06045			CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(O·) → CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06046			CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )C(OH)(O·)CHO → 0.500 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + 0.500 CO(OH)CHO + 0.500 CH(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH) + 0.500 CH · (OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00748			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub>	9.4 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 06047			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO → 0.500 + 0.500 + 0.500	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 06048			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + OH → 0.074 CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.515 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OO·) + 0.206 CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(O·) + 0.205 CH(OH) <sub>2</sub> C(OH)(O·)CH(ONO <sub>2</sub> )CHO + H <sub>2</sub> O - 0.589 O <sub>2</sub>	1.8 · 10 <sup>+09</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 06049			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + NO <sub>3</sub> → 0.074 CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) + 0.515 CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OO·) + 0.206 CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(O·) + 0.205 CH(OH) <sub>2</sub> C(OH)(O·)CH(ONO <sub>2</sub> )CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.589 O <sub>2</sub>	8.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 06050			CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> C(OH) <sub>2</sub> (OO·) → CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 06051			CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OO·) → CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 06052			CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(O·) $\xrightarrow{O_2}$ CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 06053			CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(O·) → CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + CHO(OH) - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06054			CH(OH) <sub>2</sub> C(OH)(O·)CH(ONO <sub>2</sub> )CHO → 0.500 CH · (OH) <sub>2</sub> + 0.500 CO(OH)CH(ONO <sub>2</sub> )CHO + 0.500 CH(OH) <sub>2</sub> CO(OH) + 0.500 CHOCH(ONO <sub>2</sub> )(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06055	*	*	CH <sub>2</sub> (OH)CH=CHCH <sub>2</sub> (OH) + OH → 0.115 CH <sub>2</sub> (OH)CH=CHCH(OH)(OO·) + 0.885 CH <sub>2</sub> (OH)CH(OH)CH(OO·)CH <sub>2</sub> (OH) + 0.115 H <sub>2</sub> O - O <sub>2</sub>	1.0 · 10 <sup>+10</sup>		
R <sub>o</sub> 06056			CH <sub>2</sub> (OH)CH=CHCH <sub>2</sub> (OH) + NO <sub>3</sub> → 0.115 CH <sub>2</sub> (OH)CH=CHCH(OH)(OO·) + 0.885 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OO·)CH <sub>2</sub> (OH) + 0.115 NO <sub>3</sub> <sup>-</sup> + 0.115 H <sup>+</sup> - O <sub>2</sub>	1.0 · 10 <sup>+07</sup>		
R <sub>o</sub> 06057	*	*	CH <sub>2</sub> (OH)CH=CHCH(OH)(OO·) → CH <sub>2</sub> (OH)CH=CHCHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06058			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OO·)CH <sub>2</sub> (OH) $\xrightarrow{RO_2}$ 0.200 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(O·)CH <sub>2</sub> (OH) + 0.550 CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CH <sub>2</sub> (OH) + 0.250 CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CH <sub>2</sub> (OH) + 0.350 O <sub>2</sub> + 0.150 H <sub>2</sub> O <sub>2</sub>	7.3 · 10 <sup>+08</sup>		
R <sub>o</sub> 06059			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(O·)CH <sub>2</sub> (OH) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CH <sub>2</sub> (OH) + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 06060			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(O·)CH <sub>2</sub> (OH) → 0.500 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )(OO·) + 0.500 CH <sub>2</sub> (OH)CHO + 0.500 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CHO + 0.500 CH <sub>2</sub> (OH)· - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06061			CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CH <sub>2</sub> (OH) + OH → 0.314 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CH(OH)(OO·) + 0.127 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH)(OO·)CH <sub>2</sub> (OH) + 0.127 CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(OO·)CH <sub>2</sub> (OH) + 0.314 CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CH(OH)(OO·) + 0.039 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) + 0.040 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(O·)CH <sub>2</sub> (OH) + 0.039 CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) + H <sub>2</sub> O - 0.882 O <sub>2</sub>	2.2 · 10 <sup>+09</sup>		
R <sub>o</sub> 06062			CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CH <sub>2</sub> (OH) + NO <sub>3</sub> → 0.314 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CH(OH)(OO·) + 0.127 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH)(OO·)CH <sub>2</sub> (OH) + 0.127 CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(OO·)CH <sub>2</sub> (OH) + 0.314 CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CH(OH)(OO·) + 0.039 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) + 0.040 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(O·)CH <sub>2</sub> (OH) + 0.039 CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.882 O <sub>2</sub>	2.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 06063			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CH(OH)(OO·) → CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06064			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH)(OO·)CH <sub>2</sub> (OH) → CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CH <sub>2</sub> (OH) + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06065			CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(OO·)CH <sub>2</sub> (OH) $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)CH(OH)C(ONO <sub>2</sub> )(O·)CH <sub>2</sub> (OH) + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 06066			CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CH(OH)(OO·) → CH <sub>2</sub> (OH)CH(OH)CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06067			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 06068			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)CH <sub>2</sub> (O·) → CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CH(OH)(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0α	β	γ	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 06069			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2}$	$5.0 \cdot 10^{+06}$		
			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CHO} + \text{HO}_2$			
R <sub>o</sub> 06070			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}_2(\text{O}\cdot) \rightarrow$	$5.0 \cdot 10^{+02}$		
			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$			
R <sub>o</sub> 06071			$\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{CH}_2(\text{OH}) \rightarrow$	$5.0 \cdot 10^{+02}$		
			$0.500 \text{CH}_2(\text{OH})\text{CH}(\text{OH})(\text{OO}\cdot) + 0.500 \text{CH}_2(\text{OH})\text{CO}(\text{ONO}_2) +$			
			$0.500 \text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CO}(\text{ONO}_2) + 0.500 \text{CH}_2(\text{OH})\cdot - 0.500 \text{O}_2$			
E <sub>o</sub> 00749			$\text{CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)\text{CH}_2(\text{OH}) \xrightleftharpoons{\text{H}_2\text{O}}$	$2.7 \cdot 10^{+00}$		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
			$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CH}_2(\text{OH})$			
R <sub>o</sub> 06072			$\text{CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)\text{CH}_2(\text{OH}) + \text{OH} \rightarrow$	$1.2 \cdot 10^{+09}$		
			$0.262 \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{COCH}(\text{OH})(\text{OO}\cdot) +$			
			$0.106 \text{CH}_2(\text{OH})\text{COC}(\text{ONO}_2)(\text{OO}\cdot)\text{CH}_2(\text{OH}) +$			
			$0.498 \text{CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}\cdot) +$			
			$0.062 \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{COCH}_2(\text{O}\cdot) +$			
			$0.073 \text{CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)\text{CH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.865 \text{O}_2$			
R <sub>o</sub> 06073			$\text{CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)\text{CH}_2(\text{OH}) + \text{NO}_3 \rightarrow$	$1.6 \cdot 10^{+06}$		
			$0.262 \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{COCH}(\text{OH})(\text{OO}\cdot) +$			
			$0.106 \text{CH}_2(\text{OH})\text{COC}(\text{ONO}_2)(\text{OO}\cdot)\text{CH}_2(\text{OH}) +$			
			$0.498 \text{CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}\cdot) +$			
			$0.062 \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{COCH}_2(\text{O}\cdot) +$			
			$0.073 \text{CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)\text{CH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.865 \text{O}_2$			
R <sub>o</sub> 06074			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{COCH}(\text{OH})(\text{OO}\cdot) \rightarrow$	$2.0 \cdot 10^{+02}$		
			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{COCHO} + \text{HO}_2$			
R <sub>o</sub> 06075			$\text{CH}_2(\text{OH})\text{COC}(\text{ONO}_2)(\text{OO}\cdot)\text{CH}_2(\text{OH}) \xrightarrow{\text{RO}_2}$	$1.0 \cdot 10^{+06}$		
			$\text{CH}_2(\text{OH})\text{COC}(\text{ONO}_2)(\text{O}\cdot)\text{CH}_2(\text{OH}) + 0.500 \text{O}_2$			
R <sub>o</sub> 06076			$\text{CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow$	$2.0 \cdot 10^{+02}$		
			$\text{CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)\text{CHO} + \text{HO}_2$			
R <sub>o</sub> 06077			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{COCH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{COCHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 06078			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{COCH}_2(\text{O}\cdot) \rightarrow$	$5.0 \cdot 10^{+02}$		
			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{CO}(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$			

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 06079			$\text{CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2} \text{CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 06080			$\text{CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{COCH}(\text{ONO}_2)(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 06081			$\text{CH}_2(\text{OH})\text{COC}(\text{ONO}_2)(\text{O}\cdot)\text{CH}_2(\text{OH}) \rightarrow$ $0.500 \text{CH}_2(\text{OH})\text{CO}(\text{OO}\cdot) + 0.500 \text{CH}_2(\text{OH})\text{CO}(\text{ONO}_2) +$ $0.500 \text{CH}_2(\text{OH})\text{COCO}(\text{ONO}_2) + 0.500 \text{CH}_2(\text{OH})\cdot - 0.500 \text{O}_2$	$5.0 \cdot 10^{+02}$		
R <sub>o</sub> 06082			$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CH}_2(\text{OH}) + \text{OH} \rightarrow$ $0.173 \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.070 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CH}_2(\text{OH}) +$ $0.415 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.052 \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) +$ $0.235 \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})(\text{O}\cdot)\text{CH}_2(\text{OH}) +$ $0.055 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CH}_2(\text{O}\cdot) + \text{H}_2\text{O} - 0.658 \text{O}_2$	$1.6 \cdot 10^{+09}$		
R <sub>o</sub> 06083			$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CH}_2(\text{OH}) + \text{NO}_3 \rightarrow$ $0.173 \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.070 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CH}_2(\text{OH}) +$ $0.415 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}\cdot) +$ $0.052 \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) +$ $0.235 \text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})(\text{O}\cdot)\text{CH}_2(\text{OH}) +$ $0.055 \text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CH}_2(\text{O}\cdot) + \text{NO}_3^- + \text{H}^+ - 0.658 \text{O}_2$	$1.1 \cdot 10^{+07}$		
R <sub>o</sub> 06084			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 06085			$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{OO}\cdot)\text{CH}_2(\text{OH}) \xrightarrow{\text{RO}_2}$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{C}(\text{ONO}_2)(\text{O}\cdot)\text{CH}_2(\text{OH}) + 0.500 \text{O}_2$	$1.0 \cdot 10^{+06}$		
R <sub>o</sub> 06086			$\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CH}(\text{OH})(\text{OO}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{C}(\text{OH})_2\text{CH}(\text{ONO}_2)\text{CHO} + \text{HO}_2$	$2.0 \cdot 10^{+02}$		
R <sub>o</sub> 06087			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \xrightarrow{\text{O}_2}$ $\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CHO} + \text{HO}_2$	$5.0 \cdot 10^{+06}$		
R <sub>o</sub> 06088			$\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2\text{CH}_2(\text{O}\cdot) \rightarrow$ $\text{CH}_2(\text{OH})\text{CH}(\text{ONO}_2)\text{C}(\text{OH})_2(\text{OO}\cdot) + \text{CH}_2\text{O} - \text{O}_2$	$5.0 \cdot 10^{+02}$		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 06089			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH)(O·)CH <sub>2</sub> (OH) → 0.500 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )(OO·) + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CO(OH) + 0.500 CH <sub>2</sub> (OH)· - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06090			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 06091			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06092			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> C(ONO <sub>2</sub> )(O·)CH <sub>2</sub> (OH) → 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> (OO·) + 0.500 CH <sub>2</sub> (OH)CO(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CO(ONO <sub>2</sub> ) + 0.500 CH <sub>2</sub> (OH)· - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00750			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)COCH(ONO <sub>2</sub> )CH(OH) <sub>2</sub>	1.2 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
E <sub>o</sub> 00751			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub>	7.9 · 10 <sup>+02</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 06093			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + OH → 0.168 CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO·) + 0.552 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OO·) + 0.051 CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.229 CH <sub>2</sub> (OH)C(OH)(O·)CH(ONO <sub>2</sub> )CHO + H <sub>2</sub> O - 0.720 O <sub>2</sub>	1.6 · 10 <sup>+09</sup>		
R <sub>o</sub> 06094			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + NO <sub>3</sub> → 0.168 CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO·) + 0.552 CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OO·) + 0.051 CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O·) + 0.229 CH <sub>2</sub> (OH)C(OH)(O·)CH(ONO <sub>2</sub> )CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.720 O <sub>2</sub>	8.8 · 10 <sup>+06</sup>		
R <sub>o</sub> 06095			CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH)(OO·) → CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06096			CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OO·) → CH <sub>2</sub> (OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 06097			CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 06098			CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH <sub>2</sub> (O·) → CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> (OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		

**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 06099			CH <sub>2</sub> (OH)C(OH)(O·)CH(ONO <sub>2</sub> )CHO → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(OH)CH(ONO <sub>2</sub> )CHO + 0.500 CH <sub>2</sub> (OH)CO(OH) + 0.500 CHOCH(ONO <sub>2</sub> )(OO·) - 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00752			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO $\xrightleftharpoons{H_2O}$ CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CH(OH) <sub>2</sub>	4.7 · 10 <sup>+01</sup>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 06100			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + OH → 0.435 CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(OO·) + 0.060 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)C(OH) <sub>2</sub> CHO + 0.247 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) + 0.057 CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) + 0.202 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH)(O·)CHO + H <sub>2</sub> O - 0.741 O <sub>2</sub>	1.5 · 10 <sup>+09</sup>		
R <sub>o</sub> 06101			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + NO <sub>3</sub> → 0.435 CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(OO·) + 0.060 CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)C(OH) <sub>2</sub> CHO + 0.247 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) + 0.057 CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) + 0.202 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH)(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> - 0.741 O <sub>2</sub>	8.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 06102			CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH)(OO·) → CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	2.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06103			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(OO·)C(OH) <sub>2</sub> CHO $\xrightarrow{RO_2}$ CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(O·)C(OH) <sub>2</sub> CHO + 0.500 O <sub>2</sub>	1.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 06104			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) → CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OH) + HO <sub>2</sub> - H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 06105			CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) $\xrightarrow{O_2}$ CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub>	5.0 · 10 <sup>+06</sup>		
R <sub>o</sub> 06106			CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH <sub>2</sub> (O·) → CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )(OO·) + CH <sub>2</sub> O - O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
R <sub>o</sub> 06107			CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )C(OH)(O·)CHO → 0.500 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )(OO·) + 0.500 CO(OH)CHO + 0.500 CH <sub>2</sub> (OH)CH(ONO <sub>2</sub> )CO(OH) + 0.500 CH·(OH) <sub>2</sub> - 0.500 O <sub>2</sub> - 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		



**Table G.14 (continued)** Aqueous phase processes in CAPRAM 4.0

C4.0 $\alpha$	$\beta$	$\gamma$	Process	$k_{298} / K^a$	$E_A / R^b$	Reference/comment
R <sub>o</sub> 06108			CH <sub>2</sub> (OH)C(ONO <sub>2</sub> )(O·)C(OH) <sub>2</sub> CHO → 0.500 CH <sub>2</sub> (OH)· + 0.500 CO(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + 0.500 CH <sub>2</sub> (OH)CO(ONO <sub>2</sub> ) + 0.500 CHOC(OH) <sub>2</sub> (OO·) – 0.500 O <sub>2</sub>	5.0 · 10 <sup>+02</sup>		
E <sub>o</sub> 00753			CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO $\xrightleftharpoons{H_2O}$ CH(OH) <sub>2</sub> C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CH(OH) <sub>2</sub>	<i>9.4 · 10<sup>+01</sup></i>		$k_b = 5.69 \cdot 10^{-3} \text{ s}^{-1}$ estimated
R <sub>o</sub> 06109			CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO → 0.500 + 0.500	1.0 · 10 <sup>-01</sup>		
R <sub>o</sub> 06110			CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + OH → 0.237 CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) + 0.569 CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OO·) + 0.194 CHOCH(ONO <sub>2</sub> )C(OH)(O·)CHO + H <sub>2</sub> O – 0.806 O <sub>2</sub>	1.6 · 10 <sup>+09</sup>		
R <sub>o</sub> 06111			CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + NO <sub>3</sub> → 0.237 CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) + 0.569 CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OO·) + 0.194 CHOCH(ONO <sub>2</sub> )C(OH)(O·)CHO + NO <sub>3</sub> <sup>-</sup> + H <sup>+</sup> – 0.806 O <sub>2</sub>	6.6 · 10 <sup>+06</sup>		
R <sub>o</sub> 06112			CHOCH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CO(OO·) → CO(OH)C(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CHO + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 06113			CHOC(OH) <sub>2</sub> CH(ONO <sub>2</sub> )CO(OO·) → CO(OH)CH(ONO <sub>2</sub> )C(OH) <sub>2</sub> CHO + HO <sub>2</sub> – H <sub>2</sub> O	1.0 · 10 <sup>+03</sup>		
R <sub>o</sub> 06114			CHOCH(ONO <sub>2</sub> )C(OH)(O·)CHO → 0.500 CHOCH(ONO <sub>2</sub> )(OO·) + 0.500 CO(OH)CHO + 0.500 CO(OH)CH(ONO <sub>2</sub> )CHO + 0.500 CH·(OH) <sub>2</sub> – 0.500 O <sub>2</sub> – 0.500 H <sub>2</sub> O	5.0 · 10 <sup>+02</sup>		

<sup>a</sup> $k_{298}$  is given for non-reversible reactions (labelled with R<sub>o</sub>XXXX in the first column) in M<sup>1-n</sup>s<sup>-1</sup>,  $K$  is given for equilibria (labelled with E<sub>o</sub>XXXX in the first column) in M<sup>m-n</sup> with n being the order of the forward reaction and m the order of the backward reaction. For more convenience,  $K$  values are printed italic.

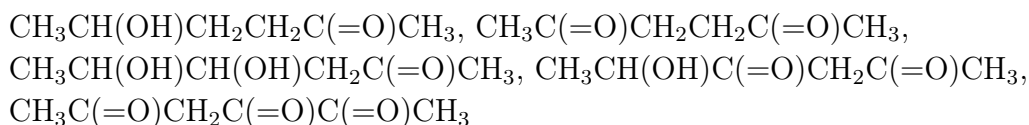
<sup>b</sup>in K



# H Detailed information about the model validation with chamber experiments

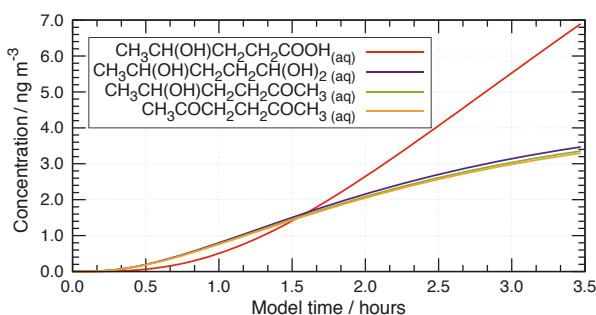
## H.1 Additional information about the initialisation of the hexane oxidation experiment

The following compounds have been used as input in the primary stack of GECKO-A for the mechanism generation:

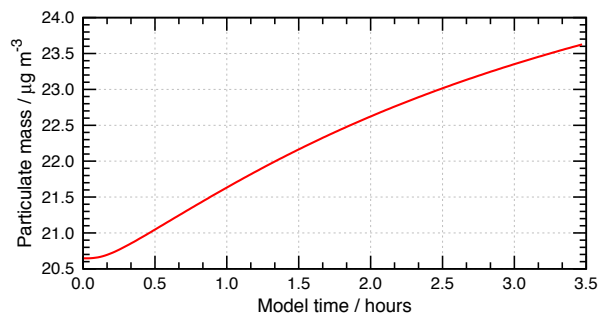


## H.2 Additional model results from the hexane oxidation experiment

(a) Selected aqueous phase compounds



(b) Particulate mass



**Figure H.1** Modelled concentration-time profiles of selected aqueous phase compounds (a) and overall particulate mass (b) in the model run simulating the hexane oxidation experiment.

### H.3 Additional information about the sensitivity runs used in the trimethylbenzene oxidation experiment

Two additional scenarios have been created to validate the generator against the experimental results from the chamber LEAK. In a first sensitivity run labelled ‘UPT’, the effective uptake of TMB oxidation products, which are formed prior to methylglyoxal (MGLY) in the oxidation chain, was implemented in the mechanism. No further oxidation of these compounds has been treated in the aqueous phase and aqueous phase concentrations are solely dependent on the Henry’s Law equilibrium. Where possible, the Henry’s Law constants (HLCs) were generated with the GECKO-A routine GROMHE (*Raventos-Duran et al.*, 2010). However, for several species an estimation with GROMHE was not possible, due to missing increments. For these compounds, the HLC has been estimated with the HENRYWIN programme part of the EPI Suite 4.1 by the US Environmental Protection Agency (*Meylan and Howard*, 2000). These compounds are indicated by footnote (c) in Table H.1.

To account for reactive uptake, another sensitivity study (‘RXN’) was introduced in which the first reaction step of each of the aqueous phase compound from the UPT scenario has been implemented. Only hydroxyl radical reactions are considered and all first generation oxidation products directly contribute to the water-soluble organic content (WSOC). Thus, all reaction products of these compounds are assumed to stay in the aqueous phase. For poly-carbonyls, the monomolecular decay as described in section 5.1 has additionally been implemented in the RXN scenario. The resulting fragments are treated explicitly as they were already part of the original TMB scenario.

Moreover, uptake was modified in the sensitivity run RXN. In contrast to the scenario UPT, the physical Henry’s Law constants have been implemented and hydrations and dissociations are treated explicitly. The radical decay and the monomolecular decay of polycarbonyls is treated for all hydration and dissociation forms. For the generation of the reactions including products and kinetic data, the generator GECKO-A has been used except for a few complicated structures, such as epoxides, where missing increments of the reaction products prevented the use of the generator. For these compounds, reaction rates have been calculated manually applying the same rules as in the GECKO-A protocol.

Moreover, the generator could not be used to generate the hydrations for epoxides with carbonyl functions as reaction products with unknown increments lead to a programme failure. However, it was possible to generate the hydration constants by using the subroutine GROMHE only. The output of this subroutine, were an overall hydration equilibrium in which all possible hydration forms are combined. For simplicity, this overall equilibrium has been implemented instead of the calculating single equilibria (see Table H.1).

Furthermore, to calculate the effective Henry’s Law constants, GECKO-A considers only the hydration of carbonyl compounds. However, acids may deprotonate affecting the HLC

as well. The solution effects have to be considered for the uptake process as the gas phase is in equilibrium with all aqueous forms of the corresponding species. Thus uptake has to consider the sum of all aqueous form, i.e. for carboxylic acids (see, e.g., *Seinfeld and Pandis*, 2006):

$$[HA]_g = K_h \cdot ([HA] + [A^-]) = K_h[HA] \cdot \left(1 + \frac{K_{diss}}{[H^+]}\right) \quad (H.1)$$

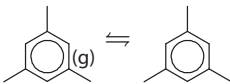
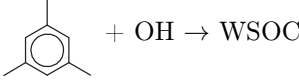
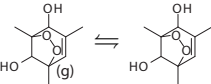
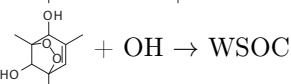
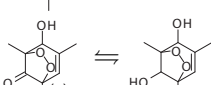
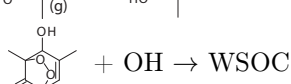
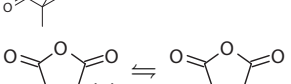
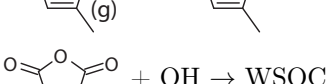
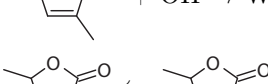
where  $HA$  is a carboxylic acid and  $A^-$  the corresponding anionic form. Square brackets denote concentrations. There resulting effective Henry's Law constant  $K_{h,eff}$  can be calculated as (*Seinfeld and Pandis*, 2006):

$$K_{h,eff} = K_h \cdot \left(1 + \frac{K_{diss}}{[H^+]}\right) \quad (H.2)$$

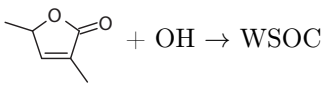
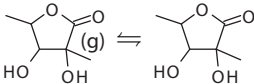
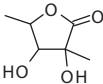
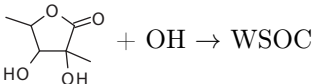
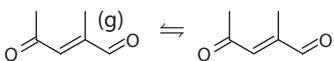
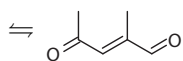
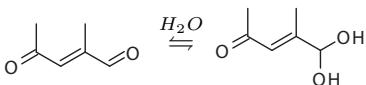
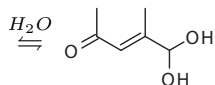
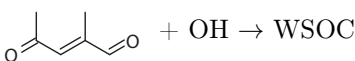
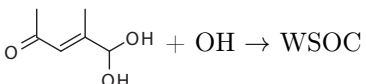
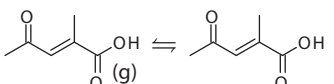
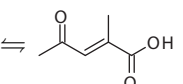
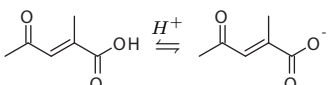
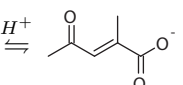
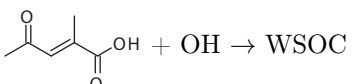
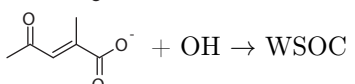
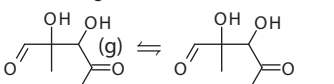
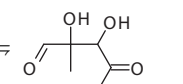
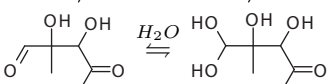
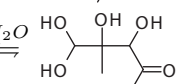
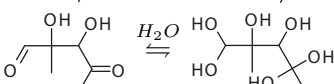
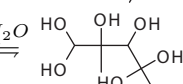
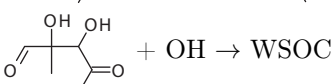
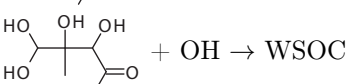
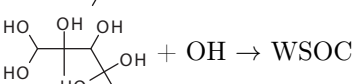
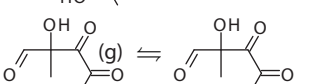
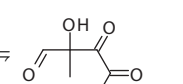
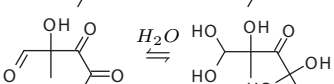
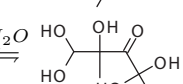
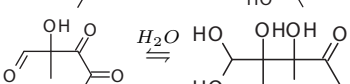
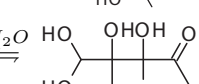
As the generator does not consider dissociations for the calculation of the effective HLCs, these values have been determined manually as indicated in Table H.1. However, at the pH of the chamber experiment, the HLC was affected only in the third digit after the decimal point.

Overall, the base run and the two sensitivity studies compromise between reaction schemes of manageable size and complexity as well as feasibility. A complete aqueous phase oxidation scheme would, to date, not have been possible due to missing descriptions of the degradation of evolving intermediates.

**Table H.1** Additional mechanism used for the sensitivity runs UPT and RXN.

Reaction	UPT <sup>(a)</sup>	RXN <sup>(a)</sup>
	$9.60 \cdot 10^{-2}$	$9.60 \cdot 10^{-2}$
		$6.40 \cdot 10^9^{(b)}$
	$2.34 \cdot 10^5$	$2.34 \cdot 10^5^{(c)}$
		$6.89 \cdot 10^9^{(d)}$
	$5.92 \cdot 10^6$	$5.92 \cdot 10^6^{(c)}$
		$1.19 \cdot 10^{10^{(d)}}$
	$3.81 \cdot 10^1$	$3.81 \cdot 10^1^{(c)}$
		$2.00 \cdot 10^9$
	$1.02 \cdot 10^1$	$1.02 \cdot 10^1^{(c)}$

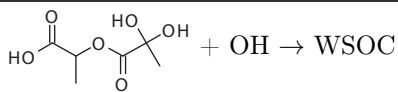
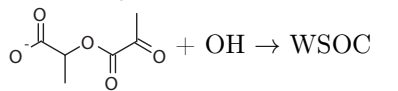
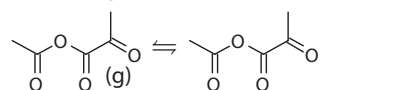
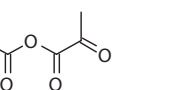
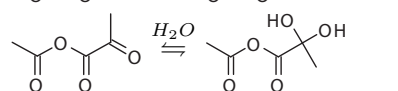
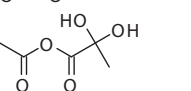
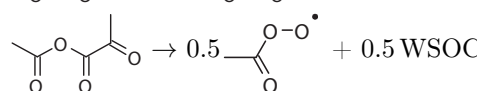
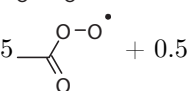
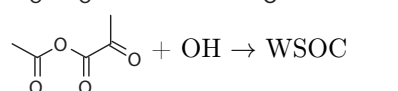
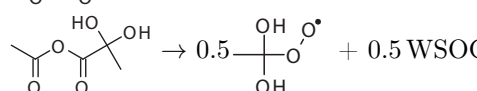
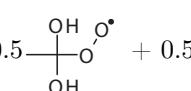
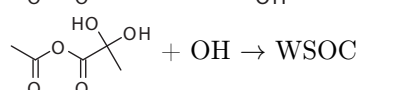
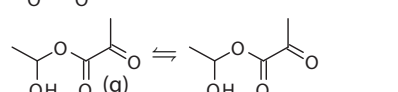
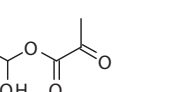
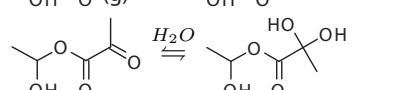
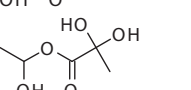
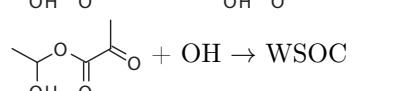
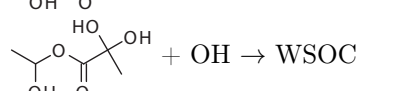
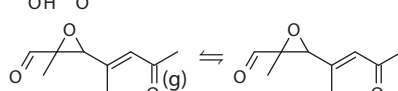
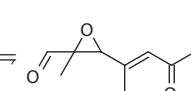
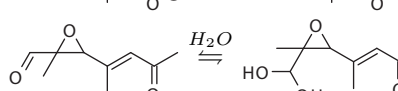
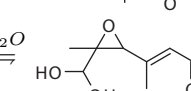
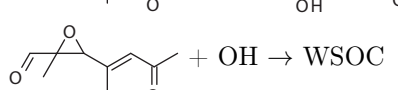
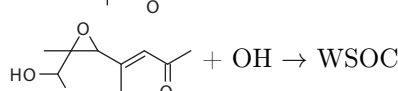
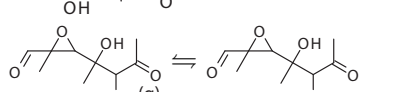
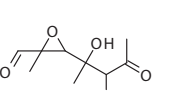
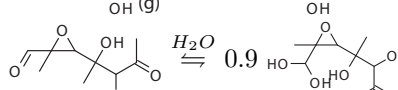
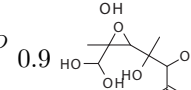
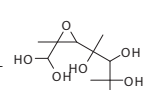
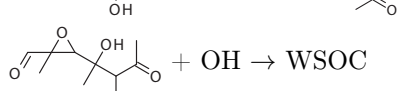
**Table H.1 (continued)** Additional mechanism used for the sensitivity runs UPT and RXN.

Reaction	UPT <sup>(a)</sup>	RXN <sup>(a)</sup>
 + OH → WSOC		1.30 · 10 <sup>9</sup>
 (g) ⇌ 	6.92 · 10 <sup>4</sup>	6.92 · 10 <sup>4</sup>
 + OH → WSOC		2.29 · 10 <sup>9</sup>
 (g) ⇌ 	2.23 · 10 <sup>4</sup>	3.10 · 10 <sup>3</sup>
 ⇌ 		6.20 · 10 <sup>0</sup>
 + OH → WSOC		6.33 · 10 <sup>10</sup>
 + OH → WSOC		1.06 · 10 <sup>11</sup>
 (g) ⇌ 	9.89 · 10 <sup>5(e)</sup>	9.89 · 10 <sup>5</sup>
 ⇌ 		2.32 · 10 <sup>-4</sup>
 + OH → WSOC		2.47 · 10 <sup>10</sup>
 + OH → WSOC		1.06 · 10 <sup>11</sup>
 (g) ⇌ 	6.76 · 10 <sup>5</sup>	1.70 · 10 <sup>4</sup>
 ⇌ 		3.39 · 10 <sup>1</sup>
 ⇌ 		3.15 · 10 <sup>0</sup>
 + OH → WSOC		1.50 · 10 <sup>9</sup>
 + OH → WSOC		1.26 · 10 <sup>9</sup>
 + OH → WSOC		1.64 · 10 <sup>9</sup>
 (g) ⇌ 	7.07 · 10 <sup>7</sup>	1.21 · 10 <sup>4</sup>
 ⇌ 		7.69 · 10 <sup>0</sup>
 ⇌ 		5.42 · 10 <sup>1</sup>

**Table H.1 (continued)** Additional mechanism used for the sensitivity runs UPT and RXN.

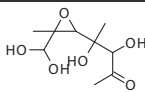
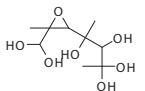
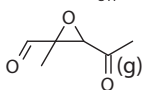
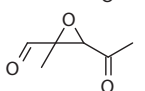
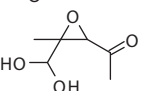
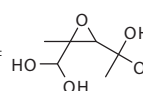
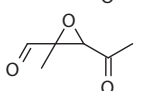
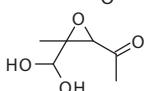
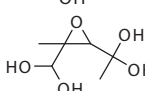
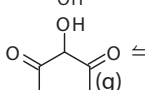
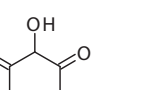

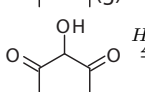
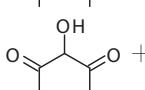
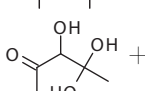
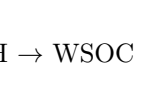

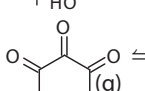
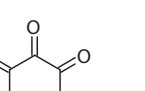

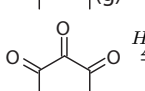
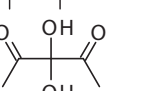

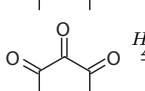
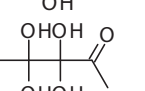

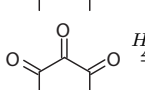
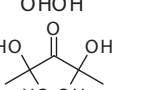

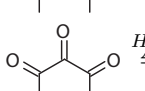
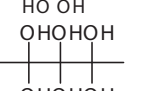

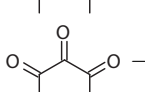
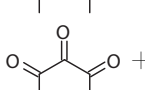
Reaction	UPT <sup>(a)</sup>	RXN <sup>(a)</sup>
$\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(=\text{O})\text{CH}_3 \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(=\text{O})\text{CH}_3$		$3.07 \cdot 10^1$
$\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(=\text{O})\text{CH}_3 \rightarrow 0.5 \text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(=\text{O})\text{O}^\bullet + 0.5 \text{WSOC}$		$1.00 \cdot 10^{-1}$
$\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(=\text{O})\text{CH}_3 + \text{OH} \rightarrow \text{WSOC}$		$1.12 \cdot 10^9$
$\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(=\text{O})\text{CH}_3 \rightarrow 0.5 \text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(=\text{O})\text{O}^\bullet + 0.5 \text{WSOC}$		$1.00 \cdot 10^{-1}$
$\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(=\text{O})\text{CH}_3 + \text{OH} \rightarrow \text{WSOC}$		$1.29 \cdot 10^9$
$\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(=\text{O})\text{CH}_3 \rightarrow 0.5 \text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(=\text{O})\text{O}^\bullet + 0.5 \text{WSOC}$		$1.00 \cdot 10^{-1}$
$\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(=\text{O})\text{CH}_3 + \text{OH} \rightarrow \text{WSOC}$		$1.31 \cdot 10^9$
$\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(=\text{O})\text{CH}_3 \rightarrow 0.5 \text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(=\text{O})\text{O}^\bullet + 0.5 \text{WSOC}$		$1.00 \cdot 10^{-1}$
$\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(=\text{O})\text{CH}_3 + \text{OH} \rightarrow \text{WSOC}$		$1.72 \cdot 10^9$
$\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OCH}_3)\text{C}(=\text{O})\text{CH}_3 \rightleftharpoons \text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OCH}_3)\text{C}(=\text{O})\text{CH}_3 \text{ (g)}$	$4.99 \cdot 10^6$	$6.31 \cdot 10^2$
$\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OCH}_3)\text{C}(=\text{O})\text{CH}_3 \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(=\text{O})\text{CH}_3$		$1.80 \cdot 10^3$
$\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OCH}_3)\text{C}(=\text{O})\text{CH}_3 \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(=\text{O})\text{CH}_3$		$3.02 \cdot 10^3$
$\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OCH}_3)\text{C}(=\text{O})\text{CH}_3 + \text{OH} \rightarrow \text{WSOC}$		$1.31 \cdot 10^9$
$\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OCH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(=\text{O})\text{CH}_3 + \text{OH} \rightarrow \text{WSOC}$		$1.41 \cdot 10^9$
$\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OCH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(=\text{O})\text{CH}_3 + \text{OH} \rightarrow \text{WSOC}$		$1.97 \cdot 10^9$
$\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OCH}_3)\text{C}(=\text{O})\text{CH}_3 \rightleftharpoons \text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OCH}_3)\text{C}(=\text{O})\text{CH}_3 \text{ (g)}$	$9.01 \cdot 10^5 \text{ (e)}$	$2.05 \cdot 10^5$
$\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OCH}_3)\text{C}(=\text{O})\text{CH}_3 \xrightleftharpoons{\text{H}_2\text{O}} \text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OH})(\text{CH}_3)\text{C}(=\text{O})\text{CH}_3$		$1.90 \cdot 10^0$
$\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OCH}_3)\text{C}(=\text{O})\text{CH}_3 \xrightleftharpoons{\text{H}^+} \text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OCH}_3)\text{C}(=\text{O})\text{CH}_3$		$1.50 \cdot 10^{-3}$
$\text{CH}_3\text{C}(\text{OH})(\text{CH}_3)\text{C}(\text{OCH}_3)\text{C}(=\text{O})\text{CH}_3 + \text{OH} \rightarrow \text{WSOC}$		$4.68 \cdot 10^8$

**Table H.1 (continued)** Additional mechanism used for the sensitivity runs UPT and RXN.

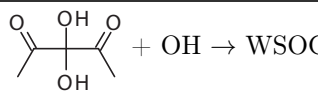
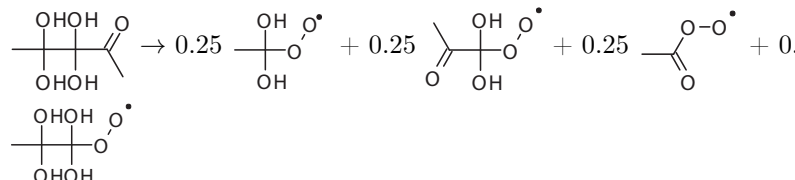
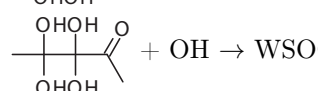
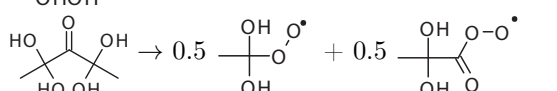
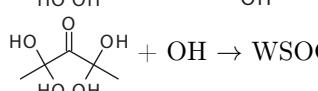
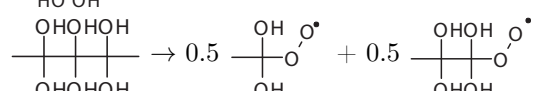
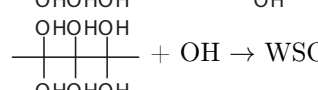
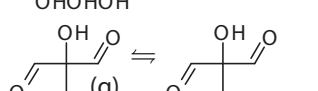
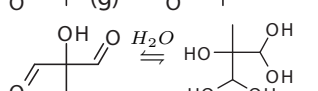
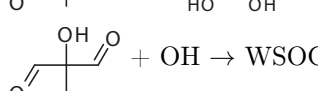
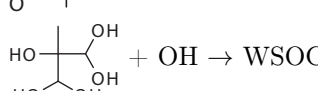
Reaction	UPT <sup>(a)</sup>	RXN <sup>(a)</sup>
 + OH → WSOC		5.50 · 10 <sup>8</sup>
 + OH → WSOC		2.13 · 10 <sup>8</sup>
 (g) ⇌ 	2.14 · 10 <sup>4</sup>	1.84 · 10 <sup>3</sup>
 $\xrightleftharpoons{H_2O}$ 		3.00 · 10 <sup>0</sup>
 → 0.5  + 0.5 WSOC		1.00 · 10 <sup>-1</sup>
 + OH → WSOC		1.09 · 10 <sup>8</sup>
 → 0.5  + 0.5 WSOC		1.00 · 10 <sup>-1</sup>
 + OH → WSOC		4.24 · 10 <sup>9</sup>
 (g) ⇌ 	7.75 · 10 <sup>3</sup>	2.85 · 10 <sup>3</sup>
 $\xrightleftharpoons{H_2O}$ 		1.72 · 10 <sup>0</sup>
 + OH → WSOC		5.68 · 10 <sup>8</sup>
 + OH → WSOC		1.35 · 10 <sup>9</sup>
 (g) ⇌ 	1.70 · 10 <sup>6</sup>	8.69 · 10 <sup>2</sup>
 $\xrightleftharpoons{H_2O}$ 		1.95 · 10 <sup>3</sup>
 + OH → WSOC		1.08 · 10 <sup>10</sup>
 + OH → WSOC		1.09 · 10 <sup>10</sup>
 (g) ⇌ 	2.54 · 10 <sup>9</sup>	6.96 · 10 <sup>5</sup>
 $\xrightleftharpoons{H_2O}$ 0.9  + 0.1 		3.65 · 10 <sup>3(f)</sup>
 + OH → WSOC		1.43 · 10 <sup>9</sup>



**Table H.1 (continued)** Additional mechanism used for the sensitivity runs UPT and RXN.

Reaction	UPT <sup>(a)</sup>	RXN <sup>(a)</sup>
 + OH → WSOC		1.91 · 10 <sup>9</sup>
 + OH → WSOC		2.29 · 10 <sup>9</sup>
 + OH → WSOC		1.07 · 10 <sup>9</sup>
 $\xrightleftharpoons{H_2O}$ 0.06  + 0.94 	7.39 · 10 <sup>4</sup>	1.04 · 10 <sup>5(f)</sup>
 + OH → WSOC		1.37 · 10 <sup>9</sup>
 + OH → WSOC		1.83 · 10 <sup>9</sup>
 + OH → WSOC		2.00 · 10 <sup>3</sup>
 $\xrightleftharpoons{H_2O}$  + 	2.84 · 10 <sup>3</sup>	3.92 · 10 <sup>-1</sup>
 + OH → WSOC		2.89 · 10 <sup>8</sup>
 + OH → WSOC		6.80 · 10 <sup>8</sup>
 $\xrightleftharpoons{H_2O}$  + 	2.66 · 10 <sup>7</sup>	3.61 · 10 <sup>4</sup>
 $\xrightleftharpoons{H_2O}$  + 		4.28 · 10 <sup>1</sup>
 $\xrightleftharpoons{H_2O}$  + 		9.85 · 10 <sup>1</sup>
 $\xrightleftharpoons{H_2O}$  + 		1.19 · 10 <sup>1</sup>
 $\xrightleftharpoons{H_2O}$  + 		5.91 · 10 <sup>1</sup>
 $\xrightarrow{H_2O}$ 0.5  + 0.5 		1.00 · 10 <sup>-1</sup>
 + OH → WSOC		1.39 · 10 <sup>8</sup>
 + OH → WSOC		1.00 · 10 <sup>-1</sup>

**Table H.1 (continued)** Additional mechanism used for the sensitivity runs UPT and RXN.

Reaction	UPT <sup>(a)</sup>	RXN <sup>(a)</sup>
		$4.19 \cdot 10^8$
		$1.00 \cdot 10^{-1}$
		$8.22 \cdot 10^8$
		$1.00 \cdot 10^{-1}$
		$8.11 \cdot 10^8$
		$1.00 \cdot 10^{-1}$
		$1.23 \cdot 10^9$
	$8.16 \cdot 10^5$	$1.40 \cdot 10^2$
		$6.28 \cdot 10^1$
		$1.91 \cdot 10^9$
		$1.68 \cdot 10^9$

<sup>(a)</sup>Given in this column are the Henry's Law constant ( $K_{H,eff}$  for UPT or  $K_H$  for RXN), the hydration constant ( $K_{hyd}$ ), the dissociation constant ( $K_{diss}$ ), or the first or second order rate constants ( $k_{1st}/k_{2nd}$ ), if part of the sensitivity study. The respective units of measure are  $M^n atm^{-1}$  for  $K_H$  and  $K_{H,eff}$ ,  $M^{-1}$  for  $K_{hyd}$ ,  $M$  for  $K_{diss}$ , and  $s^{-1}$  or  $M^{-1} s^{-1}$  for  $k_{1st}$  and  $k_{2nd}$ . The rate constants of the backward reactions of hydrations have been estimated with  $5.69 \cdot 10^{-3} s^{-1}$ , for the rate constants of the backward reactions of dissociations  $5 \cdot 10^{10} M^{-1} s^{-1}$  is used.

<sup>(b)</sup>Reference for  $k_{2nd}$ : *Schested et al.* (1975)

<sup>(c)</sup>Uptake estimated with EPI Suite 4.1 (see US Environmental Protection Agency, 2011:

<http://www.epa.gov/opptintr/exposure/pubs/episuite.htm>; *Meylan and Howard*, 2000).

<sup>(d)</sup>Rate constant calculated with the SAR by *Minakata et al.* (2009) ignoring the oxygen atoms in the  $-O-O-$  group as this group is bound solely to quaternary carbon atoms and thus in  $\beta$ -position of any reactive group. As the group itself contains no H-atoms and is, therefore, unreactive and no  $\beta$ -parameters are used in the SAR of *Minakata et al.* (2009), it was possible to derive a rate constant with the SAR without further assumptions.

<sup>(e)</sup>Contributions of dissociation to the effective Henry's Law constant calculated manually as explained in the text.

<sup>(f)</sup>Hydrations channels have been combined to an overall equilibrium as explained in the text.

## H.4 Additional results from the TMB oxidation experiment

Table H.2 shows the uncorrected values as determined by offline GC-MS analysis from the C-GIS and PTFE filter samples. For comparison with model results, blind values of the C-GIS sample A1 (begin of the experiment) have been subtracted from the other samples A2 – A14, as particles were initialised as pure  $\text{Na}_2\text{SO}_4/\text{Na}_2\text{O}_2$  seed particles and any organic content derives from contaminations.

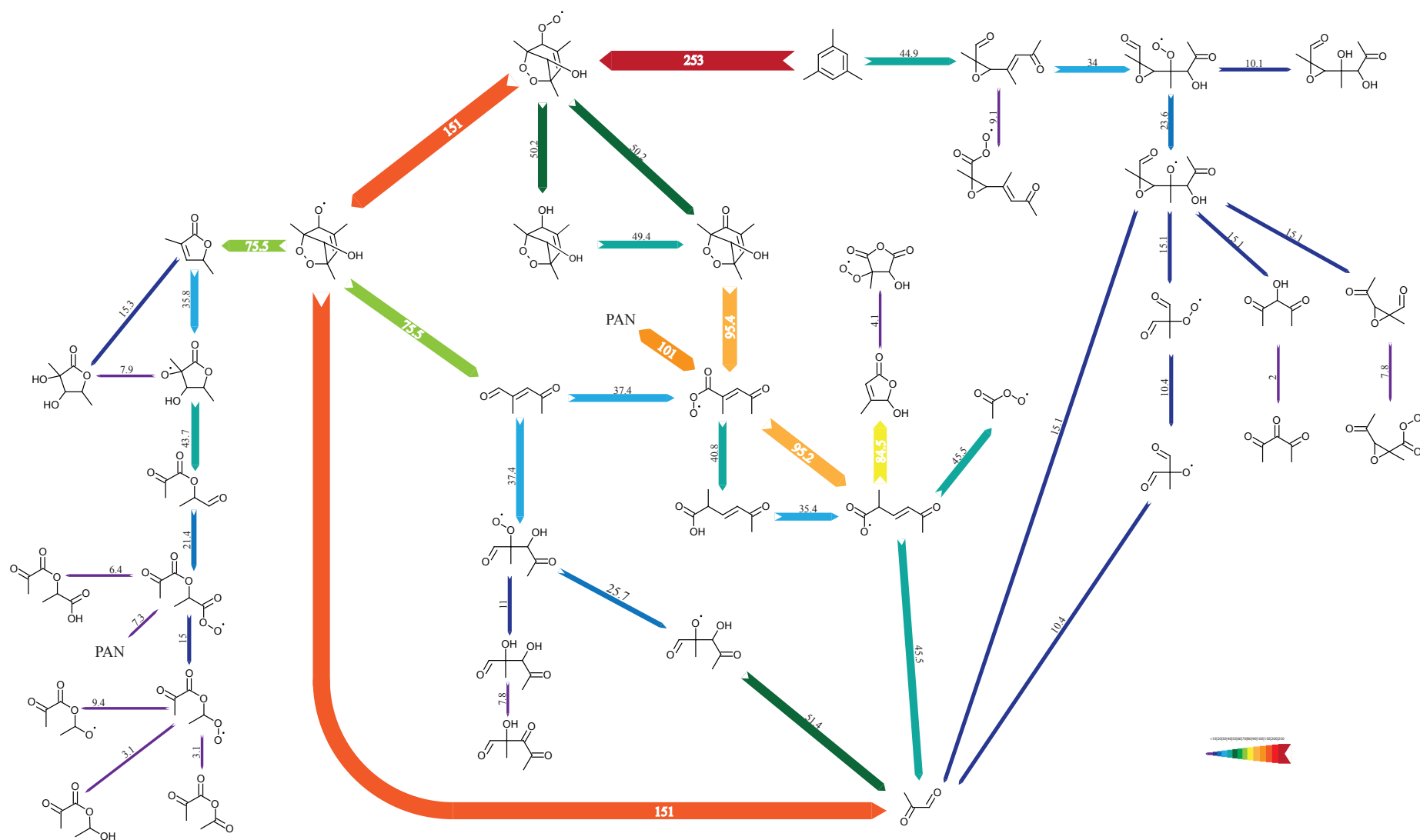
**Table H.2** Measured uncorrected concentrations in  $\mu\text{g m}^{-3}$  from the analysis of the different C-GIS samples and the PTFE filter for the compounds listed in the header. Times given in the first column refer to measurement points in hours and minutes after the injection of ozone and the start of the UV-C photolysis.

Sample	[Time]	MGLY	Formate	Acetate	Pyruvate	Oxalate	Malonate	Succinate	Malate
C-GIS samples (prior to the experiment and every 15 min)									
A00 <sup>(a)</sup>	[-00:27]	—	0.230	0.395	—	0.199	0.019	0.049	0.422
A01 <sup>(b)</sup>	[00:01]	—	0.328	0.512	—	0.212	0.016	0.105	0.748
A02	[00:16]	—	0.266	0.433	—	0.213	0.022	0.074	0.475
A03	[00:31]	—	0.340	0.783	—	0.355	0.046	0.130	0.475
A04	[00:46]	—	0.159	0.427	—	0.178	0.017	0.048	0.149
A05	[01:01]	—	0.026	0.630	—	0.185	0.014	0.150	0.004
A06	[01:16]	—	0.230	0.570	—	0.237	0.018	0.116	0.083
A07	[01:31]	—	0.137	0.436	—	0.189	0.018	0.044	0.052
A08	[01:46]	—	0.230	0.798	—	0.315	0.016	0.023	0.055
A09	[02:01]	—	0.374	1.469	—	0.651	0.043	0.087	0.079
A10	[02:16]	—	0.230	0.887	—	0.355	0.031	0.058	0.026
A11	[02:31]	—	0.477	2.169	—	0.824	0.039	0.070	0.064
A12	[02:46]	—	0.170	0.908	—	0.260	0.037	0.098	0.027
A13	[03:01]	—	0.307	1.798	—	0.474	0.028	0.021	0.018
A14	[03:16]	—	0.362	2.194	—	0.703	0.043	0.087	0.037
Filter samples (collected after the experiment)									
FS <sup>(c)</sup>	[03:36]	0.048	0.646	0.810	0.280	6.819	0.354	—	5.640

<sup>(a)</sup>Sample A0 was collected after the injection of seed particles, when conditions were stable, but prior to the injection of TMB and ozone and the start of the UV-C photolysis.

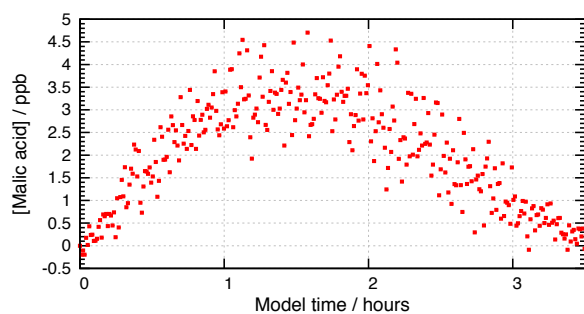
<sup>(b)</sup>Sample A1 was directly collected after start of the experiment with the injection of TMB and ozone and the start of the UV-C photolysis.

<sup>(c)</sup>The experiment was ended by switching of the UV-C lights at 03:30. Filter samples were taken at 03:36.

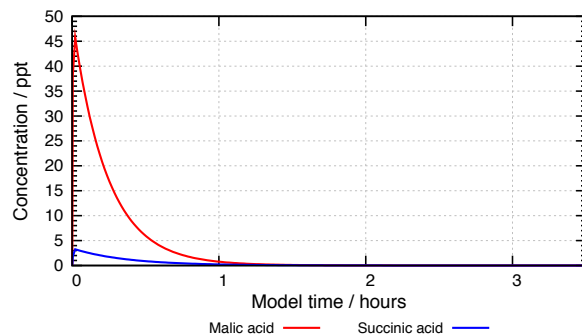


**Figure H.2** Analysis of the gas phase turnovers (in molecules cm<sup>-3</sup> s<sup>-1</sup>) from TMB to MGLY averaged over the whole experiment.

(a) LEAK observations

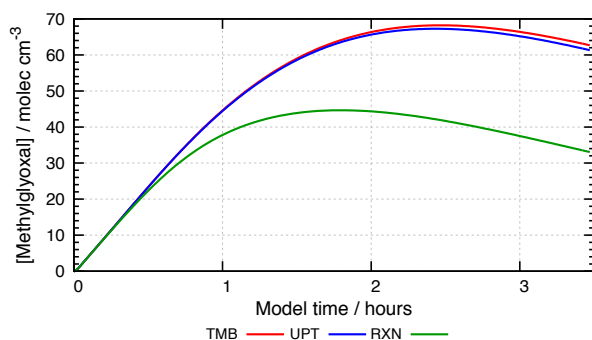


(b) Model observations

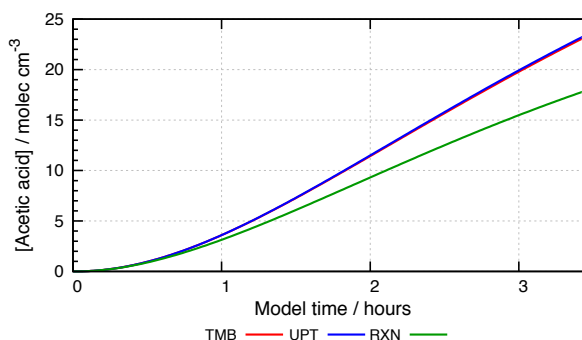


**Figure H.3** Concentrations of gas phase malic acid as monitored by the PTR-MS in the chamber (a) and modelled malic and succinic acid gas phase concentrations (b).

(a) Methylglyoxal



(b) Acetic acid



**Figure H.4** Gas phase concentrations of the most important TMB oxidation products methylglyoxal (a) and acetic acid (b) in the sensitivity runs TMB, UPT, and RXN.

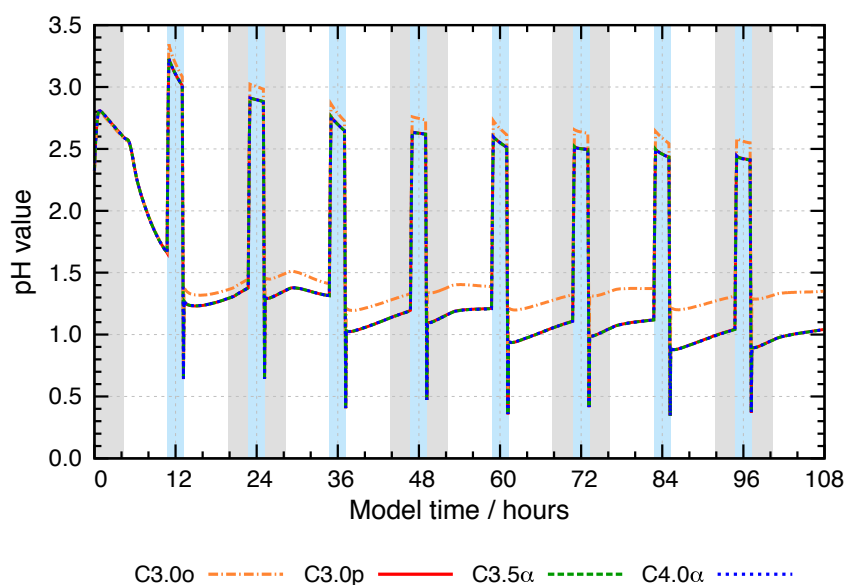


# I Additional results from the ‘real atmosphere’ scenario

## I.1 Particle acidity and SOA formation

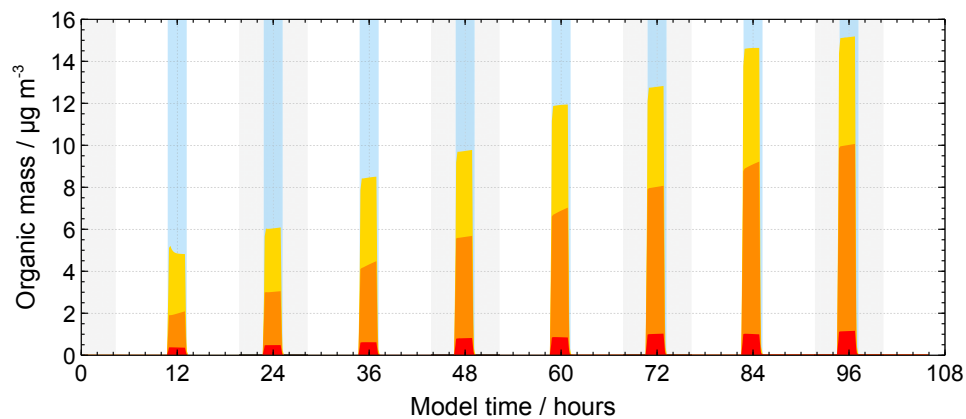
To investigate the effects of the level of detail in the organic chemistry scheme in CAPRAM 3.0o – 4.0 $\alpha$  on particle acidity, the pH value has been replotted for the different CAPRAM versions under urban conditions in Figure I.1. A discussion is provided in subsection 6.2.3 of the main part.

As the mechanism development was focused on the organic chemistry, which is more dominant under urban regimes, the discussion stresses on the urban scenario as well. The remote case is discussed briefly in the main part of the dissertation with a focus on differences of the remote scenario to the urban case. For clarification, figures concerning the remote scenario are provided in the Appendix. Figure I.2 shows the concentration-time profile of the organic mass distinguished by carbon number of the constituents under remote conditions.

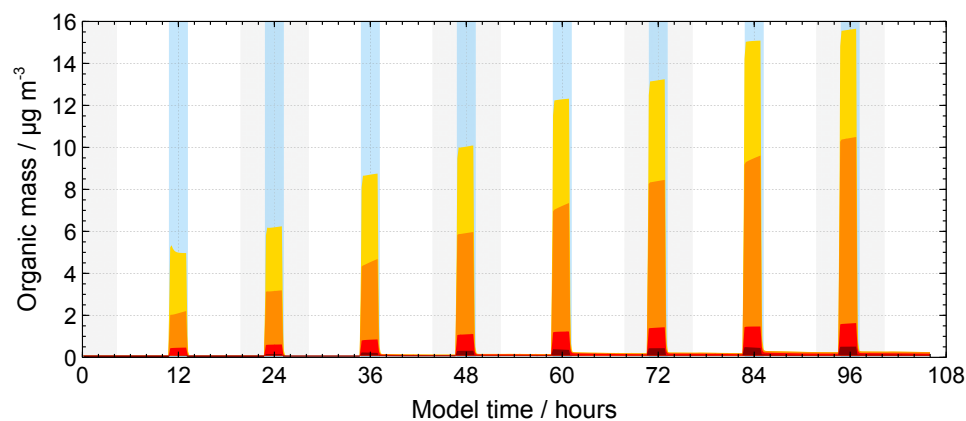


**Figure I.1** Time profiles of the particle/cloud droplet pH for the different CAPRAM mechanisms in the urban scenario.

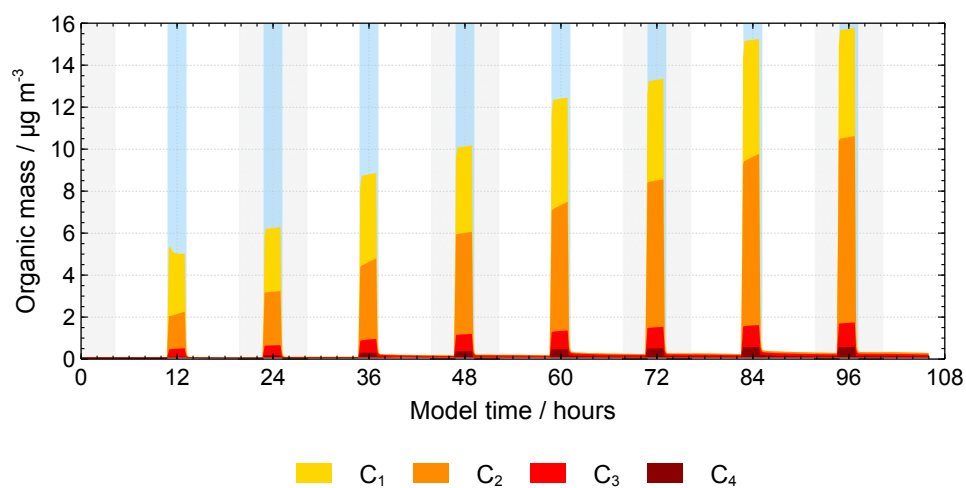
(a) CAPRAM 3.0n



(b) CAPRAM 3.5 $\alpha$



(c) CAPRAM 4.0 $\alpha$

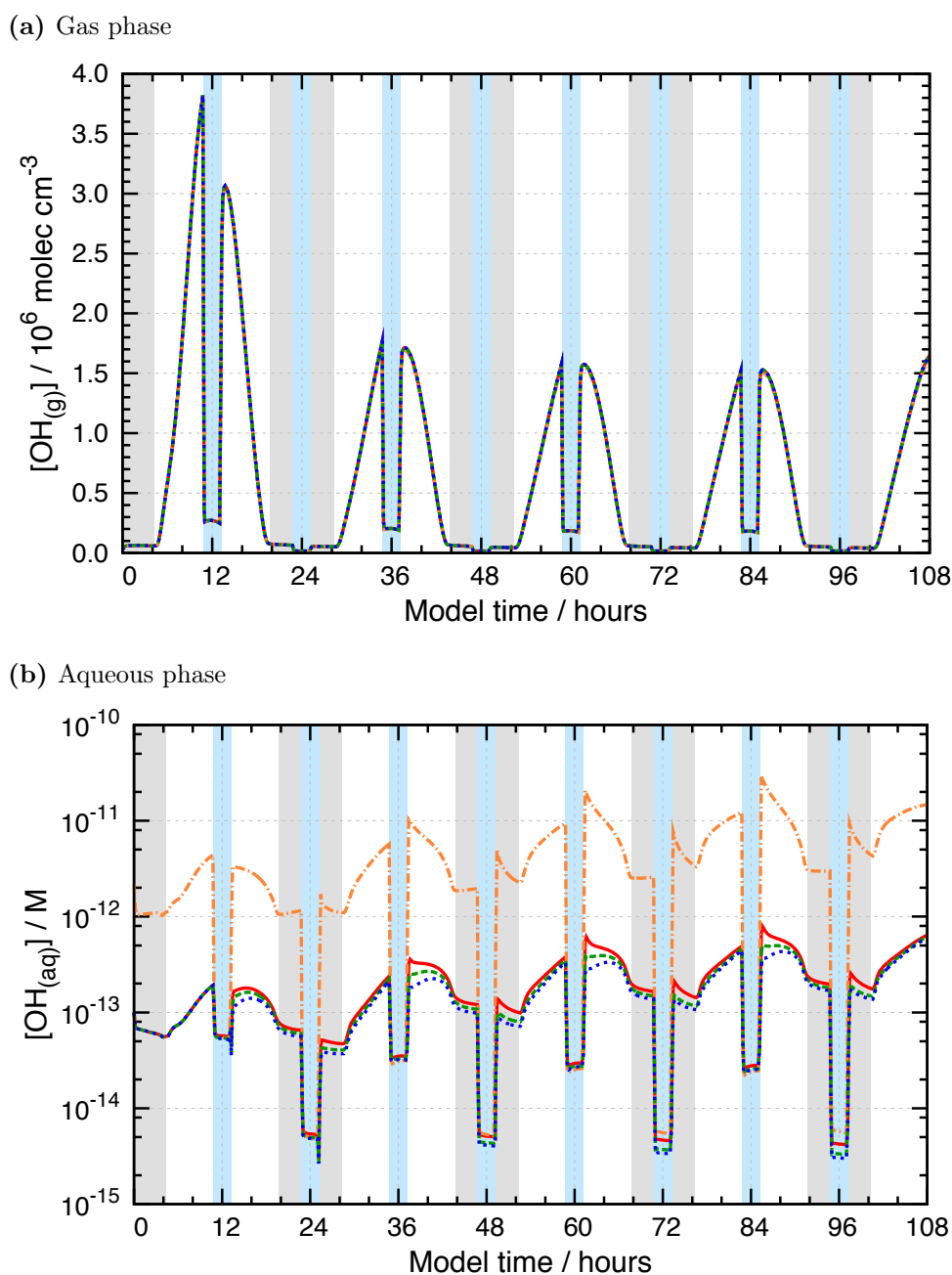


**Figure I.2** Evolution of the organic particulate mass differentiated by chain length for the 3 different mechanisms CAPRAM 3.0n, 3.5 $\alpha$ , and 4.0 $\alpha$  under remote conditions.



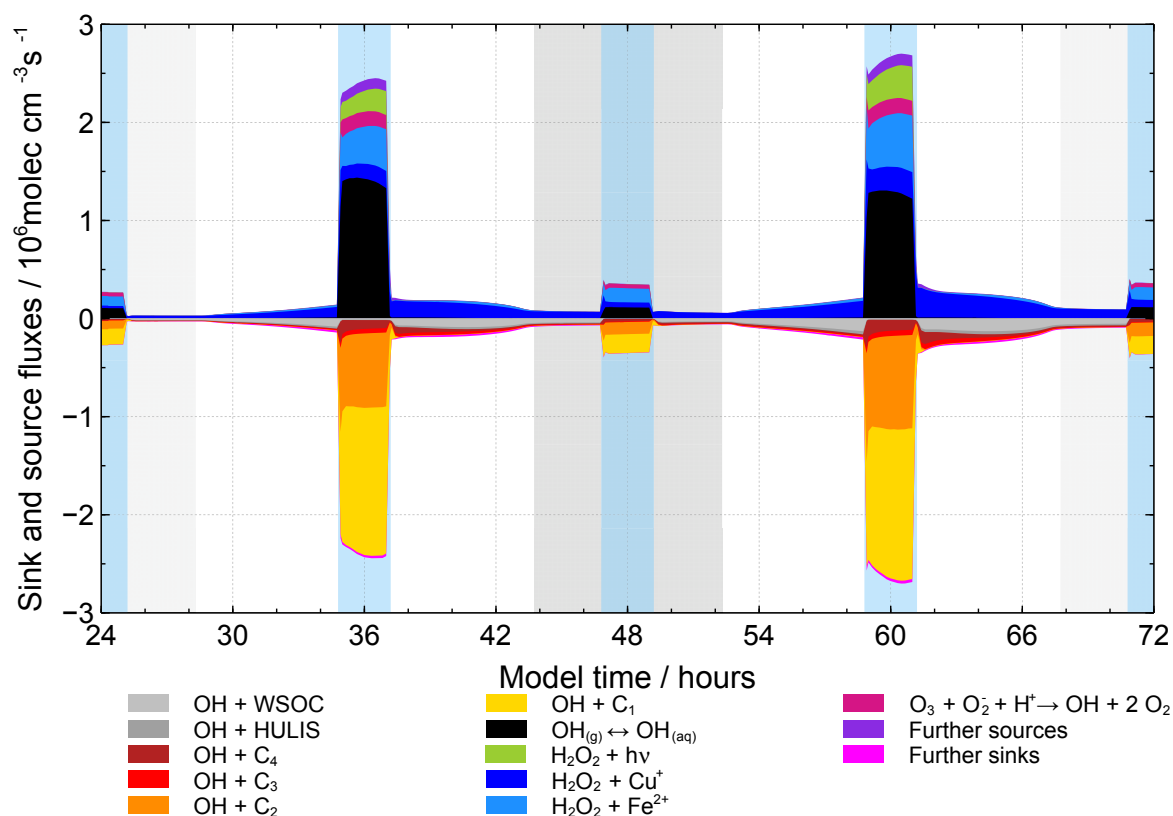
## I.2 Radical oxidants

As effects of the extended organic schemes are similar in the remote case and the urban case, but less pronounced in the remote case, the concentration-profiles of OH radicals in the gas and the aqueous phase under remote conditions have been moved to the Appendix and are shown in Figure I.3.



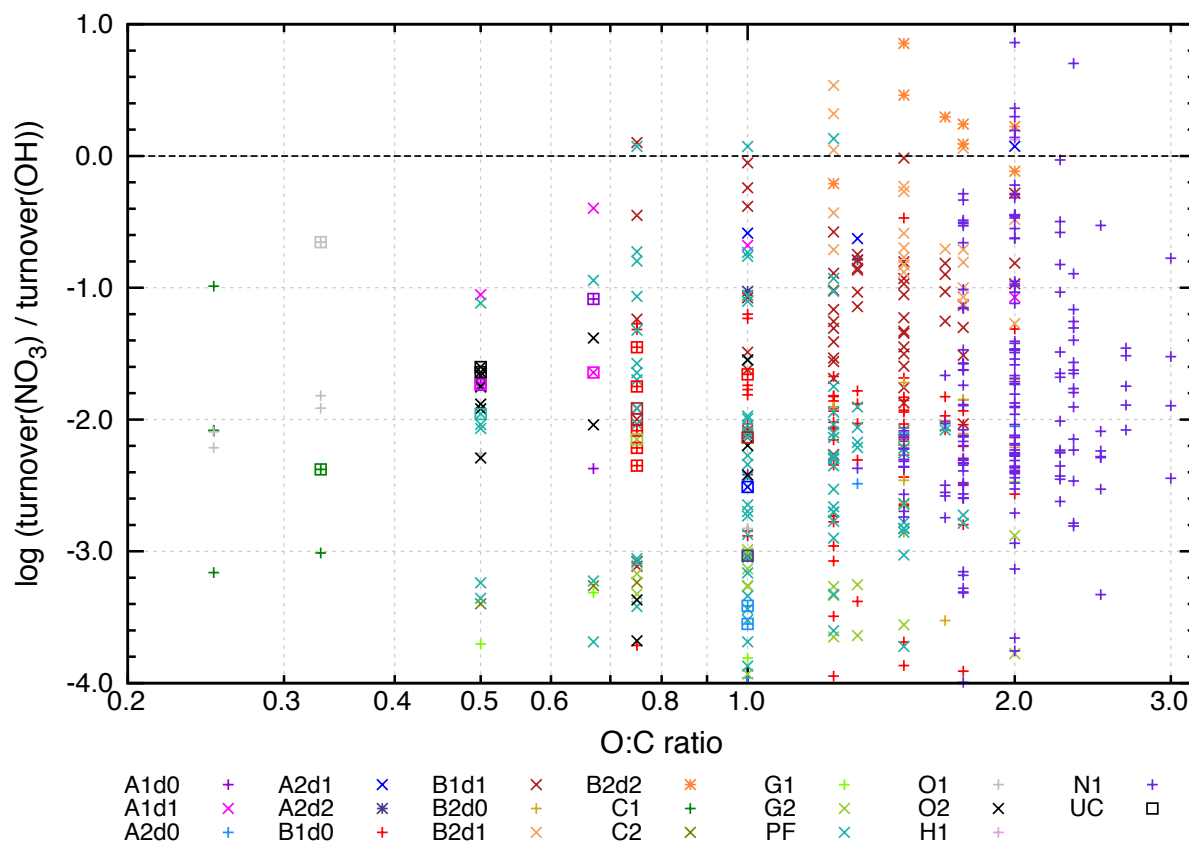
**Figure I.3** Concentration-time profiles of hydroxyl radicals in the gas (a) and the aqueous phase (b) for the various CAPRAM mechanisms under remote conditions.

Chemical fluxes contribution to the formation and degradation of hydroxyl radicals under remote conditions in the scenario using CAPRAM 3.5 $\alpha$  are given in Figure I.4. The plot is discussed in the main part in subsection 6.2.4.1 with a special emphasis on the differences to the urban scenario.



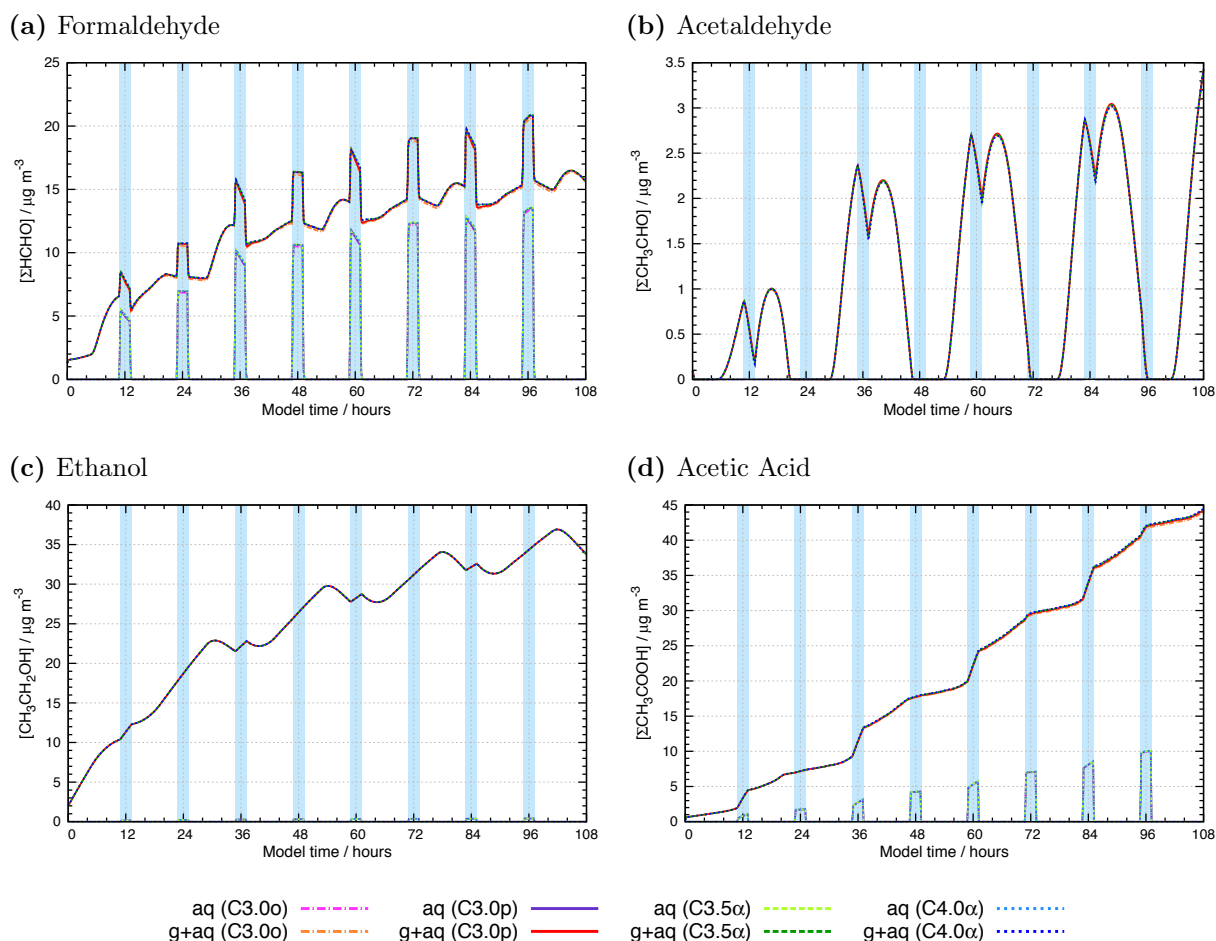
**Figure I.4** Time-resolved production (positive values) and degradation fluxes (negative values) of aqueous hydroxyl radicals for the second and third model day calculated with CAPRAM 4.0 $\alpha$  under remote conditions.

For clarification and a better legibility, the data of Figure 6.21 is replotted in Figure I.5 with rescaled axes. Moreover, unsaturated organic compounds in Figure I.5 are marked with a box in the same colour of the symbol for a more detailed analysis of the oxidation of aliphatic organic compounds by hydroxyl and nitrate radicals. A detailed discussion is provided in subsection 6.2.4.3 in the main part of the dissertation.



**Figure I.5** Comparison of the logarithmised hydroxyl radical versus nitrate radical turnovers of reactions with organic compounds against the O:C ratio distinguished by compound classes as given in the legend and explained in the text with a rescaled range for clarification.

## I.3 Organic compounds



**Figure I.6** Profiles of the overall aqueous phase concentration (including all hydrated or dissociated forms) and the sum of the gas and overall aqueous phase concentration of selected emitted monofunctional organic compounds for the various CAPRAM mechanisms under urban conditions.

# References of the Appendix

- Acero, J.L., Haderlein, S.B., Schmidt, T.C., Suter, M.J.F., and Von Gunten, U. MTBE oxidation by conventional ozonation and the combination ozone/hydrogen peroxide: Efficiency of the processes and bromate formation. *Environmental Science & Technology*, **35**(21), 4252–4259, 2001. ISSN 0013-936X. doi:10.1021/es010044n.
- Adams, G., Boag, J., Currant, J., and Michael, B. Absolute rate constants for the reaction of the hydroxyl radical with organic compounds. In *Pulse Radiolysis*, edited by M. Ebert, J.P. Keen, and S.A.J.B.J. H., 131–143. Academic Press, 1965a.
- Adams, G.E., Boag, J.W., and Michael, B.D. Reactions of hydroxyl radical. 2. Determination of absolute rate constants. *Transactions of the Faraday Society*, **61**(511P), 1417, 1965b. doi:10.1039/tf9656101417.
- Adams, G.E. and Michael, B.D. Pulse radiolysis of benzoquinone and hydroquinone. Semiquinone formation by water elimination from trihydroxy-cyclohexadienyl radicals. *Transactions of the Faraday Society*, **63**(533P), 1171, 1967. doi:10.1039/tf9676301171.
- Adams, G.E. and Willson, R.L. Pulse radiolysis studies on oxidation of organic radicals in aqueous solution. *Transactions of the Faraday Society*, **65**(563P), 2981, 1969. doi:10.1039/tf9696502981.
- Ahrens, R.W. Gamma radiolysis of aqueous solutions containing Fe(II) and selected substituted phenols. *Radiation Research*, **30**(3), 611–&, 1967. ISSN 0033-7587. doi:10.2307/3572125.
- Al-Sheikhly, M., Silverman, J., Simic, M., and Michael, B. Formation and reactions of alkyl, allyl, biallylic, and peroxy radicals from unsaturated fatty acids in micellar and monomeric aqueous solutions. *Journal of Physical Chemistry B*, **108**(45), 17618–17627, 2004. ISSN 1520-6106. doi:10.1021/jp047738d.
- Al-Suhybani, A. and Hughes, G. Pulse radiolysis of deaerated hydroquinone solutions. *Journal of the Chemical Society of Pakistan*, **8**(2), 107 – 115, 1986. ISSN 0253-5106.
- Alam, M.S., Rao, B.S.M., and Janata, E. OH reactions with aliphatic alcohols: evaluation of kinetics by direct optical absorption measurement. A pulse radiolysis study. *Radiation Physics and Chemistry*, **67**(6), 723–728, 2003. ISSN 0969-806X. doi:10.1016/S0969-806X(03)00310-4.
- Albalat, R., Claret, J., Gomez, E., Muller, C., and Sarret, M. Electrocatalytic oxidations of mesoxalic acid on a polycrystalline platinum-electrode in acid-medium. *Electrochimica*

- acta*, **34**(5), 611–618, 1989. ISSN 0013-4686. doi:10.1016/0013-4686(89)85003-0.
- Albarran, G., Bentley, J., and Schuler, R.H. Substituent effects in the reaction of OH radicals with aromatics: Toluene. *Journal of Physical Chemistry A*, **107**(39), 7770–7774, 2003. ISSN 1089-5639. doi:10.1021/jp.30550u.
- Alfassi, Z.B., Padmaja, S., Neta, P., and Huie, R.E. Rate constants for reactions of nitrate (NO<sub>3</sub>) radicals with organic compounds in water and acetonitrile. *The Journal of Physical Chemistry*, **97**(15), 3780 – 3782, 1993. doi:10.1021/j100117a025.
- Almgren, M., Grieser, F., and Thomas, J.K. Rate of exchange of surfactant monomer radicals and long-chain alcohols between micelles and aqueous-solutions. A pulse-radiolysis study. *Journal of the Chemical Society – Faraday Transactions I*, **75**(7), 1674–1687, 1979. ISSN 0300-9599. doi:10.1039/f19797501674.
- Amels, P., Elias, H., Götz, U., Steinges, U., and Wannowius, K.J. Kinetic investigation of the stability of peroxonitric acid and of its reaction with sulfur(IV) in aqueous solution. In *Heterogeneous and Liquid Phase Processes*, edited by P. Warneck, *Transport and Chemical Transformation of Pollutants in the Troposphere* (P. Borrell, P. M. Borrell, T. Cvitaš, K. Kelly, and W. Seiler, series editors), volume 2, 77–88. Springer, 1996.
- Anbar, M., Meyerste, D., and Neta, P. Reactivity of aliphatic compounds towards hydroxyl radicals. *Journal of the Chemical Society B – Physical Organic*, **8**, 742, 1966a. doi: 10.1039/j29660000742.
- Anbar, M., Meyerstein, D., and Neta, P. Reactivity of aromatic compounds toward hydroxyl radicals. *Journal of Physical Chemistry*, **70**(8), 2660, 1966b. ISSN 0022-3654. doi:10.1021/j100880a034.
- Anderson, R.F., Patel, K.B., and Stratford, M.R.L. Radical spectra and product distribution following electrophilic attack by the OH radical on 4-hydroxybenzoic acid and subsequent oxidation. *Journal of the Chemical Society – Faraday Transactions I*, **83**(10), 3177–3187, 1987. ISSN 0300-9599. doi:10.1039/f19878303177.
- Anderson, R.F. and Schulte-Frohlinde, D. Reactions induced by hydroxyl radical attack on acetylene in aqueous solution. A pulse radiolysis study. *Journal of Physical Chemistry*, **82**(1), 22–26, 1978. ISSN 0022-3654. doi:10.1021/j100490a006.
- Arakaki, T., Anastasio, C., Kuroki, Y., Nakajima, H., Okada, K., Kotani, Y., Handa, D., Azechi, S., Kimura, T., Tsuhako, A., and Miyagi, Y. A general scavenging rate constant for reaction of hydroxyl radical with organic carbon in atmospheric waters. *Environmental Science & Technology*, **47**(15), 8196 – 8203, 2013. doi:10.1021/es401927b.
- Arakaki, T., Saito, K., Okada, K., Nakajima, H., and Hitomi, Y. Contribution of fulvic acid to the photochemical formation of Fe(II) in acidic Suwannee River fulvic acid solutions. *Chemosphere*, **78**(8), 1023 – 1027, 2010. ISSN 0045-6535. doi:http://dx.doi.org/10.1016/j.chemosphere.2009.11.035.

- Ashton, L., Buxton, G.V., and Stuart, C.R. Temperature dependence of the rate of reaction of OH with some aromatic compounds in aqueous solution. Evidence for the formation of a  $\pi$ -complex intermediate? *Journal of the Chemical Society – Faraday Transactions*, **91**(11), 1631–1633, 1995. ISSN 0956-5000. doi:10.1039/ft9959101631.
- Asmus, K.D., Beck, G., Henglein, A., and Wigger, A. Pulsradiolytische Untersuchung der Oxydation und Reduktion des Nitrobenzols in wässriger Lösung. *Berichte der Bunsen-Gesellschaft für physikalische Chemie*, **70**(8), 869, 1966.
- Asmus, K.D. and Taub, I.A. Spectrum and kinetics of the hydroxynitromethane anion radical in pulse-irradiated alkaline nitromethane solutions. *Journal of Physical Chemistry*, **72**(10), 3382, 1968. ISSN 0022-3654. doi:10.1021/j100856a005.
- Atkinson, R. Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds. *Journal of Physical and Chemical Reference Data*, Monograph No. 1, 1989.
- Atkinson, R. and Arey, J. Atmospheric degradation of volatile organic compounds. *Chemical Reviews*, **103**(12), 4605 – 4638, 2003. ISSN 0009-2665. doi:10.1021/cr0206420.
- Atkinson, R., Baulch, D.L., Cox, R.A., Crowley, J.N., Hampson, R.F., Hynes, R.G., Jenkin, M.E., Rossi, M.J., and Troe, J. Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II – gas phase reactions of organic species. *Atmospheric Chemistry and Physics*, **6**(11), 3625 – 4055, 2006. ISSN 1680-7316.
- Bakalik, D.P. and Thomas, J.K. Micellar catalysis of radical reactions. A spin trapping study. *Journal of Physical Chemistry*, **81**(20), 1905–1908, 1977. ISSN 0022-3654. doi:10.1021/j100535a004.
- Baker, M.Z., Badiello, R., Tamba, M., Quintiliani, M., and Gorin, G. Pulse radiolytic study of hydrogen transfer from glutathione to organic radicals. *International Journal of Radiation Biology*, **41**(6), 595–602, 1982. ISSN 0955-3002. doi:10.1080/09553008214550691.
- Balazs, E.A., Davies, J.V., Phillips, G.O., and Scheuefele, D.S. Polyanions and their complexes. Part III. Reactions of heparin, hyaluronic acid, sodium poly(ethylenesulphonate), sodium poly(styrenesulphonate), and sodium carboxymethylcellulose with hydroxyl radicals and hydrated electrons. *Journal of the Chemical Society C: Organic*, **12**, 1420, 1968. doi:10.1039/j39680001420.
- Barb, W.G., Baxendale, J.H., George, P., and Hargrave, K.R. Reactions of ferrous and ferric ions with hydrogen peroxide. Part I. – The ferrous ion reaction. *Transactions of the Faraday Society*, **47**, 462–500, 1951. doi:10.1039/TF9514700462. URL <http://dx.doi.org/10.1039/TF9514700462>.
- Barber, D.J.W. and Thomas, J.K. Reactions of radicals with lecithin bilayers. *Radiation Research*, **74**(1), 51–65, 1978. ISSN 0033-7587. doi:10.2307/3574756.
- Barker, G.C., Fowles, P., and Stringer, B. Pulse radiolytic induced transient electrical conductance in liquid solutions. 2. Radiolysis of aqueous solutions of NO<sub>3</sub>, NO<sub>2</sub> and

- $\text{Fe}(\text{CN})_6^{3-}$ . *Transactions of the Faraday Society*, **66**(570), 1509–1519, 1970. doi:10.1039/tf9706601509.
- Barlow, S., Buxton, G.V., Murray, S.A., and Salmon, G.A. Free-radical-induced oxidation of hydroxymethanesulfonate in aqueous solution. Part 2. A pulse and steady-state radiolysis study of oxygenated solutions. *Journal of the Chemical Society – Faraday Transactions*, **93**(20), 3641–3645, 1997. ISSN 0956-5000. doi:10.1039/a703266h.
- Bartlett, W.P. and Margerum, D.W. Temperature Dependencies of the Henry’s Law Constant and the Aqueous Phase Dissociation Constant of Bromine Chloride. *Environmental Science & Technology*, **33**(19), 3410–3414, 1999. doi:10.1021/es990300k. URL <http://pubs.acs.org/doi/abs/10.1021/es990300k>. <http://pubs.acs.org/doi/pdf/10.1021/es990300k>.
- Barzaghi, P. and Herrmann, H. Kinetics and mechanisms of reactions of the nitrate radical ( $\text{NO}_3$ ) with substituted phenols in aqueous solution. *Physical Chemistry Chemical Physics*, **6**(23), 5379–5388, 2004. ISSN 1463-9076. doi:10.1039/b412933d.
- Basinski, A. and Lerke, G. Reactivity of certain aromatic-compounds with respect to OH radical. *Bulletin de l’Academie Polonaise des Sciences – Serie des Sciences Chimiques*, **20**(4), 319, 1972. ISSN 0001-4095.
- Baxendale, J.H., Ward, M.D., and Wardman, P. Heats of ionization of  $\text{HO}_2$  and OH in aqueous solution. *Transactions of the Faraday Society*, **67**(585), 2532–2537, 1971. doi:10.1039/tf9716702532.
- Beckwith, R.C., Wang, T.X., and Margerum, D.W. Equilibrium and kinetics of bromine hydrolysis. *Inorganic Chemistry*, **35**(4), 995–1000, 1996. ISSN 0020-1669. doi:10.1021/ic950909w.
- Behar, D., Fessenden, R.W., and Hornak, J.P. Electron-Spin-Resonance and pulse radiolysis investigation of the radiolysis of sodium vinyl sulfonate. *Radiation Physics and Chemistry*, **20**(4), 267–273, 1982. doi:10.1016/0146-5724(82)90036-X.
- Behnke, W., George, C., Scheer, V., and Zetzsch, C. Production and decay of  $\text{ClNO}_2$ , from the reaction of gaseous  $\text{N}_2\text{O}_5$  with NaCl solution: Bulk and aerosol experiments. *Journal of Geophysical Research – Atmospheres*, **102**(D3), 3795–3804, 1997. ISSN 2169-897X. doi:10.1029/96JD03057.
- Beilke, S. and Gravenhorst, G. Heterogeneous  $\text{SO}_2$ -oxidation in droplet phase. *Atmospheric Environment*, **12**(1-3), 231–239, 1978. ISSN 1352-2310. doi:10.1016/0004-6981(78)90203-2.
- Bell, R.P. and Evans, P.G. Kinetics of dehydration of methylene glycol in aqueous solution. *Proceedings of the Royal Society of London Series A – Mathematical and Physical Sciences*, **291**(1426), 297–323, 1966. doi:10.1098/rspa.1966.0097.
- Bell, R.P., Rand, M.H., and WynneJones, K.M.A. Kinetics of the hydration of acetaldehyde. *Transactions of the Faraday Society*, **52**(8), 1093–1102, 1956. doi:10.1039/tf9565201093.



- Benkelberg, H.J. and Warneck, P. Photodecomposition of iron(III)hydroxid and sulfato complexes in aqueous-solution – wavelength dependence of OH and SO<sub>4</sub>-quantum yields. *Journal of Physical Chemistry*, **99**(14), 5214–5221, 1995. ISSN 0022-3654. doi:10.1021/j100014a049.
- Berdnikov, V.M. Catalytic activity of the hydrated copper ion in the decomposition of hydrogen peroxide. *Russian Journal of Physical Chemistry*, **47**, 1060–1062, 1973.
- Berglund, J., Elding, L.I., Buxton, G.V., McGowan, S., and Salmon, G.A. Reaction of peroxomonosulfate radical with manganese(II) in acidic aqueous-solution. A pulse-radiolysis study. *Journal of the Chemical Society – Faraday Transactions*, **90**(21), 3309–3313, 1994. ISSN 0956-5000. doi:10.1039/ft9949003309.
- Berglund, J., Fronaeus, S., and Elding, L.I. Kinetics and mechanism for manganese-catalyzed oxidation of sulfur(IV) by oxygen in aqueous-solution. *Inorganic Chemistry*, **32**(21), 4527–4538, 1993. ISSN 0020-1669. doi:10.1021/ic00073a011.
- Betterton, E.A. The partitioning of ketones between the gas and aqueous phases. *Atmospheric Environment Part A – General Topics*, **25**(8), 1473–1477, 1991. ISSN 0004-6981. doi:10.1016/0960-1686(91)90006-S.
- Betterton, E.A. and Hoffmann, M.R. Henry Law constants of some environmentally important aldehydes. *Environmental Science & Technology*, **22**(12), 1415–1418, 1988. ISSN 0013-936X. doi:10.1021/es00177a004.
- Bielski, B.H.J., Cabelli, D.E., Arudi, R.L., and Ross, A.B. Reactivity of HO<sub>2</sub>/O<sub>2</sub><sup>-</sup> radicals in aqueous-solution. *Journal of Physical and Chemical Reference Data*, **14**(4), 1041–1100, 1985. ISSN 0047-2689. doi:10.1063/1.555739.
- Biro, A. and Wojnarovits, L. Pulse radiolysis of ethyl propionate in aqueous solution. *Journal of Radioanalytical and Nuclear Chemistry – Letters*, **166**(1), 7–14, 1992. ISSN 0236-5731. doi:10.1007/BF02167993.
- Biro, A. and Wojnarovits, L. Reaction of diethyl maleate and diethyl fumarate with hydrated electrons and hydroxyl radicals. *Radiation Physics and Chemistry*, **47**(3), 389–392, 1996. doi:10.1016/0969-806X(95)00122-E. 8th Tihany Symposium on Radiation Chemistry, BALATONSZEPLAK, HUNGARY, 1994.
- Bjergbakke, E., Sehested, K., and Rasmussen, O.L. Reaction-mechanism and rate constants in radiolysis of Fe<sup>2+</sup>–Cu<sup>2+</sup> solutions. *Radiation Research*, **66**(3), 433–442, 1976. ISSN 0033-7587. doi:10.2307/3574449.
- Bobrowski, K. Pulse radiolysis of p-hydroxycinnamic acid in aqueous solution. *Journal of the Chemical Society – Faraday Transactions 1*, **80**(6), 1377–1389, 1984. ISSN 0300-9599. doi:10.1039/f19848001377.
- Bobrowski, K. and Raghavan, N.V. Pulse radiolytic and product analysis studies of the reaction of hydroxyl radicals with cinnamic acid. The relative extent of addition to the ring and side chain. *Journal of Physical Chemistry*, **86**(22), 4432–4435, 1982. ISSN

0022-3654. doi:10.1021/j100219a033.

- Bocek, K. Relations among activity coefficients, partition coefficients and solubilities. In *Quantitative structure-activity relationships. Proceedings of the conference on chemical structure-biological activity relationships: quantitative approaches*, edited by M. Tichy, *Experientia supplementum*, volume 23, 231–240. Birkhaeuser Verlag, 1976.
- Bolkenius, F.N., Grisar, J.M., and Dejong, W. A water-soluble quaternary ammonium analog of  $\alpha$ -tocopherol, that scavenges lipoperoxyl, superoxyl and hydroxyl radicals. *Free Radical Research Communications*, **14**(5-6), 363–372, 1991. ISSN 8755-0199. doi:10.3109/10715769109093425.
- Bone, R., Cullis, P., and Wolfenden, R. Solvent effects on equilibria of addition of nucleophiles to acetaldehyde and the hydrophilic character of diols. *Journal of the American Chemical Society*, **105**(5), 1339–1343, 1983. ISSN 0002-7863. doi:10.1021/ja00343a044.
- Bongartz, A., Schweighoefer, S., Roose, C., and Schurath, U. The mass accommodation coefficient of ammonia on water. *Journal of Atmospheric Chemistry*, **20**(1), 35–58, 1995. ISSN 0167-7764. doi:10.1007/BF01099917.
- Bonifacic, M., Ljubenkovic, I., and Eckertmaksic, M. One-electron oxidation and reduction reactions of vitamin C derivatives: 6-bromo- and 6-chloro-6-deoxy-ascorbic acid. *International Journal of Radiation Biology*, **66**(2), 123–131, 1994. ISSN 0955-3002. doi:10.1080/09553009414551021.
- Bonin, J., Janik, I., Janik, D., and Bartels, D.M. Reaction of the hydroxyl radical with phenol in water up to supercritical conditions. *Journal of Physical Chemistry A*, **111**(10), 1869–1878, 2007. ISSN 1089-5639. doi:10.1021/jp0665325.
- Bors, W., Michel, C., Erben-Russ, M., Kreileder, B., Tait, D., , and Saran, M. Rate constants of sparingly water-soluble phenolic antioxidants with hydroxyl radicals. In *Oxygen Radicals in Chemistry and Biology: Proceedings Third International Conference Neuherberg*, edited by e.a. W. Bors, 95–99. de Gruyter, 1984.
- Bors, W., Saran, M., and Michel, C. Pulse-radiolytic investigations of catechols and catecholamines. 4. 3,4-Dihydroxybenzaldehyde and 3,4-dihydroxyacetophenone. *Journal of Physical Chemistry*, **83**(24), 3084–3088, 1979. ISSN 0022-3654. doi:10.1021/j100487a005.
- Bors, W., Saran, M., and Michel, C. Radical intermediates involved in the bleaching of the carotenoid crocin. hydroxyl radicals, superoxideanions and hydrated electrons. *International Journal of Radiation Biology*, **41**(5), 493–501, 1982. ISSN 0955-3002. doi:10.1080/09553008214550571.
- Bothe, E., Schuchmann, M.N., Schultefrohlinde, D., and von Sonntag, C.  $\text{HO}_2$  elimination from  $\alpha$ -hydroxyalkylperoxyl radicals in aqueous-solution. *Photochemistry and Photobiology*, **28**(4-5), 639–644, 1978. ISSN 0031-8655. doi:10.1111/j.1751-1097.1978.tb06984.x.

- Bothe, E., Schuchmann, M.N., Schultefrohlinde, D., and von Sonntag, C. Hydroxyl radical-induced oxidation of ethanol in oxygenated aqueous-solutions. A pulse-radiolysis and product study. *Zeitschrift für Naturforschung Section B. A Journal of Chemical Sciences*, **38**(2), 212–219, 1983. ISSN 0932-0776.
- Brandt, C. and van Eldik, R. Transition metal catalyzed oxidation of sulfur(IV) oxides. Atmospheric relevant processes and mechanisms. *Chemical Reviews*, **95**(1), 119 – 190, 1995. doi:10.1021/cr00033a006.
- Brede, O., Bos, J., Helmstreit, W., and Mehnert, R. Nanosecond pulse-radiolysis of 1-Methylstyrene and 1,1'-Diphenylethylene in aqueous-solution. *Zeitschrift für Chemie*, **17**(12), 447–448, 1977. ISSN 0044-2402.
- Brimblecombe, P. and Clegg, S.L. The solubility and behavior of acid gases in the marine aerosol. *Journal of Atmospheric Chemistry*, **7**(1), 1–18, 1988. ISSN 0167-7764. doi:10.1007/BF00048251.
- Broszkiewicz, R.K., Soyelemmez, T., and Schultefrohlinde, D. Reactions of OH radicals with acetylacetone in aqueous-solution. A pulse-radiolysis and electron-spin resonance study. *Zeitschrift für Naturforschung Section B. A Journal of Chemical Sciences*, **37**(3), 368–375, 1982. ISSN 0932-0776.
- Bucknall, T., Edwards, H.E., Kemsley, K.G., Moore, J.S., and Phillips, G.O. Formation of Malonaldehyde in Irradiated Carbohydrates. *Carbohydrate Research*, **62**(1), 49–59, 1978. ISSN 0008-6215. doi:10.1016/S0008-6215(00)83377-7.
- Bühler, R.E., Staehelin, J., and Hoigné, J. Ozone decomposition in water studied by pulse-radiolysis. Part 1.  $\text{HO}_2/\text{O}_2^-$  and  $\text{HO}_3/\text{O}_3^-$  as intermediates. *Journal of Physical Chemistry*, **88**(12), 2560–2564, 1984. ISSN 0022-3654.
- Buxton, G., Salmon, G., and Williams, J. The reactivity of biogenic monoterpenes towards  $\text{OH}\cdot$  and  $\text{SO}_4^-\cdot$  radicals in de-oxygenated acidic solution. *Journal of Atmospheric Chemistry*, **36**(2), 111 – 134, 2000. ISSN 0167-7764. doi:10.1023/A:1006340727148.
- Buxton, G.V., Bydder, M., and Salmon, G.A. Reactivity of chlorine atoms in aqueous solution. Part 1. The equilibrium  $\text{Cl} + \text{Cl}^- \rightleftharpoons \text{Cl}^{2-}$ . *Journal of the Chemical Society – Faraday Transactions*, **94**(5), 653 – 657, 1998. ISSN 0956-5000. doi:10.1039/a707377a.
- Buxton, G.V., Bydder, M., and Salmon, G.A. The reactivity of chlorine atoms in aqueous solution. Part II. The equilibrium  $\text{SO}_4^- + \text{Cl}^- \rightleftharpoons \text{Cl} + \text{SO}_4^{2-}$ . *Physical Chemistry Chemical Physics*, **1**(2), 269–273, 1999a. ISSN 1463-9076. doi:10.1039/a807808d.
- Buxton, G.V., Greenstock, C.L., Helman, W.P., and Ross, A.B. Critical review of rate constants for reactions of hydrated electrons, hydrogen-atoms and hydroxyl radicals ( $\text{OH}/\text{O}^-$ ) in aqueous solution. *Journal of Physical and Chemical Reference Data*, **17**(2), 513–886, 1988a. ISSN 0047-2689.
- Buxton, G.V., Malone, T.N., and Salmon, G. Pulse radiolysis study of the reaction of  $\text{SO}_5^-$  with  $\text{HO}_2$ . *Journal of the Chemical Society – Faraday Transactions*, **92**(7), 1287–1289,

- 1996a. ISSN 0956-5000. doi:10.1039/ft9969201287.
- Buxton, G.V., Malone, T.N., and Salmon, G.A. Oxidation of glyoxal initiated by OH in oxygenated aqueous solution. *Journal of the Chemical Society – Faraday Transactions*, **93**(16), 2889–2891, 1997. ISSN 0956-5000. doi:10.1039/a701468f.
- Buxton, G.V., McGowan, S., Salmon, G.A., Williams, J.E., and Woods, N.D. A study of the spectra and reactivity of oxysulphur-radical anions involved in the chain oxidation of S(IV): A pulse and  $\gamma$ -radiolysis study. *Atmospheric Environment*, **30**(14), 2483–2493, 1996b. ISSN 1352-2310. doi:10.1016/1352-2310(95)00473-4.
- Buxton, G.V., Mulazzani, Q.G., and Ross, A.B. Critical-review of rate constants for reactions of transients from metal-ions and metal-complexes in aqueous-solution. *Journal of Physical and Chemical Reference Data*, **24**(3), 1055–1349, 1995. ISSN 0047-2689.
- Buxton, G.V., Salmon, G.A., and Wang, J.Q. The equilibrium  $\text{NO}_3 + \text{Cl}^- \rightleftharpoons \text{NO}_3^- + \text{Cl}$ : A laser flash photolysis and pulse radiolysis study of the reactivity of  $\text{NO}_3$  with chloride ion in aqueous solution. *Physical Chemistry Chemical Physics*, **1**(15), 3589–3593, 1999b. ISSN 1463-9076. doi:10.1039/a903286j.
- Buxton, G.V., Salmon, G.A., and Williams, J.E. The reactivity of oxy-sulphur free radicals with oxalate in aqueous solution. In *Air Pollution Research Report 67*, edited by K.H. Becker, 357 – 362. published by the European Commission, 1999c.
- Buxton, G.V., Salmon, G.A., and Wood, N.D. A pulse-radiolysis study of the chemistry of oxysulphur radicals in aqueous-solution. In *Physico-Chemical Behaviour of Atmospheric Pollutants*, edited by G. Restelli and G. Angeletti, *Air Pollution Research Report*, volume 23, 245–250. 1990. ISBN 0-7923-0700-3. 5th European Symp on Physico-chemical Behaviour of Atmospheric Pollutants, Varese, Italy, Sep 25-28, 1989.
- Buxton, G.V., Wang, J.Q., and Salmon, G.A. Rate constants for the reactions of  $\text{NO}_3$ ,  $\text{SO}_4^-$  and Cl radicals with formate and acetate esters in aqueous solution. *Physical Chemistry Chemical Physics*, **3**(13), 2618–2621, 2001. ISSN 1463-9076. doi:10.1039/b101932p.
- Buxton, G.V., Wood, N.D., and Dyster, S. Ionisation constants of OH and  $\text{HO}_2$  in aqueous solution up to 200°C. A pulse radiolysis study. *Journal of the Chemical Society – Faraday Transactions I*, **84**(4), 1113–1121, 1988b. ISSN 0300-9599. doi:10.1039/f19888401113.
- Cabelli, D.E. and Bielski, B.H.J. A pulse-radiolysis study of some dicarboxylic acids of the citric acid cycle – The kinetics and spectral properties of the free radicals formed by reaction with the OH radical. *Zeitschrift für Naturforschung Section B. A Journal of Chemical Sciences*, **40**(12), 1731–1737, 1985. ISSN 0932-0776.
- Cabelli, D.E., Comstock, D.A., and Bielski, B.H.J. Free radical mechanisms for the oxidation of substituted ascorbates. A pulse radiolysis study of L-ascorbic acid-2-sulfate. *Radiation Research*, **95**(3), 530–540, 1983. ISSN 0033-7587. doi:10.2307/3576098.
- Campi, E. Complessi di ioni metallici con gli acidi tartronico, malico, molonico e succinico. *Annali di Chimica*, **53**, 96 – 116, 1963.

- Carter, W.P.L. Development of a condensed SAPRC-07 chemical mechanism. *Atmospheric Environment*, **44**(40), 5336 – 5345, 2010. ISSN 1352-2310. doi:10.1016/j.atmosenv.2010.01.024. 2nd Biennial Conference on Atmospheric Chemistry Mechanisms, Air Quality Res Ctr, Davis, CA, DEC, 2008.
- Cercek, B. and Ebert, M. Radiolytic transients from p-nitrophenol and their inter- and intramolecular reactions. *Advances in Chemistry Series*, **81**, 210–&, 1968. ISSN 0065-2393.
- Chameides, W.L. The photochemistry of a remote marine stratiform cloud. *Journal of Geophysical Research – Atmospheres*, **89**(ND3), 4739–4755, 1984. ISSN 2169-897X. doi:10.1029/JD089iD03p04739.
- Chang, P.B.L. and Young, T.M. Kinetics of methyl tert-butyl ether degradation and by-product formation during UV/hydrogen peroxide water treatment. *Water Research*, **34**(8), 2233–2240, 2000. ISSN 0043-1354. doi:10.1016/S0043-1354(99)00392-9.
- Chapman, J.D., Grennstock, C.L., Reuvers, A.P., McDonald, E., and Dunlop, I. Radiation chemical studies with nitrofurazone as related to its mechanism of radiosensitization. *Radiation Research*, **53**(2), 190–203, 1973. ISSN 0033-7587. doi:10.2307/3573524.
- Chen, X.F. and Schuler, R.H. Directing effects of phenyl substitution in the reaction of hydroxyl radical with aromatics: the radiolytic hydroxylation of biphenyl. *Journal of Physical Chemistry*, **97**(2), 421–425, 1993. ISSN 0022-3654. doi:10.1021/j100104a025.
- Chin, M. and Wine, P.H. A temperature-dependent competitive kinetics study of the aqueous phase reactions of OH radicals with formate, formic-acid, acetate, acetic acid and hydrated formaldehyde. In *Aquatic and Surface Photochemistry*, edited by G. Helz, R. Zepp, and D. Crosby, 85–96. American Chemical Society, 1994. ISBN 0-87371-871-2. Symposium on Aquatic and Surface Photochemistry, at the 203rd National Meeting of the American-Chemical-Society, San Francisco, CA, APR 05-10, 1992.
- Christensen, H. and Sehested, K. Pulse-radiolysis at high-temperatures and high-pressures. *Radiation Physics and Chemistry*, **18**(3-4), 723–731, 1981. doi:10.1016/0146-5724(81)90195-3.
- Christensen, H., Sehested, K., and Bjergbakke, E. Radiolysis of reactor water: Reaction of hydroxyl radicals with superoxide ( $\text{O}_2^-$ ). *Water Chemistry for Nuclear Reaction Systems*, **5**, 141–144, 1989.
- Christensen, H., Sehested, K., and Corfitzen, H. Reactions of hydroxyl radicals with hydrogen peroxide at ambient and elevated temperatures. *Journal of Physical Chemistry*, **86**(9), 1588–1590, 1982. ISSN 0022-3654. doi:10.1021/j100206a023.
- Christensen, L.K., Sehested, J., Nielsen, O.J., Wallington, T.J., Guschin, A., and Hurley, M.D. Kinetics and mechanism of the reactions of 2,3-butadione with F and Cl atoms, UV absorption spectra of  $\text{CH}_3\text{C}(\text{O})\text{C}(\text{O})\text{CH}_2\cdot$  and  $\text{CH}_3\text{C}(\text{O})\text{C}(\text{O})\text{CH}_2\text{O}_2\cdot$  radicals, and atmospheric fate of  $\text{CH}_3\text{C}(\text{O})\text{C}(\text{O})\text{CH}_2\text{O}\cdot$  radicals. *Journal of Physical Chemistry A*, **102**(45), 8913–8923, 1998. ISSN 1089-5639. doi:10.1021/jp982431y.

- Clegg, S.L. and Brimblecombe, P. Solubility of volatile electrolytes in multicomponent solutions with atmospheric applications. *ACS Symposium Series*, 1990.
- Clifton, C.L. and Huie, R.E. Rate constants for hydrogen abstraction reactions of the sulfate radical,  $\text{SO}_4^-$ . Alcohols. *International Journal of Chemical Kinetics*, **21**(8), 677–687, 1989. ISSN 0538-8066. doi:10.1002/kin.550210807.
- Cooper, W.J., Cramer, C.J., Martin, N.H., Mezyk, S.P., O'Shea, K.E., and von Sonntag, C. Free radical mechanisms for the treatment of methyl tert-butyl ether (MTBE) via advanced oxidation/reductive processes in aqueous solutions. *Chemical Reviews*, **109**(3), 1302–1345, 2009. ISSN 0009-2665. doi:10.1021/cr078024c.
- Cope, V.W., Hoffmann, M.Z., and Chen, S.N. Reactivity of the carbonate radical toward metal complexes in aqueous solution. *Journal of Physical Chemistry*, **82**(25), 2665–2669, 1978. ISSN 0022-3654. doi:10.1021/j100514a007.
- Damschen, D.E. and Martin, L.R. Aqueous aerosol oxidation of nitrous acid by  $\text{O}_2$ ,  $\text{O}_3$  and  $\text{H}_2\text{O}_2$ . *Atmospheric Environment*, **17**(10), 2005–2011, 1983. ISSN 1352-2310. doi:10.1016/0004-6981(83)90357-8.
- D'Angelantonio, M., Emmi, S.S., Poggi, G., and Beggiato, G. Reaction of the OH radical with furfural. Spectral and kinetic investigation by pulse radiolysis and by ab initio and semiempirical methods. *Journal of Physical Chemistry A*, **103**(7), 858–864, 1999. ISSN 1089-5639. doi:10.1021/jp983883d.
- Davidovits, P., Hu, J., Worsnop, D., Zahniser, M., and Kolb, C. Entry of gas molecules into liquids. *Faraday Discussions*, **100**, 65–81, 1995. ISSN 0301-7249. doi:10.1039/fd9950000065. Faraday Discussions on Atmospheric Chemistry - Measurements, Mechanics and Models, UNIV E ANGLIA, E ANGLIA, ENGLAND, APR 19-21, 1995.
- Davies, G., Kirchenbaum, L.J., and Kustin, K. Kinetics and stoichiometry of the reaction between manganese(III) and hydrogen peroxide in acid perchlorate solution. *Inorganic Chemistry*, **7**(1), 146–154, 1968. ISSN 0020-1669. doi:10.1021/ic50059a031.
- de Semainville, P.G., Anna, B.D., and George, C. Aqueous phase reactivity of nitrate radicals ( $\text{NO}_3$ ) toward dicarboxylic acids. *Zeitschrift für physikalische Chemie – International Journal of Research in Physical Chemistry & Chemical Physics*, **224**(7-8), 1247–1260, 2010a. ISSN 0942-9352. doi:10.1524/zpch.2010.6150.
- de Semainville, P.G., Anna, B.D., and George, C. Aqueous phase reactivity of nitrate radicals ( $\text{NO}_3$ ) toward dicarboxylic acids. *Zeitschrift für physikalische Chemie – International Journal of Research in Physical Chemistry & Chemical Physics*, **224**(7-8), 1247–1260, 2010b. ISSN 0942-9352. doi:10.1524/zpch.2010.6150.
- de Semainville, P.G., Hoffmann, D., George, C., and Herrmann, H. Study of nitrate radical ( $\text{NO}_3$ ) reactions with carbonyls and acids in aqueous solution as a function of temperature. *Physical Chemistry Chemical Physics*, **9**(8), 958–968, 2007a. ISSN 1463-9076. doi:10.1039/b613956f.

- de Semainville, P.G., Hoffmann, D., George, C., and Herrmann, H. Study of nitrate radical ( $\text{NO}_3$ ) reactions with carbonyls and acids in aqueous solution as a function of temperature. *Physical Chemistry Chemical Physics*, **9**(8), 958–968, 2007b. ISSN 1463-9076. doi:10.1039/b613956f.
- Diebler, H. and Sutin, N. The kinetics of some oxidation-reduction reactions involving manganese(III). *Journal of Physical Chemistry*, **68**(1), 174, 1964. ISSN 0022-3654. doi:10.1021/j100783a029.
- Doherty, M.D., Wilson, I., Wardman, P., Basra, J., Patterson, L.H., , and Cohen, G.M. Peroxidase activation of 1-naphthol to naphthoxy or naphthoxy-derived radicals and their reaction with glutathione. *Chemico-Biological Interactions*, **58**(2), 199–215, 1986. ISSN 0009-2797. doi:10.1016/S0009-2797(86)80098-9.
- Doussin, J.F. and Monod, A. Structure–activity relationship for the estimation of OH-oxidation rate constants of carbonyl compounds in the aqueous phase. *Atmospheric Chemistry and Physics*, **13**(23), 11625 – 11641, 2013. doi:10.5194/acp-13-11625-2013.
- Draganic, Z.D., Negronmendoza, A., Sehested, K., Vujosevic, S.I., Navarrogonzales, R., Albarransanchez, M.G., and Draganic, I.G. Radiolysis of aqueous-solutions of ammonium bicarbonate over a large dose range. *Radiation Physics and Chemistry*, **38**(3), 317–321, 1991.
- Eibenberger, J. *Pulse radiolytic investigations concerning the formation and the oxidation of organic radicals in aqueous solutions*. Ph.D. thesis, University of Wien, 1980.
- Ek, M., Gierer, J., and Jansbo, K. Study on the selectivity of bleaching with oxygen-containing species. *Holzforschung*, **43**(6), 391 – 396, 1989.
- El Boudali, A., Le Calvé, S., Le Bras, G., and Mellouki, A. Kinetic studies of OH reactions with a series of acetates. *The Journal of Physical Chemistry*, **100**(30), 12364 – 12368, 1996. doi:10.1021/jp9606218.
- Elliot, A.J. and Buxton, G.V. Temperature dependence of the reactions  $\text{OH} + \text{O}$  and  $\text{OH} + \text{HO}_2$  in water up to 200°C. *Journal of the Chemical Society – Faraday Transactions*, **88**(17), 2465 – 2470, 1992. ISSN 0956-5000. doi:10.1039/ft9928802465.
- Elliot, A.J. and McCracken, D.R. Effect of temperature on O-reactions and equilibria – A pulse radiolysis study. *Radiation Physics and Chemistry*, **33**(1), 69–74, 1989.
- Elliot, A.J. and Simsons, A.S. Rate constants for reactions of hydroxyl radicals as a function of temperature. *Radiation Physics and Chemistry*, **24**(2), 229–231, 1984. doi:10.1016/0146-5724(84)90056-6.
- Eriksen, T.E., Lind, J., and Merenyi, G. On the acid-base equilibrium of the carbonate radical. *Radiation Physics and Chemistry*, **26**(2), 197–199, 1985. doi:10.1016/0146-5724(85)90185-2.
- Ervens, B. *Kinetische Untersuchungen zur atmosphärischen Chemie von  $\text{SO}_4^-$ - und  $\text{Cl}_2^-$ -Radikalanionen in wäßriger Lösung*. Diploma thesis, University of Essen, 1997.

- Ervens, B., George, C., Williams, J.E., Buxton, G.V., Salmon, G.A., Bydder, M., Wilkinson, F., Dentener, F., Mirabel, P., Wolke, R., and Herrmann, H. CAPRAM 2.4 (MODAC mechanism): An extended and condensed tropospheric aqueous phase mechanism and its application. *Journal of Geophysical Research – Atmospheres*, **108**(D14), 2003a. ISSN 2156-2202. doi:10.1029/2002JD002202.
- Ervens, B., Gligorovski, S., and Herrmann, H. Temperature-dependent rate constants for hydroxyl radical reactions with organic compounds in aqueous solutions. *Physical Chemistry Chemical Physics*, **5**(9), 1811–1824, 2003b. ISSN 1463-9076. doi:10.1039/b300072a.
- Evers, E.L., Jayson, G.G., Robb, I.D., and Swallow, A.J. Determination by pulse radiolysis of the distribution of solubilizates between micellar and nonmicellar phases. Naphthalene and its reduced free radical in aqueous sodium dodecyl sulphate solutions. *Journal of the Chemical Society – Faraday Transactions 1*, **76**(3), 528–536, 1980. ISSN 0300-9599. doi:10.1039/f19807600528.
- Exner, M. *Bildung und Reaktionen von Radikalen und Radikalanionen in wäßriger Phase*. Diploma thesis, Georg-August University, Göttingen, Germany, 1990.
- Exner, M., Herrmann, H., Michel, J.W., and Zellner, R. Laser pulse initiated measurements of NO<sub>3</sub> reactions with S(IV) and organic compounds in aqueous solutions. In *Proceedings of EUROTRAC Symposium '92: Photo-oxidants: Precursors and Products Proceedings of EUROTRAC Symposium '92: Photo-oxidants: Precursors and Products Proceedings of EUROTRAC Symposium '92: Precursors and Products*, edited by P.M. Borrell, P. Borrell, T. Cvitaš, and W. Seiler, 615 – 618. SPB Academic Publishing, The Hague, NL, 1993.
- Exner, M., Herrmann, H., and Zellner, R. Laser-based studies of reactions of the nitrate radical in aqueous-solution. *Berichte der Bunsen-Gesellschaft – Physical Chemistry Chemical Physics*, **96**(3), 470–477, 1992. ISSN 0005-9021. DISCUSSION MEETING ON PHYSICS and CHEMISTRY of THE ATMOSPHERE, SCHLIERSEE, GERMANY, OCT 07-09, 1991.
- Exner, M., Herrmann, H., and Zellner, R. Rate constants for the reactions of the NO<sub>3</sub> radical with HCOOH/HCOO<sup>−</sup> and CH<sub>3</sub>COOH/CH<sub>3</sub>COO<sup>−</sup> in aqueous solution between 278 and 328 K. *Journal of Atmospheric Chemistry*, **18**(4), 359–378, 1994. ISSN 0167-7764. doi:10.1007/BF00712451.
- Ferrari, C., Roche, A., Jacob, V., Foster, P., and Baussand, P. Kinetics of the reaction of OH radicals with a series of esters under simulated conditions at 295 K. *International Journal of Chemical Kinetics*, **28**(8), 609 – 614, 1996. ISSN 1097-4601. doi:10.1002/(SICI)1097-4601(1996)28:8<609::AID-KIN6>3.0.CO;2-Z.
- Fisher, M.M. and Hamill, W.H. Electronic processes in pulse-irradiated aqueous and alcoholic systems. *Journal of Physical Chemistry*, **77**(2), 171–177, 1973. ISSN 0022-3654. doi:10.1021/j100621a006.



- Flyunt, R., Makogon, O. and Schuchmann, M.N., Asmus, K.D., and von Sonntag, C. OH-Radical-induced oxidation of methanesulfinic acid. The reactions of the methanesulfonyl radical in the absence and presence of dioxygen. *Journal of the Chemical Society – Perkin Transactions 2*, **5**, 787–792, 2001. ISSN 1472-779X. doi:10.1039/b009631h.
- Fornier de Violet, P. Polyhalide anions as intermediates in chemistry. *Review Chemical Intermediates* **4**, 121 – 169, 1981.
- Frenzel, A., Scheer, V., Sikorski, R., George, C., Behnke, W., and Zetzsch, C. Heterogeneous interconversion reactions of  $\text{BrNO}_2$ ,  $\text{ClNO}_2$ ,  $\text{Br}_2$ , and  $\text{Cl}_2$ . *Journal of Physical Chemistry A*, **102**(8), 1329–1337, 1998. ISSN 1089-5639. doi:10.1021/jp973044b.
- Fuller, E.N. Diffusion coefficients for binary gas systems at low pressures: Empirical correlations. In *Properties of Gases and Liquids*, edited by R. *et al.*, 587. McGraw Hill, New York, 1986.
- Gaffney, J.S., Streit, G.E., Spall, W.D., and Hall, J.H. Beyond Acid-Rain – Do Soluble Oxidants and Organic Toxins Interact with  $\text{SO}_2$  and  $\text{NO}_x$  to Increase Ecosystem Effects. *Environmental Science & Technology*, **21**(6), 519 – 524, 1987. ISSN 0013-936X. doi: {10.1021/es00160a001}.
- Gardner, J.A., Watson, L.R., Adewuyi, Y.G., Davidovits, P., Zahniser, M.S., Worsnop, D.R., and Kolb, C.E. Measurement of the mass accommodation coefficient of  $\text{SO}_2$  (g) on water droplets. *Journal of Geophysical Research – Atmospheres*, **92**(D9), 10887–10895, 1987. doi:10.1029/JD092iD09p10887.
- Garoma, T. and Gurol, M.D. Modeling aqueous ozone/UV process using oxalic acid as probe chemical. *Environmental Science & Technology*, **39**(20), 7964–7969, 2005. ISSN 0013-936X. doi:10.1021/es050878w.
- Geeta, S., Sharma, S.B., Rao, B.S.M., Mohan, H., Dhanya, S., and Mittal, J.P. Study of kinetics and absorption spectra of OH adducts of hydroxy derivatives of benzaldehyde and acetophenone. *Journal of Photochemistry and Photobiology A: Chemistry*, **140**(2), 99–107, 2001. ISSN 1010-6030. doi:10.1016/S1010-6030(01)00402-6.
- George, C., Ponche, J.L., Mirabel, P., Behnke, W., Scheer, V., and Zetzsch, C. Study of the uptake of  $\text{N}_2\text{O}_5$  by water and NaCl solutions. *Journal of Physical Chemistry*, **98**(35), 8780–8784, 1994. ISSN 0022-3654. doi:10.1021/j100086a031.
- George, C., Rouse, D., Perraudin, E., and Strekowski, R. A new approach for studying aqueous phase OH kinetics: application of Teflon waveguides. *Physical Chemistry Chemical Physics*, **5**(8), 1562–1569, 2003. ISSN 1463-9076. doi:10.1039/b301145n.
- Getoff, N. Advancements of radiation-induced degradation of pollutants in drinking and waste-water. *Applied Radiation and Isotopes*, **40**(7), 585–594, 1989. ISSN 0969-8043.
- Getoff, N., Schworer, F., Markovic, V.M., Sehested, K., and Nielsen, S.O. Pulse radiolysis of oxalic acid and oxalates. *Journal of Physical Chemistry*, **75**(6), 749, 1971. ISSN 0022-3654.

- Gilbert, B.C. and Whitwood, A.C. Vinyl-radical rearrangements. E.s.r. evidence for the formation of enol radical cations by the protonation at carbon of  $\beta$ -hydroxyvinyl radicals and for a 1,4-hydrogen shift in some  $\beta$ -sulphur-substituted analogues. *Journal of the Chemical Society – Perkin Transactions 2*, **11**, 1921–1927, 1989. ISSN 0300-9580. doi:10.1039/p29890001921.
- Gligorovski, S. *Laser based studies of OH radical reactions in aqueous solution*. Ph.D. thesis, University of Leipzig, 2005.
- Gligorovski, S. and Herrmann, H. Kinetics of reactions of OH with organic carbonyl compounds in aqueous solution. *Physical Chemistry Chemical Physics*, **6**(16), 4118–4126, 2004. ISSN 1463-9076. doi:10.1039/b403070b.
- Gligorovski, S., Rouse, D., George, C.H., and Herrmann, H. Rate constants for the OH reactions with oxygenated organic compounds in aqueous solution. *International Journal of Chemical Kinetics*, **41**(5), 309–326, 2009. ISSN 0538-8066. doi:10.1002/kin.20405.
- Glowa, G., Driver, P., and Wren, J.C. Irradiation of MEK – Part II: A detailed kinetic model for the degradation under of 2-butanone in aerated aqueous solutions steady-state  $\gamma$ -radiolysis conditions. *Radiation Physics and Chemistry*, **58**(1), 49–68, 2000. ISSN 0969-806X. doi:10.1016/S0969-806X(99)00360-6.
- Gohn, M. and Getoff, N. Pulse-radiolysis of 3,4-dihydroxytoluene. *Journal of the Chemical Society – Faraday Transactions I*, **73**, 1207–1215, 1977. ISSN 0300-9599. doi:10.1039/f19777301207.
- Goldstein, S., Czapski, G., Cohen, H., and Meyerstein, D. Deamination of  $\beta$ -alanine induced by hydroxyl radicals and monovalent copper ions. A pulse radiolysis study. *Inorganica chimica acta*, **192**(1), 87–93, 1992. ISSN 0020-1693. doi:10.1016/S0020-1693(00)83177-1.
- Gopakumar, K., Kini, U.R., Ashawa, S.C., Bhandari, N.S., Krishnan, G.U., and Krishnan, D. Gamma irradiation of coumarin in aqueous solution. *Radiation Effects and Defects in Solids*, **32**(3-4), 199–203, 1977. ISSN 1042-0150. doi:10.1080/00337577708233075.
- Graedel, T.E. and Weschler, C.J. Chemistry within aqueous atmospheric aerosols and raindrops. *Reviews of Geophysics*, **19**(4), 505–539, 1981. ISSN 8755-1209. doi:10.1029/RG019i004p00505.
- Greenstock, C.L. and Dunlop, I. Pulse radiolysis studies of nitrofurans. radiation chemistry of nifuroxime. *Journal of Physical Chemistry*, **77**(15), 1834–1838, 1973. ISSN 0022-3654. doi:10.1021/j100634a600.
- Grigorov, A.E., Makarov, I.E., and Pikaev, A.K. Formation of  $\text{Cl}_2^-$  in the bulk solution during the radiolysis of concentrated aqueous solutions of chlorides. *High Energy Chemistry*, **21**(2), 99–102, 1987. ISSN 0018-1439.
- Guthrie, J.P. Uncatalyzed and amine catalyzed decarboxylation of acetoacetic acid: An examination in terms of no barrier theory. *Bioorganic Chemistry*, **30**(1), 32–52, 2002. ISSN 0045-2068. doi:10.1006/bioo.2001.1231.

- Guthrie, J.P. and Jordan, F. Amine-catalyzed decarboxylation of acetoacetic acid. The rate constant for decarboxylation of a  $\beta$ -imino acid. *Journal of the American Chemical Society*, **94**(26), 9136–9141, 1972. ISSN 0002-7863. doi:10.1021/ja00781a025.
- Haag, W.R. and Yao, C.C.D. Rate constants for reaction of hydroxyl radicals with several drinking water contaminants. *Environmental Science & Technology*, **26**(5), 1005–1013, 1992. ISSN 0013-936X. doi:10.1021/es00029a021.
- Hanson, D.R., Burkholder, J.B., Howard, C.J., and Ravishankara, A.R. Measurement of OH and HO<sub>2</sub> radical uptake coefficients on water and sulfuric acid surfaces. *Journal of Physical Chemistry*, **96**(12), 4979 – 4985, 1992. ISSN 0022-3654. doi:10.1021/j100191a046.
- Hardison, D.R., Cooper, W.J., Mezyk, S.P., and Bartels, D.M. The free radical chemistry of tert-butyl formate: rate constants for hydroxyl radical, hydrated electron and hydrogen atom reaction in aqueous solution. *Radiation Physics and Chemistry*, **65**(4-5), 309–315, 2002. ISSN 0969-806X. doi:10.1016/S0969-806X(02)00333-X. Pacificchem 2000 Meeting, HONOLULU, HAWAII, DEC 14-19, 2000.
- Harned, H.S. and Owen, B.B. *The physical chemistry of electrolytic solutions*. Reinhold, New York, 3 edition, 1958.
- Hart, E.J., Gordon, S., and Thomas, J.K. Review of radiation chemistry of single-carbon compounds + some reactions of hydrated electron in aqueous solution. *Radiation Research*, **S**(4), 74, 1964. ISSN 0033-7587.
- Heckel, E., Henglein, A., and Beck, G. Pulsradiolytische Untersuchung des Radikalanions SO<sub>4</sub><sup>-</sup>. *Berichte der Bunsen-Gesellschaft für physikalische Chemie*, **70**(2), 149–&, 1966.
- Hemmes, P., Rich, L.D., Cole, D.L., and Eyring, E.M. Kinetics of hydrolysis of ferric ion in dilute aqueous solution. *Journal of Physical Chemistry*, **75**(7), 929, 1971. ISSN 0022-3654. doi:10.1021/j100677a015.
- Herrmann, H. Kinetics of aqueous phase reactions relevant for atmospheric chemistry. *Chemical Reviews*, **103**(12), 4691–4716, 2003. ISSN 0009-2665. doi:10.1021/cr020658q.
- Herrmann, H., Buxton, G., Salmon, A., Mirabel, P., George, C., Lelieveld, J., and Dentener, F. *Model development for tropospheric aerosol and cloud chemistry (MODAC)*. Final Report, No. ENV4-CT97-0388, 2000.
- Herrmann, H., Ervens, B., Nowacki, P., Wolke, R., and Zellner, R. A chemical aqueous phase radical mechanism for tropospheric chemistry. *Chemosphere*, **38**(6), 1223 – 1232, 1999. ISSN 0045-6535. doi:10.1016/S0045-6535(98)00520-7.
- Herrmann, H., Exner, M., Jacobi, H.-W., Raabe, G., Reese, A., and Zellner, R. Laboratory studies of atmospheric aqueous-phase free-radical chemistry: kinetic and spectroscopic studies of reactions of NO<sub>3</sub> and SO<sub>4</sub><sup>-</sup> radicals with aromatic compounds. *Faraday Discussions*, **100**, 129 – 153, 1995a. doi:10.1039/FD9950000129.
- Herrmann, H., Exner, M., and Zellner, R. Reactivity trends in reactions of the nitrate radical (NO<sub>3</sub>) with inorganic and organic cloudwater constituents. *Geochimica et Cosmochimica*

- Acta*, **58**(15), 3239–3244, 1994. ISSN 0016-7037. doi:10.1016/0016-7037(94)90051-5. Symposium on Topics in Global Geochemistry, in Honor of Clair C Patterson, Pasadena, CA, DEC 03-04, 1993.
- Herrmann, H., Jacobi, H.-W., Raabe, G., Reese, A., Umschlag, T., and Zellner, R. Free radical reactions in the tropospheric aqueous phase. In *The oxidizing capacity of the troposphere*, 503 – 512. Proceedings of the seventh European symposium on physico-chemical behaviour of atmospheric pollutants, Venice, Italy, 1996a.
- Herrmann, H., Jacobi, H.-W., Raabe, G., Reese, A., and Zellner, R. Laboratory studies of free radicals reactions with tropospheric aqueous phase constituents. In *Air Pollution Research Report 57: Homogenous and heterogenous chemical Processes in the Troposphere*, edited by P. Mirabel, 90–95. Office for official Publications of the European Communities, 1996b.
- Herrmann, H., Jacobi, H.-W., Reese, A., and Zellner, R. Laboratory studies of small radicals and radical anions of interest for tropospheric aqueous phase chemistry: The reactivity of  $\text{SO}_4^-$ . In *Transport and Transformation of Pollutants in the Troposphere*, edited by P.M. Borrell, T. Cvitaš, K. Kelly, and W. Seiler, *Proceedings of EUROTRAC Symposium 96*, volume 1, 407–411. Computational Mechanics Publications, Southampton, UK, 1997.
- Herrmann, H., Raabe, G., Jacobi, H.-W., and Zellner, R. Ionic strength effects in radical ion-dipole reactions in the tropospheric aqueous phase. In *Air Pollution Research Report 54: Tropospheric Oxidation Mechanisms*, edited by K.H. Becker, 471–475. Office for official Publications of the European Communities, 1995b.
- Herrmann, H., Reese, A., and Zellner, R. Time-resolved UV/VIS diode array absorption spectroscopy of  $\text{SO}_x^-$  ( $x=3, 4, 5$ ) radical anions in aqueous solution. *Journal of Molecular Structure*, **348**, 183–186, 1995c. ISSN 0022-2860. doi:10.1016/0022-2860(95)08619-7. XXIIInd European Congress on Molecular Spectroscopy - Molecular Spectroscopy and Molecular Structure 1994, ESSEN, GERMANY, SEP 11-16, 1994.
- Herrmann, H. and Zellner, R. Reactions of  $\text{NO}_3$  radicals in aqueous solution. In *N-Centered Radicals*, edited by Z.B. Alfassi, 291–243. Wiley, 1998.
- Hesper, J. *Spektroskopische und kinetische Untersuchungen von Reaktionen der Radikale  $\text{O}_2^-$  und OH in wässriger Phase*. Ph.D. thesis, University of Leipzig, 2003.
- Hesper, J. and Herrmann, H. A T-dependent study of the reaction of the superoxide radical anion ( $\text{O}_2^-$ ) with ozone in aqueous solution. In *Proceedings of EUROTRAC Symposium 2000: Transport and Transformation of Pollutants in the Troposphere*. 2003.
- Hilal, S.H., Ayyampalayam, S.N., and Carreira, L.A. Air-liquid partition coefficient for a diverse set of organic compounds: Henry's Law constant in water and hexadecane. *Environmental Science & Technology*, **42**(24), 9231 – 9236, 2008.
- Hilborn, J.W. and Pincock, J.A. Rates of decarboxylation of acyloxy radicals formed in the photocleavage of substituted 1-naphthylmethyl alkanoates. *Journal of the American*

- Chemical Society*, **113**(7), 2683–2686, 1991. ISSN 0002-7863. doi:10.1021/ja00007a049.
- Hine, J. and Mookerjee, P.K. Intrinsic hydrophilic character of organic compounds – Correlations in terms of structural contributions. *Journal of Organic Chemistry*, **40**(3), 292 – 298, 1975. ISSN 0022-3263. doi:{10.1021/jo00891a006}.
- Hoffmann, D., Weigert, B., Barzaghi, P., and Herrmann, H. Reactivity of poly-alcohols towards OH, NO<sub>3</sub> and SO<sub>4</sub><sup>-</sup> in aqueous solution. *Physical Chemistry Chemical Physics*, **11**(41), 9351–9363, 2009. ISSN 1463-9076. doi:10.1039/b908459b.
- Hoffmann, M.R. On the kinetics and mechanism of oxidation of aquated sulfur dioxide by ozone. *Atmospheric Environment*, **20**(6), 1145–1154, 1986. ISSN 1352-2310. doi:10.1016/0004-6981(86)90147-2.
- Hoigné, J. and Böhler, R.E. *Heterogenous and Liquid Phase Processes*, 110 – 115. Springer Verlag, Berlin, 1996.
- Horii, H., Abe, Y., and Taniguchi, S. Pulse Radiolysis Study of Reaction of OH Radicals with Triose Reductone. *Bulletin of the Chemical Society of Japan*, **59**(3), 721–724, 1986. ISSN 0009-2673. doi:10.1246/bcsj.59.721.
- Huie, R.E. and Clifton, C.L. Temperature dependence of the rate constants for reactions of the sulfate radical, SO<sub>4</sub><sup>-</sup>, with anions. *Journal of Physical Chemistry*, **94**(23), 8561–8567, 1990. ISSN 0022-3654. doi:10.1021/j100386a015.
- Huie, R.E., Shoute, L.C.T., and Neta, P. Temperature dependence of the rate constants for reactions of the carbonate radical with organic and inorganic reductants. *International Journal of Chemical Kinetics*, **23**(6), 541–552, 1991. ISSN 0538-8066. doi:10.1002/kin.550230606.
- Hulme, B.E., Phillips, G.O., and Land, E.J. Pulse radiolysis of 9,10-anthraquinones. Part 1. - Radicals. *Journal of the Chemical Society – Faraday Transactions 1*, **68**, 1992–&, 1972. ISSN 0300-9599. doi:10.1039/f19726801992.
- Ip, H.S.S., Huang, X.H.H., and Yu, J.Z. Effective Henry's law constants of glyoxal, glyoxylic acid, and glycolic acid. *Geophysical Research Letters*, **36**(1), 2009. ISSN 1944-8007. doi:10.1029/2008GL036212.
- Ito, O., Akiho, S., and Imo, M. Kinetic study for reactions of nitrate radical (NO<sub>3</sub>) with alcohols in solutions. *Bulletin of the Chemical Society of Japan*, **62**(5), 1606 – 1611, 1989a. ISSN 0009-2673. doi:10.1246/bcsj.62.1606.
- Ito, O., Akiho, S., and Imo, M. Kinetics for reactions of the nitrate radical (NO<sub>3</sub>) with aldehydes in acetonitrile. *Journal of Physical Chemistry*, **93**(10), 4079 – 4083, 1989b. ISSN 0022-3654. doi:10.1021/j100347a041.
- Jacob, D.J. Chemistry of OH in remote clouds and its role in the production of formic acid and peroxymonosulfate. *Journal of Geophysical Research – Atmospheres*, **91**(D9), 9807–9826, 1986. ISSN 2169-897X. doi:10.1029/JD091iD09p09807.

- Jacob, D.J., Gottlieb, E.W., and Prather, M.J. Chemistry of a polluted cloudy boundary layer. *Journal of Geophysical Research – Atmospheres*, **94**(D10), 12975–13002, 1989. ISSN 2169-897X. doi:10.1029/JD094iD10p12975.
- Jacobi, H.-W., Herrmann, H., and Zellner, R. Kinetic investigation of the  $\text{Cl}_2^-$  radical in the aqueous phase. In *Air Pollution Research Report 57: Homogenous and heterogenous chemical Processes in the Troposphere*, edited by P. Mirabel, 172–176. Office for official Publications of the European Communities, 1996.
- Jacobi, H.-W., Wicktor, F., Herrmann, H., and Zellner, R. A laser flash photolysis kinetic study of reactions of the  $\text{Cl}_2^-$  radical anion with oxygenated hydrocarbons in aqueous solution. *International Journal of Chemical Kinetics*, **31**(3), 169–181, 1999. ISSN 0538-8066. doi:10.1002/(SICI)1097-4601(1999)31:3<169::AID-KIN2>3.0.CO;2-K.
- Jacobsen, F., Holcman, J., and Sehested, K. Activation parameters of ferryl ion reactions in aqueous acid solutions. *International Journal of Chemical Kinetics*, **29**(1), 17–24, 1997a. ISSN 0538-8066. doi:10.1002/(SICI)1097-4601(1997)29:1<17::AID-KIN3>3.0.CO;2-O.
- Jacobsen, F., Holcman, J., and Sehested, K. Manganese(II)-superoxide complex in aqueous solution. *Journal of Physical Chemistry A*, **101**(7), 1324–1328, 1997b. ISSN 1089-5639. doi:10.1021/jp962867i.
- Jacobsen, F., Holcman, J., and Sehested, K. Reactions of the ferryl ion with some compounds found in cloud water. *International Journal of Chemical Kinetics*, **30**(3), 215–221, 1998. ISSN 0538-8066. doi:10.1002/(SICI)1097-4601(1998)30:3<215::AID-KIN7>3.0.CO;2-V.
- Janata, E. Direct optical observation of the formation of some aliphatic alcohol radicals. A pulse radiolysis study. *Proceedings of the Indian Academy of Sciences – Chemical Sciences*, **114**(6), 731–737, 2002. ISSN 0253-4134. 3rd Asian Photochemistry Conference (APC-2002), MUMBAI, INDIA, JAN 06-11, 2002.
- Janik, I., Ulanski, P., Rosiak, J.M., and von Sonntag, C. Hydroxyl-radical-induced reactions of the poly(vinyl methyl ether) model 2,4-dimethoxypentane in the absence and presence of dioxygen: a pulse radiolysis and product study. *Journal of the Chemical Society – Perkin Transactions 2*, **10**, 2034–2040, 2000. ISSN 1472-779X. doi:10.1039/b004776g.
- Jayne, J.T., Duan, S.X., Davidovits, P., Worsnop, D.R., Zahniser, M.S., and Kolb, C.E. Uptake of gas-phase alcohol and organic acid molecules by water surfaces. *Journal of Physical Chemistry*, **95**(16), 6329–6336, 1991. ISSN 0022-3654. doi:10.1021/j100169a047.
- Jayson, G.G., Parsons, B.J., and Swallow, A.J. Oxidation of ferrous ions by perhydroxyl radicals. *Journal of the Chemical Society – Faraday Transactions I*, **69**(1), 236–242, 1973a. ISSN 0300-9599. doi:10.1039/f19736900236.
- Jayson, G.G., Parsons, B.J., and Swallow, A.J. Some simple, highly reactive, inorganic chloride derivatives in aqueous-solution. Their formation using pulses of radiation and their role in mechanism of fricke dosimeter. *Journal of the Chemical Society – Faraday Transactions I*, **9**, 1597–1607, 1973b. ISSN 0300-9599.

- Jiang, P.Y., Katsumura, Y., Nagaishi, R., Domae, M., Ishikawa, K., Ishigure, K., and Yoshida, Y. Pulse radiolysis study of concentrated sulfuric acid solutions. Formation mechanism, yield and reactivity of sulfate radicals. *Journal of the Chemical Society – Faraday Transactions*, **88**(12), 1653–1658, 1992. ISSN 0956-5000. doi:10.1039/ft9928801653.
- Kames, J. and Schurath, U. Alkyl nitrates and bifunctional nitrates of atmospheric interest – Henry’s Law constants and their temperature dependencies. *Journal of Atmospheric Chemistry*, **15**(1), 79 – 95, 1992. ISSN 0167-7764. doi:{10.1007/BF00053611}.
- Kanodia, S., Madhavan, V., and Schuler, R.H. Oxidation of naphthalene by radiolytically produced OH radicals. *Radiation Physics and Chemistry*, **32**(5), 661–664, 1988.
- Katrib, Y., Deiber, G., Schweitzer, F., Mirabel, P., and George, C. Chemical transformation of bromine chloride at the air/water interface. *Journal of Aerosol Science*, **32**(7), 893 – 911, 2001. ISSN 0021-8502. doi:10.1016/S0021-8502(00)00114-2.
- Khaikin, G.I., Alfassi, Z.B., Huie, R.E., and Neta, P. Oxidation of ferrous and ferrocyanide Ions by peroxy radicals. *The Journal of Physical Chemistry*, **100**(17), 7072 – 7077, 1996. doi:10.1021/jp9533335.
- Khan, I. and Brimblecombe, P. Henry’s Law constants of low molecular weight (<130) organic acids. *Journal of Aerosol Science*, **23**, 897 – 900, 1992. ISSN 0021-8502. doi:[http://dx.doi.org/10.1016/0021-8502\(92\)90556-B](http://dx.doi.org/10.1016/0021-8502(92)90556-B). <ce:title>Proceedings of the 1992 European Aerosol Conference </ce:title>.
- Khan, I., Brimblecombe, P., and Clegg, S.L. Solubilities of pyruvic acid and the lower (C<sub>1</sub>–C<sub>6</sub>) carboxylic acids. Experimental determination of equilibrium vapour pressures above pure aqueous and salt solutions. *Journal of Atmospheric Chemistry*, **22**(3), 285–302, 1995. ISSN 0167-7764. doi:10.1007/BF00696639.
- Kim, B.R., Kalis, E.M., DeWulf, T., and Andrews, K.M. Henry’s Law constants for paint solvents and their implications on volatile organic compound emissions from automotive painting. *Water Environment Research*, **72**(1), 65–74, 2000. ISSN 1061-4303. doi:10.2175/106143000X137121.
- Kirchner, W., Welter, F., and Schurath, U. Trace-gas-exchange kinetics at the air-water-interface. In *Physico-Chemical Behaviour of Atmospheric Pollutants*, edited by G. RESTELLI and G. ANGELETTI, *AIR POLLUTION RESEARCH REPORT*, volume 23, 270–276. 1990. ISBN 0-7923-0700-3. 5TH EUROPEAN SYMP ON PHYSICO-CHEMICAL BEHAVIOUR of ATMOSPHERIC POLLUTANTS, VARESE, ITALY, SEP 25-28, 1989.
- Kläning, U.K., Sehested, K., and Holcman, J. Standard gibbs energy of formation of the hydroxyl radical in aqueous solution. Rate constants for the reaction  $\text{ClO}_2^- + \text{O}_3 \rightleftharpoons \text{O}_3^- + \text{ClO}_2$ . *Journal of Physical Chemistry*, **89**(5), 760–763, 1985. ISSN 0022-3654. doi:10.1021/j100251a008.

- Kläning, U.K., Sehested, K., and Wolff, T. Ozone formation in laser flash photolysis of oxoacids and oxoanions of chlorine and bromine. *Journal of the Chemical Society – Faraday Transactions I*, **80**(11), 2969–2979, 1984. ISSN 0300-9599. doi:10.1039/f19848002969.
- Kläning, U.K. and Wolff, T. Laser flash-photolysis of  $\text{HClO}$ ,  $\text{ClO}^-$ ,  $\text{HBrO}$ , and  $\text{BrO}^-$  in aqueous-solution. Reactions of Cl-atoms and Br-atoms. *Berichte der Bunsen-Gesellschaft – Physical Chemistry Chemical Physics*, **89**(3), 243–245, 1985. ISSN 0005-9021.
- Kosak-Channing, L.F. and Helz, G.R. Solubility of ozone in aqueous solutions of ionic strength at 530°C. *Environmental Science & Technology*, **17**(3), 145–149, 1983. ISSN 0013-936X. doi:10.1021/es00109a005.
- Kozlov, Y.N. and Berdnikov, V.M. Photochemical  $\text{H}_2\text{O}_2$  decomposition in presence of copper ions. Part 4. Determination of elemental reaction rate constants. *Zhurnal Fizicheskoi Khimii*, **47**(3), 598–602, 1973. ISSN 0044-4537.
- Kraljic, I. Kinetics of OH radical reactions in radiolysis, photolysis, and the fenton system. In *The Chemistry of Ionization and Excitation*, edited by G.R.A. Johnson and G. Scholes, 167–173. Taylor and Francis Ltd, 1967.
- Kumar, M. and Rao, M.H. Pulse-radiolysis study of initiation, dimerization, and propagation steps of 3,3-dimethylacrylic acid in aqueous-medium. *Journal of Macromolecular Science: Part A – Chemistry*, **A28**(5-6), 531–544, 1991. ISSN 0022-233X. doi:10.1080/00222339108052105.
- Kumar, M., Rao, M.H., Moorthy, P.N., and Rao, K.N. Structural influences on the reactivity of vinyl monomers with hydroxyl radicals and hydrated electrons studied by pulse radiolysis. *Radiation Effects Express*, **1**, 167–173, 1988.
- Kuzmin, V.A. Reactions of the  $\text{CO}_3^-$  and  $\text{SiO}_3^-$  radical anions. *High Energy Chemistry*, **6**, 338–339, 1972.
- Lammel, G., Perner, D., and Warneck, P. Decomposition of pernitric acid in aqueous solution. *Journal of Physical Chemistry*, **94**(15), 6141–6144, 1990. ISSN 0022-3654. doi:10.1021/j100378a091.
- Land, E.J. and Swallow, A.J. Some free radical reactions of camphor in relation to the action of cytochrome P450. *Journal of the Chemical Society – Faraday Transactions 1*, **75**(8), 1849–1856, 1979. ISSN 0300-9599. doi:10.1039/f19797501849.
- Langer, S., Ljungström, E., Wängberg, I., Wallington, T.J., Hurley, M.D., and Nielsen, O.J. Atmospheric chemistry of di-tert-butyl ether: Rates and products of the reactions with chlorine atoms, hydroxyl radicals, and nitrate radicals. *International Journal of Chemical Kinetics*, **28**(4), 299 – 306, 1996. ISSN 1097-4601. doi:10.1002/(SICI)1097-4601(1996)28:4<299::AID-KIN8>3.0.CO;2-Q.
- Laurence, G.S. and Thornton, A.T. Kinetics of oxidation of transition-metal ions by halogen radical anions. Part III. The oxidation of manganese(II) by dibromide and



- dichloride ions generated by flash photolysis. *Journal of the Chemical Society – Dalton Transactions*, **16**, 1637–1644, 1973. ISSN 0300-9246. doi:10.1039/dt9730001637.
- Law, K.S., Sturges, W.T., Blake, D.R., Blake, N.J., Burkholder, J.B., Butler, J.H., Cox, R.A., Haynes, P.H., Ko, M.K.W., Kreher, K., Mari, C., Pfeilsticker, K., Plane, J.M.C., Salawitch, R.J., Schiller, C., Sinnhuber, B.M., von Glasow, R., Warwick, N.J., Wuebbles, D.J., and Yvon-Lewis, S.A. Scientific Assessment of Ozone Depletion. In *Global Ozone Research and Monitoring Project – Report No. 50*, Global Ozone Research and Monitoring Project – Report No. 50, chapter 2: Halogenated Very Short Live Substances. World Meteorological Organization, Genf, Schweiz, 2007.
- Le Calvé, S., Le Bras, G., and Mellouki, A. Kinetic studies of OH reactions with a series of methyl esters. *The Journal of Physical Chemistry A*, **101**(48), 9137 – 9141, 1997a. doi:10.1021/jp972369p.
- Le Calvé, S., Le Bras, G., and Mellouki, A. Kinetic studies of OH reactions with Iso-propyl, Iso-butyl, Sec-butyl, and Tert-butyl acetate. *International Journal of Chemical Kinetics*, **29**(9), 683 – 688, 1997b. ISSN 1097-4601. doi:10.1002/(SICI)1097-4601(1997)29:9<683::AID-KIN5>3.0.CO;2-Q.
- Le Calvé, S., Le Bras, G., and Mellouki, A. Temperature Dependence for the Rate Coefficients of the Reactions of the OH Radical with a Series of formates. *The Journal of Physical Chemistry A*, **101**(30), 5489 – 5493, 1997c. doi:10.1021/jp970554x.
- Lelieveld, J. and Crutzen, P.J. The role of clouds in tropospheric photochemistry. *Journal of Atmospheric Chemistry*, **12**(3), 229–267, 1991. ISSN 0167-7764. doi:10.1007/BF00048075.
- Lide, D. and Frederikse, H. *Handbook of Chemistry and Physics*. CRC Press, Boca Raton, 76th edition, 1995.
- Lilie, J. Pulsradiolytic investigations of oxydativ ring scission of furan, thiophen and pyrrol. *Zeitschrift für Naturforschung Part B – Chemie Biochemie Biophysik Biologie und verwandten Gebiete*, **B 26**(3), 197, 1971.
- Lilie, J., Hanrahan, R.J., and Henglein, A. O<sup>-</sup> transfer reactions of the carbonate radical anion. *Radiation Physics and Chemistry*, **11**(5), 225–227, 1978. doi:10.1016/0146-5724(78)90101-2.
- Lilie, J. and Henglein, A. Pulse radiolytic studies of oxidation of unsaturated carbonyl compounds in aqueous solution - Hydrated enols as intermediate products. *Berichte der Bunsen-Gesellschaft für physikalische Chemie*, **74**(4), 388, 1970.
- Lind, J. and Eriksen, T.E. The reactions of hydroxyl radicals with alkyl disulphonic acids in aqueous solution studied by pulse radiolysis. *Radiation Physics and Chemistry*, **10**(5-6), 349–352, 1977. doi:10.1016/0146-5724(77)90043-7.
- Lind, J.A. and Kok, G.L. Henrys law determinations for aqueous-solutions of hydrogen-peroxide, methylhydroperoxide, and peroxyacetic acid. *Journal of Geophysical Research – Atmospheres*, **99**(D10), 21119, 1994. ISSN 2169-897X.

- Lind, J.A., Lazrus, A.L., and Kok, G.L. Aqueous phase oxidation of sulfur(IV) by hydrogen peroxide, methylhydroperoxide, and peroxyacetic acid. *Journal of Geophysical Research – Atmospheres*, **92**(D4), 4171–4177, 1987. ISSN 2169-897X. doi:10.1029/JD092iD04p04171.
- Løgager, T., Holcman, J., Sehested, K., and Pedersen, T. Oxidation of ferrous-ions by ozone in acidic solutions. *Inorganic Chemistry*, **31**(17), 3523–3529, 1992. ISSN 0020-1669.
- Løgager, T. and Sehested, K. Formation and decay of peroxyntic acid. A pulse radiolysis study. *Journal of Physical Chemistry*, **97**(39), 10047–10052, 1993. ISSN 0022-3654.
- Løgager, T., Sehested, K., and Holcman, J. Rate constants of the equilibrium reactions  $\text{SO}_4^- + \text{HNO}_3 \rightleftharpoons \text{HSO}_4^- + \text{NO}_3$  and  $\text{SO}_4^- + \text{NO}_3^- \rightleftharpoons \text{SO}_4^{2-} + \text{NO}_3$ . *Radiation Physics and Chemistry*, **41**(3), 539–543, 1993. ISSN 0146-5724. doi:10.1016/0969-806X(93)90017-O.
- Logan, S.R. Redox reactions of organic radicals with ferrocene/ferricenium species in aqueous solution. Part 1. Radicals derived from carboxylic acids. *Journal of the Chemical Society – Perkin Transactions 2*, **7**, 751 – 754, 1989. ISSN 0300-9580. doi:10.1039/p29890000751.
- Loomis, A.G. Solubilities of gases in water. In *International Critical Tables Vol. III: Solubilities of Gases in Water*, edited by E.W. Washburn, C.J. West, N.E. Dorsey, B.F. R., and K. A., 255–261. McGraw-Hill, 1928.
- Magneron, I., Thévenet, R., Mellouki, A., Le Bras, G., Moortgat, G.K., and Wirtz, K. A study of the photolysis and OH-initiated oxidation of acrolein and trans-crotonaldehyde. *The Journal of Physical Chemistry A*, **106**(11), 2526 – 2537, 2002. doi:10.1021/jp013413a.
- Makarov, I.E., Protasova, E.L., and Khaikin, G.I. The kinetics of radical reactions in the radiolysis of aqueous solutions of organic nitro compounds. *Russian Journal of Physical Chemistry A*, **82**(11), 1833–1837, 2008. ISSN 0036-0244. doi:10.1134/S0036024408110083.
- Marchaj, A., Kelley, D.G., Bakac, A., and Espenson, J.H. Kinetics of the reactions between alkyl radicals and molecular oxygen in aqueous solution. *Journal of Physical Chemistry*, **95**(11), 4440–4441, 1991. ISSN 0022-3654. doi:10.1021/j100164a051.
- Marsh, A.R.W. and McElroy, W.J. The dissociation constant and Henry’s Law constant of HCl in aqueous solution. *Atmospheric Environment*, **19**(7), 1075–1080, 1985. ISSN 1352-2310. doi:10.1016/0004-6981(85)90192-1.
- Martin, L.R., Mezyk, S.P., and Mincher, B.J. Determination of arrhenius and thermodynamic parameters for the aqueous reaction of the hydroxyl radical with lactic acid. *Journal of Physical Chemistry A*, **113**(1), 141–145, 2009. ISSN 1089-5639. doi: 10.1021/jp806290s.
- Maruthamuthu, M. and Dhandavel, R. Binding of bromocresol green onto poly(n-vinyl-2-pyrrolidone). *Makromolekulare Chemie – Rapid Communications*, **1**(10), 633–636, 1980. ISSN 0173-2803.
- Maruthamuthu, P. Absolute rate constants for the reactions of sulfate, phosphate and hydroxyl radicals with monomers. *Makromolekulare Chemie – Rapid Communications*,

- 1(1), 23–25, 1980. ISSN 0173-2803.
- Maruthamuthu, P. and Neta, P. Phosphate radicals. Spectra, acid-base equilibria, and reactions with inorganic compounds. *Journal of Physical Chemistry*, **82**(6), 710–713, 1978. ISSN 0022-3654. doi:10.1021/j100495a019.
- Massaut, B., Tilquin, B., and Hickel, B. Reactivity of the captodative methylmethoxyacetate (mma) toward radicals, studied by electron pulse-radiolysis in neutral aqueous-medium. *Bulletin Des Societes Chimiques Belges*, **97**(11-12), 1031–1036, 1988. ISSN 0037-9646.
- Mata-Segreda, J.F. Spontaneous hydrolysis of ethyl formate: Isobaric activation parameters. *International Journal of Chemical Kinetics*, **32**(1), 67–71, 2000. ISSN 0538-8066. doi:10.1002/(SICI)1097-4601(2000)32:1<67::AID-JCK8>3.0.CO;2-M.
- Matsushige, T., Koltzenburg, G., and Schultefrohlinde, D. Pulse-radiolysis of aqueous-solutions of acetic-acid 2-hydroxyethyl ester - Fast elimination of acetic-acid from a primary radical. *Berichte der Bunsen-Gesellschaft für physikalische Chemie*, **79**(8), 657–661, 1975. ISSN 0005-9021.
- Matthew, B.M., George, I., and Anastasio, C. Hydroperoxyl radical ( $\text{HO}_2$ ) oxidizes dibromide radical anion ( $\text{Br}_2^-$ ) to bromine ( $\text{Br}_2$ ) in aqueous solution: Implications for the formation of  $\text{Br}_2$  in the marine boundary layer. *Geophysical Research Letters*, **30**(24), 2003. ISSN 0094-8276. doi:10.1029/2003GL018572.
- McElroy, W.J. The interactions of gases with aqueous aerosol particles. *central Electr., Gen. Board, Part IV*, 1997.
- McElroy, W.J. and Waygood, S.J. Kinetics of the reactions of the  $\text{SO}_4^-$  radical with  $\text{SO}_4^-$ ,  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{H}_2\text{O}$  and  $\text{Fe}^{2+}$ . *Journal of the Chemical Society – Faraday Transactions*, **86**(14), 2557–2564, 1990. ISSN 0956-5000. doi:10.1039/ft9908602557.
- Mellouki, A., Le Bras, G., and Sidebottom, H. Kinetics and mechanisms of the oxidation of oxygenated organic compounds in the gas phase. *Chemical Reviews*, **103**(12), 5077–5096, 2003. ISSN 0009-2665. doi:10.1021/cr020526x.
- Mellouki, A., Teton, S., and Le Bras, G. Kinetics of OH radical reactions with a series of ethers. *International Journal of Chemical Kinetics*, **27**(8), 791 – 805, 1995. ISSN 1097-4601. doi:10.1002/kin.550270806.
- Mendes, P. Biochemistry by numbers: simulation of biochemical pathways with Gepasi 3. *Trends in Biochemical Sciences*, **22**(9), 361 – 363, 1997. ISSN 0968-0004. doi:10.1016/S0968-0004(97)01103-1.
- Merenyi, G. and Lind, J. Reaction mechanism of hydrogen abstraction by the bromine atom in water. *Journal of the American Chemical Society*, **116**(17), 7872–7876, 1994. ISSN 0002-7863. doi:10.1021/ja00096a050.
- Merz, J.H. and Waters, W.A. The oxidation of aromatic compounds by means of the free hydroxyl radical. *Journal of the Chemical Society*, 2427–2433, 1949. doi:10.1039/

jr9490002427.

- Meyerstein, D. Trivalent copper. Part I. Pulse radiolytic study of the chemical properties of the aquo complex. *Inorganic Chemistry*, **10**(3), 638, 1971. ISSN 0020-1669. doi:10.1021/ic50097a040.
- Meylan, W. and Howard, P. *SRC's EPI Suite, v3.20*. Syracuse Research Corporation, New York, 2000.
- Meylan, W.M. and Howard, P.H. Bond contribution method for estimating Henry's Law constants. *Environmental Toxicology and Chemistry*, **10**(10), 1283–1293, 1991. ISSN 0730-7268. doi:10.1897/1552-8618(1991)10[1283:BCMFEH]2.0.CO;2.
- Mezyk, S.P., Cooper, W.J., Bartels, D.M., O'Shea, K.E., and Wu, T.X. Radiation chemistry of alternative fuel oxygenates: Substituted ethers. *Journal of Physical Chemistry A*, **105**(14), 3521–3526, 2001. ISSN 1089-5639. doi:10.1021/jp003892y.
- Mezyk, S.P., Rance Hardison, D., Song, W., O'Shea, K.E., Bartels, D.M., and Cooper, W.J. Advanced oxidation and reduction process chemistry of methyl tert-butyl ether (MTBE) reaction intermediates in aqueous solution: 2-methoxy-2-methyl-propanal, 2-methoxy-2-methyl-propanol, and 2-methoxy-2-methyl-propanoic acid. *Chemosphere*, **77**(10), 1352–1357, 2009. ISSN 0045-6535. doi:10.1016/j.chemosphere.2009.09.029.
- Michael, B.D. and Hart, E.J. Rate constants of hydrated electron, hydrogen atom, and hydroxyl radical reactions with benzene, 1,3-cyclohexadiene, 1,4-cyclohexadiene, and cyclohexene. *Journal of Physical Chemistry*, **74**(15), 2878, 1970. ISSN 0022-3654. doi:10.1021/j100709a005.
- Middleton, P., Stockwell, W.R., and Carter, W.P.L. Aggregation and analysis of volatile organic compound emissions for regional modelling. *Atmospheric Environment Part A – General Topics*, **24**(5), 1107 – 1133, 1990. ISSN 0004-6981. doi:10.1016/0960-1686(90)90077-Z.
- Minakata, D., Li, K., Westerhoff, P., and Crittenden, J. Development of a group contribution method to predict aqueous phase hydroxyl radical (HO) reaction rate constants. *Environmental Science & Technology*, **43**(16), 6220 – 6227, 2009. ISSN 0013-936X. doi:10.1021/es900956c.
- Mirabel, P. Investigations of the uptake rate of some atmospheric trace gases. In *RINOXA Final Report*. 1996.
- Mitani, M.M., Keller, A.A., Bunton, C.A., Rinker, R.G., and Sandall, O.C. Kinetics and products of reactions of MTBE with ozone and ozone/hydrogen peroxide in water. *Journal of Hazardous Materials*, **89**(2-3), 197–212, 2002. ISSN 0304-3894. doi:10.1016/S0304-3894(01)00309-0.
- Mittal, L.J. and Mittal, J.P. Site of attack in the interaction of hydrated electrons and hydroxy radicals in the pulse-radiolysis of arylalkylamines in aqueous-solutions. *Radiation Physics and Chemistry*, **28**(4), 363–371, 1986.

- Moise, T., Rudich, Y., Rouse, D., and George, C. Multiphase decomposition of novel oxygenated organics in aqueous and organic media. *Environmental Science & Technology*, **39**(14), 5203–5208, 2005. ISSN 0013-936X. doi:10.1021/es048488h.
- Monod, A., Chevallier, E., Jolibois, R.D., Doussin, J.F., Picquet-Varrault, B., and Carlier, P. Photooxidation of methylhydroperoxide and ethylhydroperoxide in the aqueous phase under simulated cloud droplet conditions. *Atmospheric Environment*, **41**(11), 2412–2426, 2007. ISSN 1352-2310. doi:10.1016/j.atmosenv.2006.10.006.
- Monod, A. and Doussin, J.F. Structure-activity relationship for the estimation of OH-oxidation rate constants of aliphatic organic compounds in the aqueous phase: alkanes, alcohols, organic acids and bases. *Atmospheric Environment*, **42**(33), 7611 – 7622, 2008. ISSN 1352-2310. doi:10.1016/j.atmosenv.2008.06.005.
- Monod, A., Poulain, L., Grubert, S., Voisin, D., and Wortham, H. Kinetics of OH-initiated oxidation of oxygenated organic compounds in the aqueous phase: new rate constants, structure-activity relationships and atmospheric implications. *Atmospheric Environment*, **39**(40), 7667 – 7688, 2005.
- Moore, J.S., Kemsley, K.G., Davies, J.V., and Phillips, G.O. Pulse radiolysis of carbohydrates. In *Radiation Biology and Chemistry. Research Developments (Proceedings of the Association for Radiation Research)*, edited by H.E. Edwards, 99–113. Elsevier, 1979.
- Nauser, T. and Buhler, R.E. Pivalic acid as combined buffer and scavenger for studies of cloud water chemistry with pulse radiolysis. *Journal of the Chemical Society – Faraday Transactions*, **90**(24), 3651–3656, 1994. ISSN 0956-5000. doi:10.1039/ft9949003651.
- Neta, P. and Dorfman, L.M. Pulse radiolysis studies. XIII. rate constants for reaction of hydroxyl radicals with aromatic compounds in aqueous solutions. *Advances in Chemistry Series*, **81**, 222, 1968. ISSN 0065-2393.
- Neta, P., Hoffman, M.Z., and Simic, M. Electron-spin resonance and pulse radiolysis studies of reactions of oh and o-radicals with aromatic and olefinic compounds. *Journal of Physical Chemistry*, **76**(6), 847–&, 1972. ISSN 0022-3654. doi:10.1021/j100650a009.
- Neta, P. and Huie, R.E. Rate constants for reactions of NO<sub>3</sub> radicals in aqueous solutions. *Journal of Physical Chemistry*, **90**(19), 4644–4648, 1986. ISSN 0022-3654. doi:10.1021/j100410a035.
- Neta, P., Huie, R.E., and Ross, A.B. Rate constants for reactions of peroxy radicals in fluid solutions. *Journal of Physical and Chemical Reference Data*, **19**(2), 413–513, 1990. ISSN 0047-2689.
- Neta, P. and Schuler, H. Oxidation of phenol to phenoxyl radical by O<sup>•−</sup>. *Journal of the American Chemical Society*, **97**(4), 912–913, 1975. ISSN 0002-7863. doi:10.1021/ja00837a049.

- Nielsen, O.J., Sehested, J., Langer, S., Ljungström, E., and Wängberg, I. UV absorption spectra and kinetics for alkyl and alkyl peroxy radicals originating from di-tert-butyl ether. *Chemical Physics Letters*, **238**(4–6), 359 – 364, 1995. ISSN 0009-2614. doi: 10.1016/0009-2614(95)00401-O.
- Olson, T.M. and Hoffmann, M.R. Hydroxyalkylsulfonate formation: Its role as a S(IV) reservoir in atmospheric water droplets. *Atmospheric Environment*, **23**(5), 985–997, 1989. ISSN 1352-2310. doi:10.1016/0004-6981(89)90302-8.
- O'Neill, P. and Steenken, S. Pulse-radiolysis and electron-spin resonance studies on formation of phenoxyl radicals by reaction of OH radicals with methoxylated phenols and hydroxybenzoic acids. *Berichte der Bunsen-Gesellschaft für physikalische Chemie*, **81**(6), 550–556, 1977. ISSN 0005-9021.
- O'Neill, P., Steenken, S., and Schulte-Frohlinde, D. Formation of radical cations of methoxylated benzenes by reaction with hydroxyl radicals,  $\text{Tl}^{2+}$ ,  $\text{Ag}^{2+}$ , and peroxysulfate ( $\text{SO}_4^-$ ) in aqueous solution. Optical and conductometric pulse radiolysis and in situ radiolysis electron spin resonance study. *Journal of Physical Chemistry*, **79**(25), 2773–2779, 1975. ISSN 0022-3654. doi:10.1021/j100592a013.
- O'Neill, P., Steenken, S., and Schultefrohlinde, D. Formation of radical zwitterions from methoxylated benzoic acids. 2. Hydroxyl adducts as precursors. *Journal of Physical Chemistry*, **81**(1), 31–34, 1977. ISSN 0022-3654. doi:10.1021/j100516a008.
- Oturan, M.A., Pinson, J., Deprez, D., and Terlain, B. Polyhydroxylation of salicylic-acid by electrochemically generated OH radicals. *New Journal of Chemistry*, **16**(6), 705–710, 1992. ISSN 1144-0546.
- Padmaja, S., Neta, P., and Huie, R.E. Rate constants for some reactions of inorganic radicals with inorganic-ions – Temperature and solvent dependence. *International Journal of Chemical Kinetics*, **25**(6), 447–455, 1993. ISSN 0538-8066.
- Park, J.Y. and Lee, Y.N. Solubility and decomposition kinetics of nitrous acid in aqueous solution. *Journal of Physical Chemistry*, **92**(22), 6294–6302, 1988. ISSN 0022-3654. doi:10.1021/j100333a025.
- Park, S.E., Joo, H., and Kang, J.W. Photodegradation of methyl tertiary butyl ether (MTBE) vapor with immobilized titanium dioxide. *Solar Energy Materials and Solar Cells*, **80**(1), 73–84, 2003. ISSN 0927-0248. doi:10.1016/S0927-0248(03)00133-8.
- Patterson, L.K. and Hasegawa, K. Pulse-radiolysis studies in model lipid systems - Influence of aggregation on kinetic-behavior of oh induced radicals in aqueous sodium linoleate. *Berichte der Bunsen-Gesellschaft für physikalische Chemie*, **82**(9), 951–956, 1978. ISSN 0005-9021.
- Phillips, G.O., Filby, W.G., Moore, J.S., and Davies, J.V. Radiation studies of aryl glycosides. 3. Reactivity of aryl glucosides towards hydroxyl radicals and hydrated electrons. *Carbohydrate Research*, **16**(1), 105–&, 1971. ISSN 0008-6215. doi:10.1016/S0008-6215(00)86103-0.

- Phillips, G.O. and Worthington, N.W. Effects of ionizing radiations on glucuronic acid. *Radiation Research*, **43**(1), 34, 1970. ISSN 0033-7587. doi:10.2307/3572856.
- Phulkar, S., Rao, B.S.M., Schuchmann, H.P., and von Sonntag, C. Radiolysis of tertiary butyl hydroperoxide in aqueous-solution - Reductive cleavage by the solvated electron, the hydrogen-atom, and, in particular, the superoxide radical-anion. *Zeitschrift für Naturforschung Part B – Chemie Biochemie Biophysik Biologie und verwandten Gebiete*, **45**(10), 1425–1432, 1990. ISSN 0932-0776.
- Pikaev, A.K., Sibirskaya, G.K., Shirshov, E.M., Glazunov, P.Y., and Spitsyn, V.I. Pulse radiolysis of Concentrated aqueous-solutions of nitric acid. *Doklady Akademii Nauk SSSR*, **215**(3), 645–648, 1974. ISSN 0002-3264.
- Ponche, J.L., George, C., and Mirabel, P. Mass transfer at the air/water interface: Mass accommodation coefficients of SO<sub>2</sub>, HNO<sub>3</sub>, NO<sub>2</sub> and NH<sub>3</sub>. *Journal of Atmospheric Chemistry*, **16**(1), 1–21, 1993. ISSN 0167-7764. doi:10.1007/BF00696620.
- Prütz, W.A. Chemiluminescence of aqueous fluorescein solutions under x-irradiation - effect of pH. *Zeitschrift für physikalische Chemie – Frankfurt*, **83**(5-6), 309–321, 1973.
- Raabe, G. *Eine laserphotolytische Studie zur Kinetik von Reaktionen des NO<sub>3</sub>-Radikals in wäßriger Lösung*. Ph.D. thesis, University of Essen, 1996.
- Rabani, J., Klugroth, D., and Lilie, J. Pulse radiolytic investigations of the catalyzed disproportionation of peroxy radicals. Aqueous cupric ions. *Journal of Physical Chemistry*, **77**(9), 1169–1175, 1973. ISSN 0022-3654. doi:10.1021/j100628a018.
- Raventos-Duran, T., Camredon, M., Valorso, R., Mouchel-Vallon, C., and Aumont, B. Structure-activity relationships to estimate the effective Henry's law constants of organics of atmospheric interest. *Atmospheric Chemistry and Physics*, **10**(16), 7643 – 7654, 2010. ISSN 1680-7316. doi:10.5194/acp-10-7643-2010.
- Redlich, O. The dissociation of strong electrolytes. *Chemical Reviews*, **39**(2), 333–356, 1946. ISSN 0009-2665. doi:10.1021/cr60123a005.
- Redlich, O. and Hood, G.C. Ionic interaction, dissociation and molecular structure. *Discussions of the Faraday Society*, **24**, 87–93, 1957.
- Redpath, J.L., Ihara, J., and Patterson, L.K. Pulse-radiolysis studies of 8-methoxypsoralen. *International Journal of Radiation Biology*, **33**(4), 309–315, 1978. ISSN 0955-3002. doi:10.1080/09553007814550221.
- Redpath, J.L. and Willson, R.L. Reducing compounds in radioprotection and radiosensitization - Model experiments using ascorbic-acid. *International Journal of Radiation Biology*, **23**(1), 51–65, 1973. ISSN 0955-3002. doi:10.1080/09553007314550051.
- Reese, A. *UV/VIS-spektrometrische und kinetische Untersuchungen von Radikalen und Radikalanionen in wäßriger Lösung*. Ph.D. thesis, University of Essen, 1997.

- Reese, A., Herrmann, H., and Zellner, R. Kinetics and spectroscopy of organic peroxy radicals ( $\text{RO}_2$ ) in aqueous solution. In *Transport and Transformation of Pollutants in the Troposphere*, edited by P.M. Borrell, P. Borrell, T. Cvitaš, K. Kelly, and W. Seiler, *Proceedings of EUROTRAC Symposium 96*, volume 1, 377–381. Computational Mechanics Publications, Southampton, UK, 1997.
- Reese, A., Herrmann, H., and Zellner, R. Kinetic and spectroscopic investigations of the  $\text{Br}_2^-$  radical in aqueous solution. In *Proceedings of the EUROTRAC-2 98 symposium*, edited by P.M. Borrell and P. Borrell, 714–718. WIT press, 1999.
- Regimbal, J.M. and Mozurkewich, M. Peroxynitric acid decay mechanisms and kinetics at low pH. *Journal of Physical Chemistry A*, **101**(47), 8822–8829, 1997. ISSN 1089-5639. doi:10.1021/jp971908n.
- Richter, H.W. Pulse radiolysis of 4-tert-butyl-1,2-dihydroxybenzene and 4-tert-butyl-1,2-quinone. *Journal of Physical Chemistry*, **83**(9), 1123–1129, 1979. ISSN 0022-3654. doi:10.1021/j100472a003.
- Roder, M., Wojnarovits, L., and Foldiak, G. Pulse-radiolysis of aqueous-solutions of aromatic-hydrocarbons in the presence of oxygen. *Radiation Physics and Chemistry*, **36**(2), 175–176, 1990. 2ND INTERNATIONAL MEETING ON PULSE INVESTIGATIONS IN PHYSICS, CHEMISTRY AND BIOLOGY, CZERNIEJEWO, POLAND, SEP 12-17, 1988.
- Ross, A.B., Bielski, B.H.J., Buxton, G.V., Cabelli, D.E., Helman, W.P., Huie, R.E., Grodkovski, J., Neta, P., Mulazzani, Q.G., and Wilkinson, F. *NIST standard reference database 40: NDRL/NIST solution kinetics database vers. 3.0*. Gaithersburg, MD, USA, 1998.
- Rosseinsky, D.R. The reaction between mercury(I) and manganese(III) in aqueous perchlorate solution. *Journal of the Chemical Society*, 1181, 1963. doi:10.1039/jr9630001181.
- Rousse, D. and George, C. A novel long path photolysis cell-application to the reactivity of selected organic compounds toward the nitrate radical ( $\text{NO}_3$ ). *Physical Chemistry Chemical Physics*, **6**(13), 3408–3414, 2004. ISSN 1463-9076. doi:10.1039/b400175c.
- Rudakov, E.S., Volkova, L.K., and Tretyakov, V.P. Low selectivity reactions of OH radicals with alkanes in aqueous-solutions. *Reaction Kinetics and Catalysis Letters*, **16**(4), 333–337, 1981. ISSN 0133-1736.
- Rudich, Y., Talukdar, R.K., and Ravishankara, A.R. Reactive uptake of  $\text{NO}_3$  on pure water and ionic solutions. *Journal of Geophysical Research – Atmospheres*, **101**(D15), 21023–21031, 1996. ISSN 2169-897X. doi:10.1029/96JD01844.
- Rush, J.D. and Bielski, B.H.J. Pulse radiolytic studies of the reaction of perhydroxyl/superoxide  $\text{O}_2^-$  with iron(II)/iron(III) ions. The reactivity of  $\text{HO}_2/\text{O}_2^-$  with ferric ions and its implication on the occurrence of the Haber-Weiss reaction. *Journal of Physical Chemistry*, **89**(23), 5062–5066, 1985. ISSN 0022-3654. doi:10.1021/j100269a035.



- Safrany, A. and Wojnarovits, L. Radiolysis of hydroxy ethylacrylate in dilute aqueous-solutions. *Radiation Physics and Chemistry*, **41**(3), 531–537, 1993. ISSN 0146-5724. doi:10.1016/0969-806X(93)90016-N.
- Salma, I. and Láng, G.G. How many carboxyl groups does an average molecule of humic-like substances contain? *Atmospheric Chemistry and Physics*, **8**(20), 5997 – 6002, 2008. doi:10.5194/acp-8-5997-2008.
- Saveleva, O.S., Shevchuk, L.G., and Vysotskaya, N.A. Reactivity of substituted benzene, furan and pyridine in relation to hydroxyl radicals. *Zhurnal Organicheskoi Khimii*, **9**(4), 737–739, 1973. ISSN 0514-7492.
- Saveleva, O.S., Vysotska.N., and Shevchuk, L.G. Reactions of substituted phenols with hydroxyl radicals and their dissociated form  $O^-$ . *Zhurnal Organicheskoi Khimii*, **8**(2), 283–&, 1972. ISSN 0514-7492.
- Saxena, P. and Hildemann, L.M. Water-soluble organics in atmospheric particles: A critical review of the literature and application of thermodynamics to identify candidate compounds. *Journal of Atmospheric Chemistry*, **24**(1), 57–109, 1996. ISSN 0167-7764. doi:10.1007/BF00053823.
- Schaefer, T., Schindelka, J., Hoffmann, D., and Herrmann, H. Laboratory kinetic and mechanistic studies on the OH-initiated oxidation of acetone in aqueous solution. *Journal of Physical Chemistry A*, **116**(24), 6317 – 6326, 2012. ISSN 1089-5639. doi:10.1021/jp2120753.
- Scholes, G. and Willson, R.L.  $\gamma$ -Radiolysis of aqueous thymine solutions. Determination of relative reaction rates of OH radicals. *Transactions of the Faraday Society*, **63**(540P), 2983, 1967. doi:10.1039/tf9676302983.
- Schöne, L., Schindelka, J., Szeremeta, E., Schaefer, T., Hoffmann, D., Rudzinski, K.J., Szmigielski, R., and Herrmann, H. Atmospheric aqueous phase radical chemistry of the isoprene oxidation products methacrolein, methyl vinyl ketone, methacrylic acid and acrylic acid - kinetics and product studies. *Physical Chemistry Chemical Physics*, **16**(13), 6257 – 6272, 2014. doi:10.1039/C3CP54859G.
- Schöneshöfer, M. Pulse radiolysis of tropylium-ion, tropylcarbinol and tropilidene in aqueous solution. *Zeitschrift für Naturforschung Part B – Chemie Biochemie Biophysik Biologie und verwandten Gebiete*, **B 26**(11), 1120, 1971.
- Schöneshöfer, M. Pulse radiolysis studies of oxidation of ascorbic-acid by OH-radicals and halide radical anion complexes in aqueous-solution. *Zeitschrift für Naturforschung Part B – Chemie Biochemie Biophysik Biologie und verwandten Gebiete*, **B 27**(6), 649, 1972.
- Schuchmann, M.N., Schuchmann, H., Hess, M., and Von Sonntag, C.  $O_2^-$  addition to ketomalonate leads to decarboxylation: a chain reaction in oxygenated aqueous solution. *Journal of the American Chemical Society*, **113**(18), 6934 – 6937, 1991. doi:10.1021/ja00018a033.

- Schuchmann, M.N., Schuchmann, H., and von Sonntag, C. Oxidation of hydroxymalonic acid by OH radicals in the presence and in the absence of molecular oxygen. A pulse-radiolysis and product study. *Journal of Physical Chemistry*, **99**(22), 9122–9129, 1995. ISSN 0022-3654. doi:10.1021/j100022a026.
- Schuchmann, M.N. and von Sonntag, C. The rapid hydration of the acetyl radical. A pulse radiolysis study of acetaldehyde in aqueous solution. *Journal of the American Chemical Society*, **110**(17), 5698–5701, 1988. ISSN 0002-7863. doi:10.1021/ja00225a019.
- Schuchmann, M.N., Zegota, H., and von Sonntag, C. Acetate peroxy radicals,  $\text{O}_2\text{CH}_2\text{CO}_2^-$ . A study on the  $\gamma$ -radiolysis of acetate in oxygenated aqueous solution. *Zeitschrift für Naturforschung Section B. A Journal of Chemical Sciences*, **40**(2), 215–221, 1985. ISSN 0932-0776.
- Schuler, M.A., Bhatia, K., and Schuler, R.H. Radiation chemical studies on systems related to ascorbic-acid. Radiolysis of aqueous-solutions of alpha-bromotetronic acid. *Abstracts of Papers of the American Chemical Society*, 15, 1974. ISSN 0065-7727.
- Schuler, R.H. Oxidation of ascorbate anion by electron-transfer to phenoxyl radicals. *Radiation Research*, **69**(3), 417–433, 1977. ISSN 0033-7587. doi:10.2307/3574655.
- Schütze, M. and Herrmann, H. Uptake of acetone, 2-butanone, 2,3-butanedione and 2-oxopropanal on a water surface. *Physical Chemistry Chemical Physics*, **6**(5), 965–971, 2004. ISSN 1463-9076. doi:10.1039/b313474a.
- Schwartz, S.E. Mass transport considerations pertinent to aqueous phase reactions of gases in liquid water clouds. In *Chemistry of Multiphase Atmospheric Systems*, edited by W. Jaeschke, 415 – 471. Springer, Berlin, Germany, 1986.
- Schwartz, S.E. and White, W.H. Kinetics of reactive dissolution of nitrogen oxides into aqueous solution. *Advances in environmental science and technology*, **12**, 1–116, 1983.
- Schweitzer, F., Magi, L., Mirabel, P., and George, C. Uptake rate measurements of methanesulfonic acid and glyoxal by aqueous droplets. *Journal of Physical Chemistry A*, **102**(3), 593 – 600, 1998. ISSN 1089-5639. doi:10.1021/jp972451k.
- Sehested, K., Christensen, H.C., Hart, E.J., and Corfitzen, H. Rates of reaction of  $\text{O}^-$ , OH, and H with methylated benzenes in aqueous solution – optical spectra of radicals. *Journal of Physical Chemistry*, **79**(4), 310 – 315, 1975. ISSN 0022-3654. doi:10.1021/j100571a005.
- Sehested, K. and Holcman, J. Radical cations of ethyl-butylbenzene isopropyl-butylbenzene and tert-butylbenzene in aqueous-solution. *Nukleonika*, **24**(9), 941–950, 1979. ISSN 0029-5922.
- Sehested, K., Holcman, J., Bjergbakke, E., and Hart, E.J. A pulse radiolytic study of the reaction  $\text{OH} + \text{O}_3$  in aqueous medium. *Journal of Physical Chemistry*, **88**(18), 4144–4147, 1984. ISSN 0022-3654. doi:10.1021/j150662a058.
- Sehested, K., Holcman, J., and Hart, E.J. Rate constants and products of the reactions of  $\text{e}_{aq}^-$ ,  $\text{O}_2^-$  and H with ozone in aqueous solutions. *Journal of Physical Chemistry*, **87**(11),

- 1951–1954, 1983. ISSN 0022-3654. doi:10.1021/j100234a024.
- Sehested, K., Løgager, T., Holcman, J., and Nielsen, O.J. Formation and reactions of the  $\text{NO}_3$  radical in aqueous solution. In *Transport and Transformation of Pollutants in the Troposphere*, edited by P.M. Borrell, P. Borrell, T. Cvitaš, and W. Seiler, Proceedings of EUROTRAC Symposium 94, 999–1004. SPB Academic Publishing, The Hague, NL, 1994.
- Seinfeld, J.H. and Pandis, S.N. *Atmospheric Chemistry and Physics – From Air Pollution to Climate Change*. John Wiley & Sons, Inc., Hoboken, New Jersey, USA, 2nd edition, 2006. ISBN 0-0471-72018-6.
- Shastri, L.V. and Huie, R.E. Rate constants for hydrogen abstraction reactions of  $\text{NO}_3$  in aqueous solution. *International Journal of Chemical Kinetics*, **22**(5), 505–512, 1990. ISSN 0538-8066. doi:10.1002/kin.550220507.
- Shetiya, R.S., Rao, K.N., and Shankar, J. Determination of rate constants for the reactions of H, OH and  $\text{e}_{aq}^-$  with indole-3-acetic acid and other plant hormones. *Radiation Effects*, **14**(3-4), 185–189, 1972. doi:10.1080/00337577208231199. URL <http://www.tandfonline.com/doi/abs/10.1080/00337577208231199>. <http://www.tandfonline.com/doi/pdf/10.1080/00337577208231199>.
- Shetiya, R.S., Rao, K.N., and Shankar, J. OH radical rate constants of phenols using par-nitrosodimethylaniline. *Indian Journal of Chemistry Section a-Inorganic Bio-Inorganic Physical Theoretical & Analytical Chemistry*, **14**(8), 575–578, 1976. ISSN 0376-4710.
- Shevchuk, L.G., Zhikharev, V.S., and Vysotska, N.A. Kinetics of the reactions of hydroxyl radicals with benzene and pyridine derivatives. *Zhurnal Organicheskoi Khimii USSR*, **5**, 1606–1608, 1969.
- Shoute, L.C.T., Alfassi, Z.B., Neta, P., and Huie, R.E. Temperature dependence of the rate constants for reaction of dihalide and azide radicals with inorganic reductants. *Journal of Physical Chemistry*, **95**(8), 3238–3242, 1991. ISSN 0022-3654. doi:10.1021/j100161a050.
- Simhon, E., Cohen, H., and Meyerstein, D. Enhancement of the rate of addition of free-radicals to dicarboxylacetylene by pi-acid complexation to ruthenium(II)-pentaamine a pulse-radiolysis study. *Inorganica Chimica Acta*, **142**(1), 5–6, 1988. ISSN 0020-1693. doi:10.1016/S0020-1693(00)80645-3.
- Simic, M., Hoffman, M.Z., and Ebert, M. Reaction of OH and  $\text{O}^-$  radicals with aromatic carboxylate anions in aqueous solutions. *Journal of Physical Chemistry*, **77**(9), 1117–1120, 1973a. ISSN 0022-3654. doi:10.1021/j100628a007.
- Simic, M., Neta, P., and Hayon, E. Reactions of hydroxyl radicals with unsaturated aliphatic alcohols in aqueous solution. Spectroscopic and electron spin resonance radiolysis study. *Journal of Physical Chemistry*, **77**(22), 2662–2667, 1973b. ISSN 0022-3654. doi:10.1021/j100640a018.

- Snider, J.R. and Dawson, G.A. Tropospheric light alcohols, carbonyls, and acetonitrile: Concentrations in the southwestern United States and Henry's Law data. *Journal of Geophysical Research – Atmospheres*, **90**(ND2), 3797–3805, 1985. ISSN 2169-897X. doi:10.1029/JD090iD02p03797.
- Snook, M.E. and Hamilton, G.A. Oxidation and fragmentation of some phenyl-substituted alcohols and ethers by peroxydisulfate and fentons reagent. *Journal of the American Chemical Society*, **96**(3), 860–869, 1974. ISSN 0002-7863. doi:10.1021/ja00810a035.
- Soylomez, T. and Schuler, R.H. Radiolysis of aqueous-solutions of cyclopentane and cyclopentene. *Journal of Physical Chemistry*, **78**(11), 1052–1062, 1974. ISSN 0022-3654. doi:10.1021/j100604a003.
- Stefan, M. and Bolton, J. Reinvestigation of the acetone degradation mechanism in dilute aqueous solution by the UV/H<sub>2</sub>O<sub>2</sub> process. *Environmental Science & Technology*, **33**(6), 870 – 873, 1999. ISSN 0013-936X. doi:10.1021/es9808548.
- Stemmler, K. and von Gunten, U. OH radical-initiated oxidation of organic compounds in atmospheric water phases: Part 1. Reactions of peroxy radicals derived from 2-butoxyethanol in water. *Atmospheric Environment*, **34**(25), 4241–4252, 2000. ISSN 1352-2310. doi:10.1016/S1352-2310(00)00218-1.
- Sychev, A.Y., Isak, V.G., and Pfannmeller, U. Determination of the rate constants of hydroxyl radicals with organic and inorganic substances under the conditions of H<sub>2</sub>O<sub>2</sub> catalytic decomposition. *Zhurnal Fizicheskoi Khimii*, **53**(11), 2790–2793, 1979. ISSN 0044-4537.
- Tamminga, J.J., Vandenende, C.A.M., Warman, J.M., and Hummel, A. Absorption-spectra and reaction-kinetics of the radical-anion, radical cation and OH adduct(s) of 3,5-dinitroanisole studied by pulse-radiolysis. *Recueil Des Travaux Chimiques Des Pays-Bas – Journal of the Royal Netherlands Chemical Society*, **98**(5), 305–315, 1979. ISSN 0165-0513.
- Tang, I.N. and Lee, J.H. Accommodation coefficients of ozone and SO<sub>2</sub> – Implications on SO<sub>2</sub> oxidation in cloud water. *ACS Symposium Series*, **349**, 109 – 117, 1987. ISSN 0097-6156.
- Tang, Y., Thorn, R.P., Mauldin, R.L., and Wine, P.H. Kinetics and spectroscopy of the SO<sub>4</sub><sup>-</sup> radical in aqueous solution. *Journal of Photochemistry and Photobiology A: Chemistry*, **44**(3), 243–258, 1988. ISSN 1010-6030. doi:10.1016/1010-6030(88)80097-2.
- Teton, S., Mellouki, A., Le Bras, G., and Sidebottom, H. Rate constants for reactions of OH radicals with a series of asymmetrical ethers and tert-Butyl alcohol. *International Journal of Chemical Kinetics*, **28**(4), 291 – 297, 1996. ISSN 1097-4601. doi:10.1002/(SICI)1097-4601(1996)28:4<291::AID-KIN7>3.0.CO;2-Q.
- Thomas, J.K. Pulse radiolysis of aqueous solutions of methyl iodide and methyl bromide. The reactions of iodine atoms and methyl radicals in water. *Journal of Physical Chemistry*, **71**(6), 1919, 1967. ISSN 0022-3654. doi:10.1021/j100865a060.

- Thornton, A.T. and Laurence, G.S. Kinetics of oxidation of transition-metal ions by halogen radical anions. Part I. The oxidation of iron(II) by dibromide and dichloride ions generated by flash photolysis. *Journal of the Chemical Society – Dalton Transactions*, **8**, 804–813, 1973. ISSN 0300-9246. doi:10.1039/dt9730000804.
- Thüner, L.P., Barnes, I., Maurer, T., Sauer, C.G., and Becker, K.H. Kinetic study of the reaction of OH with a series of acetals at  $298 \pm 4$  K. *International Journal of Chemical Kinetics*, **31**(11), 797 – 803, 1999. ISSN 1097-4601. doi:10.1002/(SICI)1097-4601(1999)31:11<797::AID-JCK6>3.0.CO;2-C.
- Tilgner, A., Bräuer, P., Wolke, R., and Herrmann, H. Modelling multiphase chemistry in deliquescent aerosols and clouds using CAPRAM3.0i. *Journal of Atmospheric Chemistry*, **1** – 36, 2013. ISSN 0167-7764. doi:10.1007/s10874-013-9267-4.
- Tilgner, A. and Herrmann, H. Radical-driven carbonyl-to-acid conversion and acid degradation in tropospheric aqueous systems studied by CAPRAM. *Atmospheric Environment*, **44**(40), 5415 – 5422, 2010.
- Toyota, K., Kanaya, Y., Takahashi, M., and Akimoto, H. A box model study on photochemical interactions between VOCs and reactive halogen species in the marine boundary layer. *Atmospheric Chemistry and Physics*, **4**(7), 1961 – 1987, 2004. doi:10.5194/acp-4-1961-2004.
- Ulanski, P., Bothe, E., Rosiak, J.M., and von Sonntag, C. OH-radical-induced cross-linking and strand breakage of poly(vinyl alcohol) in aqueous-solution in the absence and presence of oxygen. A pulse-radiolysis and product study. *Macromolecular Chemistry and Physics*, **195**(4), 1443–1461, 1994. ISSN 1022-1352. doi:10.1002/macp.1994.021950427.
- Umschlag, T., Zellner, R., and Herrmann, H. Laser-based studies of NO<sub>3</sub> radical reactions with selected aromatic compounds in aqueous solution. *Physical Chemistry Chemical Physics*, **4**(13), 2975–2982, 2002. ISSN 1463-9076. doi:10.1039/b110263j.
- von Piechowski, M., Nauser, T., Hoigné, J., and Buhler, R.E. O<sub>2</sub><sup>-</sup> decay catalyzed by Cu<sup>2+</sup> and Cu<sup>+</sup> ions in aqueous-solutions. A pulse radiolysis study for atmospheric chemistry. *Berichte der Bunsen – Gesellschaft-Physical Chemistry Chemical Physics*, **97**(6), 762–771, 1993. ISSN 0005-9021.
- von Sonntag, C. *The chemical basis of radiation biology*. Taylor & Francis, 1987.
- Vysotskaya, N.A., Shevchuk, L.G., Gavrilova, S.P., Badovskaya, L.A., and Kulnevich, V.G. Reactivity of substituted furans with hydroxyl radicals. *Zhurnal Organicheskoi Khimii*, **19**(7), 1502–1505, 1983. ISSN 0514-7492.
- Wagner, I. and Strehlow, H. On the flash-photolysis of bromide ions in aqueous-solutions. *Berichte der Bunsen-Gesellschaft – Physical Chemistry Chemical Physics*, **91**(12), 1317–1321, 1987. ISSN 0005-9021.
- Wagner, I., Strehlow, H., and Busse, G. Flash-photolysis of nitrate ions in aqueous-solution. *Zeitschrift für physikalische Chemie – Wiesbaden*, **123**(1), 1–33, 1980. ISSN 0044-3336.

- Walling, C.. Fentons reagent revisited. *Accounts of Chemical Research*, **8**(4), 125–131, 1975. ISSN 0001-4842. doi:10.1021/ar50088a003.
- Walling, C. and El-Taliawi, G.M. Fentons Reagent .2. Reactions of carbonyl-compounds and alpha, beta-unsaturated acids. *Journal of the American Chemical Society*, **95**(3), 844–847, 1973a. ISSN 0002-7863. doi:10.1021/ja00784a035.
- Walling, C. and El-Taliawi, G.M. Fenton's reagent. III. Addition of hydroxyl radicals to acetylenes and redox reactions of vinyl radicals. *Journal of the American Chemical Society*, **95**(3), 848–850, 1973b. ISSN 0002-7863. doi:10.1021/ja00784a036.
- Walling, C., El-Taliawi, G.M., and Johnson, R.A. Fenton's reagent. IV. Structure and reactivity relations in the reactions of hydroxyl radicals and the redox reactions of radicals. *Journal of the American Chemical Society*, **96**(1), 133–139, 1974. ISSN 0002-7863. doi:10.1021/ja00808a022.
- Wallington, T.J., Dagaut, P., Liu, R., and Kurylo, M.J. The gas phase reactions of hydroxyl radicals with a series of esters over the temperature range 240 — 440 K. *International Journal of Chemical Kinetics*, **20**(2), 177 – 186, 1988. ISSN 1097-4601. doi:10.1002/kin.550200210.
- Wander, R., Neta, P., and Dorfman, L.M. Pulse radiolysis studies. XII. Kinetics and spectra of the cyclohexadienyl radicals in aqueous benzoic acid solution. *Journal of Physical Chemistry*, **72**(8), 2946–&, 1968. ISSN 0022-3654. doi:10.1021/j100854a044.
- Wang, D., Gyöergy, I. and Hildenbrand, K., and Von Sonntag, C. Free radical induced oxidation of phloroglucinol. A pulse radiolysis and EPR study. *Journal of the Chemical Society – Perkin Transactions 2*, **1**, 45–55, 1994. ISSN 0300-9580. doi:10.1039/p29940000045.
- Warneck, P. Multi-phase chemistry of C-2 and C-3 organic compounds in the marine atmosphere. *Journal of Atmospheric Chemistry*, **51**(2), 119–159, 2005. ISSN 0167-7764. doi:10.1007/s10874-005-5984-7.
- Warneck, P. and Wurzinger, C. Product quantum yields for the 305 nm photodecomposition of  $\text{NO}_3^-$  in aqueous solution. *Journal of Physical Chemistry*, **92**(22), 6278–6283, 1988. ISSN 0022-3654. doi:10.1021/j100333a022.
- Wayne, R.P., Barnes, I., Biggs, P., Burrows, J.P., Canosamas, C.E., Hjorth, J., Lebras, G., Moortgat, G.K., Perner, D., Poulet, G., Restelli, G., and Sidebottom, H. The nitrate radical - Physics, chemistry, and the atmosphere. *Atmospheric Environment Part A – General Topics*, **25**(1), 1–203, 1991. ISSN 0004-6981. doi:10.1016/0960-1686(91)90192-A.
- Weinstein-Lloyd, J. and Schwartz, S.E. Low-intensity radiolysis study of free-radical reactions in cloudwater: Hydrogen peroxide production and destruction. *Environmental Science & Technology*, **25**(4), 791 – 800, 1991. doi:10.1021/es00016a027.
- Weller, C., Horn, S., and Herrmann, H. Effects of Fe(III)-concentration, speciation, excitation-wavelength and light intensity on the quantum yield of iron(III)-oxalato complex photolysis. *Journal of Photochemistry and Photobiology A: Chemistry*, **255**(0),

- 41 – 49, 2013. ISSN 1010-6030. doi:<http://dx.doi.org/10.1016/j.jphotochem.2013.01.014>.
- Wells, C.F. and Davies, G. A spectrophotometric investigation of the aquomanganese(III) ion in perchlorate media. *Journal of the Chemical Society A – Inorganic Physical Theoretical*, **11**, 1858, 1967. doi:10.1039/j19670001858.
- Weschler, C.J., Mandich, M.L., and Graedel, T.E. Speciation, photosensitivity, and reactions of transition metal ions in atmospheric droplets. *Journal of Geophysical Research – Atmospheres*, **91**(D4), 5189–5204, 1986. ISSN 2169-897X. doi:10.1029/JD091iD04p05189.
- Wilhelm, E., Battino, R., and Wilcock, R.J. Low-pressure solubility of gases in liquid water. *Chemical Reviews*, **77**(2), 219–262, 1977. ISSN 0009-2665. doi:10.1021/cr60306a003.
- Willson, R.L., Greenstock, C.L., Adams, G.E., Wageman, R., and Dorfman, L.M. Standardization of hydroxyl radical rate data from radiation chemistry. *International Journal for Radiation Physics and Chemistry*, **3**(3), 211–&, 1971. ISSN 0020-7055. doi:10.1016/0020-7055(71)90023-4.
- Wine, P.H., Tang, Y., Thorn, R.P., Wells, J.R., and Davis, D.D. Kinetics of aqueous phase reactions of the  $\text{SO}_4^-$  radical with potential importance in cloud chemistry. *Journal of Geophysical Research – Atmospheres*, **94**(D1), 1085–1094, 1989. doi:10.1029/JD094iD01p01085.
- Witter, R.A. and Neta, P. Mode of reaction of hydrogen-atoms with organic compounds in aqueous-solutions. *Journal of Organic Chemistry*, **38**(3), 484–487, 1973. ISSN 0022-3263. doi:10.1021/jo00943a016.
- Yang, X., Wang, J., and Wang, T. Rate constants for the reaction of  $\text{NO}_3^-$  and  $\text{SO}_4^-$  radicals with oxalic acid and oxalate anions in aqueous solution. *Chinese Chemical Letters*, **15**(5), 583 – 586, 2004.
- Ye, M.Y. and Schuler, R.H. Determination of oxidation products in radiolysis of halophenols with pulse radiolysis, HPLC, and ion chromatography. *Journal of Liquid Chromatography*, **13**(17), 3369–3387, 1990. ISSN 0148-3919. doi:10.1080/01483919008049108.
- Zakatova, N., Minkhadzhiddinova, D., and Sharpatyi, V. Role of OH-radicals in the radiolytic decomposition of carbohydrates and polysaccharides. *Bulletin of the Academy of Sciences of the USSR, Division of chemical science*, **18**(7), 1520–1520, 1969. ISSN 0568-5230. doi:10.1007/BF00908773. URL <http://dx.doi.org/10.1007/BF00908773>.
- Zegota, H., Schuchmann, M.N., Schulz, D., and von Sonntag, C. Acetonylperoxyl radicals,  $\text{CH}_3\text{COCH}_2\text{O}_2$  – A study on the  $\gamma$ -radiolysis and pulse-radiolysis of acetone in oxygenated aqueous-solutions. *Zeitschrift für Naturforschung Section B. A Journal of Chemical Sciences*, **41**(8), 1015–1022, 1986. ISSN 0932-0776.
- Zehavi, D. and Rabani, J. Oxidation of aqueous bromide ions by hydroxyl radicals. Pulse radiolytic investigation. *Journal of Physical Chemistry*, **76**(3), 312, 1972. ISSN 0022-3654. doi:10.1021/j100647a006.

- Zellner, R., Exner, M., and Herrmann, H. Absolute OH quantum yields in the laser photolysis of nitrate, nitrite and dissolved H<sub>2</sub>O<sub>2</sub> at 308 and 351 nm in the temperature range 278 – 353 K. *Journal of Atmospheric Chemistry*, **10**(4), 411–425, 1990. ISSN 0167-7764. doi:10.1007/BF00115783.
- Zellner, R., Herrmann, H., Exner, M., Jacobi, H.-W., Raabe, G., and Reese, A. Formation and reactions of oxidants in the aqueous phase. In *Heterogeneous and Liquid Phase Processes*, edited by P. Warneck, 146–152. Springer, 1996.
- Zepp, R.G., Faust, B.C., and Hoigné, J. Hydroxyl radical formation in aqueous reactions (pH 3-8) of iron(II) with hydrogen peroxide: the photo-Fenton reaction. *Environmental Science & Technology*, **26**(2), 313 – 319, 1992. doi:10.1021/es00026a011.
- Zevos, N. and Sehested, K. Pulse-radiolysis of aqueous naphthalene solutions. *Journal of Physical Chemistry*, **82**(2), 138–141, 1978. ISSN 0022-3654. doi:10.1021/j100491a004.
- Zhou, X.L. and Mopper, K. APPA apparent partition coefficients of 15 carbonyl compounds between air and seawater and between air and freshwater; implications for air-sea exchange. *Environmental Science & Technology*, **24**(12), 1864–1869, 1990. ISSN 0013-936X. doi:10.1021/es00082a013.
- Ziajka, J., Beer, F., and Warneck, P. Iron-catalysed oxidation of bisulphite aqueous solution: Evidence for a free radical chain mechanism. *Atmospheric Environment*, **28**(15), 2549–2552, 1994. ISSN 1352-2310. doi:10.1016/1352-2310(94)90405-7.
- Zona, R., Solar, S., Sehested, K., Holcman, J., and Mezyk, S.P. OH-radical induced oxidation of phenoxyacetic acid and 2,4-dichlorophenoxyacetic acid. Primary radical steps and products. *Journal of Physical Chemistry A*, **106**(29), 6743–6749, 2002. ISSN 1089-5639. doi:10.1021/jp0201251.