

This is a repository copy of *Mechanism development and modelling of tropospheric multiphase halogen chemistry: The CAPRAM Halogen Module 2.0 (HM2)*.

White Rose Research Online URL for this paper:

<https://eprints.whiterose.ac.uk/id/eprint/191784/>

Article:

Bräuer, Peter orcid.org/0000-0002-3815-7631, Tilgner, Andreas, Wolke, Ralf et al. (1 more author) (2013) Mechanism development and modelling of tropospheric multiphase halogen chemistry: The CAPRAM Halogen Module 2.0 (HM2). *Journal of Atmospheric Chemistry*. pp. 19-52. ISSN: 0167-7764

<https://doi.org/10.1007/s10874-013-9249-6>

Reuse

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

Mechanism development and modelling of the tropospheric multiphase halogen chemistry: The CAPRAM Halogen Module 2.0

Electronic Supplementary Material
Journal of Atmospheric Chemistry

Bräuer, P., Tilgner, A., Wolke, R., and Herrmann, H.*

Leibniz-Institut für Troposphärenforschung
Permoserstr. 15, 04318 Leipzig, Germany

February 15, 2013

*herrmann@tropos.de

Contents

S1 Detailed Results from the open ocean runs with the Halogen Module 2.0	3
S1.1 Chlorine chemistry	3
S1.2 Bromine chemistry	6
S1.3 Iodine chemistry	8
S1.3.1 Inorganic iodine chemistry	8
S1.3.2 Organic iodine chemistry	13
S1.4 Influence of halogen chemistry on the aqueous phase oxalate oxidation	13
S1.5 Comparison of the model results with results from previous model studies	16
S2 Model setup	18
S2.1 Model initialisation	18
S2.2 Cloud scenario	19
S2.3 Calculation of photolysis rates	19
S2.4 Changes to original setup	20
S2.5 Additional setup of the Halogen Modul 2.0	22
S3 Reaction mechanism	24
S3.1 Changes to Photolysis reactions in CAPRAM 3.0i	24
S3.2 Phase transfer	27
S3.3 Gas phase chemistry	30
S3.4 Photolysis reactions	52
S3.5 Aqueous phase chemistry	57
S4 Estimation of rate constants of reactions with lumped species	71
S5 Estimation of gas phase diffusion coefficients	72
References	74

List of Tables

(S1)	Most important source and sink reactions contributing to the production and destruction of I atoms.	8
(S2)	Maximum concentrations of important halogen species from selected model studies. .	16
(S3)	Changes to the original emission scenario in CAPRAM 3.0i and older versions	20
(S4)	Changes to the original initial concentrations in CAPRAM 3.0i and older versions . .	20
(S5)	Emissions of halogen species	22
(S6)	Depositions of halogen species	22
(S7)	Initial concentrations of halogen species	23
(S8)	Parameters for the updated gas phase photolysis reactions in RACM-MIM2ext	24
(S9)	Parameters for the updated aqueous phase photolysis reactions in CAPRAM 3.0i . .	26
(S10)	Henry's Law constants	27
(S11)	Mass accommodation coefficients and gas phase diffusion coefficients	28
(S12)	Gas phase reactions	30
(S13)	Parameters for pressure dependent reactions	50
(S14)	Parameters for gas phase photolysis reactions	52
(S15)	Parameters for aqueous phase photolysis reactions	55
(S16)	Aqueous phase irreversible reactions	57
(S17)	Aqueous phase equilibria	67
(S18)	Kinetic data used for synthesising rate constants of the reactions of chlorine with the lumped model species HC3, HC5, HC8 and TOL	71
(S19)	Overall rate constants of the reactions of chlorine with the model species HC3, HC5, HC8 and TOL	72

List of Figures

(S1)	Modelled Cl concentration-time profiles in the gas phase over the whole modelling period of 108h for the different scenarios.	4
(S2)	Modelled concentration-time profiles of selected chlorine species in the gas phase on the second model day (scenario HM2).	5
(S3)	Modelled concentration-time profiles of selected bromine species in the gas phase on the second model day (scenario HM2).	7
(S4)	Modelled concentration-time profiles of selected iodine species in the gas phase on the second model day (scenario HM2).	10
(S5)	Modelled concentration-time profiles of selected iodine species in the aqueous phase over the whole modelling period of 108 h (scenario HM2).	12
(S6)	Modelled concentration-time profiles of the various alkyl iodides in the gas phase for the whole modelling period of 108h (scenario HM2).	13
(S7)	Modelled time-resolved contributions of the various oxidants to the aqueous phase degradation of the sum of all dissociation states of oxalic acid for the whole modelling period of 108h (scenario HM2).	14
(S8)	Modelled concentration-time profiles of the speciation of the different oxidation states of oxalic acid for the whole modelling period of 108h (scenario HM2).	15
(S9)	Modelled concentration-time profiles of OH _(aq) and Cl ₂ ⁻ for the whole modelling period of 108h (scenario HM2).	15
(S10)	Schematic of the cloud scenario used in the model runs.	19
(S11)	Estimation of diffusion volumes.	73

S1 Detailed Results from the open ocean runs with the Halogen Module 2.0

In this section, a more detailed description of the halogen chemistry is given in addition to the description in section 4 of the article. Reaction fluxes are quantified and their relative contributions to the overall sinks are given.

S1.1 Chlorine chemistry

Discussion of chlorine atom concentration profiles and its reaction fluxes

As explained in the article, the photolysis of molecular chlorine impacts the concentration-time profiles of chlorine atoms especially during morning hours. The effect of morning peaks as described in [Pechtl and von Glasow \(2007\)](#) is stronger than in this study. While the concentrations of the second model day are very similar to the ones of this study, differences arise on the third model day. In the study of [Pechtl and von Glasow \(2007\)](#), the influence of the accumulated Cl_2 during the night increases so much that it causes a peak in the morning concentration of Cl atoms from the third model day on. This effect is not seen in the concentration profile of the base run of the present study, in which again only a steeper slope occurs in the concentration profile in the morning, yet no peak is found. Also, from the 4th model day on, the maximum concentration starts to decrease in the model study of [Pechtl and von Glasow \(2007\)](#) using cloud-free conditions. Their base run ends with a maximum concentration of about $7.5 \times 10^4 \text{ molecules cm}^{-3}$ on the last day and an overall maximum of about $1 \times 10^5 \text{ molecules cm}^{-3}$ on the 3rd model day. However, in the present study the concentration rises over the whole model run for cloud-free conditions leading to maximum concentration of about $1.2 \times 10^5 \text{ molecules cm}^{-3}$ on the last day. Only when clouds are present, the Cl maximum concentrations do not rise from day to day. For a better comparison with the work of [Pechtl and von Glasow \(2007\)](#), the modelled Cl concentrations of the different scenarios of the present study are given over the modelling period of 108h in Fig. S1. They can be directly compared to Fig. 1 in the work of [Pechtl and von Glasow \(2007\)](#).

In the following, the description of the reaction fluxes given in section 4.1.1 of the article is amended by a quantification of the reaction fluxes. The analyses of the source and sink fluxes for chlorine atoms reveal that the reaction of ClO with NO and the decomposition of ClO_2 are important non-photolysis sources for Cl atoms. The latter flux is only a net flux resulting from the fast equilibrium of Cl with O_2 recombination and ClO_2 destruction. While the average net flux over the whole model period is $5.8 \times 10^3 \text{ molecules cm}^{-3} \text{ s}^{-1}$, the real average forward and reverse fluxes of this equilibrium are astonishingly high with $2.1 \times 10^9 \text{ molecules cm}^{-3} \text{ s}^{-1}$, respectively. The reaction of ClO with NO is also only a backward reaction of the most important sink reaction of chlorine atoms with ozone as described later in the text. For a better evaluation of the real sinks and sources, net fluxes have been calculated. The fast re-cycling of forward and backward reactions was subtracted from each other to avoid null-cycles. Furthermore, percentages of the overall sinks and sources given in the following are derived after the elimination of all null-cycles. Most important sinks for gaseous chlorine atoms are the reactions with ozone and alkanes forming ClO and HCl, respectively. The only important gas phase loss reaction for HCl is the reaction with hydroxyl radicals, where Cl is regenerated. However, sink and source fluxes are only in the same order of magnitude during cloud periods, while during non-cloud periods production fluxes dominate with $3.2 \times 10^5 \text{ molecules cm}^{-3} \text{ s}^{-1}$ over sink fluxes, which total to $2.3 \times 10^3 \text{ molecules cm}^{-3} \text{ s}^{-1}$. The ClO radicals generated during the ozone destruction by Cl atoms are either directly recycled to Cl atoms in a null-cycle (as described above) or react with HO_2 radicals to hypochlorous acid as proposed by previous studies (see e.g., [von Glasow and Crutzen, 2007](#) and references therein). Most model results confirm the results of previous investigations, however, some refinements to the ozone destruction cycle have to be made as explained in the next section.

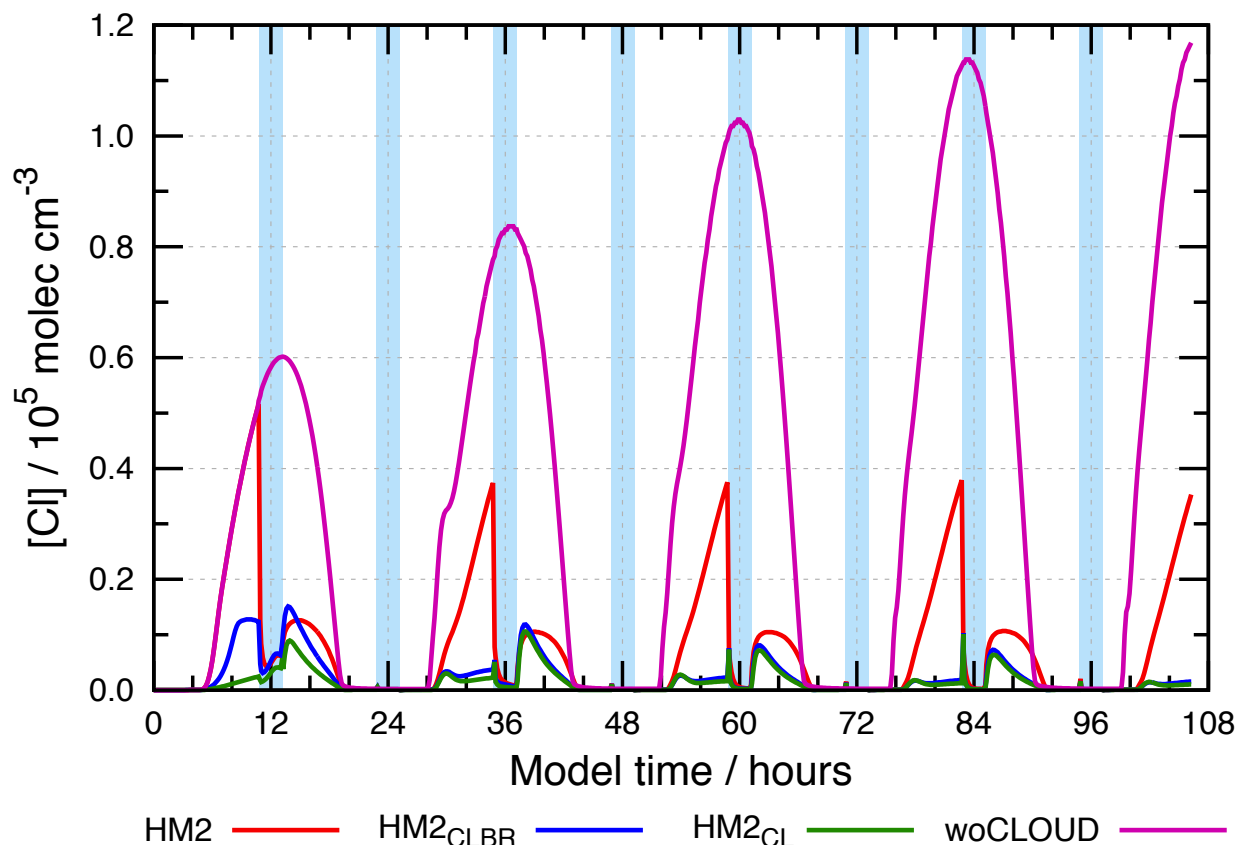


Figure S1 Modelled Cl concentration-time profiles in the gas phase over the whole modelling period of 108h for the different scenarios. Blue bars indicate in-cloud residence times of the air parcel.

Participation of chlorine species in the ozone destruction cycle under non-cloud conditions and chlorine activation

The direct recycling of ClO to Cl has been investigated by means of time-resolved flux analyses. The reaction of ClO with NO has been determined as the main pathway with a flux of $1.7 \times 10^4 \text{ molecules cm}^{-3} \text{ s}^{-1}$. Photolysis is of minor importance with fluxes one order of magnitude smaller ($1.1 \times 10^3 \text{ molecules cm}^{-3} \text{ s}^{-1}$).

Under cloud-free conditions, about two third of ClO react with HO₂ and 18% with methyl peroxide radicals to form HOCl, respectively. 25% of the HOCl formed partition into the aqueous phase and 75% photolyse in the gas phase to form Cl again. Further sinks for ClO are the reaction with NO₂ to ClONO₂, which will then either decompose to ClO and NO₂ or photolyse to Cl and NO₃. However, after the subtraction of all null-cycles, this process is only important during cloud periods as described in the next subsection. Yet, due to the short residence time of 15% of the air parcel in clouds, the overall loss is not more than 5%.

After the uptake of HOCl into the aqueous phase, the activation of chloride by hypochlorous acid as part of the ozone destruction cycle is only a minor sink for chloride. Most of the Cl⁻ (about 70%) is activated by HOI leading to ICl, which degasses and acts as the main source for chlorine atoms in the gas phase. The detailed flux analyses underline the importance of iodine species and their influence on chlorine chemistry, especially in the case of the activation of particulate chloride by HOI to yield ICl as suggested first by Vogt et al. (1999).

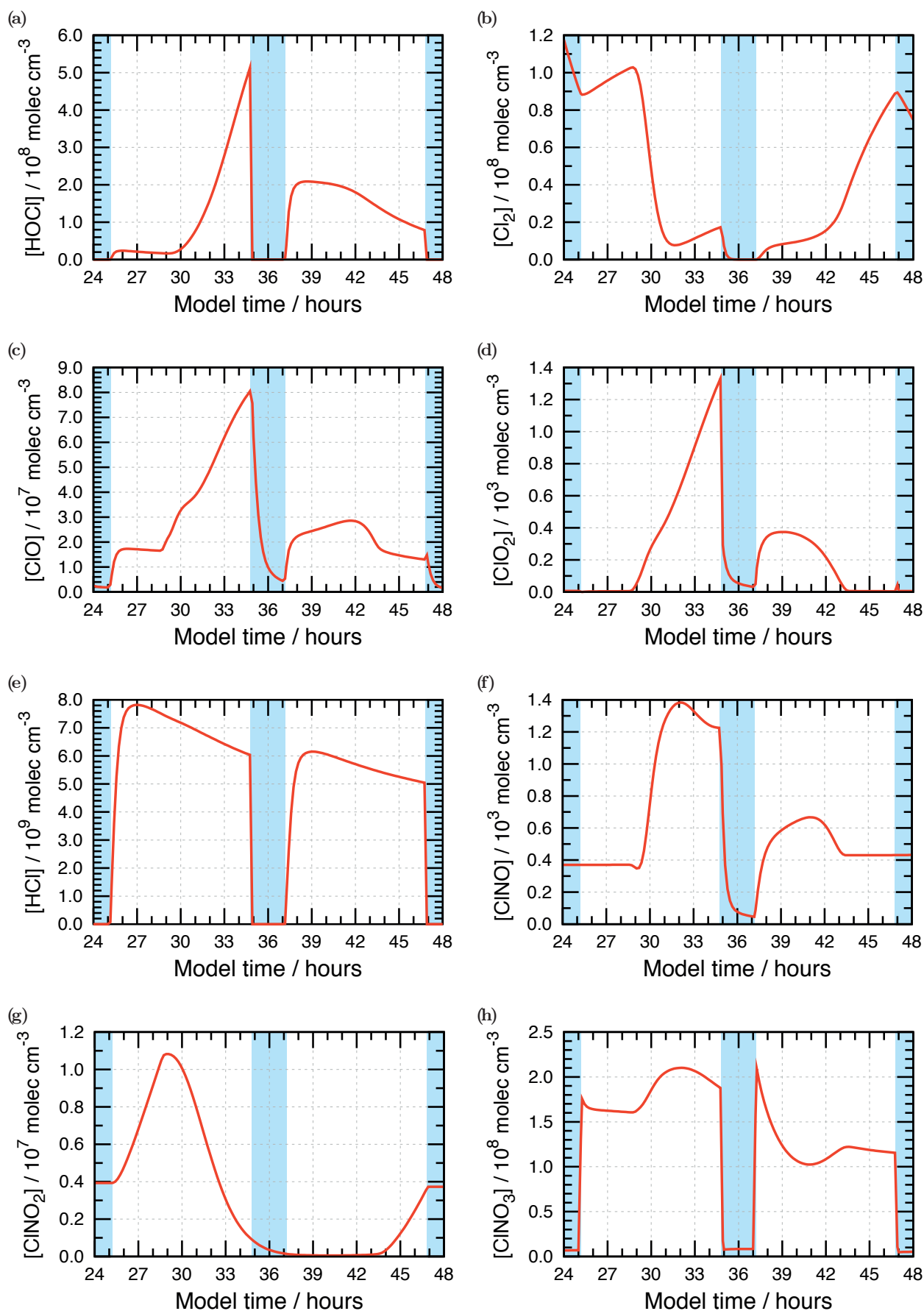


Figure S2 Modelled concentration-time profiles of selected chlorine species in the gas phase on the second model day (scenario HM2). Blue bars indicate in-cloud residence times of the air parcel.

Under in-cloud conditions, chlorine chemistry is suppressed, because there is no Cl^- activation by HOI during cloud events. Thus, the main production channel for chlorine species is missing, which leads to decreased concentrations and, as a consequence, to decreased fluxes of chlorine species.

This can be seen in Fig. 2 and 3 of the article for chlorine atoms and in Fig. S2 for other important chlorine species. In Fig. 2 of the article, the concentrations of the run HM2 are always lower than the concentrations of the run woCLOUD, in which only deliquescent particle chemistry is treated. Differences before the cloud period originate from the first model day, where already two cloud passages occurred lowering Cl concentrations on the second model day. From Fig. 3 of the article can be seen that fluxes of Cl atoms are decreased during cloud periods as well.

Under in-cloud conditions, the main source for Cl atoms in the gas phase is the direct release from the aqueous phase making up about 68% of the total sources with a flux of $8.8 \times 10^3 \text{ molecules cm}^{-3} \text{ s}^{-1}$. Photolysis as a source for $\text{Cl}_{(\text{g})}$ is less important under in-cloud conditions. Only Cl_2 photolysis with fluxes of $2.1 \times 10^3 \text{ molecules cm}^{-3} \text{ s}^{-1}$ accounts for 17% to the total sources of chlorine atoms. A minor contribution results from the OH initiated oxidation of chlorinated alkanes. The decomposition of ClCO with a flux of $6.9 \times 10^2 \text{ molecules cm}^{-3} \text{ s}^{-1}$ amounts to 4% of the total sources. Sinks for Cl remain the same as under in-cloud conditions, yet with slightly lower absolute fluxes. In a cloud, the importance of the reaction of chlorine with ozone is dramatically reduced. After the elimination of all null-cycles, only 7% of Cl react with ozone ($9.0 \times 10^2 \text{ molecules cm}^{-3} \text{ s}^{-1}$), while the main part of chlorine reacts with organics. In the latter reaction HCl is formed, which partitions into the aqueous phase and accumulates there.

Under in-cloud conditions, only 24% ($1.8 \times 10^3 \text{ molecules cm}^{-3} \text{ s}^{-1}$) of the ClO react with hydroperoxyl radicals to form hypochlorous acid. The reaction with methyl peroxy radicals is less affected and still accounts for 13% of all losses under in-cloud conditions. A large fraction of ClO ($3.8 \times 10^3 \text{ molecules cm}^{-3} \text{ s}^{-1}$) reacts with NO_2 to form ClNO_3 . During the day, this makes up 38% of the total ClO sinks, while in the night-time, this is the dominant sink with 97%. ClNO_3 accumulates in the aqueous phase upon phase transfer. Under in-cloud conditions, all of the HOCl partitions into the aqueous phase, but in contrast to deliquescent particle conditions, it reacts with hydrogen peroxide and sulphuric acid to form HCl, which accumulates in cloud droplets. Cl atoms in cloud droplets take part in multiple and complex reaction cycles. They are formed by the equilibrium of ClOH^- with H^+ , the first originating mainly from the reaction of chloride with hydroxyl radicals and the hydrolysis of the Cl_2^- radical anion. A reaction flux of $6.1 \times 10^3 \text{ molecules cm}^{-3} \text{ s}^{-1}$ closes the reaction cycles by the reaction of Cl and Cl^- to Cl_2^- .

A direct phase transfer of chlorine atoms from the aqueous phase with a release rate of $8.8 \times 10^3 \text{ molecules cm}^{-3} \text{ s}^{-1}$ is the main source of chlorine atoms in the gas phase. It should be noted that the reactions of Cl atoms with organic compounds have to be regarded far from being complete and hence the direct transfer of halogen atoms is probably overestimated at this time. As a part of this, and different to other mechanisms, there is no estimated overall rate constant for chlorine with dissolved organic matter (DOM). Hence, Cl atom sinks in the aqueous phase might be underestimated.

S1.2 Bromine chemistry

For a better understanding of the various cycles of bromine species, section 4.1.2 of the article is completed by Fig. S3 with plots of the concentration-time profiles of the most important gas phase bromine species including the mixed halide molecule BrCl.

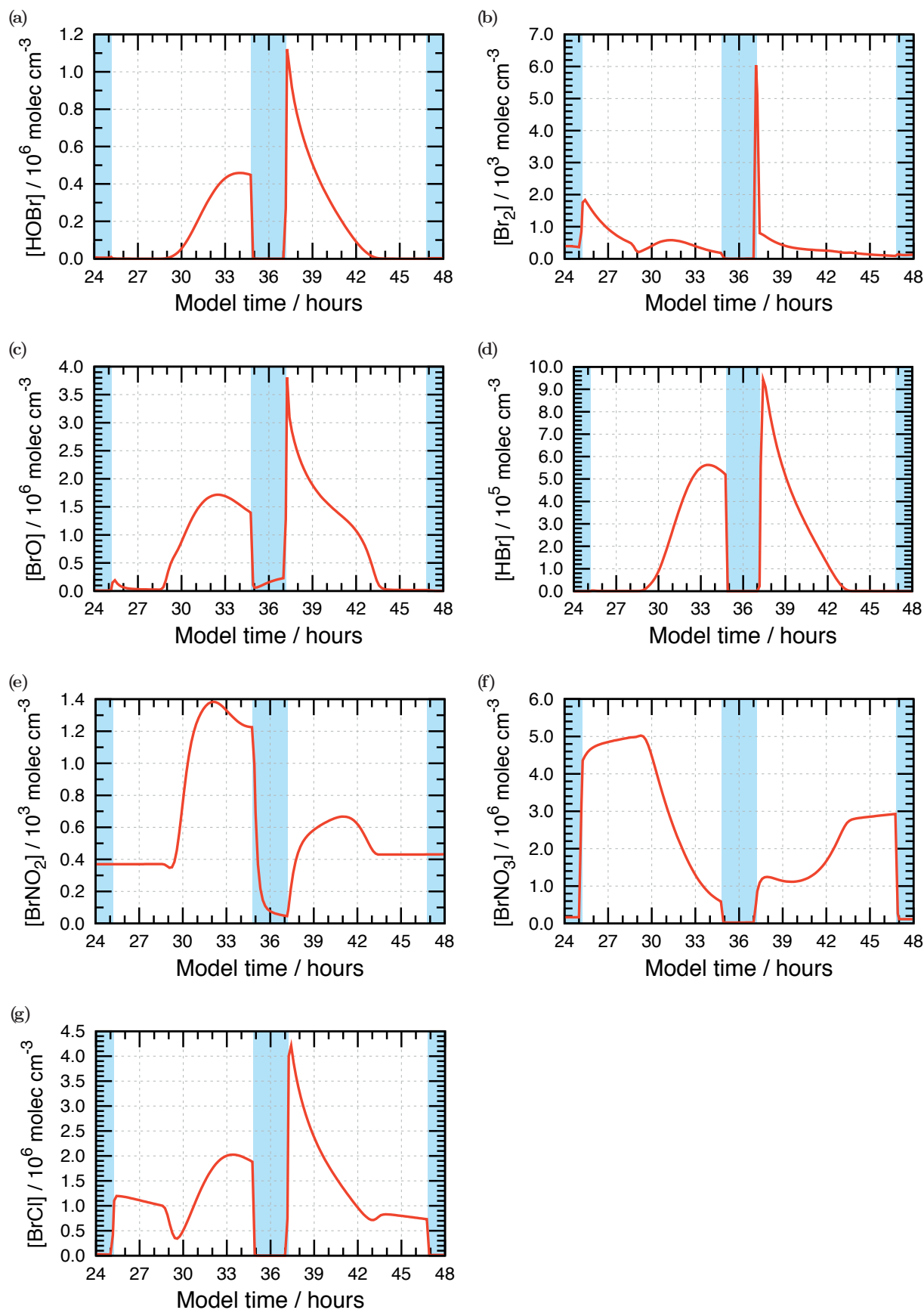


Figure S3 Modelled concentration-time profiles of selected bromine species in the gas phase on the second model day (scenario HM2). Blue bars indicate in-cloud residence times of the air parcel.

S1.3 Iodine chemistry

S1.3.1 Inorganic iodine chemistry

Inorganic iodine cycles leading to IBr formation under in-cloud conditions

In this paragraph, the cycles leading to the different behaviour of IBr under in-cloud conditions are explained in more detail. Under in-cloud conditions, the main source of IBr is not anymore the dissociation of the trihalide anion IClBr^- as described in section 4.1.2 of the article. This flux is now only $14.3 \text{ molecules cm}^{-3} \text{ s}^{-1}$ totalling to 6% of the sources. The largest fraction (94% of the total sources) with a flux of $219 \text{ molecules cm}^{-3} \text{ s}^{-1}$ originates from the iodide activation by hypobromous acid. In the only sink process for IBr, it is hydrolysed to HOI and dissociated HBr. HOI oxidises sulphur(IV) to sulphur(VI), where I^- is produced, which is a source species for IBr in the reaction with HOBr. Bromide is recycled to HOBr in a reaction chain producing the BrCl_2^- radical anion by the reaction with Cl_2 , which dissociates to BrCl and Cl^- . BrCl then hydrolyses to HOBr, which will form IBr again. Thus, all sink reactions are converted to source reactions and IBr accumulates in the aqueous phase. Upon cloud evaporation, IBr is released into the gas phase causing a peak in the concentration profile.

Participation of iodine species in the ozone destruction cycle under non-cloud conditions and chlorine activation

This section quantifies the reaction fluxes in the ozone destruction cycle under non-cloud conditions. Tab. S1 lists the most important sources and sinks for iodine atoms after the elimination of all null-cycles together with the chemical fluxes and the relativ contributions to the overall sources and sinks. For a better understanding, the concentration-time profiles of the most important inorganic halogen species are shown in Fig. S4, page 10.

Table S1 Most important source and sink reactions contributing to the production and destruction of I atoms. Given are the absolute chemical fluxes after the elimination of null-cycles averaged over the whole model run of 108 hours as well as their relative contributions to the overall sources/sinks in per cent. For net fluxes, the individual reactions and their fluxes are given below the net reaction/flux as well.

Label	Reaction	Chemical flux [molec $\text{cm}^{-3} \text{ s}^{-1}$]	Relative contri- bution to overall sources/sinks [%]
P _g 47	$\text{ICl} \xrightarrow{h\nu} \text{I} + \text{Cl}$	4.8×10^4	69
P _g 42	$\text{HOI} \xrightarrow{h\nu} \text{I} + \text{OH}$	1.4×10^4	21
P _g 36	$\text{I}_2 \xrightarrow{h\nu} 2\text{I}$	1.9×10^3	3
G234	$\text{IO} + \text{IO} \longrightarrow \text{products}$	3.0×10^3	4
G254	$\text{IO} + \text{ClO} \longrightarrow \text{products}$	1.8×10^3	3
	$\text{I} + \text{O}_3 \longrightarrow \text{IO} + \text{O}_2$	-7.7×10^4	-100
G230	* $\text{I} + \text{O}_3 \longrightarrow \text{IO} + \text{O}_2$	-8.6×10^4	
G243	* $\text{IO} + \text{NO} \longrightarrow \text{I} + \text{NO}_2$	5.8×10^3	
P _g 37	* $\text{IO} \xrightarrow{h\nu} \text{I} + \text{O}(^3\text{P})$	3.4×10^3	

The only significant loss of iodine atoms in the gas phase is the reaction with ozone with a flux of $1.0 \times 10^5 \text{ molecules cm}^{-3} \text{ s}^{-1}$. For the IO radicals formed, the reaction with HO_2 is the dominant sink. $7.5 \times 10^4 \text{ molecules cm}^{-3} \text{ s}^{-1}$ or 75% of all loss fluxes are resulting from this reaction. Further fluxes are of minor importance and account for interactions with NO_x (7%) or trigger fast cycles between the iodine oxides IO, OIO, and I_2O_2 as well as atomic and molecular iodine with fluxes in the order of $10^3 \text{ molecules cm}^{-3} \text{ s}^{-1}$ (6%). About 23% of the hypoiodous acid formed from the reaction of IO with HO_2 photolyse, the remaining part ($5.9 \times 10^4 \text{ molecules cm}^{-3} \text{ s}^{-1}$) partitions into the aqueous phase, in which it activates chloride to ICl . Iodine chloride is rapidly released into the gas phase, in which it triggers both the iodine and chlorine chemistry. This is in good agreement with previous studies, e.g. by Vogt et al. (1999).

Participation of iodine species in the ozone destruction cycle under in-cloud conditions and iodate formation

This section details the reaction fluxes of the IO uptake during in-cloud residence times of the air parcel. The ozone destruction cycle is disturbed as only 9% of the IO formed react with HO_2 . The main fraction of IO (84%, $1.5 \times 10^4 \text{ molecules cm}^{-3} \text{ s}^{-1}$) partitions into the aqueous phase and hence gas phase IO concentrations are decreased when a cloud is formed. In the aqueous phase, the IO radicals recombine to yield, with water, hypoiodous and iodous acid. Thus, at the beginning of the cloud period, aqueous IO concentrations show a peak and as the aqueous IO reacts further, concentrations are decreased over time as can be seen from Fig. S5a, page 12. The reaction product of the IO recombination, iodous acid, dissociates and reacts with hydrogen peroxide to form iodate, which accumulates as iodic acid. So again, HIO_2 shows only a peak at the beginning of the cloud period (see Fig. S5b, page 12) when it is formed from the large source of IO radicals. Concentrations decrease rapidly as HIO_2 reacts further to HIO_3 whose accumulation over time can be seen in Fig. S5b (page 12) as well.

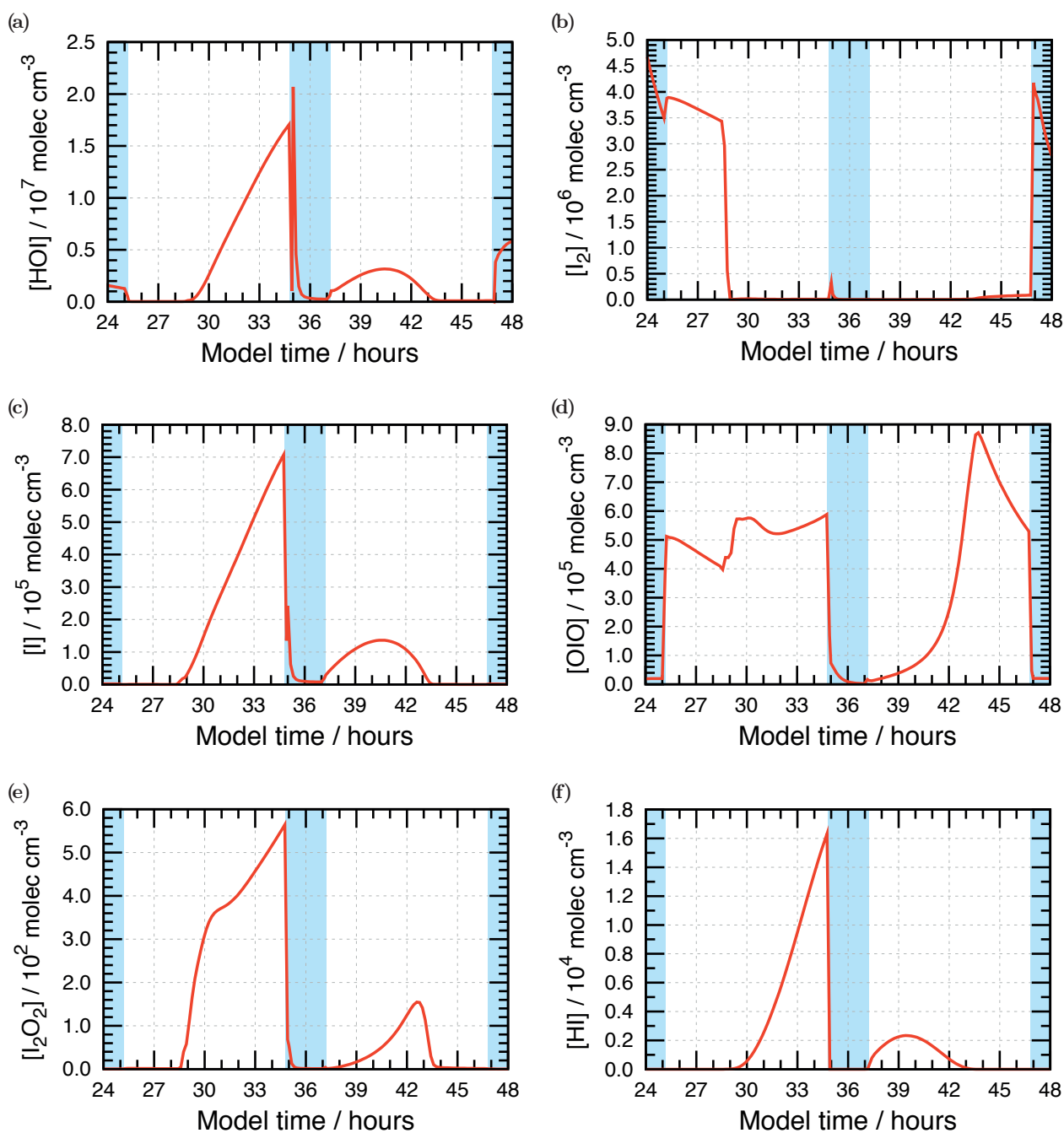


Figure S4 Modelled concentration-time profiles of selected iodine species in the gas phase on the second model day (scenario HM2). Blue bars indicate in-cloud residence times of the air parcel.

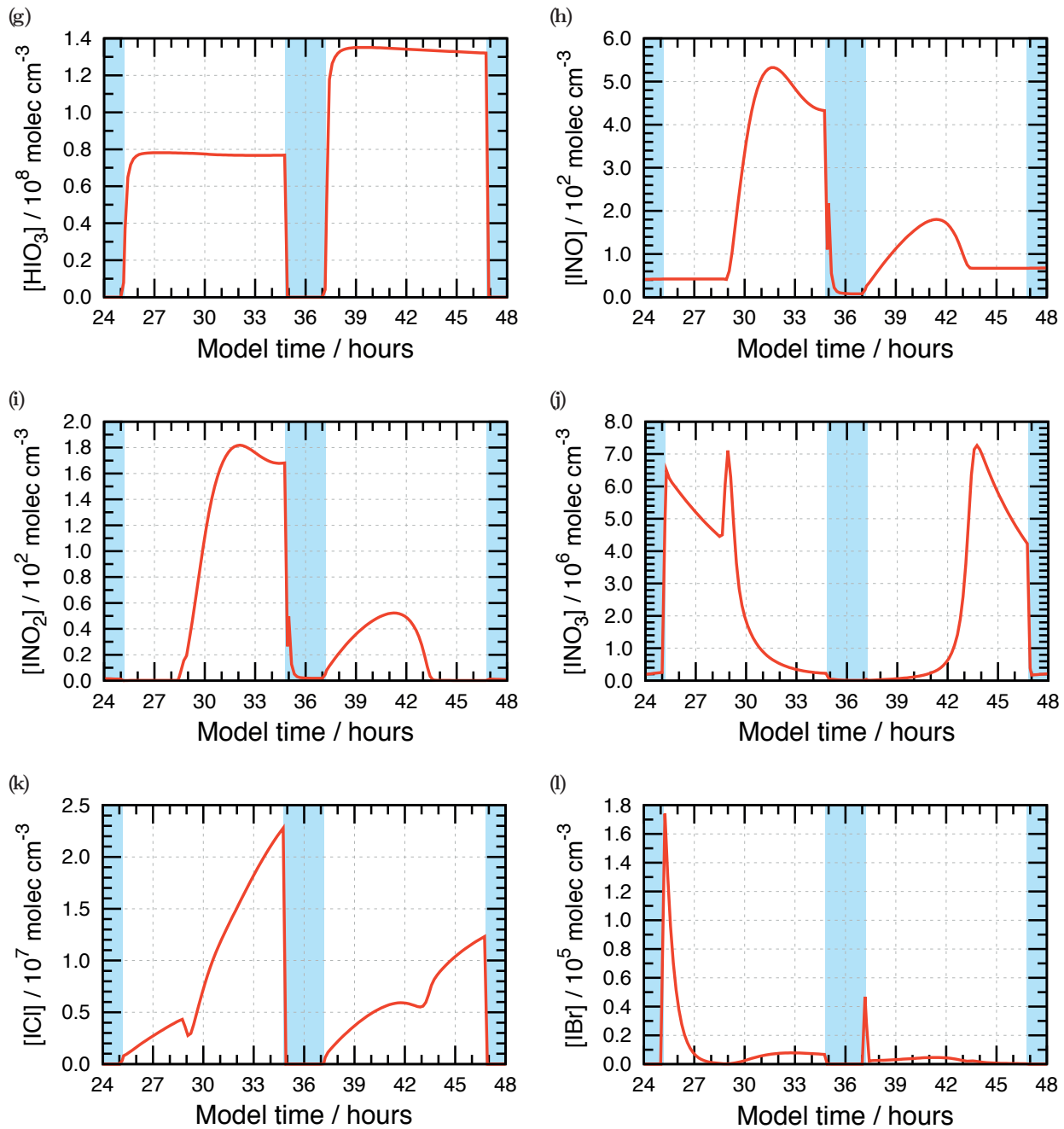
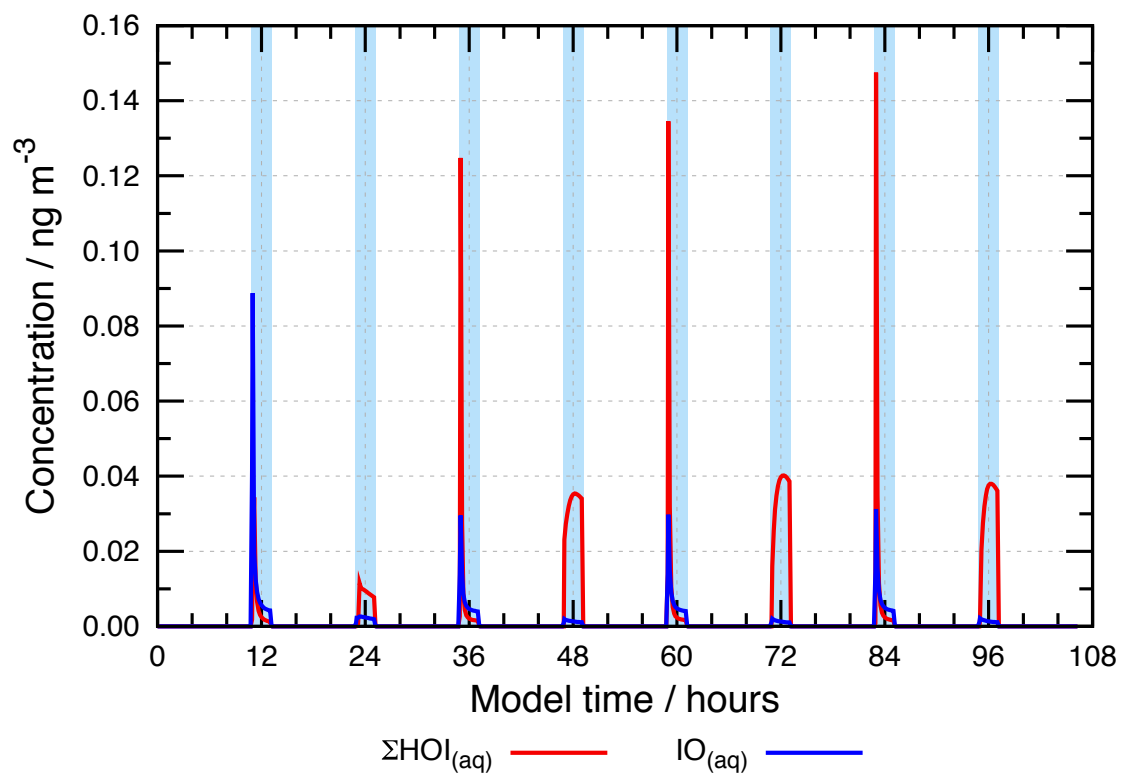


Figure S4 (continued) Modelled concentration-time profiles of selected bromine species in the gas phase on the second model day (scenario HM2). Blue bars indicate in-cloud residence times of the air parcel.

(a) $\text{IO}_{(\text{aq})}$ and $\Sigma\text{HOI}_{(\text{aq})}$



(b) $\Sigma\text{HIO}_{2(\text{aq})}$ and $\Sigma\text{HIO}_{3(\text{aq})}$

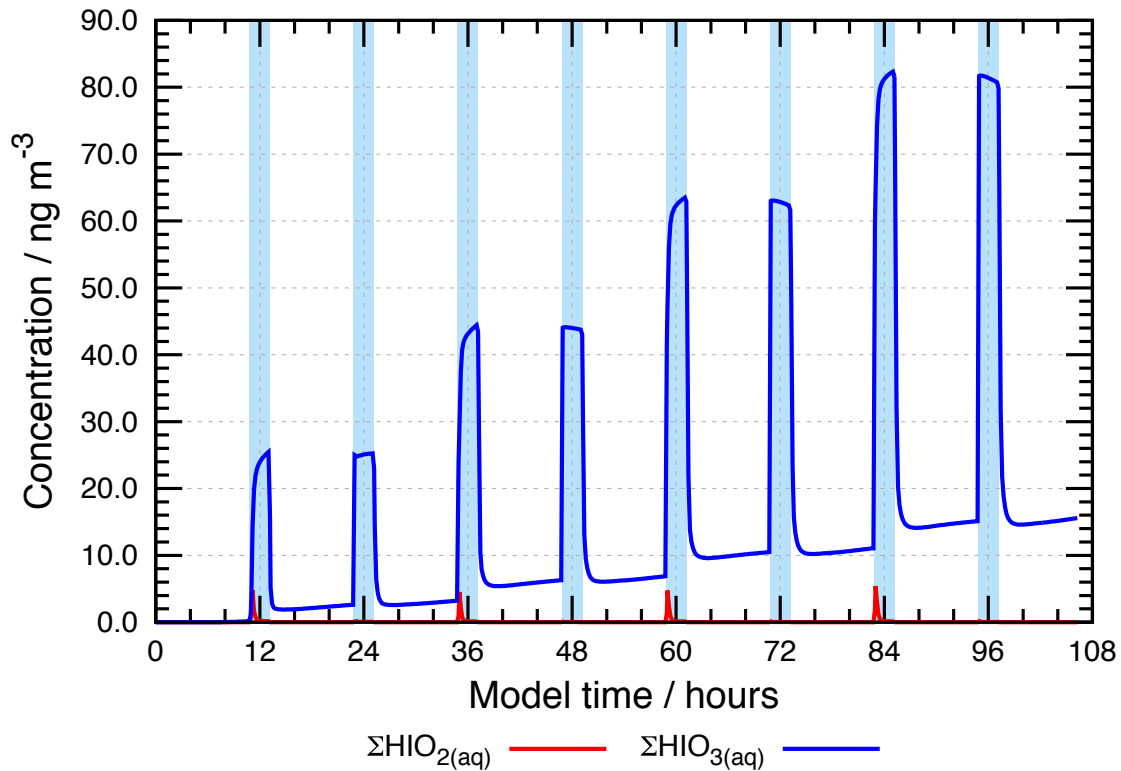


Figure S5 Modelled concentration-time profiles of selected iodine species in the aqueous phase over the whole modelling period of 108 h (scenario HM2). For HOI, HIO₂, and HIO₃ the sum of the dissociated and undissociated forms was used for the concentration-time profiles (indicated by Σ). Blue bars indicate in-cloud residence times of the air parcel.

S1.3.2 Organic iodine chemistry

For a better understanding of the decay of iodocarbons emitted from the ocean's surface, the concentration-time profiles are shown in Fig. S6.

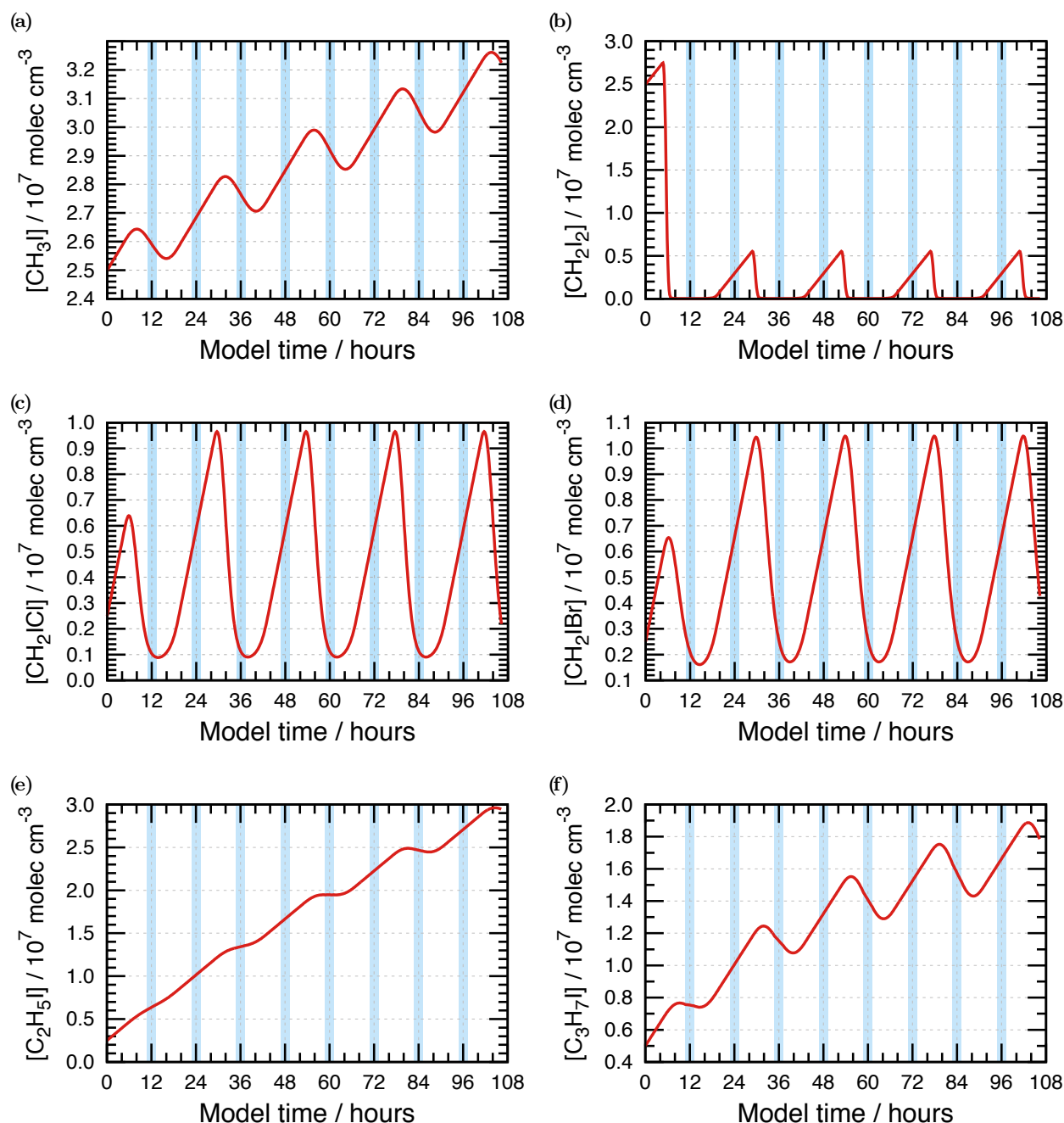


Figure S6 Modelled concentration-time profiles of the various alkyl iodides in the gas phase for the whole modelling period of 108h (scenario HM2). Blue bars indicate in-cloud residence times of the air parcel.

S1.4 Influence of halogen chemistry on the aqueous phase oxalate oxidation

In this section, the oxidation of oxalate is discussed in more detail. Halogens contribute to the oxalate oxidation during non-cloud periods via electron transfer reaction of the Cl_2^- radical anion.

In Fig. S7 the relative contributions of all sinks are plotted over time. It can be clearly seen that under non-cloud conditions the oxidation is dominated by Cl_2^- , while under in-cloud conditions OH is the main oxidant. Only during night-time in-cloud conditions, NO_3 contributes with about 40% to the total sinks. In Fig. S8 the speciation of the different dissociation states of oxalic acid is given. Under non-cloud conditions, the di-anion is the dominant form, while under in-cloud conditions the mono-anion predominantly exists. The reactivities are comparable for both forms and are in the order of $10^6 \text{ M}^{-1} \text{ s}^{-1}$ for Cl_2^- and in the order of $10^8 \text{ M}^{-1} \text{ s}^{-1}$ for OH. Therefore, the aqueous phase concentrations of these two species dictate the degradation process. They are given in Fig. S9. Please, note the logarithmic scale of the ordinate. The reactivity of OH is always about 2 orders of magnitude higher than that of Cl_2^- . However, during non-cloud periods the concentrations of Cl_2^- are between 4 to 5 orders of magnitude higher (in the range of 10^9 mol l^{-1}), which more than compensates the higher reactivities of the hydroxyl radical. Thus, the oxidation of oxalic acid is dominated by this species. During in-cloud residence times of the air parcel, oxalate is exposed to higher OH radical concentrations (1 to 2 orders of magnitude higher than Cl_2^- in the range of $10^{-12} \text{ mol l}^{-1}$) with higher reactivities than the chlorine radical di-anion and, hence, its oxidation is dominated by OH.

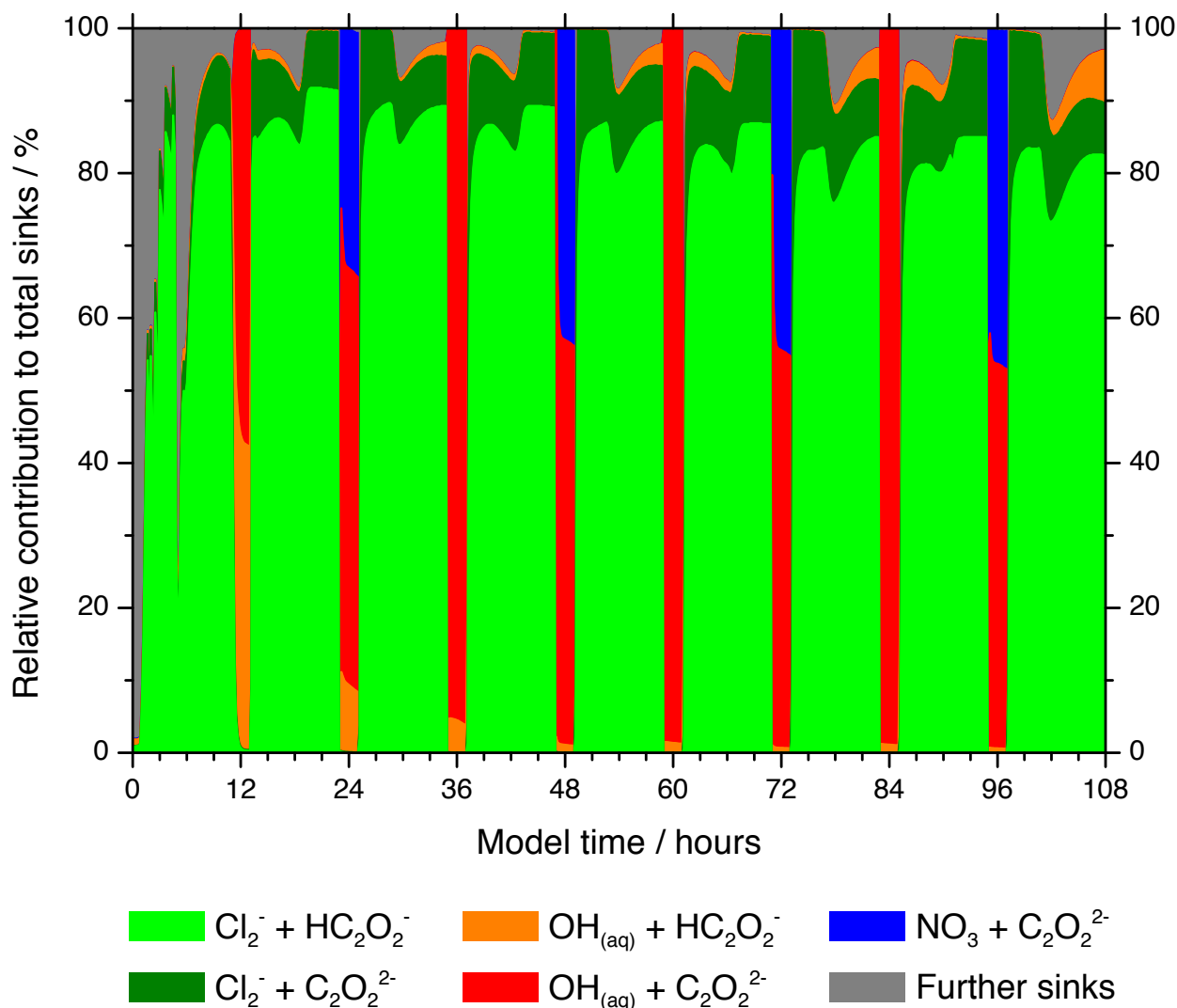


Figure S7 Modelled time-resolved contributions of the various oxidants to the aqueous phase degradation of the sum of all dissociation states of oxalic acid for the whole modelling period of 108h (scenario HM2). The respective total average sink fluxes under non-cloud, daytime in-cloud, and night-time in-cloud conditions are 5.7×10^2 , 6.8×10^2 , and $1.2 \text{ molecules cm}^{-3} \text{ s}^{-1}$.

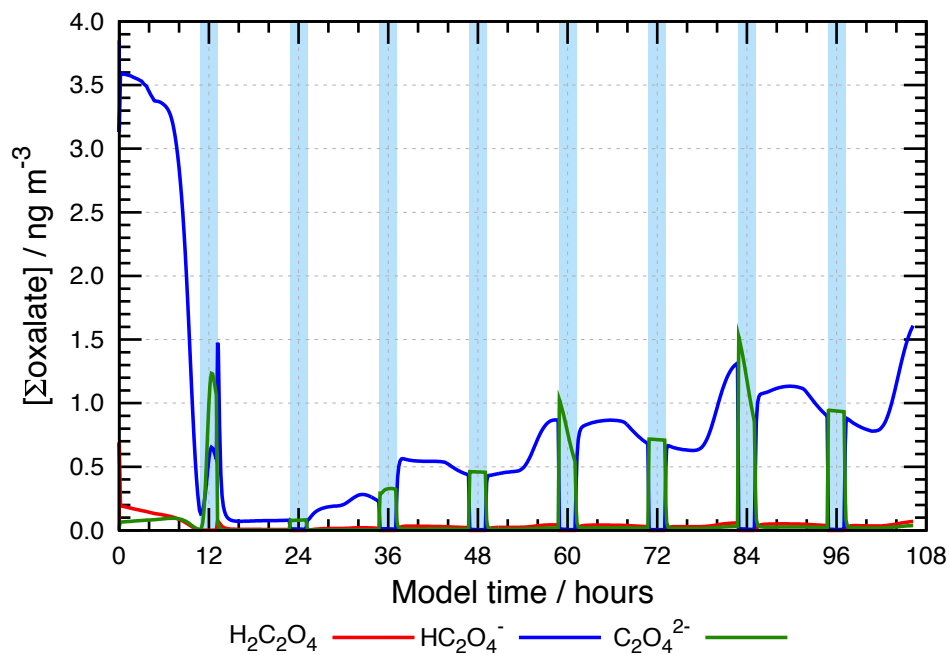


Figure S8 Modelled concentration-time profiles of the speciation of the different oxidation states of oxalic acid for the whole modelling period of 108h (scenario HM2). Blue bars indicate in-cloud residence times of the air parcel.

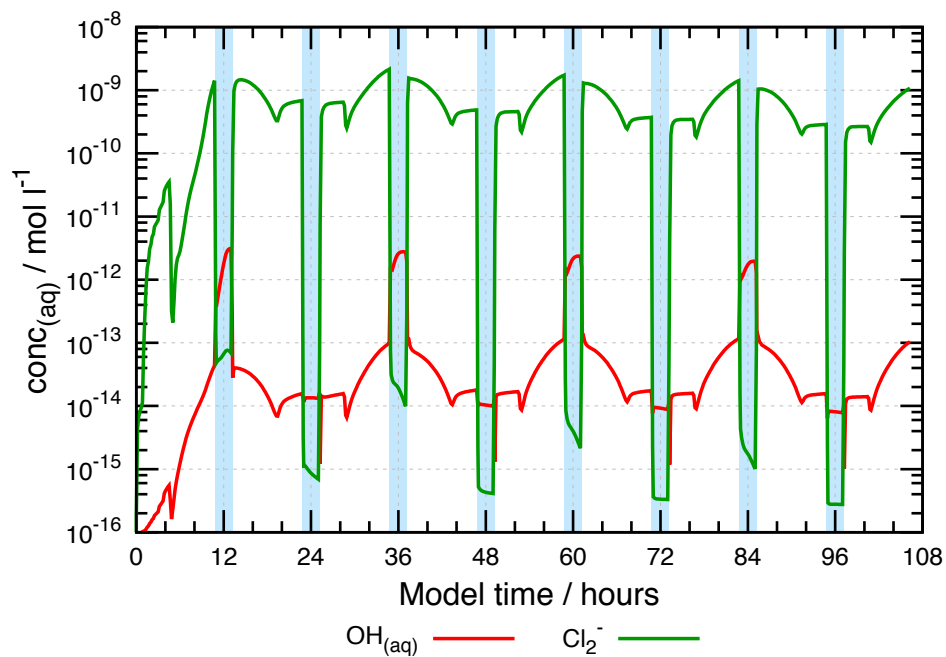


Figure S9 Modelled concentration-time profiles of $\text{OH}_{(\text{aq})}$ and Cl_2^- for the whole modelling period of 108h (scenario HM2). Blue bars indicate in-cloud residence times of the air parcel.

S1.5 Comparison of the model results with results from previous model studies

In this section, an overview of the maximum concentrations of important halogen species from this and previous model studies is given. Results are compiled in Tab. S2 and discussed in section 4 of the article.

Table S2 Maximum concentrations of important halogen species from selected model studies. Values are taken from the result plots given in the referenced publications.

Species	Maximum value [molec cm ⁻³]	Reference ^a
Cl	$\sim 1.5 \times 10^4$	Sander and Crutzen (1996) ¹
	$\sim 10^3$	Vogt et al. (1996) ²
	$\sim 2 \times 10^4$	Sander et al. (1997) ³
	$\sim 7 \times 10^3$	Vogt et al. (1999) ²
	$\sim 9 \times 10^4$	Pechtl and von Glasow (2007) ¹
	$\sim 3 \times 10^4$	Pechtl and von Glasow (2007) ²
	$\sim 1 - 2.5 \times 10^5$	Lowe et al. (2009) ⁴
	5.2×10^4	this work ^b
	3.7×10^4	this work ^c
ClO	$\sim 1.4 \times 10^6$	Sander and Crutzen (1996) ¹
	$\sim 10^7$	Vogt et al. (1996) ²
	$\sim 10^8$	Sander et al. (1997) ³
	$\sim 1.2 \times 10^7$	Vogt et al. (1999) ²
	$\sim 10^7 - 4.5 \times 10^8$	Lowe et al. (2009) ⁴
	1.3×10^8	this work ^b
	8.0×10^7	this work ^c
HOCl	$\sim 1 \times 10^8$	Sander and Crutzen (1996) ¹
	$\sim 5 \times 10^7$	Vogt et al. (1996) ²
	$\sim 6 \times 10^7$	Vogt et al. (1999) ²
	$\sim 2.4 \times 10^9$	Pechtl and von Glasow (2007) ¹
	$\sim 1.2 \times 10^8$	Pechtl and von Glasow (2007) ²
	$< 3 \times 10^9$	Lowe et al. (2009) ⁴
	7.8×10^8	this work ^b
	5.1×10^8	this work ^c
Cl ₂	$\sim 9 \times 10^8$	Sander and Crutzen (1996) ¹
	$\sim 5 \times 10^6$	Vogt et al. (1996) ²
	$\sim 8 \times 10^6$	Vogt et al. (1999) ²
	$\sim 2.3 \times 10^9$	Pechtl and von Glasow (2007) ¹
	$\sim 7.5 \times 10^7$	Pechtl and von Glasow (2007) ²
	1.5×10^8	this work ^b
	1.2×10^8	this work ^c
Br	$\sim 7 \times 10^5$	Sander and Crutzen (1996) ¹
	$\sim 3.5 \times 10^5$	Vogt et al. (1996) ²
	$\sim 2 \times 10^9$	Sander et al. (1997) ³
	$\sim 1.8 \times 10^6$	Vogt et al. (1999) ²

Table S2 (continued) Maximum concentrations of important halogen species from selected model studies. Values are taken from the result plots given in the referenced publications.

	$\sim 4.5 - 7.5 \times 10^6$	Lowe et al. (2009) ⁴
	6.5×10^5	this work ^b
	2.1×10^5	this work ^c
BrO	$\sim 2 \times 10^7$	Sander and Crutzen (1996) ¹
	$\sim 10^7$	Vogt et al. (1996) ²
	$\sim 2 \times 10^9$	Sander et al. (1997) ³
	$\sim 4 \times 10^7$	Vogt et al. (1999) ²
	$\sim 1.2 \times 10^8$	von Glasow et al. (2002a) ²
	$\sim 4.5 \times 10^7$	von Glasow et al. (2002b) ⁵
	$\sim 1 - 1.2 \times 10^8$	Lowe et al. (2009) ⁴
	2.1×10^7	this work ^b
	3.8×10^6	this work ^c
HOBr	$\sim 6.8 \times 10^8$	Sander and Crutzen (1996) ¹
	$\sim 2 \times 10^8$	Vogt et al. (1996) ²
	$\sim 5 \times 10^8$	Sander et al. (1997) ³
	$\sim 9 \times 10^7$	Vogt et al. (1999) ²
	$\sim 9.5 \times 10^7$	von Glasow et al. (2002a) ²
	$\sim 7 \times 10^6$	von Glasow et al. (2002b) ⁵
	$\sim 2.2 - 5 \times 10^8$	Lowe et al. (2009) ⁴
	3.6×10^6	this work ^b
	1.1×10^6	this work ^c
Br₂	$\sim 3.2 \times 10^8$	Sander and Crutzen (1996) ¹
	$\sim 8 \times 10^7$	Vogt et al. (1996) ²
	$\sim 5 \times 10^7$	Vogt et al. (1999) ²
	$\sim 6.3 \times 10^7$	von Glasow et al. (2002a) ²
	5.0×10^6	this work ^b
	6.0×10^3	this work ^c
BrCl	$\sim 6.8 \times 10^7$	Sander and Crutzen (1996) ¹
	$\sim 9 \times 10^7$	Vogt et al. (1996) ²
	$\sim 2 \times 10^8$	Sander et al. (1997) ³
	$\sim 1 \times 10^8$	Vogt et al. (1999) ²
	$\sim 1.1 \times 10^8$	von Glasow et al. (2002a) ²
	$\sim 2.8 - 4 \times 10^8$	Lowe et al. (2009) ⁴
	1.9×10^7	this work ^b
	4.2×10^6	this work ^c
IO	$\sim 2.2 \times 10^7$	Vogt et al. (1999) ²
	$\sim 7 \times 10^7$	Sander et al. (1997) ³
	$\sim 4 \times 10^7$	von Glasow et al. (2002a) ²
	$\sim 7.5 \times 10^7$	Pechtl et al. (2006) ⁶
	$\sim 2.5 \times 10^7$	Pechtl et al. (2006) ⁷
	$\sim 1.5 - 4.5 \times 10^7$	Lowe et al. (2009) ⁴
	$\sim 5 \times 10^6$	Jones et al. (2010) ⁸

Table S2 (continued) Maximum concentrations of important halogen species from selected model studies. Values are taken from the result plots given in the referenced publications.

	$\sim 7.5 \times 10^7$	Jones et al. (2010) ⁹
	2.4×10^7	this work ^b
	1.6×10^6	this work ^c
HOI	$\sim 5 \times 10^7$	Vogt et al. (1999) ²
	$\sim 6.5 \times 10^7$	von Glasow et al. (2002a) ²
	$\sim 4.5 \times 10^8$	Pechtl et al. (2006) ⁷
	$\sim 0.9 - 2.5 \times 10^8$	Lowe et al. (2009) ⁴
	2.4×10^7	this work ^b
	2.1×10^7	this work ^c
ICl	$\sim 2 \times 10^6$	Sander et al. (1997) ³
	$\sim 4.6 \times 10^7$	von Glasow et al. (2002a) ²
	$\sim 0.5 - 1.8 \times 10^8$	Lowe et al. (2009) ⁴
	3.1×10^7	this work ^b
	2.3×10^7	this work ^c

^aModel conditions are given in the footnotes below; ^boverall maximum concentration for the base run HM2; ^cmaximum concentration on the second model day for the base run HM2

¹polluted MBL, permanently cloud-free; ²remote MBL, permanently cloud-free; ³MBL in the arctic spring; ⁴clean MBL, permanently cloud-free for different treatments of the microphysics; ⁵remote MBL, permanently cloudy; ⁶coastal MBL, permanently cloud-free; continuous alkyl iodide emissions (their scenario 1); ⁷coastal MBL, permanently cloud-free; hot spot emissions of alkyl iodides/I₂ (their scenario 3); ⁸open ocean, permanently cloud-free; ⁹open ocean, permanently cloud-free with additional I₂ emissions

S2 Model setup

S2.1 Model initialisation

No spin-up time is used in the model runs. Within the first 15 model seconds the microphysics and aerosol distribution is set and the pH value is calculated according to the charge balance. Thereafter, chemistry is calculated and the pH value is determined explicitly every time-step according to the H⁺ concentration.

S2.2 Cloud scenario

In Figure S10, the cloud scenario used is depicted. A description can be found in the article in section 3.

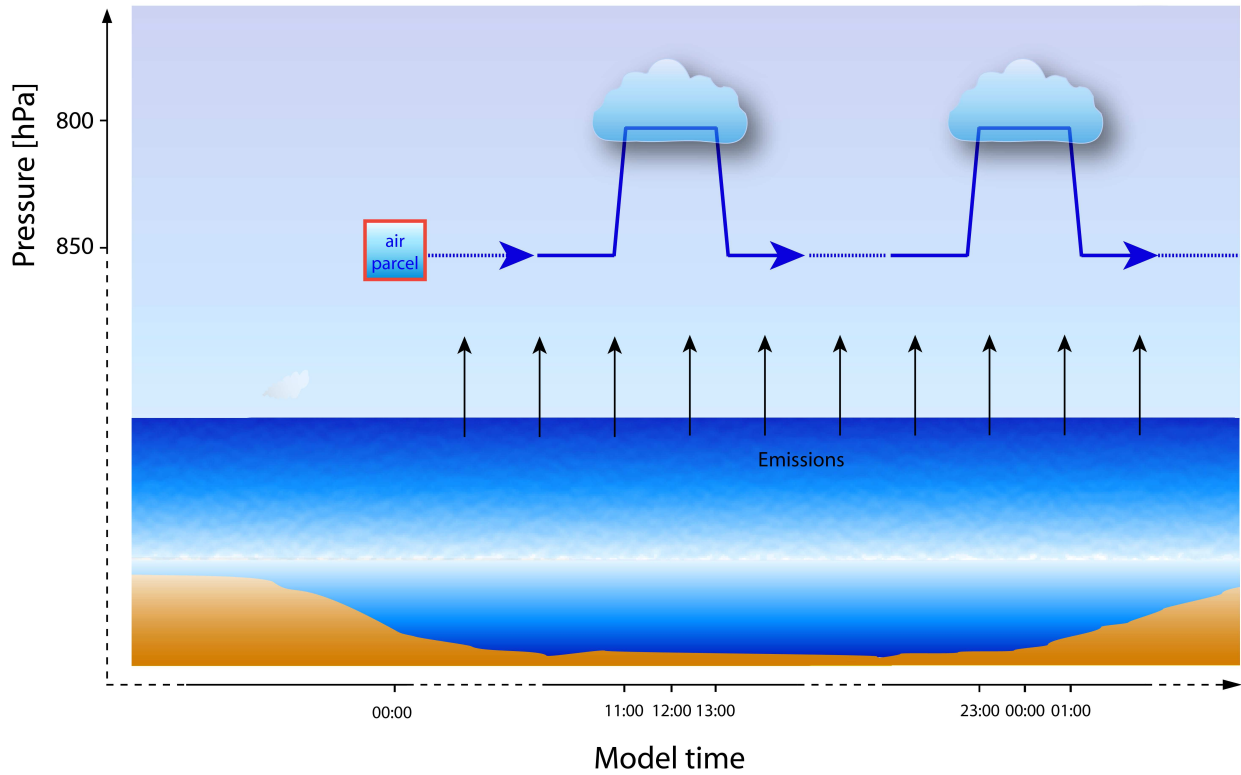


Figure S10 Schematic of the cloud scenario used in the model runs.

S2.3 Calculation of photolysis rates

Photolysis rates were calculated for the lower troposphere at 45°N and clear sky conditions. The aerosol distribution and absorption of important trace gases was taken over from the TUV model. Photolysis rates were determined every 15 minutes for June 21st. A parameterisation was derived from the calculated photolysis rates according to the MCM mechanism:

$$j = l \times \cos^m \chi \times \exp\{-n \times \sec \chi\},$$

where the parameters, l , m , and n were determined. They serve as input for the model SPACCIM, which uses the diurnal profile of the photolysis rate and varies it according to the latitude and the time. For cloud periods, no variation of the photolysis rates is used. Since there are areas in clouds with increased photolysis rates at the top and decreased photolysis rates at the bottom of the cloud and there is no exact definition of the position of the air parcel within the cloud, the variation during cloud periods was renounced.

S2.4 Changes to original setup

Table S3 Changes to the original emission scenario in CAPRAM 3.0i and older versions

Species	Open ocean [$\text{cm}^{-2} \text{s}^{-1}$]	Reference
NO	2.50×10^8	Thompson and Zafriou (1983)
ETH ^a	1.00×10^7	Plass-Dülmer et al. (1993)
HC3 ^b	2.00×10^7	estimated based on emission rates by Plass-Dülmer et al. (1993) and Broadgate et al. (1997) and the compounds belonging to the model species HC3 as explained in section S4
ETE ^c	2.40×10^8	Plass-Dülmer et al. (1993)
C ₃ H ₆	1.00×10^8	Plass-Dülmer et al. (1993)
ETI ^d	1.00×10^7	Plass-Dülmer et al. (1993)
CH ₃ CHO	3.60×10^9	Toyota et al. (2004)
C ₂ H ₅ CHO	5.47×10^9	Singh et al. (2003)
ISO ^e	3.20×10^7	Arnold et al. (2009)

^aETH = ethane; ^bHC3 = alkanes, alcohols, esters, and alkynes with OH rate constant (298 K, 1 atm) less than $3.4 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$; ^cETE = ethylene; ^dETI = acetylene; ^eISO = isoprene

Table S4 Changes to the original initial concentrations in CAPRAM 3.0i and older versions

Species	Open ocean [cm^{-3}]	Reference/comment
O ₃	7.50×10^{11}	Sander et al. (1997)
H ₂ O ₂	1.50×10^{10}	Lowe et al. (2009)
NO	2.50×10^8	Lowe et al. (2009)
NO ₂	5.00×10^8	Lowe et al. (2009)
HONO	2.50×10^8	Warneck (2005)
HNO ₃	2.50×10^9	Warneck (2005)
CH ₄	4.50×10^{13}	Lowe et al. (2009)
HC3 ^a	2.31×10^{10}	adjusted emissions according to the delumping of acetylene
C ₃ H ₆	1.60×10^9	delumped from OLT

Table S4 (continued) Changes to the initial concentrations in CAPRAM 3.0i and older versions

Species	Open ocean [cm^{-3}]	Reference/comment
OLT ^b	9.50×10^8	adjusted emissions according to the delumping of propylene
ETI ^c	2.42×10^9	delumped from HC3
HCHO	5.00×10^9	Warneck (2005)
CH ₃ CHO	5.12×10^9	Singh et al. (2003)
C ₂ H ₅ CHO	1.50×10^9	Singh et al. (2003)
CH ₃ OCH ₃	1.10×10^{10}	Singh et al. (2003)
CH ₃ OH	1.40×10^{10}	Singh et al. (2003)
ETOH ^d	2.00×10^9	Warneck (2005)
ORA1 ^e	6.25×10^9	Warneck (2005)
CH ₃ COOH	5.00×10^9	Warneck (2005)
OP1 ^f	5.00×10^9	Warneck (2005)
PAN ^g	2.50×10^8	Lowe et al. (2009)
ISO ^h	7.90×10^8	average of Yokouchi et al. (1999) and Matsunaga et al. (2002)

^⓪update of CAPRAM; ^aHC3 = alkanes, alcohols, esters, and alkynes with OH rate constant (298 K, 1 atm) less than $3.4 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$;

^bOLT = terminal alkenes; ^cETI = acetylene; ^dETOH = ethanol; ^eORA1 = formic acid; ^fOP1 = methyl hydrogen peroxide; ^gPAN = peroxyacetyl nitrate and higher saturated PANs; ^hISO = isoprene

S2.5 Additional setup of the Halogen Modul 2.0

Table S5 Emissions of halogen species

Species	Open ocean [$\text{cm}^{-2} \text{s}^{-1}$]	Reference
C ₂ Cl ₄	3.2×10^6	Keene et al. (2008)
C ₂ HCl ₃	4.0×10^6	Keene et al. (2008)
CH ₃ CCl ₃	—	Keene et al. (2008)
CHCl ₃	6.4×10^7	Keene et al. (2008)
CH ₂ Cl ₂	3.2×10^7	Keene et al. (2008)
CH ₃ Cl	9.1×10^7	Keene et al. (2008)
CHBr ₃	1.1×10^7	Yang et al. (2005)
CH ₂ Br ₂	4.6×10^6	Yang et al. (2005)
CH ₃ Br	9.7×10^6	Yang et al. (2005)
C ₃ H ₇ I	1.0×10^7	Lowe et al. (2009)
C ₂ H ₅ I	1.0×10^7	assumed
CH ₂ I ₂	1.5×10^7	assumed
CH ₃ I	6.0×10^6	Lowe et al. (2009)
CH ₂ ICl	2.0×10^7	Lowe et al. (2009)
CH ₂ IBr	2.0×10^7	Lowe et al. (2009)

Table S6 Depositions of halogen species

Species	Open ocean [s^{-1}] ^a	Reference
HCl [⊗]	2.0×10^{-5}	Lowe et al. (2009)
HOCl	2.0×10^{-6}	Lowe et al. (2009)
HBr	2.0×10^{-5}	Lowe et al. (2009)
HOBr	2.0×10^{-6}	Lowe et al. (2009)
HI	1.0×10^{-5}	Lowe et al. (2009)
HOI	1.0×10^{-5}	Lowe et al. (2009)

Table S6 (continued) Depositions of halogen species

Species	Open ocean [s^{-1}] ^a	Reference
INO ₂	1.0×10^{-5}	Lowe et al. (2009)
INO ₃	1.0×10^{-5}	Lowe et al. (2009)

^a $\frac{v_d}{h} = [\text{cm s}^{-1}]/[\text{cm}] \hat{=} [\text{s}^{-1}]$ with $h = 10^5 \text{ cm}$; [⊗]already implemented in CAPRAM

Table S7 Initial concentrations of halogen species

Species	Open ocean [cm^{-3}]	Reference/comment
HCl [⊗]	2.5×10^9	Lowe et al. (2009)
C ₂ Cl ₄	3.0×10^8	mean based on data presented in Zhou et al. (2005)
C ₂ HCl ₃	1.3×10^8	mean based on data presented in Zhou et al. (2005)
CH ₃ CCl ₃	—	
CHCl ₃	2.5×10^8	mean based on data presented in Law et al. (2007)
CH ₂ Cl ₂	3.3×10^8	mean based on data presented in Law et al. (2007)
CH ₃ Cl	1.4×10^{10}	Moore et al. (1996)
CHBr ₃	2.5×10^7	mean based on data presented in Zhou et al. (2005)
CH ₂ Br ₂	3.1×10^7	mean based on data presented in Zhou et al. (2005)
CH ₃ Br	2.8×10^8	Groszko and Moore (1998)
C ₃ H ₇ I	5.0×10^6	assumed
C ₂ H ₅ I	2.5×10^6	assumed
CH ₂ I ₂	2.5×10^7	assumed
CH ₃ I	2.5×10^7	Moore and Groszko (1999)
CH ₂ ICl	2.5×10^6	assumed
CH ₂ IBr	2.5×10^6	assumed

[⊗]update of CAPRAM

S3 Reaction mechanism

S3.1 Changes to Photolysis reactions in CAPRAM 3.0i

Photolysis reactions are calcuted offline. With the developement of the Halogen Module 2.0 photolysis processes have been revised and the parameterisation has been changed from the *ABC*-type (Röth, E. P., 1992) to the *MCM*-type (Jenkin et al., 1997, Saunders et al., 2003). Parameters for photolysis processes have been derived from calculations with the Tropospheric Ultraviolet and Visible Model TUV 4.6 (Madronich and Flocke, 1997). Input data concerning cross sections and quantum yields have been used unchanged from the model input as given by the authors.

For aqueous phase photolysis reactions, a modified version of TUV 4.1 has been used (Deguillaume et al., 2004). Input parameters are taken from references as described in Table S9.

In both cases calculations have been performed for 45°N on June 21st under clear sky conditions.

Table S8 Parameters for the updated gas phase photolysis reactions in RACM-MIM2ext

Reaction	I/s^{-1}	m	n
$\text{NO}_2 \xrightarrow{h\nu} \text{NO} + \text{O}(^3\text{P})$	1.041×10^{-2}	0.404	0.250
$\text{O}_3 \xrightarrow{h\nu} \text{O}_2 + \text{O}(^1\text{D})$	7.531×10^{-5}	1.886	0.382
$\text{O}_3 \xrightarrow{h\nu} \text{O}_2 + \text{O}(^3\text{P})$	5.685×10^{-4}	0.273	0.132
$\text{HONO} \xrightarrow{h\nu} \text{OH} + \text{NO}$	3.149×10^{-3}	0.430	0.263
$\text{HNO}_3 \xrightarrow{h\nu} \text{OH} + \text{NO}_2$	1.173×10^{-6}	1.385	0.271
$\text{HNO}_4 \xrightarrow{h\nu} 0.65 \text{HO}_2 + 0.65 \text{NO}_2 + 0.35 \text{OH} + 0.35 \text{NO}_3$	9.036×10^{-6}	1.262	0.327
$\text{NO}_3 \xrightarrow{h\nu} \text{NO} + \text{O}_2$	2.919×10^{-2}	0.115	0.164
$\text{NO}_3 \xrightarrow{h\nu} \text{NO}_2 + \text{O}(^3\text{P})$	2.349×10^{-1}	0.122	0.180
$\text{N}_2\text{O}_5 \xrightarrow{h\nu} \text{NO}_3 + \text{NO} + \text{O}(^3\text{P})$	2.071×10^{-7}	2.185	3.974
$\text{N}_2\text{O}_5 \xrightarrow{h\nu} \text{NO}_3 + \text{NO}_2$	7.083×10^{-5}	0.887	0.237
$\text{H}_2\text{O}_2 \xrightarrow{h\nu} 2 \text{OH}$	1.189×10^{-5}	0.924	0.249
$\text{HCHO} \xrightarrow{h\nu} \text{H}_2 + \text{CO}$	7.681×10^{-5}	0.685	0.273
$\text{HCHO} \xrightarrow{h\nu, 2\text{O}_2} 2 \text{HO}_2 + \text{CO}$	5.681×10^{-5}	0.943	0.328

Table S8 (continued) Parameters for the updated gas phase photolysis reactions in RACM-MIM2ext

Reaction	l/s^{-1}	m	n
ALD ^a $\xrightarrow{h\nu, 2O_2}$ MO ₂ ^b + HO ₂ + CO	1.163×10^{-5}	1.303	0.418
CH ₃ CHO $\xrightarrow{h\nu, 2O_2}$ MO ₂ + HO ₂ + CO	1.163×10^{-5}	1.303	0.418
C ₂ H ₅ CHO $\xrightarrow{h\nu, 2O_2}$ MO ₂ + HO ₂ + CO	3.546×10^{-5}	1.226	0.325
C ₃ H ₇ CHO $\xrightarrow{h\nu, 2O_2}$ MO ₂ + HO ₂ + CO	4.476×10^{-5}	0.805	0.338
OP1 ^c $\xrightarrow{h\nu, O_2}$ HCHO + HO ₂ + OH	9.017×10^{-6}	0.870	0.244
OP2 ^d $\xrightarrow{h\nu, O_2}$ 0.47 ALD + 0.49 CH ₃ CHO + 0.02 C ₂ H ₅ CHO + 0.02 C ₃ H ₇ CHO + HO ₂ + OH	9.017×10^{-6}	0.870	0.244
PAA ^e $\xrightarrow{h\nu}$ MO ₂ + OH	1.400×10^{-6}	1.059	0.265
KET ^f $\xrightarrow{h\nu, 2O_2}$ ACO ₃ ^g + ETHP ^h	1.029×10^{-6}	1.983	0.459
CH ₃ COCH ₃ $\xrightarrow{h\nu, 2O_2}$ ACO ₃ + ETHP	1.029×10^{-6}	1.983	0.459
C ₂ H ₅ COCH ₃ $\xrightarrow{h\nu, 2O_2}$ ACO ₃ + ETHP	1.340×10^{-6}	1.201	0.335
CH ₃ COCH(CH ₃) ₂ $\xrightarrow{h\nu, 2O_2}$ ACO ₃ + ETHP	1.029×10^{-6}	1.983	0.459
GLY ⁱ $\xrightarrow{h\nu, 2O_2}$ 2 CO + 2 HO ₂	9.610×10^{-5}	0.325	0.240
GLY $\xrightarrow{h\nu}$ HCHO + CO	3.026×10^{-5}	0.323	0.241
MGLY ^j $\xrightarrow{h\nu, 2O_2}$ ACO ₃ + CO + HO ₂	1.853×10^{-4}	0.583	0.225
DCB ^k $\xrightarrow{h\nu, 2O_2}$ 0.98 HO ₂ + 0.02 ACO ₃ + TCO ₃ ^l	1.624×10^{-4}	0.244	0.267
ONIT ^m $\xrightarrow{h\nu, O_2}$ 0.094 ALD + 0.098 CH ₃ CHO + 0.004 C ₂ H ₅ CHO + 0.004 C ₃ H ₇ CHO + 0.120 KET + 0.408 CH ₃ COCH ₃ + 0.216 C ₂ H ₅ COCH ₃ + 0.056 CH ₃ COCH(CH ₃) ₂ + HO ₂ + NO ₂	4.615×10^{-6}	1.293	0.286
HKET ⁿ $\xrightarrow{h\nu, 2O_2}$ HCHO + HO ₂ + ACO ₃	3.552×10^{-6}	1.282	0.234
MACR ^o $\xrightarrow{h\nu, O_2}$ CO + HCHO + HO ₂ + ACO ₃	8.692×10^{-6}	0.582	0.261
MVK ^p $\xrightarrow{h\nu, O_2}$ CO + HCHO + HO ₂ + ACO ₃	6.990×10^{-6}	0.821	0.260
CH ₂ (OH)CHO $\xrightarrow{h\nu, 2O_2}$ HCHO + CO + 2 HO ₂	9.737×10^{-6}	1.264	0.327

Photolysis reactions are parameterised with $j = l \times \cos^m \chi \times \exp \{-n \times \sec \chi\}$ according to [Jenkin et al. \(1997\)](#).

^aALD = higher aldehydes; ^bMO₂ = methyl peroxy radical; ^cOP1 = methyl hydrogen peroxide; ^dOP2 = higher organic peroxides; ^ePAA = peroxyacetic acid and higher analogues; ^fKET = ketones; ^gACO₃ = acetyl peroxy radical and higher saturated acyl peroxy radicals; ^hETHP = peroxy radical formed from ETH; ⁱGLY = glyoxal; ^jMGLY = methylglyoxal; ^kDCB = unsaturated dicarbonyls; ^lTCO₃ = unsaturated acyl peroxy radicals; ^mONIT = organic nitrates; ⁿHKET = hydroxy ketone; ^oMACR = methacrolein and other unsaturated monoaldehydes; ^pMVK = methyl vinyl ketone

Table S9 Parameters for the updated aqueous phase photolysis reactions in CAPRAM 3.0i

Reaction	l/s^{-1}	m	n	Reference/comment
$\text{Fe}(\text{OH})^{2+} \xrightarrow{h\nu} \text{Fe}^{2+} + \text{OH}$	4.764×10^{-2}	0.829	0.291	absorption spectra from Weschler et al. (1986) /quantum yields from Benkelberg and Warneck (1995)
$\text{Fe}(\text{OH})_2^+ \xrightarrow{h\nu} \text{Fe}^{2+} + \text{OH} + \text{OH}^-$	1.343×10^{-2}	0.855	0.300	absorption spectra from Weschler et al. (1986) /quantum yields from Benkelberg and Warneck (1995)
$\text{NO}_3^- \xrightarrow{h\nu} \text{NO}_2 + \text{OH} + \text{OH}^-$	6.109×10^{-7}	1.076	0.409	absorption spectra from Graedel and Weschler (1981) /quantum yields from Zellner et al. (1990)
$\text{NO}_2^- \xrightarrow{h\nu} \text{NO} + \text{OH} + \text{OH}^-$	7.245×10^{-5}	0.480	0.303	absorption spectra from Graedel and Weschler (1981) /quantum yields from Zellner et al. (1990)
$\text{HONO} \xrightarrow{h\nu} \text{OH} + \text{NO}$	2.999×10^{-4}	0.439	0.308	Graedel and Weschler (1981)
$\text{Fe}^{3+} \xrightarrow{h\nu} \text{Fe}^{2+} + \text{OH} + \text{H}^+$	1.224×10^{-5}	1.467	0.248	absorption spectra from Weschler et al. (1986) /quantum yields from Benkelberg and Warneck (1995)
$\text{Fe}(\text{SO}_4)^+ \xrightarrow{h\nu} \text{Fe}^{2+} + \text{SO}_4^-$	8.215×10^{-5}	0.885	0.313	Benkelberg and Warneck (1995)
$\text{H}_2\text{O}_2 \xrightarrow{h\nu} 2\text{OH}$	8.625×10^{-6}	1.043	0.271	absorption spectra from Graedel and Weschler (1981) /quantum yields from Zellner et al. (1990)
$\text{Fe}(\text{C}_2\text{O}_4)_2^- \xrightarrow{h\nu} \text{Fe}^{2+} + \text{C}_2\text{O}_4^{2-} + \text{CO}_2 + \text{CO}_2^-$	7.993×10^{-2}	0.625	0.279	IfT measurements
$\text{Fe}(\text{C}_2\text{O}_4)_3^{3-} \xrightarrow{h\nu} \text{Fe}^{2+} + 2\text{C}_2\text{O}_4^{2-} + \text{CO}_2 + \text{CO}_2^-$	4.659×10^{-2}	0.561	0.276	IfT measurements
$\text{OP1}^a \xrightarrow{h\nu} \text{CH}_3\text{O} + \text{OH}$	8.625×10^{-5}	1.043	0.271	estimated same as H_2O_2
$\text{NO}_3 \xrightarrow{h\nu} \text{NO} + \text{O}_2$	2.584×10^{-3}	0.072	0.196	Graedel and Weschler (1981)
$\text{NO}_3 \xrightarrow{h\nu} \text{NO}_2 + \text{O}(^3\text{P})$	2.325×10^{-2}	0.072	0.196	Graedel and Weschler (1981)
$\text{O}_3 \xrightarrow{h\nu} 2\text{OH} + \text{O}_2$	3.652×10^{-4}	0.515	0.044	Graedel and Weschler (1981)

Photolysis reactions are parameterised with $j = l \times \cos^m \chi \times \exp \{-n \times \sec \chi\}$.

^aOP1 = methyl hydrogen peroxide

S3.2 Phase transfer

Table S10 Henry's Law constants

	Species	$K_H(298\text{ K}) / \text{M atm}^{-1}$	$\Delta H/R / \text{K}$	Reference/comment
H1 \otimes	Cl ₂	9.15×10^{-2}	-2490	Wilhelm et al. (1977)
H2 \oplus	Cl	0.2		Mozurkewich (1995)
H3 \ominus	ClO	660	-5862	estimated ($K_{H, \text{H3}} \approx K_{H, \text{H6}}$), correction of Halogen Module 1.0
H4 \oplus	ClO ₂	1.0	3300	Lide et al. (1995)
H5 \otimes	HCl	1.1	-2020	Marsh and McElroy (1985)
H6 \ominus	HOCl	660	-5862	Huthwelker et al. (1995), correction of Halogen Module 1.0
H7	ClNO	5.0×10^{-2}		upper limit, Scheer et al. (1997)
H8 \otimes	ClNO ₂	4.6×10^{-2}		upper limit, Frenzel et al. (1998)
H9	ClNO ₃	2.1×10^5	-8700	estimated same as nitric acid
H10	CH ₂ ClCO ₃	669	-5893	estimated same as acetylperoxyl radical
H11	CH ₂ ClCOOH	5.5×10^3	-5890	estimated same as acetic acid
H12	CH ₃ COCClO	1.4	-7541	estimated same as methylglyoxal
H13	COCl ₂	7.0×10^{-2}		Law et al. (2007)
H14	CHOC1	3.0×10^3	-7216	estimated same as formaldehyde
H15 \otimes	Br ₂	0.76	-4100	Law et al. (2007)
H16 \oplus	Br	1.2		Mozurkewich (1995)
H17 \oplus	BrO	93	-5862	estimated ($K_{H, \text{H17}} \approx K_{H, \text{H19}}$)
H18 \ominus	HBr	1.3	-10239	Brimblecombe and Clegg (1989)
H19 \ominus	HOBr	93	-5862	von Glasow et al. (2002a), temperature dependency estimated same as H6
H20 \otimes	BrNO ₂	0.3		Frenzel et al. (1998)
H21	BrNO ₃	2.1×10^5	-8700	estimated same as nitric acid
H22 \ominus	BrCl	0.94	-5600	Bartlett and Margerum (1999)
H23	CH ₂ BrCO ₃	669	-5893	estimated same as acetylperoxyl radical
H24	CH ₂ BrCOOH	5.5×10^3	-5890	estimated same as acetic acid

Table S10 (continued) Henry's Law constants

	Species	$K_H(298\text{ K}) / \text{M atm}^{-1}$	$\Delta H/R / \text{K}$	Reference/comment
H25	CH ₃ COCBrO	1.4	-7541	estimated same as methylglyoxal
H26	COBr ₂	7.0×10^{-2}		estimated ($K_H, \text{H26} \approx K_H, \text{H13}$)
H27	CHOBr	3.0×10^3	-7216	estimated same as formaldehyde
H28	I ₂	3.0	-4431	Palmer et al. (1985)
H29	I	8.0×10^{-2}		Mozurkewich (1986)
H30	IO	450	-5862	von Glasow et al. (2002a) , estimated ($K_H, \text{H30} \approx K_H, \text{H6}$)
H31	OIO	2.1×10^5	-8700	estimated same as nitric acid
H32	I ₂ O ₂	2.1×10^5	-8700	estimated same as nitric acid
H33	HI	2.5	-9800	Brimblecombe and Clegg (1989)
H34	HOI	450	-5862	von Glasow et al. (2002a) , estimated ($K_H, \text{H34} \approx K_H, \text{H6}$)
H35	HIO ₃	2.1×10^5	-8700	estimated same as nitric acid
H36	INO ₂	2.1×10^5	-8700	estimated same as nitric acid
H37	INO ₃	2.1×10^5	-8700	estimated same as nitric acid
H38	ICl	110	-5600	von Glasow et al. (2002a) , temperature dependency estimated same as bromine chloride
H39	IBr	24	-5600	von Glasow et al. (2002a) , temperature dependency estimated same as bromine chloride
H40	CH ₂ ICO ₃	669	-5893	estimated same as acetylperoxyl radical
H41	CH ₂ ICOOH	5.5×10^3	-5890	estimated same as acetic acid
H42	COI ₂	7.0×10^{-2}		estimated ($K_H, \text{H42} \approx K_H, \text{H13}$)
H43	CHOI	3.0×10^3	-7216	estimated same as formaldehyde

⊗already implemented in CAPRAM; ⊕already implemented in the Halogen Module 1.0; ⊖update of the Halogen Module 1.0

Table S11 Mass accommodation coefficients and gas phase diffusion coefficients

	Species	α	Reference	D_g^a	Reference	Comment
H1 ⊗	Cl ₂	0.08		1.28	Schwartz (1986)	α estimated

Table S11 (continued) Mass accommodation coefficients and gas phase diffusion coefficients

	Species	α	Reference	D_g^a	Reference	Comment
H2 \ominus	Cl	0.05		1.82	Fuller (1986)	α estimated same as OH, ^b
H3 \ominus	ClO	0.064		1.55	Fuller (1986)	α estimated, ^b
H4 \ominus	ClO ₂	0.05		1.39	Fuller (1986)	α estimated same as OH, ^b
H5 \ominus	HCl	0.1026	Schweitzer et al. (2000)	1.89	Marsh and McElroy (1985)	
H6 \ominus	HOCl	0.5	Abbatt and Waschewsky (1998)	1.51	Fuller (1986)	α estimated same as H19, ^b
H7	ClNO	0.01		1.39	Fuller (1986)	α estimated same as H8, ^c
H8 \ominus	ClNO ₂	0.01	Schweitzer et al. (1998)	1.27	Fuller (1986)	^b
H9	ClNO ₃	0.1	Schweitzer et al. (1998)	1.18	Fuller (1986)	^c
H10	CH ₂ ClCO ₃	0.019		0.94	Fuller (1986)	α estimated same as acetylperoxyl radical, ^c
H11	CH ₂ ClCOOH	0.0322		0.97	Fuller (1986)	α estimated same as acetic acid, ^c
H12	CH ₃ COCClO	0.03		0.88	Fuller (1986)	α estimated same as methylglyoxal, ^c
H13	COCl ₂	0.02		1.02	Fuller (1986)	α estimated same as formaldehyde, ^c
H14	CHOC1	0.02		1.23	Fuller (1986)	α estimated same as formaldehyde, ^c
H15 \otimes	Br ₂	0.08		1.00	Schwartz (1986)	α estimated
H16 \ominus	Br	0.05		1.29	Fuller (1986)	α estimated same as OH, ^{b, d}
H17 \ominus	BrO	0.06	Sander and Crutzen (1996)	1.19	Fuller (1986)	^{b, d}
H18 \ominus	HBr	0.0481	Schweitzer et al. (2000)	1.26	Fuller (1986)	^{b, d}
H19 \ominus	HOBr	0.5	Abbatt and Waschewsky (1998)	1.16	Fuller (1986)	^{b, d}
H20 \ominus	BrNO ₂	0.01	Schweitzer et al. (1998)	1.06	Fuller (1986)	^{b, d}
H21	BrNO ₃	0.8	Hanson et al. (1996)	1.01	Fuller (1986)	^{b, d}
H22 \ominus	BrCl	0.33	(Katrib et al.)	1.05	Fuller (1986)	^{b, d}
H23	CH ₂ BrCO ₃	0.019		0.84	Fuller (1986)	α estimated same as acetylperoxyl radical, ^{c, d}
H24	CH ₂ BrCOOH	0.0322		0.84	Fuller (1986)	α estimated same as acetic acid, ^c
H25	CH ₃ COCClO	0.03		0.79	Fuller (1986)	α estimated same as methylglyoxal, ^{c, d}
H26	COBr ₂	0.02		0.81	Fuller (1986)	α estimated same as formaldehyde, ^{c, d}
H27	CHOCBr	0.02		1.02	Fuller (1986)	α estimated same as formaldehyde, ^{c, d}
H28	I ₂	0.0126	Pechtl et al. (2005)	0.86	Fuller (1986)	α estimated, ^{c, e}

Table S11 (continued) Mass accommodation coefficients and gas phase diffusion coefficients

	Species	α	Reference	D_g^a	Reference	Comment
H29	I	0.05		1.16	Fuller (1986)	α estimated same as OH, ^{c, f}
H30	IO	0.558	Pechtl et al. (2005)	1.10	Fuller (1986)	α estimated, ^{c, f}
H31	OIO	1.00	Pechtl et al. (2005)	1.04	Fuller (1986)	α estimated, ^{c, f}
H32	I ₂ O ₂	0.123	Pechtl et al. (2005)	0.80	Fuller (1986)	α estimated, ^{c, f}
H33	HI	0.057	Schweitzer et al. (2000)	1.14	Fuller (1986)	α estimated, ^{c, f}
H34	HOI	0.5	Pechtl et al. (2005)	1.08	Fuller (1986)	α estimated, ^{c, f}
H35	HIO ₃	0.0126	Pechtl et al. (2005)	0.98	Fuller (1986)	α estimated, ^{c, f}
H36	INO ₂	0.123	Pechtl et al. (2005)	0.99	Fuller (1986)	α estimated, ^{c, f}
H37	INO ₃	0.123	Pechtl et al. (2005)	0.96	Fuller (1986)	α estimated, ^{c, f}
H38	ICl	0.0126	Pechtl et al. (2005)	0.98	Fuller (1986)	α estimated, ^{c, f}
H39	IBr	0.0126	Pechtl et al. (2005)	0.88	Fuller (1986)	α estimated, ^{c, f}
H40	CH ₂ ICO ₃	0.019		0.80	Fuller (1986)	α estimated same as acetylperoxyl radical, ^{c, f}
H41	CH ₂ ICOOH	0.0322		0.82	Fuller (1986)	α estimated same as acetic acid, ^c
H42	COI ₂	0.02		0.76	Fuller (1986)	α estimated same as formaldehyde, ^{b, d}
H43	CHOI	0.02		0.96	Fuller (1986)	α estimated same as formaldehyde, ^{b, d}

[⊗]already implemented in CAPRAM; [⊙]update of CAPRAM; [⊕]already implemented in the Halogen Module 1.0; [⊖]update of the Halogen Module 1.0

^ain 10⁵ m² s⁻¹ at 288 K; ^bcorrection of D_g in the Halogen Module 1.0; ^c D_g calculated with the FSG method (Fuller, 1986); ^d v_{Br} estimated with 34.8; ^e v_{I_2} estimated with 77.3; ^f v_I estimated with 40

S3.3 Gas phase chemistry

Table S12 Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	E_A/R^b	Comment	Reference
G1 [⊖]	Cl + O ₃ → ClO + O ₂	1.21×10^{-11}	250		Atk07
G2	Cl + H ₂ $\xrightarrow{O_2}$ HCl + HO ₂	1.68×10^{-14}	2310		Atk07
G3	Cl + HO ₂ → HCl + O ₂	3.40×10^{-11}			Atk07

Table S12 (continued) Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	E_A/R^b	Comment	Reference
G4	$\text{Cl} + \text{HO}_2 \rightarrow \text{ClO} + \text{OH}$	9.30×10^{-12}	570		Atk07
G5	$\text{Cl} + \text{H}_2\text{O}_2 \rightarrow \text{HCl} + \text{HO}_2$	4.10×10^{-13}	980		Atk07
G6	$\text{Cl}_2 + \text{OH} \rightarrow \text{HOCl} + \text{Cl}$	6.42×10^{-14}	1200		Atk07
P _g 1 \ominus	$\text{Cl}_2 \xrightarrow{h\nu} 2 \text{Cl}$	(2.99×10^{-3})		$\Phi = 1.0^{\text{Cal/Pit66}}$; see Tab. S14	Dem97
G7 \ominus	$\text{ClO} + \text{O}_3 \rightarrow \text{ClO}_2 + \text{O}_2$	1.13×10^{-17}	3600	upper limit	Atk07
G8	$\text{ClO} + \text{O}_3 \rightarrow \text{OCIO} + \text{O}_2$	1.48×10^{-18}	4000	upper limit	Atk07
G9	$\text{ClO} + \text{OH} \rightarrow$ $0.94 \text{HO}_2 + 0.94 \text{Cl} + 0.06 \text{HCl} + 0.06 \text{O}_2$	2.00×10^{-11}	-300		Atk07
G10 \ominus	$\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2$	6.89×10^{-12}	-340		Atk07
G11	$\text{ClO} + \text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2$	4.82×10^{-15}	1590		Atk07
G12	$\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{ClO}_2$	8.06×10^{-15}	2450		Atk07
G13	$\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{OCIO}$	3.53×10^{-15}	1370		Atk07
G14	$\text{ClO} + \text{ClO} \xrightarrow{\text{M}} \text{Cl}_2\text{O}_2$	1.52×10^{-15}		TYP: TROE; see Tab. S13	San06
P _g 2	$\text{ClO} \xrightarrow{h\nu} \text{Cl} + \text{O}$	(2.64×10^{-4})		$\Phi = 1.0^i$; see Tab. S14	San06
G15	$\text{Cl} + \text{O}_2 \xrightarrow{\text{M}} \text{ClO}_2$	5.17×10^{-14}		TYP: TROE; see Tab. S13	San06
G16 \ominus	$\text{ClO}_2 \xrightarrow{\text{M}} \text{Cl} + \text{O}_2$	6.23×10^{-13}	1820		Atk07
G17	$\text{Cl} + \text{ClO}_2 \rightarrow 0.95 \text{Cl}_2 + 0.95 \text{O}_2 + 0.1 \text{ClO}$	2.42×10^{-10}			San06
G18	$\text{Cl}_2\text{O}_2 \xrightarrow{\text{M}} 2 \text{ClO}$	2.87×10^{-3}		TYP: TROEXP; see Tab. S13	Atk07
G19	$\text{Cl}_2\text{O}_2 + \text{O}_3 \rightarrow \text{ClO} + \text{ClO}_2 + \text{O}_2$	1.00×10^{-19}		upper limit	Atk07
G20	$\text{Cl}_2\text{O}_2 + \text{Cl} \rightarrow \text{Cl}_2 + \text{ClO}_2$	9.45×10^{-11}	-65		Atk07
P _g 4	$\text{Cl}_2\text{O}_2 \xrightarrow{h\nu} \text{Cl} + \text{ClO}_2$	(1.83×10^{-3})		$\Phi = 1.0^i$; see Tab. S14	San03
G21	$\text{OCIO} + \text{OH} \rightarrow \text{HOCl} + \text{O}_2$	1.05×10^{-11}	-600		Atk07
G22	$\text{Cl} + \text{OCIO} \rightarrow 2 \text{ClO}$	5.66×10^{-11}	-170		Atk07
G23	$\text{ClO} + \text{OCIO} \xrightarrow{\text{M}} \text{Cl}_2\text{O}_3$	1.08×10^{-19}		TYP: TROE; see Tab. S13	Atk07
P _g 3	$\text{OCIO} \xrightarrow{h\nu} \text{ClO} + \text{O}$	(0.10)		$\Phi = 1.0^i$; see Tab. S14	San06
G24	$\text{Cl}_2\text{O}_3 \xrightarrow{\text{M}} \text{ClO} + \text{OCIO}$	6.17×10^{-2}		TYP: TROEXP; see Tab. S13	Atk07

Table S12 (continued) Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	E_A/R^b	Comment	Reference
P _g 5	$\text{Cl}_2\text{O}_3 \xrightarrow{h\nu} \text{ClO} + \text{OCIO}$	(9.80×10^{-4})		$\Phi = 1.0^i$; further products omitted; see Tab. S14	Atk07
G25 [⊖]	$\text{HCl} + \text{OH} \rightarrow \text{Cl} + \text{H}_2\text{O}$	7.86×10^{-13}	230		Atk07
G26	$\text{HOCl} + \text{OH} \rightarrow \text{ClO} + \text{H}_2\text{O}$	5.60×10^{-13}	500	E_A/R estimated	San06
G27	$\text{HOCl} + \text{Cl} \rightarrow$ $0.76 \text{HCl} + 0.76 \text{ClO} + 0.24 \text{Cl}_2 + 0.24 \text{OH}$	1.62×10^{-12}	130	branching ratios from Vogt and Schindler (1993)	San06
P _g 6 [⊖]	$\text{HOCl} \xrightarrow{h\nu} \text{Cl} + \text{OH}$	(3.63×10^{-4})		$\Phi = 1.0$; see Tab. S14	Atk07
G28	$\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$	1.67×10^{-11}	-295		Atk07
G29	$\text{OCIO} + \text{NO} \rightarrow \text{ClO} + \text{NO}_2$	3.56×10^{-13}	-350		Atk07
G30	$\text{Cl} + \text{NO}_3 \rightarrow \text{ClO} + \text{NO}_2$	2.40×10^{-11}			Atk07
G31	$\text{ClO} + \text{NO}_3 \rightarrow 0.68 \text{ClO}_2 + 0.32 \text{OCIO} + \text{NO}_2$	4.61×10^{-13}			Kuk94
G32	$\text{Cl} + \text{NO} \xrightarrow{\text{M}} \text{ClNO}$	1.92×10^{-12}		TYP: SPEC2; see Tab. S13	San06
G33	$\text{Cl} + \text{ClNO} \rightarrow \text{Cl}_2 + \text{NO}$	8.11×10^{-11}	-100		San06
P _g 7	$\text{ClNO} \xrightarrow{h\nu} \text{Cl} + \text{NO}$	(5.48×10^{-4})		see Tab. S14	Atk07
G34	$\text{Cl} + \text{NO}_2 \xrightarrow{\text{M}} \text{ClNO}_2$	5.80×10^{-14}		TYP: TROE; see Tab. S13	San06
G35	$\text{ClNO}_2 + \text{OH} \rightarrow \text{HOCl} + \text{NO}_2$	3.62×10^{-14}	1250		Atk07
P _g 8 [⊖]	$\text{ClNO}_2 \xrightarrow{h\nu} \text{Cl} + \text{NO}_2$	(4.81×10^{-4})		see Tab. S14	Atk07
G36	$\text{ClO} + \text{NO}_2 \xrightarrow{\text{M}} \text{ClNO}_3$	1.85×10^{-19}		TYP: TROEF; see Tab. S13	Atk07
G37	$\text{ClNO}_3 \xrightarrow{\text{M}} \text{ClO} + \text{NO}_2$	1.47×10^{-3}	11438	TYP: SPEC4	And/Fah90
G38	$\text{ClNO}_3 + \text{OH} \rightarrow$ $0.5 \text{ClO} + 0.5 \text{HNO}_3 + 0.5 \text{HOCl} + 0.5 \text{NO}_3$	3.97×10^{-13}	330	branching ratios from Pechtl et al. (2005)	Atk07
G39	$\text{ClNO}_3 + \text{Cl} \rightarrow \text{Cl}_2 + \text{NO}_3$	1.01×10^{-11}	-145		Atk07
P _g 9	$\text{ClNO}_3 \xrightarrow{h\nu} \text{Cl} + \text{NO}_3$	(5.16×10^{-5})		$\Phi = 0.6 - 1.0$; see Tab. S14	Dem97
P _g 10	$\text{ClNO}_3 \xrightarrow{h\nu} \text{ClO} + \text{NO}_2$	(1.09×10^{-5})		$\Phi = 0.4 - 0.0$; see Tab. S14	Dem97
G40 [⊖]	$\text{Cl} + \text{CH}_4 \xrightarrow{\text{O}_2} \text{HCl} + \text{MO}_2$	1.03×10^{-13}	1240	g, A	Atk06
G41	$\text{Cl} + \text{OP1} \rightarrow \text{HCl} + \text{MO}_2$	5.70×10^{-11}		A, B	San06

Table S12 (continued) Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	E_A/R^b	Comment	Reference
G42	$\text{Cl} + \text{MO}_2 \rightarrow 0.5 \text{HCHO} + 0.5 \text{ClO} + 0.5 \text{HO}_2 - 0.5 \text{O}_2 + 0.5 \text{HCl} + 0.5 \text{ORA1}$	1.60×10^{-10}		branching ratios as in Pechtl et al. (2005) with revised products for H-abstraction, ^{A, C}	<i>San06</i>
G43	$\text{ClO} + \text{MO}_2 \xrightarrow{\text{O}_2} \text{ClO}_2 + \text{HCHO} + \text{HO}_2$	1.63×10^{-12}	238	further products omitted, ^{h, A}	<i>Atk08</i>
G44	$\text{Cl} + \text{ETH} \xrightarrow{\text{O}_2} \text{HCl} + \text{ETHP}$	5.93×10^{-11}	100	^{g, D, E}	<i>Atk06</i>
G45	$\text{Cl} + \text{HC3} \xrightarrow{\text{O}_2} \text{HCl} + \text{HC3P}$	1.47×10^{-10}	-13	estimated, ^{F, G}	
G46	$\text{Cl} + \text{HC5} \xrightarrow{\text{O}_2} \text{HCl} + \text{HC5P}$	2.14×10^{-10}		estimated, ^{H, I}	
G47	$\text{Cl} + \text{HC8} \xrightarrow{\text{O}_2} \text{HCl} + \text{HC8P}$	4.38×10^{-10}		estimated, ^{J, K}	
G48	$\text{Cl} + \text{TOL} \xrightarrow{\text{O}_2} \text{HCl} + \text{TOLP}$	5.15×10^{-11}		estimated, ^{L, M}	
G49	$\text{Cl} + \text{HCHO} \xrightarrow{\text{O}_2} \text{HCl} + \text{CO} + \text{HO}_2$	7.23×10^{-11}	34	^h	<i>Atk06</i>
G50	$\text{ClO} + \text{HCHO} \xrightarrow{\text{O}_2} \text{HOCl} + \text{CO} + \text{HO}_2$	8.70×10^{-16}	2100	upper limit	<i>San06</i>
G51	$\text{Cl} + \text{CH}_3\text{CHO} \xrightarrow{\text{O}_2} \text{HCl} + \text{ACO}_3$	8.00×10^{-11}		^N	<i>Atk06</i>
G52	$\text{Cl} + \text{ALD} \xrightarrow{\text{O}_2} \text{HCl} + \text{ACO}_3$	8.00×10^{-11}		estimated ($k_{\text{G52}} \approx k_{\text{G51}}$), ^{N, O}	
G53	$\text{Cl} + \text{CH}_3\text{COCH}_3 \xrightarrow{\text{O}_2} \text{HCl} + \text{KETP}$	2.08×10^{-11}	815		<i>Atk06</i>
G54	$\text{Cl} + \text{KET} \xrightarrow{\text{O}_2} \text{HCl} + \text{KETP}$	2.08×10^{-11}	815	estimated ($k_{\text{G54}} \approx k_{\text{G53}}$), ^{P, Q}	
G55	$\text{Cl} + \text{CH}_3\text{COCH}_2\text{CH}_3 \xrightarrow{\text{O}_2} \text{HCl} + \text{KETP}$	3.60×10^{-11}		^Q	<i>Atk06</i>
G56	$\text{Cl} + \text{HKET} \xrightarrow{\text{O}_2} \text{HCl} + \text{HO}_2 + \text{MGLY}$	5.70×10^{-11}		^{R, S}	<i>Orl99</i>
G57	$\text{Cl} + \text{MGLY} \xrightarrow{\text{O}_2} \text{HCl} + \text{ACO}_3$	4.80×10^{-11}		^{N, S}	<i>Gre90</i>
G58	$\text{Cl} + \text{GLY} \xrightarrow{\text{O}_2} \text{HCl} + 2 \text{CO} + \text{HO}_2$	3.80×10^{-11}		^T	<i>Nik85</i>
G59	$\text{Cl} + \text{CHOCH}_2\text{OH} \xrightarrow{\text{O}_2} \text{HCl} + \text{ACO}_3$	7.00×10^{-11}		^N	<i>Nik87</i>
G60	$\text{Cl} + \text{ETI} \xrightarrow{\text{O}_2, \text{M}} 0.26 \text{CHOC1} + 0.21 \text{Cl} + 0.53 \text{HCl} + 0.21 \text{GLY} + 1.32 \text{CO} + 0.79 \text{HO}_2$	4.60×10^{-11}		TYP: TROE; see Tab. S13 ; ^{d, T U}	<i>Atk06</i>
G61	$\text{Cl} + \text{ETE} \xrightarrow{\text{O}_2, \text{M}} \text{CH}_2\text{ClCH}_2\text{O}_2$	8.46×10^{-11}		TYP: TROE; see Tab. S13 ; ^{g, V}	<i>Atk06</i>
G62	$\text{CH}_2\text{ClCH}_2\text{O}_2 + \text{MO}_2 \rightarrow 0.2 \text{CH}_2\text{ClCH}_2\text{OH} + 0.8 \text{HCHO} + 0.2 \text{CH}_2\text{ClCHO} + 0.2 \text{CH}_3\text{OH} + 0.4 \text{O}_2 + 0.6 \text{CH}_2\text{ClCH}_2\text{O} + 0.6 \text{HO}_2$	2.00×10^{-12}		estimated ($\text{RO}_2 = \text{MO}_2$), ^A	<i>MCM</i>

Table S12 (continued) Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	E_A/R^b	Comment	Reference
G63	$\text{CH}_2\text{ClCH}_2\text{O}_2 + \text{CH}_2\text{ClCH}_2\text{O}_2 \rightarrow$ $1.28 \text{CH}_2\text{ClCH}_2\text{O} + 0.36 \text{CH}_2\text{ClCH}_2\text{OH} +$ $0.36 \text{CH}_2\text{ClCHO} + \text{O}_2$	3.29×10^{-12}	-1300	branching ratio at 298 K	Atk08
G64	$\text{CH}_2\text{ClCH}_2\text{O}_2 + \text{NO} \rightarrow \text{CH}_2\text{ClCH}_2\text{O} + \text{NO}_2$	9.70×10^{-12}			Atk08
G65	$\text{CH}_2\text{ClCH}_2\text{OH} + \text{OH} \xrightarrow{\text{O}_2}$ $\text{CH}_2\text{ClCHO} + \text{H}_2\text{O} + \text{HO}_2$	4.60×10^{-12}			MCM
G66	$\text{CH}_2\text{ClCH}_2\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{ClCHO} + \text{HO}_2$	9.48×10^{-15}	550		MCM
G67	$\text{CH}_2\text{ClCHO} + \text{OH} \xrightarrow{\text{O}_2} \text{CH}_2\text{ClCO}_3 + \text{H}_2\text{O}$	3.10×10^{-12}		<i>g</i>	Atk08
P _g 13	$\text{CH}_2\text{ClCHO} \xrightarrow{h\nu, 2\text{O}_2} \text{CH}_2\text{ClO}_2 + \text{CO} + \text{HO}_2$	(3.26×10^{-5})		see Tab. S14	MCM
G68	$\text{CH}_2\text{ClCO}_3 + \text{HO}_2 \rightarrow 0.71 \text{CH}_2\text{ClCO}_3\text{H} +$ $0.71 \text{O}_2 + 0.29 \text{CH}_2\text{ClCOOH} + 0.29 \text{O}_3$	1.41×10^{-11}	-1040		MCM
G69	$\text{CH}_2\text{ClCO}_3 + \text{MO}_2 \rightarrow$ $0.3 \text{CH}_2\text{ClCOOH} + \text{HCHO} + 0.7 \text{CH}_2\text{ClO}_2 +$ $0.7 \text{CO}_2 + 0.7 \text{HO}_2 - 0.4 \text{O}_2$	1.00×10^{-11}		estimated ($\text{RO}_2 = \text{MO}_2$), ^A	MCM
G70	$\text{CH}_2\text{ClCO}_3 + \text{NO} \xrightarrow{\text{O}_2}$ $\text{CH}_2\text{ClO}_2 + \text{CO}_2 + \text{NO}_2$	2.00×10^{-11}	-270		MCM
G71	$\text{CH}_2\text{ClCO}_3 + \text{NO}_2 \xrightarrow{\text{M}} \text{CH}_2\text{ClC}(\text{O})\text{OONO}_2$	1.11×10^{-11}		TYP: TROEF; see Tab. S13	MCM
G72	$\text{CH}_2\text{ClC}(\text{O})\text{OONO}_2 \xrightarrow{\text{M}} \text{CH}_2\text{ClCO}_3 + \text{NO}_2$	3.48×10^{-4}		TYP: TROEXP; see Tab. S13	MCM
G73	$\text{CH}_2\text{ClC}(\text{O})\text{OONO}_2 + \text{OH} \rightarrow$ $\text{O}_2\text{CHClC}(\text{O})\text{OONO}_2 + \text{H}_2\text{O}$	6.26×10^{-13}		<i>e</i>	MCM
G74	$\text{O}_2\text{CHClC}(\text{O})\text{OONO}_2 + \text{NO} \rightarrow$ $\text{CHOCl} + \text{CO} + \text{O}_2 + 2\text{NO}_2$	1.36×10^{-11}	-360	estimated	
G75	$\text{CH}_2\text{ClCO}_3\text{H} + \text{OH} \rightarrow \text{CH}_2\text{ClCO}_3 + \text{H}_2\text{O}$	4.29×10^{-12}			MCM
P _g 14	$\text{CH}_2\text{ClCO}_3\text{H} \xrightarrow{h\nu, \text{O}_2} \text{CH}_2\text{ClO}_2 + \text{CO}_2 + \text{OH}$	(5.79×10^{-6})		see Tab. S14	MCM
G76	$\text{CH}_2\text{ClCOOH} + \text{OH} \xrightarrow{\text{O}_2}$ $\text{CH}_2\text{ClO}_2 + \text{CO}_2 + \text{H}_2\text{O}$	3.59×10^{-12}	-190		MCM
G77	$\text{Cl} + \text{C}_3\text{H}_6 \xrightarrow{\text{O}_2, \text{M}} \text{CH}_3\text{CHO}_2\text{CH}_2\text{Cl}$	2.52×10^{-10}		TYP: TROE; see Tab. S13	Atk06

Table S12 (continued) Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	E_A/R^b	Comment	Reference
G78	$\text{CH}_3\text{CHO}_2\text{CH}_2\text{Cl} + \text{MO}_2 \rightarrow$ $0.2 \text{CH}_3\text{CHOHCH}_2\text{Cl} + 0.8 \text{HCHO} +$ $0.2 \text{CH}_3\text{COCH}_2\text{Cl} + 0.2 \text{CH}_3\text{OH} + 0.4 \text{O}_2 +$ $0.6 \text{CH}_3\text{CHOCH}_2\text{Cl} + 0.6 \text{HO}_2$	4.00×10^{-14}		estimated ($\text{RO}_2 = \text{MO}_2$), ^{c, A}	MCM
G79	$\text{CH}_3\text{CHO}_2\text{CH}_2\text{Cl} + \text{NO} \rightarrow$ $\text{CH}_3\text{CHOCH}_2\text{Cl} + \text{NO}_2$	9.04×10^{-12}	-360	further products omitted, ^c	Atk06
G80	$\text{CH}_3\text{CHOHCH}_2\text{Cl} + \text{OH} \xrightarrow{\text{O}_2}$ $\text{CH}_3\text{COCH}_2\text{Cl} + \text{H}_2\text{O} + \text{HO}_2$	5.09×10^{-12}	-200	products as in MCM, ^c	Atk06
G81	$\text{CH}_3\text{CHOCH}_2\text{Cl} + \text{O}_2 \rightarrow$ $\text{CH}_3\text{COCH}_2\text{Cl} + \text{HO}_2$	6.93×10^{-15}	230	^c	Atk06
G82	$\text{CH}_3\text{COCH}_2\text{Cl} + \text{OH} \xrightarrow{\text{O}_2}$ $\text{CH}_3\text{COCHClO}_2 + \text{H}_2\text{O}$	1.05×10^{-13}	1320	^{c, g}	Atk06
P _g 11	$\text{CH}_3\text{COCH}_2\text{Cl} \xrightarrow{h\nu} 0.7 \text{COCl} + 0.7 \text{ACO}_3 +$ $0.3 \text{CH}_2\text{ClCO}_3 + 0.3 \text{MO}_2 - 1.3 \text{O}_2$	(3.83×10^{-3})		$\Phi = 1.0^i$; see Tab. S14	San06
G83	$\text{CH}_3\text{COCHClO}_2 + \text{MO}_2 \rightarrow$ $0.2 \text{CH}_3\text{COCHClOH} + 0.8 \text{HCHO} +$ $0.2 \text{CH}_3\text{COCClO} + 0.2 \text{CH}_3\text{OH} - 0.2 \text{O}_2 +$ $0.6 \text{ACO}_3 + 0.6 \text{CHOC}_2\text{H}_5 + 0.6 \text{HO}_2$	2.00×10^{-12}		estimated ($\text{RO}_2 = \text{MO}_2$), ^{c, A, N}	MCM
G84	$\text{CH}_3\text{COCHClO}_2 + \text{NO} \xrightarrow{\text{O}_2}$ $\text{ACO}_3 + \text{CHOC}_2\text{H}_5 + \text{NO}_2$	8.00×10^{-12}		^{c, N}	Atk06
G85	$\text{CH}_3\text{COCHClOH} + \text{OH} \xrightarrow{\text{O}_2}$ $\text{CH}_3\text{COCClO} + \text{H}_2\text{O} + \text{HO}_2$	3.00×10^{-12}		^c	MCM
P _g 12	$\text{CH}_3\text{COCClO} \xrightarrow{h\nu, \text{O}_2} \text{COCl} + \text{ACO}_3$	(2.78×10^{-5})		estimated same as methylglyoxal; see Tab. S14	MCM
G86	$\text{C}_2\text{Cl}_4 + \text{OH} \xrightarrow{\text{O}_2} \text{CCl}_2\text{OHCCl}_2\text{O}_2$	1.60×10^{-13}	920	^g	Atk08
G87	$\text{CCl}_2\text{OHCCl}_2\text{O}_2 + \text{MO}_2 \rightarrow$ $0.3 \text{CCl}_2\text{OHCCl}_2\text{OH} + \text{HCHO} + 1.4 \text{COCl}_2 +$ $1.4 \text{HO}_2 - 0.4 \text{O}_2$	9.20×10^{-14}		estimated ($\text{RO}_2 = \text{MO}_2$), ^{d, A}	MCM
G88	$\text{CCl}_2\text{OHCCl}_2\text{O}_2 + \text{NO} \xrightarrow{\text{O}_2}$ $2 \text{COCl}_2 + \text{HO}_2 + \text{NO}_2$	1.87×10^{-11}	-360		MCM

Table S12 (continued) Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	E_A/R^b	Comment	Reference
G89	$\text{CCl}_2\text{OHCCl}_2\text{OH} + \text{OH} \xrightarrow{\text{O}_2}$ $2\text{COCl}_2 + \text{H}_2\text{O} + \text{HO}_2$	7.18×10^{-14}		d	MCM
G90	$\text{C}_2\text{HCl}_3 + \text{OH} \xrightarrow{\text{O}_2}$ $0.5\text{CHClOHCCl}_2\text{O}_2 + 0.5\text{CCl}_2\text{OHCHClO}_2$	2.0×10^{-12}	-565	branching ratios as in MCM, g	Atk08
G91	$\text{CHClOHCCl}_2\text{O}_2 + \text{MO}_2 \rightarrow$ $0.3\text{CCl}_2\text{OHCHClOH} + \text{HCHO} + 0.7\text{COCl}_2 +$ $0.7\text{CHOCl} + 1.4\text{HO}_2 - 0.4\text{O}_2$	9.20×10^{-14}		estimated ($\text{RO}_2 = \text{MO}_2$), d, A	MCM
G92	$\text{CHClOHCCl}_2\text{O}_2 + \text{NO} \xrightarrow{\text{O}_2}$ $\text{COCl}_2 + \text{CHOCl} + \text{NO}_2 + \text{HO}_2$	1.87×10^{-11}	-360	d	MCM
G93	$\text{CCl}_2\text{OHCHClO}_2 + \text{MO}_2 \rightarrow$ $0.2\text{CCl}_2\text{OHCHClOH} + 0.8\text{HCHO} +$ $0.2\text{CCl}_2\text{OHCClO} + 0.2\text{CH}_3\text{OH} - 0.2\text{O}_2 +$ $0.6\text{COCl}_2 + 0.6\text{CHOCl} + 1.2\text{HO}_2$	8.80×10^{-13}		estimated ($\text{RO}_2 = \text{MO}_2$), d, A	MCM
G94	$\text{CCl}_2\text{OHCHClO}_2 + \text{NO} \xrightarrow{\text{O}_2}$ $\text{COCl}_2 + \text{CHOCl} + \text{NO}_2 + \text{HO}_2$	1.87×10^{-11}	-360	d	MCM
G95	$\text{CCl}_2\text{OHCHClOH} + \text{OH} \xrightarrow{\text{O}_2}$ $\text{CCl}_2\text{OHCClO} + \text{H}_2\text{O} + \text{HO}_2$	2.85×10^{-13}			MCM
G96	$\text{CCl}_2\text{OHCClO} + \text{OH} \rightarrow$ $\text{COCl}_2 + \text{CO} + \text{Cl} + \text{H}_2\text{O}$	3.59×10^{-14}			MCM
P _g 15	$\text{CCl}_2\text{OHCClO} \xrightarrow{h\nu, \text{O}_2}$ $\text{COCl}_2 + \text{CO} + \text{Cl} + \text{HO}_2$	(1.99×10^{-5})		see Tab. S14	MCM
G97	$\text{CH}_3\text{CCl}_3 + \text{OH} \xrightarrow{\text{O}_2} \text{CCl}_3\text{CH}_2\text{O}_2 + \text{H}_2\text{O}$	9.56×10^{-15}	1440	g	Atk08
G98	$\text{CH}_3\text{CCl}_3 + \text{Cl} \xrightarrow{\text{O}_2} \text{CCl}_3\text{CH}_2\text{O}_2 + \text{HCl}$	6.89×10^{-15}	1790	g	Atk08
G99	$\text{CCl}_3\text{CH}_2\text{O}_2 + \text{MO}_2 \rightarrow$ $0.2\text{CCl}_3\text{CH}_2\text{OH} + 0.8\text{HCHO} + 0.2\text{CCl}_3\text{CHO} +$ $0.2\text{CH}_3\text{OH} + 0.4\text{O}_2 + 0.6\text{CCl}_3\text{CH}_2\text{O} + 0.6\text{HO}_2$	2.00×10^{-12}		estimated ($\text{RO}_2 = \text{MO}_2$); A	MCM

Table S12 (continued) Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	E_A/R^b	Comment	Reference
G100	$\text{CCl}_3\text{CH}_2\text{O}_2 + \text{NO} \rightarrow \text{CCl}_3\text{CH}_2\text{O} + \text{NO}_2$	1.36×10^{-11}	-360		MCM
G101	$\text{CCl}_3\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CCl}_3\text{CHO} + \text{HO}_2$	9.48×10^{-15}	550		MCM
G102	$\text{CCl}_3\text{CH}_2\text{OH} + \text{OH} \xrightarrow{\text{O}_2}$ $\text{CCl}_3\text{CHO} + \text{H}_2\text{O} + \text{HO}_2$	2.56×10^{-12}			MCM
G103	$\text{CCl}_3\text{CHO} + \text{OH} \xrightarrow{\text{O}_2} \text{CCl}_3\text{CO}_3 + \text{H}_2\text{O}$	8.04×10^{-13}	240		Atk08
P _g 16	$\text{CCl}_3\text{CHO} \xrightarrow{h\nu, 3/2\text{O}_2} \text{Cl} + \text{COCl}_2 + \text{CO} + \text{HO}_2$	(1.06×10^{-4})		$\Phi = 1.0$; see Tab. S14	Atk08
G104	$\text{CCl}_3\text{CO}_3 + \text{MO}_2 \xrightarrow{\text{O}_2}$ $\text{CCl}_3\text{O}_2 + \text{CO}_2 + \text{HCHO} + \text{HO}_2 + \text{O}_2$	1.00×10^{-11}		estimated ($\text{RO}_2 = \text{MO}_2$); ^A	MCM
G105	$\text{CCl}_3\text{CO}_3 + \text{NO} \xrightarrow{\text{O}_2} \text{CCl}_3\text{O}_2 + \text{CO}_2 + \text{NO}_2$	2.00×10^{-11}	-270	<i>g</i>	MCM
G106	$\text{CCl}_3\text{CO}_3 + \text{NO}_2 \xrightarrow{\text{M}} \text{CCl}_3\text{C}(\text{O})\text{OONO}_2$	1.11×10^{-11}		TYP: TROEF; see Tab. S13	MCM
G107	$\text{CCl}_3\text{C}(\text{O})\text{OONO}_2 \xrightarrow{\text{M}} \text{CCl}_3\text{CO}_3 + \text{NO}_2$	3.48×10^{-4}		TYP: TROEXP; see Tab. S13	MCM
G108	$\text{CHCl}_3 + \text{OH} \xrightarrow{\text{O}_2} \text{CCl}_3\text{O}_2 + \text{H}_2\text{O}$	1.04×10^{-13}	850	<i>g</i>	Atk08
G109	$\text{CHCl}_3 + \text{Cl} \xrightarrow{\text{O}_2} \text{CCl}_3\text{O}_2 + \text{HCl}$	1.10×10^{-13}	920	<i>g</i>	Atk08
G110	$\text{CCl}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{COCl}_2 + \text{HOCl} + \text{O}_2$	5.09×10^{-12}	-710		Atk08
G111	$\text{CCl}_3\text{O}_2 + \text{MO}_2 \rightarrow 0.3 \text{CCl}_3\text{OH} + \text{HCHO} +$ $0.3 \text{O}_2 + 0.7 \text{CCl}_3\text{O} + 0.7 \text{HO}_2$	6.60×10^{-12}		branching ratios from MCM, ^A	IUPAC
G112	$\text{CCl}_3\text{O}_2 + \text{CCl}_3\text{O}_2 \rightarrow 2 \text{CCl}_3\text{O} + \text{O}_2$	3.95×10^{-12}	-740		Atk08
G113	$\text{CCl}_3\text{O}_2 + \text{NO} \rightarrow \text{COCl}_2 + \text{Cl} + \text{NO}_2$	1.81×10^{-11}	-270		San06
G114	$\text{CCl}_3\text{O}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{CCl}_3\text{OONO}_2$	1.41×10^{-12}		TYP: TROEF; see Tab. S13	Atk08
G115	$\text{CCl}_3\text{OONO}_2 \xrightarrow{\text{M}} \text{CCl}_3\text{O}_2 + \text{NO}_2$	0.26		TYP: TROEXP; see Tab. S13	Atk08
G116	$\text{CCl}_3\text{OH} + \text{OH} \rightarrow \text{CCl}_3\text{O} + \text{H}_2\text{O}$	3.60×10^{-14}			MCM
G117	$\text{CCl}_3\text{O} \xrightarrow{\text{M}} \text{COCl}_2 + \text{Cl}$	7.91×10^6	4600	TYP: SPEC4	Atk08
G118	$\text{CH}_2\text{Cl}_2 + \text{OH} \xrightarrow{\text{O}_2} \text{CHCl}_2\text{O}_2 + \text{H}_2\text{O}$	1.00×10^{-13}	860	<i>g</i>	Atk08
G119	$\text{CH}_2\text{Cl}_2 + \text{Cl} \xrightarrow{\text{O}_2} \text{CHCl}_2\text{O}_2 + \text{HCl}$	3.40×10^{-13}	850	<i>g</i>	Atk08

Table S12 (continued) Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	E_A/R^b	Comment	Reference
G120	$\text{CHCl}_2\text{O}_2 + \text{HO}_2 \rightarrow 0.3 \text{CHOC}l + 0.3 \text{HO}Cl + 0.7 \text{COCl}_2 + 0.7 \text{H}_2\text{O} + \text{O}_2$	5.87×10^{-12}	-700		Atk08
G121	$\text{CHCl}_2\text{O}_2 + \text{MO}_2 \rightarrow 0.2 \text{COCl}_2 + 0.2 \text{CH}_3\text{OH} + 0.2 \text{CHCl}_2\text{OH} + 0.8 \text{HCHO} + 0.4 \text{O}_2 + 0.6 \text{HO}_2 + 0.6 \text{CHOC}l + 0.6 \text{Cl}$	2.00×10^{-12}		estimated ($\text{RO}_2 = \text{MO}_2$), ^{d, A}	MCM
G122	$\text{CHCl}_2\text{O}_2 + \text{CHCl}_2\text{O}_2 \rightarrow 2 \text{CHOC}l + 2 \text{Cl} + \text{O}_2$	7.00×10^{-12}			Atk08
G123	$\text{CHCl}_2\text{O}_2 + \text{NO} \rightarrow \text{CHOC}l + \text{Cl} + \text{NO}_2$	1.87×10^{-11}	-360	^d	MCM
G124	$\text{CHCl}_2\text{OH} + \text{OH} \xrightarrow{\text{O}_2} \text{COCl}_2 + \text{H}_2\text{O} + \text{HO}_2$	9.34×10^{-13}			MCM
G125	$\text{COCl}_2 + \text{OH} \rightarrow \text{COCl} + \text{HOCl}$	5.00×10^{-15}		upper limit	Atk08
G126	$\text{CH}_3\text{Cl} + \text{OH} \xrightarrow{\text{O}_2} \text{CH}_2\text{ClO}_2 + \text{H}_2\text{O}$	3.62×10^{-14}	1210		Atk08
G127	$\text{CH}_3\text{Cl} + \text{Cl} \xrightarrow{\text{O}_2} \text{CH}_2\text{ClO}_2 + \text{HCl}$	4.85×10^{-13}	1150		Atk08
G128	$\text{CH}_2\text{ClO}_2 + \text{HO}_2 \rightarrow 0.3 \text{CH}_2\text{ClO}_2\text{H} + 0.7 \text{CHOC}l + 0.7 \text{H}_2\text{O} + \text{O}_2$	5.01×10^{-12}	-820		Atk08
G129	$\text{CH}_2\text{ClO}_2 + \text{MO}_2 \rightarrow 0.2 \text{CH}_2\text{ClOH} + 0.8 \text{HCHO} + 0.2 \text{CHOC}l + 0.2 \text{CH}_3\text{OH} + 0.4 \text{O}_2 + 0.6 \text{CH}_2\text{ClO} + 0.6 \text{HO}_2$	2.50×10^{-12}		branching ratios from corresponding RO_2 reaction in MCM, ^A	IUPAC
G130	$\text{CH}_2\text{ClO}_2 + \text{CH}_2\text{ClO}_2 \rightarrow 2 \text{CH}_2\text{ClO} + \text{O}_2$	3.52×10^{-12}	-870		Atk08
G131	$\text{CH}_2\text{ClO}_2 + \text{NO} \rightarrow \text{CH}_2\text{ClO} + \text{NO}_2$	1.92×10^{-11}	-300		San06
G132	$\text{CH}_2\text{ClO}_2\text{H} + \text{OH} \rightarrow \text{CH}_2\text{ClO}_2 + \text{H}_2\text{O}$	3.59×10^{-12}	-190		MCM
G133	$\text{CH}_2\text{ClO}_2\text{H} + \text{OH} \rightarrow \text{CHOC}l + \text{OH} + \text{H}_2\text{O}$	4.14×10^{-12}			MCM
P _g 17	$\text{CH}_2\text{ClO}_2\text{H} \xrightarrow{h\nu} \text{CH}_2\text{ClO} + \text{OH}$	(5.79×10^{-6})		see Tab. S14	MCM
G134	$\text{CH}_2\text{ClOH} + \text{OH} \xrightarrow{\text{O}_2} \text{CHOC}l + \text{H}_2\text{O} + \text{HO}_2$	1.08×10^{-12}			MCM
G135	$\text{CH}_2\text{ClO} + \text{O}_2 \rightarrow \text{CHOC}l + \text{HO}_2$	9.48×10^{-15}	550		MCM
G136	$\text{CHOC}l + \text{OH} \rightarrow \text{COCl} + \text{H}_2\text{O}$	5.00×10^{-13}		upper limit	Atk08
G137	$\text{CHOC}l + \text{Cl} \rightarrow \text{HCl} + \text{COCl}$	7.48×10^{-13}	710		Atk08

Table S12 (continued) Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	E_A/R^b	Comment	Reference
P _g 18	$\text{CHOC1} \xrightarrow{h\nu, \text{O}_2} \text{Cl} + \text{CO} + \text{HO}_2$	(2.71×10^{-7})		$\Phi = 1.0^{\text{Fan/Liu01}}$; see Tab. S14	Atk08
G138	$\text{COCl} \xrightarrow{\text{M}} \text{CO} + \text{Cl}$	4.98×10^5	2960	TYP: SPEC4	Atk07
G139	$\text{CO} + \text{Cl} \xrightarrow{\text{M}} \text{COCl}$	3.33×10^{-14}		TYP: SPEC2; see Tab. S13	Atk07
G140 \oplus	$\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2$	1.16×10^{-12}	800	better reference	Atk07
G141 \ominus	$\text{Br} + \text{HO}_2 \rightarrow \text{HBr} + \text{O}_2$	1.70×10^{-12}	450		Atk07
G142	$\text{Br} + \text{H}_2\text{O}_2 \rightarrow \text{HBr} + \text{HO}_2$	4.25×10^{-16}	3000		San06
G143	$\text{Br}_2 + \text{OH} \rightarrow \text{HOBr} + \text{Br}$	4.48×10^{-11}	-240		Atk07
P _g 19 \ominus	$\text{Br}_2 \xrightarrow{h\nu} 2 \text{Br}$	(3.86×10^{-2})		$\Phi = 1.0^{\text{Fan/Liu01}}$; see Tab. S14	See/Bri64
G144 \ominus	$\text{BrO} + \text{O}_3 \rightarrow 0.9 \text{Br} + 0.1 \text{OBrO} + 1.9 \text{O}_2$	2.17×10^{-17}	3200	products from Atkinson et al. (2007); upper limit	San06
G145	$\text{BrO} + \text{OH} \rightarrow \text{Br} + \text{HO}_2$	4.16×10^{-11}	-250		Atk07
G146 \ominus	$\text{BrO} + \text{HO}_2 \rightarrow \text{HOBr} + \text{O}_2$	2.41×10^{-11}	-500	further products omitted	Atk07
G147	$\text{BrO} + \text{BrO} \rightarrow 1.7 \text{Br} + 0.15 \text{Br}_2 + \text{O}_2$	3.24×10^{-12}	-210		Atk07
P _g 20	$\text{BrO} \xrightarrow{h\nu} \text{Br} + \text{O}(^3\text{P})$	(4.86×10^{-2})		$\Phi = 1.0$; see Tab. S14	San03
P _g 21	$\text{OBrO} \xrightarrow{h\nu} \text{BrO} + \text{O}(^3\text{P})$	(0.56)		$\Phi = 1.0^{\text{Fle05, i}}$; see Tab. S14	San06
P _g 22 \ominus	$\text{HOBr} \xrightarrow{h\nu} \text{Br} + \text{OH}$	(2.80×10^{-3})		$\Phi = 1.0$; see Tab. S14	San03
G148 \ominus	$\text{HBr} + \text{OH} \rightarrow \text{Br} + \text{H}_2\text{O}$	1.13×10^{-11}	-155		Atk07
G149	$\text{Br} + \text{NO}_2 \xrightarrow{\text{M}} \text{BrNO}_2$	1.43×10^{-12}		TYP: TROEF; see Tab. S13	Atk07
P _g 23 \ominus	$\text{BrNO}_2 \xrightarrow{h\nu} \text{Br} + \text{NO}_2$	(5.87×10^{-3})		$\Phi = 1.0$; see Tab. S14	Atk07
G150	$\text{Br} + \text{NO}_3 \rightarrow \text{BrO} + \text{NO}_2$	1.60×10^{-11}			Atk07
G151	$\text{BrO} + \text{NO} \rightarrow \text{Br} + \text{NO}_2$	2.08×10^{-11}	-260		Atk07
G152	$\text{BrO} + \text{NO}_2 \xrightarrow{\text{M}} \text{BrNO}_3$	1.87×10^{-12}		TYP: TROEF; see Tab. S13	Atk07
G153	$\text{BrNO}_3 \rightarrow \text{BrO} + \text{NO}_2$	2.75×10^{-5}	12360		Orl/Tyn96
G154	$\text{BrNO}_3 + \text{Br} \rightarrow \text{Br}_2 + \text{NO}_3$	4.9×10^{-11}			Orl/Tyn96
P _g 24	$\text{BrNO}_3 \xrightarrow{h\nu} \text{Br} + \text{NO}_3$	(1.26×10^{-3})		$\Phi = 0.71$; see Tab. S14	San03
P _g 25	$\text{BrNO}_3 \xrightarrow{h\nu} \text{BrO} + \text{NO}_2$	(5.13×10^{-4})		$\Phi = 0.29$; see Tab. S14	San03

Table S12 (continued) Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	E_A/R^b	Comment	Reference
G155	$\text{HBr} + \text{NO}_3 \rightarrow \text{Br} + \text{HNO}_3$	1.0×10^{-16}		upper limit	Atk07
G156	$\text{Br} + \text{Cl}_2\text{O}_2 \rightarrow \text{BrCl} + \text{ClO}_2$	3.34×10^{-12}	170		Atk07
G157	$\text{Br} + \text{OCIO} \rightarrow \text{BrO} + \text{ClO}$	3.44×10^{-13}	1300		Atk07
G158	$\text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{OCIO}$	6.77×10^{-12}	-430		Atk07
G159	$\text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{ClO}_2$	6.07×10^{-12}	-220		Atk07
G160	$\text{BrO} + \text{ClO} \rightarrow \text{BrCl} + \text{O}_2$	1.03×10^{-12}	-170		Atk07
G161	$\text{Br}_2 + \text{Cl} \rightarrow \text{BrCl} + \text{Br}$	3.62×10^{-10}	-135		Bed98
G162	$\text{BrCl} + \text{Br} \rightarrow \text{Br}_2 + \text{Cl}$	3.32×10^{-15}			Bau81
G163	$\text{Br} + \text{Cl}_2 \rightarrow \text{BrCl} + \text{Cl}$	1.10×10^{-15}			Dol/Leo87
G164	$\text{BrCl} + \text{Cl} \rightarrow \text{Br} + \text{Cl}_2$	1.45×10^{-11}			Cly/Cru72
P _g 26 \ominus	$\text{BrCl} \xrightarrow{h\nu} \text{Br} + \text{Cl}$	(1.32×10^{-2})		$\Phi = 1.0$; see Tab. S14	Atk07
G165	$\text{Br} + \text{OP1} \rightarrow \text{HBr} + \text{MO}_2$	1.18×10^{-14}	1610	<i>A, B</i>	Kon/Ben84
G166	$\text{BrO} + \text{MO}_2 \rightarrow 0.25 \text{BrO}_2 + 0.25 \text{HCHO} + 0.25 \text{HO}_2 - 0.25 \text{O}_2 + 0.75 \text{HOBr} + 0.75 \text{ORA1}$	6.01×10^{-12}	-800	<i>A, C</i>	IUPAC
G167 \oplus	$\text{Br} + \text{HCHO} \xrightarrow{\text{O}_2} \text{HBr} + \text{CO} + \text{HO}_2$	1.16×10^{-12}	800	better reference	San06
G168	$\text{BrO} + \text{HCHO} \xrightarrow{\text{O}_2} \text{HOBr} + \text{CO} + \text{HO}_2$	1.50×10^{-14}			Han99
G169	$\text{Br} + \text{CH}_3\text{CHO} \xrightarrow{\text{O}_2} \text{HBr} + \text{ACO}_3$	3.84×10^{-12}	460	<i>N</i>	Atk06
G170	$\text{Br} + \text{ALD} \xrightarrow{\text{O}_2} \text{HBr} + \text{ACO}_3$	3.84×10^{-12}	460	estimated ($k_{\text{G170}} \approx k_{\text{G169}}$), <i>N, O</i>	Atk06
G171	$\text{Br} + \text{ETI} \xrightarrow{\text{O}_2, M} 0.17 \text{CHOBr} + 0.09 \text{Br} + 0.74 \text{HBr} + 0.09 \text{GLY} + 1.65 \text{CO} + 0.91 \text{HO}_2$	2.78×10^{-14}	-440	<i>d, T U</i>	Atk06
G172	$\text{Br} + \text{ETE} \xrightarrow{\text{M}, \text{O}_2} \text{CH}_2\text{BrCH}_2\text{O}_2$	2.25×10^{-13}	-277	fitted to Arrhenius expression, <i>g, U</i>	Atk06
G173	$\text{CH}_2\text{BrCH}_2\text{O}_2 + \text{MO}_2 \rightarrow 0.2 \text{CH}_2\text{BrCH}_2\text{OH} + 0.8 \text{HCHO} + 0.2 \text{CH}_2\text{BrCHO} + 0.2 \text{CH}_3\text{OH} + 0.4 \text{O}_2 + 0.6 \text{CH}_2\text{BrCH}_2\text{O} + 0.6 \text{HO}_2$	2.00×10^{-12}		estimated ($\text{RO}_2 = \text{MO}_2$), <i>e A</i>	MCM
G174	$\text{CH}_2\text{BrCH}_2\text{O}_2 + \text{CH}_2\text{BrCH}_2\text{O}_2 \rightarrow 1.14 \text{CH}_2\text{BrCH}_2\text{O} + 0.43 \text{CH}_2\text{BrCH}_2\text{OH} + 0.43 \text{CH}_2\text{BrCHO} + \text{O}_2$	3.98×10^{-12}	-1250		Atk08

Table S12 (continued) Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	E_A/R^b	Comment	Reference
G175	$\text{CH}_2\text{BrCH}_2\text{O}_2 + \text{NO} \rightarrow \text{CH}_2\text{BrCH}_2\text{O} + \text{NO}_2$	9.70×10^{-12}		<i>e</i>	Atk08
G176	$\text{CH}_2\text{BrCH}_2\text{OH} + \text{OH} \xrightarrow{\text{O}_2}$ $\text{CH}_2\text{BrCHO} + \text{H}_2\text{O} + \text{HO}_2$	4.60×10^{-12}		<i>e</i>	MCM
G177	$\text{CH}_2\text{BrCH}_2\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{BrCHO} + \text{HO}_2$	9.48×10^{-15}	550	<i>e</i>	MCM
G178	$\text{CH}_2\text{BrCHO} + \text{OH} \xrightarrow{\text{O}_2} \text{CH}_2\text{BrCO}_3 + \text{H}_2\text{O}$	3.10×10^{-12}		<i>e, g</i>	Atk08
P _g 29	$\text{CH}_2\text{BrCHO} \xrightarrow{h\nu, 2\text{O}_2} \text{CH}_2\text{BrO}_2 + \text{CO} + \text{HO}_2$	(3.26×10^{-5})		estimated same as P _g 13, see Tab. S14	MCM
G179	$\text{CH}_2\text{BrCO}_3 + \text{HO}_2 \rightarrow 0.71 \text{CH}_2\text{BrCO}_3\text{H} +$ $0.71 \text{O}_2 + 0.29 \text{CH}_2\text{BrCOOH} + 0.29 \text{O}_3$	1.41×10^{-11}	-1040	<i>e</i>	MCM
G180	$\text{CH}_2\text{BrCO}_3 + \text{MO}_2 \xrightarrow{\text{O}_2}$ $0.3 \text{CH}_2\text{BrCOOH} + \text{HCHO} + 0.7 \text{CH}_2\text{BrO}_2 +$ $0.7 \text{CO}_2 + 0.7 \text{HO}_2 - 0.4 \text{O}_2$	1.00×10^{-11}		estimated ($\text{RO}_2 = \text{MO}_2$), <i>e A</i>	MCM
G181	$\text{CH}_2\text{BrCO}_3 + \text{NO} \xrightarrow{\text{O}_2}$ $\text{CH}_2\text{BrO}_2 + \text{CO}_2 + \text{NO}_2$	2.00×10^{-11}	-270	<i>e</i>	MCM
G182	$\text{CH}_2\text{BrCO}_3 + \text{NO}_2 \xrightarrow{\text{M}} \text{CH}_2\text{BrC}(\text{O})\text{OONO}_2$	1.11×10^{-11}		TYP: TROEF; see Tab. S13, <i>e</i>	MCM
G183	$\text{CH}_2\text{BrC}(\text{O})\text{OONO}_2 \xrightarrow{\text{M}} \text{CH}_2\text{BrCO}_3 + \text{NO}_2$	3.48×10^{-4}		TYP: TROEXP; see Tab. S13, <i>e</i>	MCM
G184	$\text{CH}_2\text{BrC}(\text{O})\text{OONO}_2 + \text{OH} \rightarrow$ $\text{O}_2\text{CHBrC}(\text{O})\text{OONO}_2 + \text{H}_2\text{O}$	6.26×10^{-13}		<i>e</i>	MCM
G185	$\text{O}_2\text{CHBrC}(\text{O})\text{OONO}_2 + \text{NO} \rightarrow \text{C}(\text{O})\text{OONO}_2 +$ $\text{NOCHBr} + \text{CO} + \text{O}_2 + 2\text{NO}_2$	1.36×10^{-11}	-360	estimated	
G186	$\text{CH}_2\text{BrCO}_3\text{H} + \text{OH} \rightarrow \text{CH}_2\text{BrCO}_3 + \text{H}_2\text{O}$	4.29×10^{-12}		<i>e</i>	MCM
P _g 30	$\text{CH}_2\text{BrCO}_3\text{H} \xrightarrow{h\nu, \text{O}_2} \text{CH}_2\text{BrO}_2 + \text{CO}_2 + \text{OH}$	(5.79×10^{-6})		estimated same as P _g 14, see Tab. S14	MCM
G187	$\text{CH}_2\text{BrCOOH} + \text{OH} \xrightarrow{\text{O}_2}$ $\text{CH}_2\text{BrO}_2 + \text{CO}_2 + \text{H}_2\text{O}$	3.59×10^{-12}	-190	<i>e</i>	MCM
G188	$\text{Br} + \text{C}_3\text{H}_6 \xrightarrow{\text{M}, \text{O}_2} \text{CH}_3\text{CHO}_2\text{CH}_2\text{Br}$	3.60×10^{-12}		<i>g</i>	Atk06

Table S12 (continued) Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	E_A/R^b	Comment	Reference
G189	$\text{CH}_3\text{CHO}_2\text{CH}_2\text{Br} + \text{MO}_2 \rightarrow$ $0.2 \text{CH}_3\text{CHOHCH}_2\text{Br} + 0.8 \text{HCHO} +$ $0.2 \text{CH}_3\text{COCH}_2\text{Br} + 0.2 \text{CH}_3\text{OH} + 0.4 \text{O}_2 +$ $0.6 \text{CH}_3\text{CHOCH}_2\text{Br} + 0.6 \text{HO}_2$	4.00×10^{-14}		estimated ($\text{RO}_2 = \text{MO}_2$), ^{c, A}	MCM
G190	$\text{CH}_3\text{CHO}_2\text{CH}_2\text{Br} + \text{NO} \rightarrow$ $\text{CH}_3\text{CHOCH}_2\text{Br} + \text{NO}_2$	9.04×10^{-12}	-360	further products omitted, ^c	Atk06
G191	$\text{CH}_3\text{CHOHCH}_2\text{Br} + \text{OH} \xrightarrow{\text{O}_2}$ $\text{CH}_3\text{COCH}_2\text{Br} + \text{H}_2\text{O} + \text{HO}_2$	5.09×10^{-12}	-200	further products omitted, ^c	Atk06
G192	$\text{CH}_3\text{CHOCH}_2\text{Br} + \text{O}_2 \rightarrow$ $\text{CH}_3\text{COCH}_2\text{Br} + \text{HO}_2$	6.93×10^{-15}	230	^c	Atk06
G193	$\text{CH}_3\text{COCH}_2\text{Br} + \text{OH} \xrightarrow{\text{O}_2}$ $\text{CH}_3\text{COCHBrO}_2 + \text{H}_2\text{O}$	1.05×10^{-13}	1320	^{c, g}	Atk06
P _g 27	$\text{CH}_3\text{COCH}_2\text{Br} \xrightarrow{h\nu} 0.7 \text{COBr} + 0.7 \text{ACO}_3 +$ $0.3 \text{CH}_2\text{BrCO}_3 + 0.3 \text{MO}_2 - 1.3 \text{O}_2$	(5.87×10^{-3})		$\Phi = 1.0^i$; see Tab. S14	San06
G194	$\text{CH}_3\text{COCHBrO}_2 + \text{MO}_2 \rightarrow$ $0.2 \text{CH}_3\text{COCHBrOH} + 0.8 \text{HCHO} +$ $0.2 \text{CH}_3\text{COCBrO} + 0.2 \text{CH}_3\text{OH} - 0.2 \text{O}_2 +$ $0.6 \text{ACO}_3 + 0.6 \text{CHOBr} + 0.6 \text{HO}_2$	2.00×10^{-12}		estimated ($\text{RO}_2 = \text{MO}_2$), ^{c, A, N}	MCM
G195	$\text{CH}_3\text{COCHBrO}_2 + \text{NO} \xrightarrow{\text{O}_2}$ $\text{ACO}_3 + \text{CHOBr} + \text{NO}_2$	8.00×10^{-12}		^{c, N}	Atk06
G196	$\text{CH}_3\text{COCHBrOH} + \text{OH} \xrightarrow{\text{O}_2}$ $\text{CH}_3\text{COCBrO} + \text{H}_2\text{O} + \text{HO}_2$	3.00×10^{-12}		^c	MCM
P _g 28	$\text{CH}_3\text{COCBrO} \xrightarrow{h\nu, \text{O}_2} \text{COBr} + \text{ACO}_3$	(2.78×10^{-5})		estimated same as methylglyoxal; see Tab. S14	MCM
G197	$\text{CHBr}_3 + \text{OH} \xrightarrow{\text{O}_2} \text{CBr}_3\text{O}_2 + \text{H}_2\text{O}$	1.80×10^{-13}	600		San06
G198	$\text{CHBr}_3 + \text{Cl} \xrightarrow{\text{O}_2} \text{CBr}_3\text{O}_2 + \text{HCl}$	2.80×10^{-13}	850		San06
P _g 31	$\text{CHBr}_3 \xrightarrow{h\nu, \text{O}_2} \text{Br} + \text{CHBr}_2\text{O}_2$	(1.77×10^{-6})		$\Phi = 1.0^i$; see Tab. S14	Dem97
G199	$\text{CBr}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{COBr}_2 + \text{HOBr} + \text{O}_2$	5.09×10^{-12}	-710	^e	Atk08

Table S12 (continued) Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	E_A/R^b	Comment	Reference
G200	$\text{CBr}_3\text{O}_2 + \text{MO}_2 \rightarrow 0.3 \text{CBr}_3\text{OH} + 0.3 \text{O}_2 + \text{HCHO} + 0.7 \text{CBr}_3\text{O} + 0.7 \text{HO}_2$	6.60×10^{-12}		branching ratios from MCM, ^{e, A}	MCM
G201	$\text{CBr}_3\text{O}_2 + \text{CBr}_3\text{O}_2 \rightarrow 2 \text{CBr}_3\text{O} + \text{O}_2$	3.95×10^{-12}	-740	^e	Atk08
G202	$\text{CBr}_3\text{O}_2 + \text{NO} \rightarrow \text{COBr}_2 + \text{Br} + \text{NO}_2$	1.81×10^{-11}	-270	^e	San06
G203	$\text{CBr}_3\text{O}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{CBr}_3\text{OONO}_2$	1.41×10^{-12}		TYP: TROEF; see Tab. S13; ^e	Atk08
G204	$\text{CBr}_3\text{OONO}_2 \xrightarrow{\text{M}} \text{CBr}_3\text{O}_2 + \text{NO}_2$	0.26		TYP: TROEXP; see Tab. S13; ^e	Atk08
G205	$\text{CBr}_3\text{OH} + \text{OH} \rightarrow \text{CBr}_3\text{O} + \text{H}_2\text{O}$	3.60×10^{-14}		^e	MCM
G206	$\text{CBr}_3\text{O} \rightarrow \text{COBr}_2 + \text{Br}$	7.91×10^6	4600	^e	Atk08
G207	$\text{CH}_2\text{Br}_2 + \text{OH} \xrightarrow{\text{O}_2} \text{CHBr}_2\text{O}_2 + \text{H}_2\text{O}$	1.11×10^{-13}	775		Atk08
G208	$\text{CH}_2\text{Br}_2 + \text{Cl} \xrightarrow{\text{O}_2} \text{CHBr}_2\text{O}_2 + \text{HCl}$	4.30×10^{-13}	800		San06
P _g 32	$\text{CH}_2\text{Br}_2 \xrightarrow{h\nu, \text{O}_2} \text{Br} + \text{CH}_2\text{BrO}_2$	(8.22×10^{-10})		$\Phi = 1.0^i$; see Tab. S14	Atk08
G209	$\text{CHBr}_2\text{O}_2 + \text{HO}_2 \rightarrow 0.3 \text{CHOBr} + 0.3 \text{HOBr} + 0.7 \text{COBr}_2 + 0.7 \text{H}_2\text{O} + \text{O}_2$	5.87×10^{-12}	-700	^e	Atk08
G210	$\text{CHBr}_2\text{O}_2 + \text{MO}_2 \rightarrow 0.2 \text{CHBr}_2\text{OH} + 0.8 \text{HCHO} + 0.2 \text{COBr}_2 + 0.2 \text{CH}_3\text{OH} + 0.4 \text{O}_2 + 0.6 \text{CHOBr} + 0.6 \text{Br} + 0.6 \text{HO}_2$	2.00×10^{-12}		estimated ($\text{RO}_2 = \text{MO}_2$), ^{d, e, A}	MCM
G211	$\text{CHBr}_2\text{O}_2 + \text{CHBr}_2\text{O}_2 \rightarrow 2 \text{CHOBr} + 2 \text{Br} + \text{O}_2$	7.00×10^{-12}		^e	Atk08
G212	$\text{CHBr}_2\text{O}_2 + \text{NO} \rightarrow \text{CHOBr} + \text{Br} + \text{NO}_2$	1.70×10^{-11}			Atk08
G213	$\text{CHBr}_2\text{OH} + \text{OH} \xrightarrow{\text{O}_2} \text{COBr}_2 + \text{H}_2\text{O} + \text{HO}_2$	9.34×10^{-13}		^e	MCM
G214	$\text{COBr}_2 + \text{OH} \rightarrow \text{COBr} + \text{HOBr}$	5.00×10^{-15}		upper limit, ^e	Atk08
P _g 33	$\text{COBr}_2 \xrightarrow{h\nu} 2 \text{Br} + \text{CO}$	(3.32×10^{-6})		$\Phi = 1.0^i$; products estimated the same as in the phosgene reaction in MCM; see Tab. S14	San06
G215	$\text{CH}_3\text{Br} + \text{OH} \xrightarrow{\text{O}_2} \text{CH}_2\text{BrO}_2 + \text{H}_2\text{O}$	2.88×10^{-14}	1215		Atk08
G216	$\text{CH}_3\text{Br} + \text{Cl} \xrightarrow{\text{O}_2} \text{CH}_2\text{BrO}_2 + \text{HCl}$	4.42×10^{-13}	1030		San06

Table S12 (continued) Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	E_A/R^b	Comment	Reference
G217	$\text{CH}_2\text{BrO}_2 + \text{HO}_2 \rightarrow$ $0.85 \text{CH}_2\text{BrO}_2\text{H} + 0.15 \text{CHOBr} + 0.15 \text{H}_2\text{O} + \text{O}_2$	6.70×10^{-12}			Atk08
G218	$\text{CH}_2\text{BrO}_2 + \text{MO}_2 \rightarrow$ $0.2 \text{CH}_2\text{BrOH} + 0.8 \text{HCHO} + 0.2 \text{CHOBr} +$ $0.2 \text{CH}_3\text{OH} + 0.4 \text{O}_2 + 0.6 \text{CH}_2\text{BrO} + 0.6 \text{HO}_2$	2.00×10^{-12}		estimated ($\text{RO}_2 = \text{MO}_2$), ^A	MCM
G219	$\text{CH}_2\text{BrO}_2 + \text{CH}_2\text{BrO}_2 \rightarrow 2 \text{CH}_2\text{BrO} + \text{O}_2$	1.05×10^{-12}		products from Atkinson et al. (2008b)	Vil/Les95
G220	$\text{CH}_2\text{BrO}_2 + \text{NO} \rightarrow \text{CH}_2\text{BrO} + \text{NO}_2$	1.10×10^{-11}			Atk08
G221	$\text{CH}_2\text{BrO}_2\text{H} + \text{OH} \rightarrow \text{CH}_2\text{BrO}_2 + \text{H}_2\text{O}$	3.59×10^{-12}	-190		MCM
G222	$\text{CH}_2\text{BrO}_2\text{H} + \text{OH} \rightarrow \text{CHOBr} + \text{OH} + \text{H}_2\text{O}$	5.79×10^{-12}			MCM
P _g 34	$\text{CH}_2\text{BrO}_2\text{H} \xrightarrow{h\nu} \text{CH}_2\text{BrO} + \text{OH}$	5.79×10^{-6}		see Tab. S14	MCM
G223	$\text{CH}_2\text{BrOH} + \text{OH} \xrightarrow{\text{O}_2} \text{CHOBr} + \text{H}_2\text{O} + \text{HO}_2$	1.06×10^{-12}			MCM
G224	$\text{CH}_2\text{BrO} + \text{O}_2 \rightarrow \text{CHOBr} + \text{HO}_2$	9.48×10^{-15}	550		MCM
G225	$\text{CHOBr} + \text{OH} \rightarrow \text{Br} + \text{CO} + \text{H}_2\text{O}$	1.16×10^{-12}			MCM
G226	$\text{CHOBr} + \text{Cl} \rightarrow \text{COBr} + \text{HCl}$	7.48×10^{-13}	710	^e	Atk08
P _g 35	$\text{CHOBr} \xrightarrow{h\nu, \text{O}_2} \text{Br} + \text{CO} + \text{HO}_2$	(1.77×10^{-5})		$\Phi = 1.0^i$; see Tab. S14	San06
G227	$\text{COBr} \xrightarrow{\text{M}} \text{CO} + \text{Br}$	4.98×10^5	2960	TYP: SPEC4, ^e	Atk07
G228	$\text{CO} + \text{Br} \xrightarrow{\text{M}} \text{COBr}$	3.33×10^{-14}		TYP: SPEC2; see Tab. S13, ^e	Atk07
G229	$\text{I} + \text{I} \rightarrow \text{I}_2$	2.99×10^{-11}			Hip73
G230	$\text{I} + \text{O}_3 \rightarrow \text{IO} + \text{O}_2$	1.30×10^{-12}	830		Atk07
G231	$\text{I}_2 + \text{OH} \rightarrow \text{I} + \text{HOI}$	2.10×10^{-10}			Atk07
P _g 36	$\text{I}_2 \xrightarrow{h\nu} 2\text{I}$	(0.18)		$\Phi = 1.0$; see Tab. S14	Atk07
G232	$\text{I} + \text{HO}_2 \rightarrow \text{HI} + \text{O}_2$	3.87×10^{-13}	1090		Atk07
G233	$\text{IO} + \text{HO}_2 \rightarrow \text{HOI} + \text{O}_2$	8.57×10^{-11}	-540		Atk07
G234	$\text{IO} + \text{IO} \rightarrow 0.38 \text{OIO} + 0.485 \text{I}_2\text{O}_2 + 0.6 \text{I} +$ $0.135 \text{O}_2 + 0.025 \text{I}_2$	8.03×10^{-11}	-500	branching ratios from Sander and Kerkweg (2005)	San06
P _g 37	$\text{IO} \xrightarrow{h\nu} \text{I} + \text{O}(^3\text{P})$	(2.07×10^{-3})		$\Phi = 1.0$; see Tab. S14	Atk07
G235	$\text{OIO} + \text{OH} \rightarrow 0.5 \text{HIO}_3 + 0.5 \text{HOI} + 0.5 \text{O}_2$	2.00×10^{-10}		assumed	Gla02a

Table S12 (continued) Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	E_A/R^b	Comment	Reference
G236	$\text{OIO} + \text{OIO} \rightarrow \text{I}_2\text{O}_2 + \text{O}_2$	5.00×10^{-11}		assumed	Gla02b
P _g 38	$\text{OIO} \xrightarrow{h\nu} \text{I} + \text{O}_2$	(3.37×10^{-2})		$\Phi = 0.15$; upper limit; see Tab. S14	San06
P _g 39	$\text{OIO} \xrightarrow{h\nu} \text{IO} + \text{O}(^3\text{P})$	(1.57×10^{-3})		$\Phi = 0.007$; upper limit; see Tab. S14	San06
G237	$\text{I}_2\text{O}_2 \rightarrow 2\text{IO}$	20.0		assumed	Jim03
P _g 40	$\text{I}_2\text{O}_2 \xrightarrow{h\nu} 2\text{I} + \text{O}_2$	(1.83×10^{-3})		$\Phi = 1.0^i$; see Tab. S14	San03
G238	$\text{HI} + \text{OH} \rightarrow \text{I} + \text{H}_2\text{O}$	7.00×10^{-11}	-440		Atk07
P _g 41	$\text{HI} \xrightarrow{h\nu, \text{O}_2} \text{I} + \text{HO}_2$	(1.58×10^{-4})		$\Phi = 1.0$; see Tab. S14	Atk07
P _g 42	$\text{HOI} \xrightarrow{h\nu, \text{O}_2} \text{I} + \text{OH}$	(1.16×10^{-2})		$\Phi = 1.0$; see Tab. S14	Atk07
G239	$\text{I} + \text{NO} \xrightarrow{\text{M}} \text{INO}$	9.38×10^{-14}		TYP: TROE; see Tab. S13	Atk07
P _g 43	$\text{INO} \xrightarrow{h\nu} \text{I} + \text{NO}$	(3.84×10^{-3})		$\Phi = 1.0^i$; see Tab. S14	San06
G240	$\text{I} + \text{NO}_2 \xrightarrow{\text{M}} \text{INO}_2$	1.10×10^{-70}		TYP: TROEF; see Tab. S13	Atk07
P _g 44	$\text{INO}_2 \xrightarrow{h\nu} \text{I} + \text{NO}_2$	(3.89×10^{-3})		$\Phi = 1.0^i$; see Tab. S14	San06
G241	$\text{I} + \text{NO}_3 \rightarrow \text{IO} + \text{NO}_2$	4.50×10^{-10}			Cha92
G242	$\text{I}_2 + \text{NO}_3 \rightarrow \text{I} + \text{INO}_3$	1.50×10^{-12}			Atk07
G243	$\text{IO} + \text{NO} \rightarrow \text{I} + \text{NO}_2$	1.96×10^{-11}	-300		Atk07
G244	$\text{IO} + \text{NO}_2 \xrightarrow{\text{M}} \text{INO}_3$	4.13×10^{-12}		TYP: TROEF; see Tab. S13	Atk07
P _g 45	$\text{INO}_3 \xrightarrow{h\nu} \text{I} + \text{NO}_3$	(5.17×10^{-2})		$\Phi = 0.85$ (estimated same as BrNO_3 in Sander et al. (2006)), see Tab. S14	San06
P _g 46	$\text{INO}_3 \xrightarrow{h\nu} \text{IO} + \text{NO}_2$	(9.11×10^{-3})		$\Phi = 0.15$ (estimated same as BrNO_3 in Sander et al. (2006)), see Tab. S14	San06
G245	$\text{OIO} + \text{NO} \rightarrow \text{IO} + \text{NO}_2$	6.78×10^{-12}	-542		Atk07
G246	$\text{HI} + \text{NO}_3 \rightarrow \text{I} + \text{HNO}_3$	2.80×10^{-15}	1830		Atk07
G247	$\text{INO} + \text{INO} \rightarrow \text{I}_2 + 2\text{NO}$	1.28×10^{-14}	2620		Atk07
G248	$\text{INO}_2 + \text{INO}_2 \rightarrow \text{I}_2 + 2\text{NO}_2$	1.73×10^{-15}	1670		Atk07
G249	$\text{INO}_2 \xrightarrow{\text{M}} \text{I} + \text{NO}_2$	2.4		estimated; TYP: SPEC2	Gla02a
G250	$\text{INO}_3 \xrightarrow{\text{M}} \text{IO} + \text{NO}_2$	2.92×10^{-3}	12060	TYP: SPEC4	Atk07

Table S12 (continued) Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	E_A/R^b	Comment	Reference
G251	$I_2 + Cl \rightarrow I + ICl$	2.10×10^{-10}			Bed96
G252	$I_2 + Br \rightarrow I + IBr$	1.20×10^{-10}			Bed97
G253	$I + BrO \rightarrow IO + Br$	1.20×10^{-11}			San06
G254	$IO + ClO \rightarrow$ $0.8 I + 0.55 OClO + 0.25 Cl + 0.2 ICl + 0.45 O_2$	1.20×10^{-11}	-280		Atk07
G255	$IO + BrO \rightarrow 0.8 OIO + Br + 0.2 I + 0.2 O_2$	8.31×10^{-11}	-510		Atk07
P _g 47	$ICl \xrightarrow{h\nu} I + Cl$	(2.77×10^{-2})		$\Phi = 1.0$; see Tab. S14; exited atoms are treated like atoms in ground state	Atk07
P _g 48	$IBr \xrightarrow{h\nu} I + Br$	(8.21×10^{-2})		$\Phi = 1.0$; see Tab. S14; exited atoms are treated like atoms in ground state	Atk07
G256	$C_3H_7I + OH \xrightarrow{O_2} CH_3CIO_2CH_3 + H_2O$	1.60×10^{-12}		further products omitted, ^g	Cot03
P _g 49	$C_3H_7I \xrightarrow{h\nu, O_2} I + CH_3CHO_2CH_3$	(3.00×10^{-5})		$\Phi = 1.0$; see Tab. S14; exited atoms are treated like atoms in ground state	San06
G257	$CH_3CIO_2CH_3 + MO_2 \xrightarrow{O_2}$ $CH_3CIOCH_3 + HCHO + HO_2 + O_2$	2.40×10^{-14}		estimated ($RO_2 = MO_2$), ^{c, A}	MCM
G258	$CH_3CIO_2CH_3 + CH_3CIO_2CH_3 \rightarrow$ $2 CH_3CIOCH_3 + O_2$	5.57×10^{-16}	2200	^c	Atk06
G259	$CH_3CIO_2CH_3 + NO \rightarrow CH_3CIOCH_3 + NO_2$	9.04×10^{-12}	-360	^c	Atk06
G260	$CH_3CIOCH_3 \rightarrow CH_3COCH_3 + I$	10		estimated	
G261	$C_2H_5I + OH \xrightarrow{O_2}$ $0.13 CH_3CHIO_2 + 0.87 CH_2ICH_2O_2 + H_2O$	3.69×10^{-13}	800	products as in MCM, ^e	San06
P _g 50	$C_2H_5I \xrightarrow{h\nu, O_2} I + CH_3CH_2O_2$	(1.08×10^{-5})		$\Phi = 1.0$; see Tab. S14; exited atoms are treated like atoms in ground state	San06
G262	$CH_2ICH_2O_2 + MO_2 \xrightarrow{O_2}$ $0.2 CH_2ICH_2OH + 0.8 HCHO + 0.2 CH_2ICHO +$ $0.2 CH_3OH + 0.4 O_2 + 0.6 CH_2ICH_2O + 0.6 HO_2$	2.00×10^{-12}		estimated ($RO_2 = MO_2$), ^{e, A}	MCM

Table S12 (continued) Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	E_A/R^b	Comment	Reference
G263	$\text{CH}_2\text{ICH}_2\text{O}_2 + \text{CH}_2\text{ICH}_2\text{O}_2 \rightarrow$ $1.14 \text{CH}_2\text{ICH}_2\text{O} + 0.43 \text{CH}_2\text{ICH}_2\text{OH} +$ $0.43 \text{CH}_2\text{ICHO} + \text{O}_2$	3.98×10^{-12}	-1250	<i>f</i>	Atk08
G264	$\text{CH}_2\text{ICH}_2\text{O}_2 + \text{NO} \rightarrow \text{CH}_2\text{ICH}_2\text{O} + \text{NO}_2$	9.70×10^{-12}		<i>e</i>	Atk08
G265	$\text{CH}_2\text{ICH}_2\text{OH} + \text{OH} \xrightarrow{\text{O}_2}$ $\text{CH}_2\text{ICHO} + \text{H}_2\text{O} + \text{HO}_2$	4.60×10^{-12}		<i>e</i>	MCM
G266	$\text{CH}_2\text{ICH}_2\text{O} + \text{O}_2 \rightarrow \text{CH}_2\text{ICHO} + \text{HO}_2$	9.48×10^{-15}	550	<i>e</i>	MCM
G267	$\text{CH}_2\text{ICHO} + \text{OH} \xrightarrow{\text{O}_2} \text{CH}_2\text{ICO}_3 + \text{H}_2\text{O}$	3.10×10^{-12}		<i>e, g</i>	Atk08
P _g 51	$\text{CH}_2\text{ICHO} \xrightarrow{h\nu, 2\text{O}_2} \text{CH}_2\text{IO}_2 + \text{CO} + \text{HO}_2$	(3.26×10^{-5})		estimated same as P _g 13, see Tab. S14	MCM
G268	$\text{CH}_2\text{ICO}_3 + \text{HO}_2 \rightarrow 0.71 \text{CH}_2\text{ICO}_3\text{H} +$ $0.71 \text{O}_2 + 0.29 \text{CH}_2\text{ICOOH} + 0.29 \text{O}_3$	1.41×10^{-11}	-1040	<i>e</i>	MCM
G269	$\text{CH}_2\text{ICO}_3 + \text{MO}_2 \xrightarrow{2\text{O}_3}$ $0.3 \text{CH}_2\text{ICOOH} + \text{HCHO} - 0.4 \text{O}_2 +$ $0.7 \text{CH}_2\text{IO}_2 + 0.7 \text{CO}_2 + 0.7 \text{HO}_2$	1.00×10^{-11}		estimated ($\text{RO}_2 = \text{MO}_2$), <i>e, A</i>	MCM
G270	$\text{CH}_2\text{ICO}_3 + \text{NO} \xrightarrow{\text{O}_2} \text{CH}_2\text{IO}_2 + \text{CO}_2 + \text{NO}_2$	2.00×10^{-11}	-270	<i>e</i>	MCM
G271	$\text{CH}_2\text{ICO}_3 + \text{NO}_2 \xrightarrow{\text{M}} \text{CH}_2\text{IC}(\text{O})\text{OONO}_2$	1.11×10^{-11}		TYP: TROEF; see Tab. S13, <i>e</i>	MCM
G272	$\text{CH}_2\text{IC}(\text{O})\text{OONO}_2 \xrightarrow{\text{M}} \text{CH}_2\text{ICO}_3 + \text{NO}_2$	3.48×10^{-4}		TYP: TROEXP; see Tab. S13, <i>e</i>	MCM
G273	$\text{CH}_2\text{IC}(\text{O})\text{OONO}_2 + \text{OH} \rightarrow$ $\text{O}_2\text{CHIC}(\text{O})\text{OONO}_2 + \text{H}_2\text{O}$	6.26×10^{-13}		<i>e</i>	MCM
G274	$\text{O}_2\text{CHIC}(\text{O})\text{OONO}_2 + \text{NO} \rightarrow$ $\text{CHOI} + \text{CO} + \text{O}_2 + 2\text{NO}_2$	1.36×10^{-11}	-360	estimated	
G275	$\text{CH}_2\text{ICO}_3\text{H} + \text{OH} \rightarrow \text{CH}_2\text{ICO}_3 + \text{H}_2\text{O}$	4.29×10^{-12}		<i>e</i>	MCM
P _g 52	$\text{CH}_2\text{ICO}_3\text{H} \xrightarrow{h\nu, \text{O}_2} \text{CH}_2\text{IO}_2 + \text{CO}_2 + \text{OH}$	(5.79×10^{-6})		estimated (wie P _g 14), see Tab. S14	MCM
G276	$\text{CH}_2\text{ICOOH} + \text{OH} \xrightarrow{\text{O}_2}$ $\text{CH}_2\text{IO}_2 + \text{CO}_2 + \text{H}_2\text{O}$	3.59×10^{-12}	-190	<i>e</i>	MCM
G277	$\text{CH}_3\text{CHIO}_2 + \text{MO}_2 \rightarrow 0.2 \text{CH}_3\text{CHIOH} +$ $0.8 \text{HCHO} + 0.2 \text{CH}_3\text{CIO} + 0.2 \text{CH}_3\text{OH} +$ $0.4 \text{O}_2 + 0.6 \text{CH}_3\text{CHO} + 0.6 \text{I} + 0.6 \text{HO}_2$	8.80×10^{-13}		estimated ($\text{RO}_2 = \text{MO}_2$), <i>d, e, A</i>	MCM

Table S12 (continued) Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	E_A/R^b	Comment	Reference
G278	$\text{CH}_3\text{CHIO}_2 + \text{NO} \rightarrow \text{CH}_3\text{CHO} + \text{I} + \text{NO}_2$	1.87×10^{-11}	-360	d, e	MCM
G279	$\text{CH}_3\text{CHIOH} + \text{OH} \xrightarrow{\text{O}_2}$ $\text{CH}_3\text{CIO} + \text{H}_2\text{O} + \text{HO}_2$	2.77×10^{-12}		e	MCM
G280	$\text{CH}_3\text{CIO} + \text{OH} \xrightarrow{\text{O}_2} \text{CIOCH}_2\text{O}_2 + \text{H}_2\text{O}$	3.88×10^{-14}		e	MCM
G281	$\text{CIOCH}_2\text{O}_2 + \text{MO}_2 \rightarrow$ $\text{I} + \text{CO} + 2\text{HCHO} + \text{HO}_2$	2.00×10^{-12}		d, e, A	MCM
G282	$\text{CIOCH}_2\text{O}_2 + \text{NO} \rightarrow$ $\text{I} + \text{CO} + \text{HCHO} + \text{NO}_2$	1.36×10^{-11}	-360	d, e	MCM
G283	$\text{CH}_2\text{I}_2 + \text{OH} \xrightarrow{\text{O}_2} \text{CHI}_2\text{O}_2 + \text{H}_2\text{O}$	2.75×10^{-14}	929	estimated	
G284	$\text{CH}_2\text{I}_2 + \text{Cl} \xrightarrow{\text{O}_2} \text{CHI}_2\text{O}_2 + \text{HCl}$	4.70×10^{-13}	1135	estimated	
P _g 53	$\text{CH}_2\text{I}_2 \xrightarrow{h\nu, \text{O}_2} \text{I} + \text{CH}_2\text{IO}_2$	(1.13×10^{-2})		$\Phi = 1.0$; see Tab. S14; exited atoms are treated like atoms in ground state	San06
G285	$\text{CHI}_2\text{O}_2 + \text{HO}_2 \rightarrow$ $0.3\text{CHOI} + 0.3\text{HOI} + 0.7\text{COI}_2 + 0.7\text{H}_2\text{O} + \text{O}_2$	5.87×10^{-12}	-700	e	Atk08
G286	$\text{CHI}_2\text{O}_2 + \text{MO}_2 \rightarrow 0.2\text{CHI}_2\text{OH} +$ $0.8\text{HCHO} + 0.2\text{COI}_2 + 0.2\text{CH}_3\text{OH} +$ $0.4\text{O}_2 + 0.6\text{CHOI} + 0.6\text{I} + 0.6\text{HO}_2$	2.00×10^{-12}		estimated ($\text{RO}_2 = \text{MO}_2$), e, A	MCM
G287	$\text{CHI}_2\text{O}_2 + \text{CHI}_2\text{O}_2 \rightarrow 2\text{CHOI} + 2\text{I} + \text{O}_2$	7.00×10^{-12}		e	Atk08
G288	$\text{CHI}_2\text{O}_2 + \text{NO} \rightarrow \text{CHOI} + \text{I} + \text{NO}_2$	1.70×10^{-11}		h	Atk08
G289	$\text{CHI}_2\text{OH} + \text{OH} \xrightarrow{\text{O}_2} \text{COI}_2 + \text{H}_2\text{O} + \text{HO}_2$	9.34×10^{-13}		e	MCM
G290	$\text{COI}_2 + \text{OH} \rightarrow \text{COI} + \text{HOI}$	5.00×10^{-15}		upper limit, e	Atk08
G291	$\text{CH}_3\text{I} + \text{OH} \xrightarrow{\text{O}_2} \text{CH}_2\text{IO}_2 + \text{H}_2\text{O}$	1.00×10^{-13}	1120		Atk08
G292	$\text{CH}_3\text{I} + \text{Cl} \xrightarrow{\text{O}_2} \text{CH}_2\text{IO}_2 + \text{HCl}$	1.01×10^{-12}	1000		San06
P _g 54	$\text{CH}_3\text{I} \xrightarrow{h\nu, \text{O}_2} \text{I} + \text{MO}_2$	(9.55×10^{-6})		$\Phi = 1.0$; see Tab. S14; exited atoms are treated like atoms in ground state, A	San06

Table S12 (continued) Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	E_A/R^b	Comment	Reference
G293	$\text{CH}_2\text{IO}_2 + \text{HO}_2 \rightarrow$ $0.85 \text{CH}_2\text{IO}_2\text{H} + 0.15 \text{CHOI} + 0.15 \text{H}_2\text{O} + \text{O}_2$	6.70×10^{-12}		<i>f</i>	Atk08
G294	$\text{CH}_2\text{IO}_2 + \text{MO}_2 \rightarrow$ $0.2 \text{CH}_2\text{IOH} + 0.8 \text{HCHO} + 0.2 \text{CHOI} +$ $0.2 \text{CH}_3\text{OH} + 0.4 \text{O}_2 + 0.6 \text{CH}_2\text{IO} + 0.6 \text{HO}_2$	2.00×10^{-12}		<i>e, A</i>	MCM
G295	$\text{CH}_2\text{IO}_2 + \text{CH}_2\text{IO}_2 \rightarrow 2 \text{CH}_2\text{IO} + \text{O}_2$	1.05×10^{-12}		<i>f</i>	Vil/Les95, Atk08
G296	$\text{CH}_2\text{IO}_2 + \text{NO} \rightarrow \text{CH}_2\text{IO} + \text{NO}_2$	1.10×10^{-11}		<i>f</i>	Atk08
G297	$\text{CH}_2\text{IO}_2\text{H} + \text{OH} \rightarrow \text{CH}_2\text{IO}_2 + \text{H}_2\text{O}$	3.59×10^{-12}	-190	<i>e</i>	MCM
G298	$\text{CH}_2\text{IO}_2\text{H} + \text{OH} \rightarrow \text{CHOI} + \text{OH} + \text{H}_2\text{O}$	5.79×10^{-12}		<i>f</i>	MCM
P _g 55	$\text{CH}_2\text{IO}_2\text{H} \xrightarrow{h\nu} \text{CH}_2\text{IO} + \text{OH}$	(5.79×10^{-6})		estimated same as P _g 17, see Tab. S14	MCM
G299	$\text{CH}_2\text{IOH} + \text{OH} \xrightarrow{\text{O}_2} \text{CHOI} + \text{H}_2\text{O} + \text{HO}_2$	1.06×10^{-12}		<i>f</i>	MCM
G300	$\text{CH}_2\text{IO} + \text{O}_2 \rightarrow \text{CHOI} + \text{HO}_2$	9.48×10^{-15}	550	<i>e</i>	MCM
G301	$\text{CHOI} + \text{OH} \rightarrow \text{I} + \text{CO} + \text{H}_2\text{O}$	1.16×10^{-12}		<i>f</i>	MCM
G302	$\text{CHOI} + \text{Cl} \rightarrow \text{COI} + \text{HCl}$	7.48×10^{-13}	710	<i>e</i>	Atk08
P _g 56	$\text{CHOI} \xrightarrow{h\nu, \text{O}_2} \text{I} + \text{CO} + \text{HO}_2$	(2.71×10^{-7})		estimated same as P _g 18, see Tab. S14	Atk08
G303	$\text{COI} \xrightarrow{\text{M}} \text{CO} + \text{I}$	4.98×10^5	2960	TYP: SPEC4, ^e	Atk07
G304	$\text{CO} + \text{I} \xrightarrow{\text{M}} \text{COI}$	3.33×10^{-14}		TYP: SPEC2; see Tab. S13, ^e	Atk07
P _g 57	$\text{CH}_2\text{ICl} \xrightarrow{h\nu, \text{O}_2} \text{I} + \text{CH}_2\text{ClO}_2$	(2.04×10^{-4})		$\Phi = 1.0$ (estimated); see Tab. S14	Atk08

Table S12 (continued) Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	E_A/R^b	Comment	Reference
P _g 58	$\text{CH}_2\text{IBr} \xrightarrow{h\nu, \text{O}_2} \text{I} + \text{CH}_2\text{BrO}_2$	(6.87×10^{-4})		$\Phi = 1.0$; see Tab. S14	Atk08

[⊕]already implemented in the Halogen Module 1.0; [⊖]update of the Halogen Module 1.0

^ain cm³ molecules⁻¹ s⁻¹ (*slanted* values in parentheses represent j_{max} in s⁻¹ for photolysis reactions); ^bin K; ^cestimated X = H (X = Cl, Br, I); ^dreactions combined; ^eestimated X = Cl (X = Br, I); ^festimated I = Br; ^gimmediate reaction with oxygen; ^himmediate hydrogen abstraction; ⁱestimated
^AMO₂ = methyl peroxy radical; ^BOP1 = methyl hydrogen peroxide; ^CORA1 = formic acid; ^DETH = ethane; ^EETHP = peroxy radical formed from ETH; ^FHC3 = alkanes, alcohols, esters, and alkynes with OH rate constant (298 K, 1 atm) less than 3.4×10^{-12} cm³ molecules⁻¹ s⁻¹; ^GHC3P = peroxy radical formed from HC3; ^HHC5 = alkanes, alcohols, esters, and alkynes with OH rate constant (298 K, 1 atm) between 3.4×10^{-12} cm³ molecules⁻¹ s⁻¹ and 6.8×10^{-12} cm³ molecules⁻¹ s⁻¹; ^IHC5P = peroxy radical formed from HC5; ^JHC8 = alkanes, alcohols, esters, and alkynes with OH rate constant (298 K, 1 atm) greater than 6.8×10^{-12} cm³ molecules⁻¹ s⁻¹; ^KHC8P = peroxy radical formed from HC8; ^LTOL = Toluene and less reactive aromatics; ^MTOLP = peroxy radical formed from TOL; ^NACO₃ = acetylperoxy and higher saturated acylperoxy radicals; ^OALD = higher aldehydes; ^PKET = ketones; ^QKETP = peroxy radical formed from KET; ^RHKET = hydroxy ketone; ^SMGLY = methylglyoxal; ^TGLY = glyoxal; ^UETI = acetylene; ^VETE = ethylene
Atk07 Atkinson et al. (2007); Dem97 DeMore et al. (1997); Cal/Pit66 Calvert and Pitts (1966); San06 Sander et al. (2006); San03 Sander et al. (2003); Kuk94 Kukui et al. (1994); And/Fah90 Mallard et al. (1998) mit Werten von Anderson and Fahey (1990); Atk06 Atkinson et al. (2006); Atk08 Atkinson et al. (2008b); Orl99 Orlando et al. (1999); Gre90 Green et al. (1990); Nik85 Niki et al. (1985); Nik87 Niki et al. (1987); MCM Pilling et al. (2008); IUPAC Atkinson et al. (2008a); See/Bri64 Seery and Britton (1964); Fan/Liu01 Fang and Liu (2001); Fle05 Fleischmann et al. (2005); Orl/Tyn96 Orlando and Tyndall (1996); Bed98 Bedjanian et al. (1998); Bau81 Baulch et al. (1981); Dol/Leo87 Dolson and Leone (1987); Cly/Cru72 Clyne and Cruse (1972); Kon/Ben84 Kondo and Benson (1984); Han99 Hansen et al. (1999); Vil/Les95 Villenave and Lesclaux (1995); Hip73 Hippler et al. (1973); Gla02a von Glasow et al. (2002a) (ESM); Jim03 Jimenez et al. (2003); Gla02b von Glasow et al. (2002a); Cha92 Chambers et al. (1992); Bed96 Bedjanian et al. (1996) Bed97 Bedjanian et al. (1997)

Table S13 Parameters for pressure dependent reactions

	Reaction	TYPE	k_0^a	k_∞^a	F_C^b
G14	$\text{ClO} + \text{ClO} \xrightarrow{\text{M}} \text{Cl}_2\text{O}_2$	TROE	$1.6 \times 10^{-32} (T/300)^{-4.5}$	$2.0 \times 10^{-12} (T/300)^{-2.4}$	
G15	$\text{Cl} + \text{O}_2 \xrightarrow{\text{M}} \text{ClO}_2$	TROE	$2.2 \times 10^{-33} (T/300)^{-3.1}$	1.8×10^{-10}	
G18	$\text{Cl}_2\text{O}_2 \xrightarrow{\text{M}} 2 \text{ClO}$	TROEXP	$3.7 \times 10^{-7} \text{e}^{-7690/T}$	$7.9 \times 10^{15} \text{e}^{-8820/T}$	0,45
G23	$\text{ClO} + \text{OCLO} \xrightarrow{\text{M}} \text{Cl}_2\text{O}_3$	TROE	$6.2 \times 10^{-32} (T/300)^{-4.7}$	2.4×10^{-11}	
G24	$\text{Cl}_2\text{O}_3 \xrightarrow{\text{M}} \text{ClO} + \text{OCLO}$	TROEXP	$1.4 \times 10^{-10} \text{e}^{-3810/T}$	$2.5 \times 10^{12} \text{e}^{-4940/T}$	
G32	$\text{Cl} + \text{NO} \xrightarrow{\text{M}} \text{ClNO}$	SPEC2	$7.6 \times 10^{-32} (T/300)^{-1.8}$		
G34	$\text{Cl} + \text{NO}_2 \xrightarrow{\text{M}} \text{ClNO}_2$	TROE	$1.8 \times 10^{-31} (T/300)^{-2}$	$1.0 \times 10^{-10} (T/300)^{-1}$	

Table S13 (continued) Parameters for pressure dependent reactions

	Reaction	TYPE	k_0^a	k_∞^a	F_C^b
G36	$\text{ClO} + \text{NO}_2 \xrightarrow{\text{M}} \text{ClNO}_3$	TROEF	$1.6 \times 10^{-31}(T/300)^{-3.4}$	7.0×10^{-11}	0.4
G60	$\text{Cl} + \text{ETI}^c \xrightarrow{\text{O}_2, \text{M}}$ $0.26 \text{CHOC}l + 0.21 \text{Cl} + 0.53 \text{HCl} +$ $0.21 \text{GLY}^d + 1.32 \text{CO} + 0.79 \text{HO}_2$	TROE	$6.10 \times 10^{-30}(T/300)^{-3.0}$	2.0×10^{-10}	
G61	$\text{Cl} + \text{ETE}^e \xrightarrow{\text{O}_2, \text{M}} \text{CH}_2\text{ClCH}_2\text{OO}$	TROEF	$1.85 \times 10^{-29}(T/300)^{-3.3}$	6.0×10^{-10}	0.4
G71	$\text{CH}_2\text{ClCO}_3 + \text{NO}_2 \xrightarrow{\text{M}}$ $\text{CH}_2\text{ClC}(\text{O})\text{OONO}_2$	TROEF	$2.7 \times 10^{-28}(T/300)^{-7.1}$	$1.2 \times 10^{-11}(T/300)^{-0.9}$	0.3
G72	$\text{CH}_2\text{ClC}(\text{O})\text{OONO}_2 \xrightarrow{\text{M}}$ $\text{CH}_2\text{ClCO}_3 + \text{NO}_2$	TROEXP	$4.9 \times 10^{-3}\text{e}^{-12100/T}$	$5.4 \times 10^{16}\text{e}^{-13830/T}$	0.3
G77	$\text{Cl} + \text{C}_3\text{H}_6 \xrightarrow{\text{O}_2, \text{M}} \text{CH}_3\text{CHOOCH}_2\text{Cl}$	TROE	4.0×10^{-28}	2.8×10^{-10}	
G106	$\text{CCl}_3\text{CO}_3 + \text{NO}_2 \xrightarrow{\text{M}} \text{CCl}_3\text{C}(\text{O})\text{OONO}_2$	TROEF	$2.7 \times 10^{-28}(T/300)^{-7.1}$	$1.2 \times 10^{-11}(T/300)^{-0.9}$	0.3
G107	$\text{CCl}_3\text{C}(\text{O})\text{OONO}_2 \xrightarrow{\text{M}} \text{CCl}_3\text{CO}_3 + \text{NO}_2$	TROEXP	$4.9 \times 10^{-3}\text{e}^{-12100/T}$	$5.4 \times 10^{16}\text{e}^{-13830/T}$	0.3
G114	$\text{CCl}_3\text{OO} + \text{NO}_2 \xrightarrow{\text{M}} \text{CCl}_3\text{OONO}_2$	TROEF	$9.2 \times 10^{-29}(T/300)^{-6.0}$	$1.5 \times 10^{-12}(T/300)^{-0.7}$	0.32
G115	$\text{CCl}_3\text{OONO}_2 \xrightarrow{\text{M}} \text{CCl}_3\text{OO} + \text{NO}_2$	TROEXP	$4.3 \times 10^{-3}\text{e}^{-10235/T}$	$4.8 \times 10^{16}\text{e}^{-11820/T}$	0.32
G139	$\text{CO} + \text{Cl} \xrightarrow{\text{M}} \text{COCl}$	SPEC2	$1.3 \times 10^{-33}(T/300)^{-3.8}$		
G149	$\text{Br} + \text{NO}_2 \xrightarrow{\text{M}} \text{BrNO}_2$	TROEF	$4.2 \times 10^{-31}(T/300)^{-2.4}$	2.7×10^{-11}	0.55
G152	$\text{BrO} + \text{NO}_2 \xrightarrow{\text{M}} \text{BrNO}_3$	TROEF	$4.7 \times 10^{-31}(T/300)^{-3.1}$	1.8×10^{-11}	0.4
G182	$\text{CH}_2\text{BrCO}_3 + \text{NO}_2 \xrightarrow{\text{M}}$ $\text{CH}_2\text{BrC}(\text{O})\text{OONO}_2$	TROEF	$2.7 \times 10^{-28}(T/300)^{-7.1}$	$1.2 \times 10^{-11}(T/300)^{-0.9}$	0.3
G183	$\text{CH}_2\text{BrC}(\text{O})\text{OONO}_2 \xrightarrow{\text{M}}$ $\text{CH}_2\text{BrCO}_3 + \text{NO}_2$	TROEXP	$4.9 \times 10^{-3}\text{e}^{-12100/T}$	$5.4 \times 10^{16}\text{e}^{-13830/T}$	0.3
G203	$\text{CBr}_3\text{OO} + \text{NO}_2 \xrightarrow{\text{M}} \text{CBr}_3\text{OONO}_2$	TROEF	$9.2 \times 10^{-29}(T/300)^{-6.0}$	$1.5 \times 10^{-12}(T/300)^{-0.7}$	0.32
G204	$\text{CBr}_3\text{OONO}_2 \xrightarrow{\text{M}} \text{CBr}_3\text{OO} + \text{NO}_2$	TROEXP	$4.3 \times 10^{-3}\text{e}^{-10235/T}$	$4.8 \times 10^{16}\text{e}^{-11820/T}$	0.32
G228	$\text{CO} + \text{Br} \xrightarrow{\text{M}} \text{COBr}$	SPEC2	$1.3 \times 10^{-33}(T/300)^{-3.8}$		
G239	$\text{I} + \text{NO} \xrightarrow{\text{M}} \text{INO}$	TROE	$1.8 \times 10^{-32}(T/300)^{-1.0}$	1.7×10^{-11}	
G240	$\text{I} + \text{NO}_2 \xrightarrow{\text{M}} \text{INO}_2$	TROEF	$3.0 \times 10^{-31}(T/300)^{-1.0}$	6.6×10^{-11}	0.63

Table S13 (continued) Parameters for pressure dependent reactions

	Reaction	TYPE	k_0^a	k_∞^a	F_C^b
G244	$\text{IO} + \text{NO}_2 \xrightarrow{\text{M}} \text{INO}_3$	TROEF	$7.7 \times 10^{-31}(T/300)^{-5.0}$	1.6×10^{-11}	0.4
G271	$\text{CH}_2\text{ICO}_3 + \text{NO}_2 \xrightarrow{\text{M}} \text{CH}_2\text{IC(O)OONO}_2$	TROEF	$2.7 \times 10^{-28}(T/300)^{-7.1}$	$1.2 \times 10^{-11}(T/300)^{-0.9}$	0.3
G272	$\text{CH}_2\text{IC(O)OONO}_2 \xrightarrow{\text{M}} \text{CH}_2\text{ICO}_3 + \text{NO}_2$	TROEXP	$4.9 \times 10^{-3}\text{e}^{-12100/T}$	$5.4 \times 10^{16}\text{e}^{-13830/T}$	0.3
G304	$\text{CO} + \text{I} \xrightarrow{\text{M}} \text{COI}$	SPEC2	$1.3 \times 10^{-33}(T/300)^{-3.8}$		

Rate constants calculated with TROE formula: $k(T) = \frac{k_0[\text{M}]}{1 + \frac{k_0[\text{M}]}{k_\infty}} \cdot F_C^{(1+\lg(k_0[\text{M}]/k_\infty))^{-2}}$

^ain $\frac{\text{cm}^3\text{n}}{\text{molecules}^n \text{ s}}$, n = order of reaction; ^bif other than $F_C = 0.6$; ^cETI = acetylene; ^dGLY = glyoxal; ^eETE = ethylene

S3.4 Photolysis reactions

Table S14 Parameters for gas phase photolysis reactions

	Reaction	I/s^{-1}	m	n	Reference/comment
P _g 1 [⊖]	$\text{Cl}_2 \xrightarrow{h\nu} 2\text{Cl}$	3.827×10^{-3}	0.543	0.244	DeMore et al. (1997) with quantum yields from Calvert and Pitts (1966)
P _g 2	$\text{ClO} \xrightarrow{h\nu} \text{Cl} + \text{O}(^3\text{P})$	4.755×10^{-4}	1.258	0.588	Sander et al. (2006) ^a
P _g 3	$\text{OClO} \xrightarrow{h\nu} \text{ClO} + \text{O}(^3\text{P})$	0.133	0.416	0.244	Sander et al. (2006) ^a
P _g 4	$\text{Cl}_2\text{O}_2 \xrightarrow{h\nu} \text{Cl} + \text{ClO}_2$	2.294×10^{-3}	0.745	0.223	Sander et al. (2003) ^a
P _g 5	$\text{Cl}_2\text{O}_3 \xrightarrow{h\nu} \text{ClO} + \text{OClO}$	1.558×10^{-3}	1.324	0.462	further products omitted, Atkinson et al. (2007) ^a
P _g 6 [⊖]	$\text{HOCl} \xrightarrow{h\nu} \text{Cl} + \text{OH}$	4.615×10^{-4}	0.656	0.240	Atkinson et al. (2007)
P _g 7	$\text{ClNO} \xrightarrow{h\nu} \text{Cl} + \text{NO}$	4.755×10^{-3}	0.408	0.217	Atkinson et al. (2007)
P _g 8 [⊖]	$\text{ClNO}_2 \xrightarrow{h\nu} \text{Cl} + \text{NO}_2$	6.219×10^{-4}	0.774	0.255	Atkinson et al. (2007)
P _g 9	$\text{ClNO}_3 \xrightarrow{h\nu} \text{Cl} + \text{NO}_3$	6.420×10^{-5}	0.648	0.217	DeMore et al. (1997)

Table S14 (continued) Parameters for gas phase photolysis reactions

	Reaction	I/s^{-1}	m	n	Reference/comment
P _g 10	$ClNO_3 \xrightarrow{h\nu} ClO + NO_2$	1.393×10^{-5}	1.052	0.243	DeMore et al. (1997)
P _g 11	$CH_3COCH_2Cl \xrightarrow{h\nu} 0.7 COCl + 0.7 ACO_3 + 0.3 CH_2ClCO_3 + 0.3 MO_2 - 1.3 O_2$	1.675×10^{-4}	1.003	0.296	Sander et al. (2006) ^{a, c, d}
P _g 12	$CH_3COCClO \xrightarrow{h\nu, O_2} COCl + ACO_3$	1.853×10^{-4}	0.583	0.225	estimated same as methylglyoxal ^c
P _g 13	$CH_2ClCHO \xrightarrow{h\nu, 2O_2} CH_2ClO_2 + CO + HO_2$	4.642×10^{-5}	0.762	0.353	Pilling et al. (2008)
P _g 14	$CH_2ClCO_3H \xrightarrow{h\nu, O_2} CH_2ClO_2 + CO_2 + OH$	7.649×10^{-6}	0.682	0.279	Pilling et al. (2008)
P _g 15	$CCl_2OHCClO \xrightarrow{h\nu, O_2} COCl_2 + CO + Cl + HO_2$	2.792×10^{-5}	0.805	0.338	Pilling et al. (2008)
P _g 16	$CCl_3CHO \xrightarrow{h\nu, 3/2 O_2} Cl + COCl_2 + CO + HO_2$	1.442×10^{-4}	1.027	0.302	Atkinson et al. (2008b)
P _g 17	$CH_2ClO_2H \xrightarrow{h\nu} CH_2ClO + OH$	7.649×10^{-6}	0.682	0.279	Pilling et al. (2008)
P _g 18	$CHOC l \xrightarrow{h\nu, O_2} Cl + CO + HO_2$	3.905×10^{-7}	1.936	0.362	Atkinson et al. (2008b) with quantum yields from Fang and Liu (2001)
P _g 19 [⊖]	$Br_2 \xrightarrow{h\nu} 2 Br$	4.773×10^{-2}	0.193	0.213	Seery and Britton (1964) with quantum yields from Fang and Liu (2001)
P _g 20	$BrO \xrightarrow{h\nu} Br + O(^3P)$	6.368×10^{-2}	0.605	0.269	Sander et al. (2003)
P _g 21	$OBrO \xrightarrow{h\nu} BrO + O(^3P)$	0.688	0.144	0.198	Sander et al. (2006) with quantum yields from Fleischmann et al. (2005)
P _g 22 [⊖]	$HOBr \xrightarrow{h\nu} Br + OH$	3.464×10^{-3}	0.441	0.214	Sander et al. (2003)
P _g 23 [⊖]	$BrNO_2 \xrightarrow{h\nu} Br + NO_2$	7.443×10^{-3}	0.355	0.236	Atkinson et al. (2007)
P _g 24	$BrNO_3 \xrightarrow{h\nu} Br + NO_3$	1.558×10^{-3}	0.490	0.216	Sander et al. (2003)
P _g 25	$BrNO_3 \xrightarrow{h\nu} BrO + NO_2$	6.363×10^{-4}	0.492	0.215	Sander et al. (2003)
P _g 26 [⊖]	$BrCl \xrightarrow{h\nu} Br + Cl$	1.650×10^{-2}	0.297	0.224	Atkinson et al. (2007)
P _g 27	$CH_3COCH_2Br \xrightarrow{h\nu} 0.7 COBr + 0.7 ACO_3 + 0.3 CH_2BrCO_3 + 0.3 MO_2 - 1.3 O_2$	3.523×10^{-4}	0.885	0.283	Sander et al. (2006) ^{a, c, d}
P _g 28	$CH_3COCBrO \xrightarrow{h\nu, O_2} COBr + ACO_3$	1.853×10^{-4}	0.583	0.225	estimated same as methylglyoxal ^c

Table S14 (continued) Parameters for gas phase photolysis reactions

	Reaction	I/s^{-1}	m	n	Reference/comment
P _g 29	$CH_2BrCHO \xrightarrow{h\nu, 2O_2} CH_2BrO_2 + CO + HO_2$	4.642×10^{-5}	0.762	0.353	estimated same as P _g 13, Pilling et al. (2008)
P _g 30	$CH_2BrCO_3H \xrightarrow{h\nu, O_2} CH_2BrO_2 + CO_2 + OH$	7.649×10^{-6}	0.682	0.279	estimated same as P _g 14, Pilling et al. (2008)
P _g 31	$CHBr_3 \xrightarrow{h\nu, O_2} Br + CHBr_2O_2$	2.228×10^{-6}	1.471	0.230	DeMore et al. (1997)
P _g 32	$CH_2Br_2 \xrightarrow{h\nu, O_2} Br + CH_2BrO_2$	5.600×10^{-9}	2.763	1.922	Atkinson et al. (2008b)
P _g 33	$COBr_2 \xrightarrow{h\nu} 2Br + CO$	4.377×10^{-6}	1.360	0.273	Sander et al. (2006) products estimated same as phosgene from Pilling et al. (2008)
P _g 34	$CH_2BrO_2H \xrightarrow{h\nu} CH_2BrO + OH$	7.649×10^{-6}	0.682	0.279	Pilling et al. (2008)
P _g 35	$CHOBr \xrightarrow{h\nu, O_2} Br + CO + HO_2$	2.547×10^{-5}	1.393	0.361	Sander et al. (2006)
P _g 36	$I_2 \xrightarrow{h\nu} 2I$	0.217	0.125	0.185	Atkinson et al. (2007)
P _g 37	$IO \xrightarrow{h\nu} I + O(^3P)$	2.640×10^{-3}	0.240	0.240	Atkinson et al. (2007)
P _g 38	$OIO \xrightarrow{h\nu} I + O_2$	4.054×10^{-2}	0.119	0.185	Sander et al. (2006)
P _g 39	$OIO \xrightarrow{h\nu} IO + O(^3P)$	1.894×10^{-3}	0.119	0.185	Sander et al. (2006)
P _g 40	$I_2O_2 \xrightarrow{h\nu} 2I + O_2$	2.294×10^{-3}	0.745	0.223	estimated same as P _g 4, products from von Glasow et al. (2002a)
P _g 41	$HI \xrightarrow{h\nu, O_2} I + HO_2$	2.104×10^{-4}	1.123	0.281	Atkinson et al. (2007)
P _g 42	$HOI \xrightarrow{h\nu, O_2} I + OH$	1.469×10^{-2}	0.342	0.236	Atkinson et al. (2007)
P _g 43	$INO \xrightarrow{h\nu} I + NO$	4.849×10^{-3}	0.284	0.232	Sander et al. (2006)
P _g 44	$INO_2 \xrightarrow{h\nu} I + NO_2$	5.036×10^{-3}	0.568	0.256	Sander et al. (2006)
P _g 45	$INO_3 \xrightarrow{h\nu} I + NO_3$	6.599×10^{-2}	0.528	0.244	Sander et al. (2006)
P _g 46	$INO_3 \xrightarrow{h\nu} IO + NO_2$	1.165×10^{-2}	0.528	0.244	Sander et al. (2006)
P _g 47	$ICl \xrightarrow{h\nu} I + Cl$	3.403×10^{-2}	0.179	0.207	Atkinson et al. (2007) ^b
P _g 48	$IBr \xrightarrow{h\nu} I + Br$	0.1	0.149	0.197	Atkinson et al. (2007) ^b
P _g 49	$C_3H_7I \xrightarrow{h\nu, O_2} I + HC_3P$	3.731×10^{-5}	1.292	0.217	Sander et al. (2006) ^{b, e}

Table S14 (continued) Parameters for gas phase photolysis reactions

	Reaction	l/s^{-1}	m	n	Reference/comment
P _g 50	$C_2H_5I \xrightarrow{h\nu, O_2} I + EHP$	1.386×10^{-5}	1.324	0.224	Sander et al. (2006) ^{b, f}
P _g 51	$CH_2ICHO \xrightarrow{h\nu, 2O_2} CH_2IO_2 + CO + HO_2$	4.642×10^{-5}	0.762	0.353	estimated same as P _g 13, Pilling et al. (2008)
P _g 52	$CH_2ICO_3H \xrightarrow{h\nu, O_2} CH_2IO_2 + CO_2 + OH$	7.649×10^{-6}	0.682	0.279	estimated same as P _g 14, Pilling et al. (2008)
P _g 53	$CH_2I_2 \xrightarrow{h\nu, O_2} I + CH_2IO_2$	1.496×10^{-2}	0.801	0.265	Sander et al. (2006) ^b
P _g 54	$CH_3I \xrightarrow{h\nu, O_2} I + MO_2$	1.206×10^{-5}	1.254	0.231	Sander et al. (2006) ^{b, d}
P _g 55	$CH_2IO_2H \xrightarrow{h\nu} CH_2IO + OH$	7.649×10^{-6}	0.682	0.279	estimated same as P _g 17, Pilling et al. (2008)
P _g 56	$CHOI \xrightarrow{h\nu, O_2} I + CO + HO_2$	2.547×10^{-5}	1.393	0.361	estimated same as P _g 35
P _g 57	$CH_2ICl \xrightarrow{h\nu, O_2} I + CH_2ClO_2$	2.038×10^{-4}	1.057	0.238	Atkinson et al. (2008b)
P _g 58	$CH_2IBr \xrightarrow{h\nu, O_2} I + CH_2BrO_2$	8.824×10^{-4}	0.976	0.250	Atkinson et al. (2008b)

Photolysis reactions are parameterised with $j = l \times \cos^m \chi \times \exp \{-n \times \sec \chi\}$.

^aquantum yield estimated with $\Phi = 1$, ^bexcited atoms are treated like atoms in ground state, ^cMO₂ = methyl peroxy radical, ^dACO₃ = acetyl peroxy radical,

^eHC3P = peroxy radical formed from alkanes, alcohols, esters, and alkynes with OH rate constant (298 K, 1 atm) less than $3.4 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$,

^f EHP = ethyl peroxy radical

Table S15 Parameters for aqueous phase photolysis reactions

	Reaction	l/s^{-1}	m	n	Reference/comment
P _a 1	$Cl_2 \xrightarrow{h\nu} 2Cl$	2.548×10^{-5}	0.612	0.298	Zimmerman and Strong (1957) with quantum yields from Grossweiner and Matheson (1955)
P _a 2	$HOCl \xrightarrow{h\nu} Cl + OH$	2.517×10^{-5}	0.892	0.289	Zimmerman and Strong (1957) ^a
P _a 3	$ClO^- \xrightarrow{h\nu, H_2O} Cl + OH^- + OH$	4.205×10^{-4}	0.870	0.284	Anbar and Dostrovsky (1954) with quantum yields from Herrmann (2007)

Table S15 (continued) Parameters for aqueous phase photolysis reactions

	Reaction	l/s^{-1}	m	n	Reference/comment
P _a 4	$\text{Cl}_3^- \xrightarrow{h\nu} \text{Cl}_2 + \text{Cl}^-$	5.140×10^{-4}	0.843	0.103	Zimmerman and Strong (1957) ^a
P _a 5	$\text{Br}_2 \xrightarrow{h\nu} 2 \text{Br}$	4.501×10^{-4}	0.154	0.262	Buckles and Mills (1953) ^b with quantum yields from Grossweiner and Matheson (1955)
P _a 6	$\text{HOBr} \xrightarrow{h\nu} \text{Br} + \text{OH}$	1.396×10^{-4}	0.584	0.289	Anbar and Dostrovsky (1954) ^a
P _a 7	$\text{BrO}^- \xrightarrow{h\nu, \text{H}_2\text{O}} \text{Br} + \text{OH}^- + \text{OH}$	7.510×10^{-4}	0.548	0.300	Anbar and Dostrovsky (1954) ^a
P _a 8	$\text{BrCl} \xrightarrow{h\nu} \text{Br} + \text{Cl}$	6.121×10^{-3}	0.456	0.298	Pungor et al. (1959) ^a
P _a 9	$\text{I}_2 \xrightarrow{h\nu} 2 \text{I}$	1.816×10^{-5}	0.088	0.243	Buckles and Mills (1953) ^b with quantum yields from Grossweiner and Matheson (1955)
P _a 10	$\text{ICl} \xrightarrow{h\nu} \text{I} + \text{Cl}$	3.909×10^{-3}	0.130	0.239	Buckles and Mills (1953) ^{a, b}
P _a 11	$\text{IBr} \xrightarrow{h\nu} \text{I} + \text{Br}$	7.940×10^{-3}	0.108	0.250	Buckles and Mills (1954) ^{a, b}

Photolysis reactions are parameterised with $j = l \times \cos^m \chi \times \exp \{-n \times \sec \chi\}$.

^aquantum yield estimated with $\Phi = 0.1$; ^bestimated with measurement of the extinction coefficient ϵ in the solvent carbon tetrachloride (CCl_4)

S3.5 Aqueous phase chemistry

Table S16 Aqueous phase irreversible reactions

	Reaction	k_{298}^a	E_A/R^b	Comment	Reference
A1	$\text{Cl} + \text{Cl} \rightarrow \text{Cl}_2$	8.75×10^7			Wu80
A2	$\text{Cl}_2^- + \text{Cl} \rightarrow \text{Cl}_2 + \text{Cl}^-$	2.1×10^9			Yu/Bak03
A3 \ominus	$\text{Cl}_2^- + \text{Cl}_2^- \rightarrow \text{Cl}_2 + 2\text{Cl}^-$	1.8×10^9			Jac99
A4	$\text{Cl}^- + \text{O}_3 \rightarrow \text{ClO}^- + \text{O}_2$	3.0×10^{-3}			Hoi85
A5	$\text{Cl} + \text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{Cl}^- + \text{HO}_2$	2.0×10^9			Yu/Bak03
A6 \otimes	$\text{Cl}_2^- + \text{H}_2\text{O}_2 \rightarrow 2\text{Cl}^- + \text{H}^+ + \text{HO}_2$	5×10^4	3340		Jac99
A7 \ominus	$\text{Cl}_2^- + \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{Cl}^- + \text{ClOH}^-$	23.4		revised products from Yu and Barker (2003)	Jac96/Bux98
A8 \otimes	$\text{Cl}_2^- + \text{HO}_2 \rightarrow 2\text{Cl}^- + \text{H}^+ + \text{O}_2$	1.3×10^{10}			Jac96
A9 \otimes	$\text{Cl}_2^- + \text{O}_2^- \rightarrow 2\text{Cl}^- + \text{O}_2$	6.0×10^9			Jac96
A10	$\text{Cl}_2^- + \text{OH} \rightarrow \text{HOCl} + \text{Cl}^-$	1.0×10^9			Wag86
A11 \otimes	$\text{Cl}_2^- + \text{OH}^- \rightarrow 2\text{Cl}^- + \text{OH}$	4.0×10^6			Jac96
A12	$\text{Cl}_3^- + \text{HO}_2 \rightarrow \text{Cl}_2^- + \text{H}^+ + \text{Cl}^- + \text{O}_2$	1.0×10^9			Bje81
A13	$\text{Cl}_3^- + \text{O}_2^- \rightarrow \text{Cl}_2^- + \text{Cl}^- + \text{O}_2$	3.8×10^9		estimated	Mat/Ana06
P _a 4	$\text{Cl}_3^- \xrightarrow{h\nu} \text{Cl}_2 + \text{Cl}^-$	(4.64×10^{-4})		$\Phi = 0.1^c$; see Tab. S15	Zim/Str57
A14 \oplus	$\text{Cl}_2 + \text{HO}_2 \rightarrow \text{Cl}_2^- + \text{H}^+ + \text{O}_2$	1.0×10^9			Bje81
A15 \oplus	$\text{Cl}_2 + \text{O}_2^- \rightarrow \text{Cl}_2^- + \text{O}_2$	1.0×10^9		estimated ($k_{\text{A15}} \approx k_{\text{A14}}$)	Her03
P _a 1	$\text{Cl}_2 \xrightarrow{h\nu} 2\text{Cl}$	(1.89×10^{-5})		$\Phi = 0.01^{\text{Gro/Mat55}}$; see Tab. S15	Zim/Str57
A16	$\text{HOCl} + \text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{Cl}^- + \text{H}_2\text{O} + \text{O}_2$	1.1×10^4			Con47
A17	$\text{ClO}^- + \text{H}_2\text{O}_2 \rightarrow \text{Cl}^- + \text{H}_2\text{O} + \text{O}_2$	1.7×10^5			Con47
A18 \oplus	$\text{HOCl} + \text{HO}_2 \rightarrow \text{Cl} + \text{H}_2\text{O} + \text{O}_2$	7.5×10^6		estimated ($k_{\text{A18}} \approx k_{\text{A19}}$)	Her03
A19 \oplus	$\text{HOCl} + \text{O}_2^- \rightarrow \text{Cl} + \text{OH}^- + \text{O}_2$	7.5×10^6			Lon/Bie80
A20	$\text{ClO}^- + \text{O}_2^- \xrightarrow{\text{H}_2\text{O}} \text{Cl} + 2\text{OH}^- + \text{O}_2$	2.0×10^8		estimated	Mat/Ana06
A21 \oplus	$\text{HOCl} + \text{OH} \rightarrow \text{ClO} + \text{H}_2\text{O}$	2.0×10^9		estimated ($k_{\text{A21}} \approx k_{\text{A105}}$)	Her03
A22	$\text{ClO}^- + \text{OH} \rightarrow \text{ClO} + \text{OH}^-$	8.8×10^9			Bux/Sub72

Table S16 (continued) Aqueous phase irreversible reactions

	Reaction	k_{298}^a	E_A/R^b	Comment	Reference
P_a2	$\text{HOCl} \xrightarrow{h\nu} \text{Cl} + \text{OH}$	(1.89×10^{-5})		$\Phi = 0.1^c$; see Tab. S15	<i>Anb/Dos54</i>
P_a3	$\text{ClO}^- \xrightarrow{h\nu} \text{Cl} + \text{OH}^- + \text{OH}$	(3.17×10^{-4})		$\Phi = 4.8155 \cdot \exp\{-0.0113\lambda\}$, fit to measurements of Herrmann (2007) ; see Tab. S15	<i>Zim/Str57</i>
A23 \otimes	$\text{Cl}_2^- + \text{HSO}_3^- \rightarrow 2 \text{Cl}^- + \text{H}^+ + \text{SO}_3^-$	1.7×10^8	400		<i>Jacua96</i>
A24 \otimes	$\text{Cl}_2^- + \text{SO}_3^{2-} \rightarrow 2 \text{Cl}^- + \text{SO}_3^-$	6.2×10^7			<i>Jacua96</i>
A25	$\text{HOCl} + \text{SO}_3^{2-} \rightarrow \text{Cl}^- + \text{HSO}_4^-$	7.6×10^8			<i>Fog89</i>
A26 \oplus	$\text{HOCl} + \text{HSO}_3^- \rightarrow \text{Cl}^- + \text{H}^+ + \text{HSO}_4^-$	7.6×10^8		estimated ($k_{\text{A26}} \approx k_{\text{A25}}$)	<i>Her03</i>
A27	$\text{Cl}^- + \text{HSO}_5^- \rightarrow \text{HOCl} + \text{SO}_4^{2-}$	1.8×10^{-3}	7352		<i>For60</i>
A28 \otimes	$\text{Cl}_2^- + \text{CH}_2\text{OH}\text{SO}_3^- \rightarrow 2 \text{Cl}^- + \text{CH}_2\text{OH}\text{SO}_3$	5.0×10^5			<i>Bar97</i>
A29 \otimes	$\text{Cl}_2^- + \text{NO}_2^- \rightarrow 2 \text{Cl}^- + \text{NO}_2$	6.0×10^7			<i>Jac96</i>
A30 \otimes	$\text{Cl}^- + \text{NO}_2^+ \rightarrow \text{ClNO}_2$	1.0×10^{10}			<i>Geo99</i>
A31 \otimes	$\text{Cl}_2^- + \text{Fe}^{2+} \rightarrow 2 \text{Cl}^- + \text{Fe}^{3+}$	1.0×10^7	3030		<i>Tho/Lau73</i>
A32 \otimes	$\text{Cl}_2^- + \text{Fe}^{2+} \rightarrow \text{FeCl}^{2+} + \text{Cl}^-$	4.0×10^6	3490		<i>Tho/Lau73</i>
A33 \otimes	$\text{Cl}^- + \text{FeO}^{2+} \xrightarrow{\text{H}_2\text{O}} \text{Fe}^{3+} + \text{ClOH}^- + \text{OH}^-$	100			<i>Jacs98</i>
A34 \otimes	$\text{Cl}_2^- + \text{Mn}^{2+} \rightarrow \text{MnCl}_2^+$	2.0×10^7	4090		<i>Lau/Tho73</i>
A35 \otimes	$\text{MnCl}_2^+ \rightarrow \text{Cl}_2^- + \text{Mn}^{2+}$	3.0×10^5			<i>Lau/Tho73</i>
A36 \otimes	$\text{MnCl}_2^+ \rightarrow 2 \text{Cl}^- + \text{Mn}^{3+}$	2.1×10^5			<i>Lau/Tho73</i>
A37 \otimes	$\text{Cl}_2^- + \text{Cu}^+ \rightarrow 2 \text{Cl}^- + \text{Cu}^{2+}$	1.0×10^8		estimated ($k_{\text{A37}} \approx 10 \cdot k_{\text{A31}}$)	
A38	$\text{Cl} + \text{CO}_3^{2-} \rightarrow \text{Cl}^- + \text{CO}_3^-$	5.0×10^8			<i>Mer/Son95</i>
A39	$\text{Cl} + \text{HCO}_3^- \rightarrow \text{Cl}^- + \text{H}^+ + \text{CO}_3^-$	2.2×10^8			<i>Mer/Son95</i>
A40 \otimes	$\text{Cl}_2^- + \text{CO}_3^{2-} \rightarrow 2 \text{Cl}^- + \text{CO}_3^-$	2.7×10^6		estimated	
A41 \otimes	$\text{Cl}_2^- + \text{HCO}_3^- \rightarrow 2 \text{Cl}^- + \text{H}^+ + \text{CO}_3^-$	2.7×10^6		estimated	
A42 \otimes	$\text{Cl}_2^- + \text{CH}_3\text{OOH} \rightarrow \text{H}^+ + 2 \text{Cl}^- + \text{CH}_3\text{OO}$	5.0×10^4	3340	estimated ($k_{\text{A42}} \approx k_{\text{A6}}$)	
A43	$\text{Cl} + \text{CH}_3\text{OH} \rightarrow \text{H}^+ + \text{Cl}^- + \text{CH}_2\text{OH}$	1.0×10^9	4089		<i>Wic03</i>
A44 \odot	$\text{Cl}_2^- + \text{CH}_3\text{OH} \rightarrow \text{H}^+ + 2 \text{Cl}^- + \text{CH}_2\text{OH}$	5.1×10^4	5533		<i>Jac99</i>
A45	$\text{Cl} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{H}^+ + \text{Cl}^- + \text{CH}_3\text{CHOH}$	1.6×10^9			<i>Par06</i>

Table S16 (continued) Aqueous phase irreversible reactions

	Reaction	k_{298}^a	E_A/R^b	Comment	Reference
A46 \otimes	$\text{Cl}_2^- + \text{C}_2\text{H}_5\text{OH} \rightarrow 2\text{Cl}^- + \text{H}^+ + \text{CH}_3\text{CHOH}$	1.2×10^5		better reference	Jac99
A47	$\text{Cl} + \text{C}_3\text{H}_7\text{OH} \rightarrow \text{H}^+ + \text{Cl}^- + \text{C}_2\text{H}_5\text{CHOH}$	2.2×10^9	2285		Wic03
A48	$\text{Cl}_2^- + \text{C}_3\text{H}_7\text{OH} \rightarrow 2\text{Cl}^- + \text{H}^+ + \text{C}_2\text{H}_5\text{CHOH}$	1.0×10^5			Jac99
A49	$\text{Cl} + \text{CH}_3\text{CHOHCH}_3 \rightarrow$ $\text{H}^+ + \text{Cl}^- + \text{CH}_3\text{COHCH}_3$	3.2×10^9	2766		Wic03
A50	$\text{Cl}_2^- + \text{CH}_3\text{CHOHCH}_3 \rightarrow$ $2\text{Cl}^- + \text{H}^+ + \text{CH}_3\text{COHCH}_3$	1.9×10^5			Jac99
A51	$\text{Cl} + \text{CH}_2(\text{OH})_2 \rightarrow \text{H}^+ + \text{Cl}^- + \text{CH}(\text{OH})_2$	1.4×10^9	3127	hydration calculated from K with ~ 1	Wic03
A52 \otimes	$\text{Cl}_2^- + \text{CH}_2(\text{OH})_2 \rightarrow 2\text{Cl}^- + \text{H}^+ + \text{CH}(\text{OH})_2$	3.6×10^4	4330		Jac99
A53	$\text{Cl} + \text{CH}_3\text{CHO} \rightarrow \text{H}^+ + \text{Cl}^- + \text{CH}_3\text{CO}$	6.0×10^8	1928		Par06
A54	$\text{Cl} + \text{CH}_3\text{CH}(\text{OH})_2 \rightarrow$ $\text{H}^+ + \text{Cl}^- + \text{CH}_3\text{C}(\text{OH})_2$	6.0×10^8	1928	hydration calculated from K with 1:1	Par06
A55 \otimes	$\text{Cl}_2^- + \text{CH}_3\text{CHO} \rightarrow 2\text{Cl}^- + \text{H}^+ + \text{CH}_3\text{CO}$	4.0×10^4			Jac96
A56 \otimes	$\text{Cl}_2^- + \text{CH}_3\text{CH}(\text{OH})_2 \rightarrow$ $\text{H}^+ + 2\text{Cl}^- + \text{CH}_3\text{C}(\text{OH})_2$	4.0×10^4			Jac96
A57	$\text{Cl} + \text{C}_2\text{H}_5\text{CHO} \rightarrow \text{H}^+ + \text{Cl}^- + \text{C}_2\text{H}_5\text{CO}$	7.5×10^8	1566		Par06
A58	$\text{Cl} + \text{C}_2\text{H}_5\text{CH}(\text{OH})_2 \rightarrow$ $\text{H}^+ + \text{Cl}^- + \text{C}_2\text{H}_5\text{C}(\text{OH})_2$	7.5×10^8	1566	hydration calculated from K with 1:1	Par06
A59	$\text{Cl} + \text{C}_3\text{H}_7\text{CHO} \rightarrow \text{H}^+ + \text{Cl}^- + \text{C}_3\text{H}_7\text{CO}$	2.2×10^9	1686	hydration calculated from K with 2:1	Par06
A60	$\text{Cl} + \text{C}_3\text{H}_7\text{CH}(\text{OH})_2 \rightarrow$ $\text{H}^+ + \text{Cl}^- + \text{C}_3\text{H}_7\text{C}(\text{OH})_2$	1.1×10^9	1686	(unhydrated/hydrated)	Par06
A61	$\text{Cl} + \text{CH}_3\text{COCH}_3 \rightarrow \text{H}^+ + \text{Cl}^- + \text{CH}_3\text{COCH}_2$	7.8×10^7			Wic03
A62	$\text{Cl}_2^- + \text{CH}_3\text{COCH}_3 \rightarrow$ $2\text{Cl}^- + \text{H}^+ + \text{CH}_3\text{COCH}_2$	1.4×10^3			Jac99
A63	$\text{Cl} + \text{HCOOH} \rightarrow \text{H}^+ + \text{Cl}^- + \text{COOH}$	2.8×10^9	2405		Wic03
A64	$\text{Cl} + \text{HCOO}^- \rightarrow \text{Cl}^- + \text{COOH}$	4.2×10^9	1924		Bux00
A65 \otimes	$\text{Cl}_2^- + \text{HCOOH} \rightarrow 2\text{Cl}^- + \text{H}^+ + \text{COOH}$	8.0×10^4	4450		Jac99
A66 \otimes	$\text{Cl}_2^- + \text{HCOO}^- \rightarrow 2\text{Cl}^- + \text{COOH}$	1.3×10^6			Jac99

Table S16 (continued) Aqueous phase irreversible reactions

	Reaction	k_{298}^a	E_A/R^b	Comment	Reference
A67	$\text{Cl} + \text{CH}_3\text{COOH} \rightarrow \text{H}^+ + \text{Cl}^- + \text{CH}_2\text{COOH}$	1.0×10^8	4930		Wic03
A68	$\text{Cl} + \text{CH}_3\text{COO}^- \rightarrow \text{Cl}^- + \text{CH}_3 + \text{CO}_2$	3.7×10^9	1684		Bux00
A69 \otimes	$\text{Cl}_2^- + \text{CH}_3\text{COOH} \rightarrow$ $2\text{Cl}^- + \text{H}^+ + \text{CH}_2\text{COOH}$	1.5×10^3	4930		Jac99
A70 \otimes	$\text{Cl}_2^- + \text{CH}_3\text{COO}^- \rightarrow 2\text{Cl}^- + \text{CH}_3 + \text{CO}_2$	2.6×10^5	4800		Jac99
A71	$\text{Cl} + \text{C}_2\text{H}_5\text{COOH} \rightarrow$ $\text{H}^+ + \text{Cl}^- + \text{CH}_3\text{CHCOOH}$	1.2×10^9	5292		Wic03
A72	$\text{Cl} + \text{C}_2\text{H}_5\text{COO}^- \rightarrow \text{Cl}^- + \text{CH}_3\text{CHCOO}^-$	1.2×10^9	5292	estimated ($k_{\text{A72}} \approx k_{\text{A71}}$)	
A73 \otimes	$\text{Cl}_2^- + \text{HC}_2\text{O}_4^- \rightarrow 2\text{Cl}^- + \text{H}^+ + \text{C}_2\text{O}_4^-$	1.3×10^6		estimated (ETR)	
A74 \otimes	$\text{Cl}_2^- + \text{C}_2\text{O}_4^{2-} \rightarrow 2\text{Cl}^- + \text{C}_2\text{O}_4^-$	4.0×10^6		estimated (ETR)	
A75 \otimes	$\text{Cl}_2^- + \text{CH}(\text{OH})_2\text{CH}(\text{OH})_2 \rightarrow$ $2\text{Cl}^- + \text{H}^+ + \text{C}(\text{OH})_2\text{CH}(\text{OH})_2$	4.0×10^4			
A76 \otimes	$\text{Cl}_2^- + \text{CH}(\text{OH})_2\text{C}(\text{O})\text{OH} \rightarrow$ $2\text{Cl}^- + \text{H}^+ + \text{C}(\text{OH})_2\text{C}(\text{O})\text{OH}$	4.0×10^4		estimated ($k_{\text{A76}} \approx k_{\text{A75}}$)	
A77	$\text{CH}_2\text{ClC}(\text{OH})_2\text{O}_2 \rightarrow \text{CH}_2\text{ClCOOH} + \text{HO}_2$	1.0×10^3		estimated (Cl = H)	
A78	$\text{CH}_2\text{ClC}(\text{OH})_2\text{O}_2 \rightarrow$ $\text{CH}_2\text{ClCOO}^- + 2\text{H}^+ + \text{O}_2^-$	1.0×10^5		estimated (Cl = H)	
A79	$\text{CH}_3\text{COCClO} + \text{H}_2\text{O} \rightarrow$ $\text{CH}_3\text{COCO}^\circ\text{H} + \text{H}^+ + \text{Cl}^-$	350		estimated same as acetyl chloride	Pra01
A80	$\text{CHOC}^\circ\text{Cl} \rightarrow \text{CO} + \text{H}^+ + \text{Cl}^-$	1.0×10^4			Pra01
A81	$\text{CHOC}^\circ\text{Cl} + \text{OH}^- \rightarrow \text{HCOO}^- + \text{H}^+ + \text{Cl}^-$	2.5×10^4			Pra01
A82	$\text{COCl}_2 + \text{H}_2\text{O} \rightarrow \text{ClCOOH} + \text{H}^+ + \text{Cl}^-$	10			Pra01
A83	$\text{COCl}_2 + \text{OH}^- \rightarrow \text{ClCOOH} + \text{Cl}^-$	2.8×10^4			Pra01
A84	$\text{ClCOOH} \rightarrow \text{CO}_2 + \text{H}^+ + \text{Cl}^-$	1.0×10^5		lower limit	Pra01
A85	$\text{Br} + \text{Br} \rightarrow \text{Br}_2$	1.0×10^9		estimated	Kla/Wol85
A86 \otimes	$\text{Br}_2^- + \text{Br}_2^- \rightarrow \text{Br}_2 + 2\text{Br}^-$	1.7×10^9			Ree99
A87	$\text{Br}^- + \text{O}_3 \rightarrow \text{BrO}^- + \text{O}_2$	210	4450		Haa/Hoi83
A88	$\text{Br} + \text{HO}_2 \rightarrow \text{H}^+ + \text{Br}^- + \text{O}_2$	1.6×10^8			Wag/Str87

Table S16 (continued) Aqueous phase irreversible reactions

	Reaction	k_{298}^a	E_A/R^b	Comment	Reference
A89	$\text{Br} + \text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{Br}^- + \text{HO}_2$	4.0×10^9			<i>Sut65</i>
A90 \oplus	$\text{Br}_2 + \text{HO}_2 \rightarrow \text{H}^+ + \text{Br}_2^- + \text{O}_2$	1.1×10^8			<i>Sut/Dow72</i>
A91 \oplus	$\text{Br}_2 + \text{O}_2^- \rightarrow \text{Br}_2^- + \text{O}_2$	5.6×10^9			<i>Sut/Dow72</i>
A92	$\text{Br}_2 + \text{H}_2\text{O}_2 \rightarrow 2\text{H}^+ + 2\text{Br}^- + \text{O}_2$	1.3×10^3			<i>Wag/Str87</i>
A93	$\text{Br}_2^- + \text{OH} \rightarrow \text{Br}^- + \text{HOBr}$	1.0×10^9			<i>Wag/Str87</i>
A94 \otimes	$\text{Br}_2^- + \text{OH}^- \rightarrow 2\text{Br}^- + \text{OH}$	1.1×10^4			<i>Jac96</i>
A95 \oslash	$\text{Br}_2^- + \text{HO}_2 \rightarrow 2\text{Br}^- + \text{H}^+ + \text{O}_2$	4.4×10^9			<i>Mat03</i>
A96	$\text{Br}_2^- + \text{HO}_2 \xrightarrow{\text{H}^+} \text{Br}_2 + \text{H}_2\text{O}_2$	4.4×10^9			<i>Mat03</i>
A97 \otimes	$\text{Br}_2^- + \text{O}_2^- \rightarrow 2\text{Br}^- + \text{O}_2$	1.7×10^8			<i>Wag/Str87</i>
A98 \otimes	$\text{Br}_2^- + \text{H}_2\text{O}_2 \rightarrow 2\text{Br}^- + \text{H}^+ + \text{HO}_2$	1.0×10^5			<i>Ree97</i>
P _a 5	$\text{Br}_2 \xrightarrow{h\nu} 2\text{Br}$	(3.46×10^{-4})		$\Phi = 0.01^{\text{Gro/Mat55}}$; ϵ estimated with measurement in CCl_4 ; see Tab. S15	<i>Buc/Mil53</i>
A99	$\text{Br}_3^- + \text{HO}_2 \rightarrow \text{Br}_2^- + \text{H}^+ + \text{Br}^- + \text{O}_2$	1.0×10^7			<i>Sut/Dow72</i>
A100	$\text{Br}_3^- + \text{O}_2^- \rightarrow \text{Br}_2^- + \text{Br}^- + \text{O}_2$	3.8×10^9			<i>Sut/Dow72</i>
A101 \oplus	$\text{BrO} + \text{BrO} \xrightarrow{\text{H}_2\text{O}} \text{BrO}_2^- + \text{BrO}^- + 2\text{H}^+$	2.8×10^9			<i>Kla/Wol85</i>
A102 \oplus	$\text{BrO}_2^- + \text{BrO} \rightarrow \text{BrO}_2 + \text{BrO}^-$	4.0×10^8			<i>Ami/Tre70</i>
A103 \oplus	$\text{Br}_2^- + \text{BrO}_2^- \rightarrow 2\text{Br}^- + \text{BrO}_2$	8.0×10^7			<i>Bux/Dai68</i>
A104 \oplus	$\text{BrO}_2^- + \text{OH} \rightarrow \text{BrO}_2 + \text{OH}^-$	1.8×10^9			<i>Bux/Dai68</i>
A105 \oplus	$\text{HOBr} + \text{OH} \rightarrow \text{BrO} + \text{H}_2\text{O}$	2.0×10^9			<i>Kla/Wol85</i>
A106	$\text{BrO}^- + \text{OH} \rightarrow \text{BrO} + \text{OH}^-$	4.5×10^9			<i>Bux/Dai68</i>
A107 \oplus	$\text{HOBr} + \text{HO}_2 \rightarrow \text{Br} + \text{H}_2\text{O} + \text{O}_2$	1.0×10^9		estimated	<i>Sut/Dow72</i>
A108 \oplus	$\text{HOBr} + \text{O}_2^- \rightarrow \text{Br} + \text{OH}^- + \text{O}_2$	3.5×10^9			<i>Schw/Bie86</i>
A109	$\text{BrO}^- + \text{O}_2^- \xrightarrow{\text{H}_2\text{O}} \text{Br} + 2\text{OH}^- + \text{O}_2$	2.0×10^8		upper limit	<i>Schw/Bie86</i>
A110	$\text{HOBr} + \text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{Br}^- + \text{H}_2\text{O} + \text{O}_2$	3.5×10^6			<i>You50</i>
A111	$\text{BrO}^- + \text{H}_2\text{O}_2 \rightarrow \text{Br}^- + \text{H}_2\text{O} + \text{O}_2$	2.0×10^5		estimated	<i>Mat/Ana06</i>
P _a 6	$\text{HOBr} \xrightarrow{h\nu} \text{Br} + \text{OH}$	(1.05×10^{-4})		$\Phi = 0.1^c$; see Tab. S15	<i>Anb/Dos54</i>

Table S16 (continued) Aqueous phase irreversible reactions

	Reaction	k_{298}^a	E_A/R^b	Comment	Reference
P_a7	$\text{BrO}^- \xrightarrow{h\nu} \text{Br} + \text{OH}^- + \text{OH}$	(5.56×10^{-4})		$\Phi = 0.1^c$; see Tab. S15	<i>Anb/Dos54</i>
A112 \otimes	$\text{Br}_2^- + \text{HSO}_3^- \rightarrow 2\text{Br}^- + \text{H}^+ + \text{SO}_3^-$	5.0×10^7	780		<i>Jac96</i>
A113 \otimes	$\text{Br}_2^- + \text{SO}_3^{2-} \rightarrow 2\text{Br}^- + \text{SO}_3^-$	3.3×10^7	650		<i>Jac96</i>
A114 \otimes	$\text{Br}^- + \text{SO}_4^- \rightarrow \text{Br} + \text{SO}_4^{2-}$	2.1×10^9			<i>Her97</i>
A115	$\text{HOBr} + \text{SO}_3^{2-} \rightarrow \text{Br}^- + \text{HSO}_4^-$	5.0×10^9			<i>Tro/Mar91</i>
A116 \oplus	$\text{HOBr} + \text{HSO}_3^- \rightarrow \text{H}^+ + \text{Br}^- + \text{HSO}_4^-$	5.0×10^9		estimated ($k_{\text{A116}} \approx k_{\text{A115}}$)	<i>Fog89</i>
A117	$\text{Br}^- + \text{HSO}_5^- \rightarrow \text{HOBr} + \text{SO}_4^{2-}$	1.0	5338		<i>For60</i>
A118 \otimes	$\text{Br}_2^- + \text{CH}_2\text{OH}\text{SO}_3^- \rightarrow 2\text{Br}^- + \text{CH}_2\text{OH}\text{SO}_3$	5.0×10^4		estimated ($k_{\text{A118}} \approx 0.1 \cdot k_{\text{A28}}$)	
A119 \otimes	$\text{Br}^- + \text{NO}_3 \rightarrow \text{Br} + \text{NO}_3^-$	3.8×10^9			<i>Zel96</i>
A120 \otimes	$\text{Br}_2^- + \text{NO}_2^- \rightarrow 2\text{Br}^- + \text{NO}_2$	1.2×10^7	1720		<i>Jac96</i>
A121 \otimes	$\text{Br}^- + \text{NO}_2^+ \rightarrow \text{BrNO}_2$	1.0×10^{10}			<i>Geo99</i>
A122 \otimes	$\text{Br}^- + \text{BrNO}_2 \rightarrow \text{Br}_2 + \text{NO}_2^-$	2.55×10^4			<i>Geo99</i>
A123 \otimes	$\text{Br}_2^- + \text{Fe}^{2+} \rightarrow 2\text{Br}^- + \text{Fe}^{3+}$	3.6×10^6	3330		<i>Tho/Lau73</i>
A124 \otimes	$\text{MnBr}_2^+ \rightarrow 2\text{Br}^- + \text{Mn}^{3+}$	2.2×10^5			<i>Tho/Lau73</i>
A125 \otimes	$\text{Br}_2^- + \text{Mn}^{2+} \rightarrow \text{MnBr}_2^+$	6.3×10^6	4330		<i>Tho/Lau73</i>
A126 \otimes	$\text{MnBr}_2^+ \rightarrow \text{Br}_2^- + \text{Mn}^{2+}$	3.0×10^5			<i>Tho/Lau73</i>
A127 \otimes	$\text{Br}_2^- + \text{Cu}^+ \rightarrow 2\text{Br}^- + \text{Cu}^{2+}$	3.6×10^6		estimated ($k_{\text{A127}} \approx k_{\text{A123}}$)	
A128	$\text{Br} + \text{HCO}_3^- \rightarrow \text{H}^+ + \text{Br}^- + \text{CO}_3^-$	1.0×10^6		estimated	<i>Mat/Ana06</i>
A129	$\text{Br}_2^- + \text{CO}_3^{2-} \rightarrow 2\text{Br}^- + \text{CO}_3^-$	1.1×10^5			<i>Hui91</i>
A130 \otimes	$\text{Br}_2^- + \text{HCO}_3^- \rightarrow 2\text{Br}^- + \text{H}^+ + \text{CO}_3^-$	1.1×10^5		estimated	
A131	$\text{Br}_2^- + \text{Cl}_2^- \rightarrow \text{Br}_2 + 2\text{Cl}^-$	4.0×10^9		estimated	<i>Mat/Ana06</i>
A132 \oplus	$\text{Br}^- + \text{HOCl} \xrightarrow{\text{H}^+} \text{BrCl} + \text{H}_2\text{O}$	1.3×10^6			<i>Kum/Mar87</i>
A133	$\text{Br}^- + \text{ClO}^- \xrightarrow{\text{H}^+} \text{BrCl} + \text{OH}^-$	3.65×10^{10}			<i>Kum/Mar87</i>
A134 \otimes	$\text{Br}^- + \text{ClNO}_2 \rightarrow \text{BrCl} + \text{NO}_2^-$	5.0×10^6			<i>Geo99</i>
A135 \otimes	$\text{BrNO}_2 + \text{Cl}^- \rightarrow \text{BrCl} + \text{NO}_2^-$	10			<i>Geo99</i>
P_a8	$\text{BrCl} \xrightarrow{h\nu} \text{Br} + \text{Cl}$	(4.54×10^{-3})		$\Phi = 0.1^c$; see Tab. S15	<i>Pun59</i>

Table S16 (continued) Aqueous phase irreversible reactions

	Reaction	k_{298}^a	E_A/R^b	Comment	Reference
A136 \otimes	$\text{Br}_2^- + \text{CH}_3\text{OOH} \rightarrow 2\text{Br}^- + \text{H}^+ + \text{CH}_3\text{OO}$	1.0×10^5		estimated ($k_{\text{A136}} \approx k_{\text{A98}}$)	
A137	$\text{Br} + \text{CH}_3\text{OH} \rightarrow \text{H}^+ + \text{Br}^- + \text{CH}_2\text{OH}$	4.1×10^4	3368		Par06
A138 \otimes	$\text{Br}_2^- + \text{CH}_3\text{OH} \rightarrow 2\text{Br}^- + \text{H}^+ + \text{CH}_2\text{OH}$	1.0×10^3			Ree97
A139	$\text{Br} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{H}^+ + \text{Br}^- + \text{CH}_3\text{CHOH}$	8.2×10^5	2285		Par06
A140 \otimes	$\text{Br}_2^- + \text{C}_2\text{H}_5\text{OH} \rightarrow 2\text{Br}^- + \text{H}^+ + \text{CH}_3\text{CHOH}$	3.8×10^3			Ree99
A141	$\text{Br} + \text{C}_3\text{H}_7\text{OH} \rightarrow \text{H}^+ + \text{Br}^- + \text{C}_2\text{H}_5\text{CHOH}$	3.8×10^5	1564		Par06
A142	$\text{Br} + \text{CH}_3\text{CHOHCH}_3 \rightarrow$ $\text{H}^+ + \text{Br}^- + \text{CH}_3\text{COHCH}_3$	1.8×10^6	3127		Par06
A143	$\text{Br} + \text{CH}_2(\text{OH})_2 \rightarrow \text{H}^+ + \text{Br}^- + \text{CH}(\text{OH})_2$	3.0×10^5	3608	hydration calculated from K with ~ 1	Par06
A144 \otimes	$\text{Br}_2^- + \text{CH}_2(\text{OH})_2 \rightarrow 2\text{Br}^- + \text{H}^+ + \text{CH}(\text{OH})_2$	3.0×10^3		estimated	
A145	$\text{Br} + \text{CH}_3\text{CHO} \rightarrow \text{H}^+ + \text{Br}^- + \text{CH}_3\text{CO}$	1.75×10^7	1804		Par06
A146	$\text{Br} + \text{CH}_3\text{CH}(\text{OH}_2) \rightarrow$ $\text{H}^+ + \text{Br}^- + \text{CH}_3\text{C}(\text{OH}_2)$	1.75×10^7	1804	hydration calculated from K with 1:1	Par06
A147 \otimes	$\text{Br}_2^- + \text{CH}_3\text{CHO} \rightarrow 2\text{Br}^- + \text{H}^+ + \text{CH}_3\text{CO}$	2.15×10^5	2526		Par06
A148 \otimes	$\text{Br}_2^- + \text{CH}_3\text{CH}(\text{OH})_2 \rightarrow$ $2\text{Br}^- + \text{H}^+ + \text{CH}_3\text{C}(\text{OH})_2$	2.15×10^5	2526		Par06
A149	$\text{Br} + \text{C}_2\text{H}_5\text{CHO} \rightarrow \text{H}^+ + \text{Br}^- + \text{C}_2\text{H}_5\text{CO}$	2.85×10^7	842		Par06
A150	$\text{Br} + \text{C}_2\text{H}_5\text{CH}(\text{OH}_2) \rightarrow$ $\text{H}^+ + \text{Br}^- + \text{C}_2\text{H}_5\text{C}(\text{OH}_2)$	2.85×10^7	842	hydration calculated from K with 1:1	Par06
A151	$\text{Br}_2^- + \text{C}_2\text{H}_5\text{CHO} \rightarrow 2\text{Br}^- + \text{H}^+ + \text{C}_2\text{H}_5\text{CO}$	4.95×10^5	3614		Par06
A152	$\text{Br}_2^- + \text{C}_2\text{H}_5\text{CH}(\text{OH}_2) \rightarrow$ $2\text{Br}^- + \text{H}^+ + \text{C}_2\text{H}_5\text{C}(\text{OH}_2)$	4.95×10^5	3614		Par06
A153	$\text{Br} + \text{C}_3\text{H}_7\text{CHO} \rightarrow \text{H}^+ + \text{Br}^- + \text{C}_3\text{H}_7\text{CO}$	6.67×10^7	1203	hydration calculated from K with 2:1	Par06
A154	$\text{Br} + \text{C}_3\text{H}_7\text{CH}(\text{OH}_2) \rightarrow$ $\text{H}^+ + \text{Br}^- + \text{C}_3\text{H}_7\text{C}(\text{OH}_2)$	3.33×10^7	1203	(unhydrated/hydrated)	Par06
A155	$\text{Br}_2^- + \text{C}_3\text{H}_7\text{CHO} \rightarrow 2\text{Br}^- + \text{H}^+ + \text{C}_3\text{H}_7\text{CO}$	2.6×10^5	2289		Par06
A156	$\text{Br}_2^- + \text{C}_3\text{H}_7\text{CH}(\text{OH}_2) \rightarrow$ $2\text{Br}^- + \text{H}^+ + \text{C}_3\text{H}_7\text{C}(\text{OH}_2)$	1.3×10^5	2289		Par06

Table S16 (continued) Aqueous phase irreversible reactions

	Reaction	k_{298}^a	E_A/R^b	Comment	Reference
A157	$\text{Br} + \text{HCOOH} \rightarrow \text{H}^+ + \text{Br}^- + \text{COOH}$	7.7×10^5	2288		Par06
A158	$\text{Br} + \text{HCOO}^- \rightarrow \text{Br}^- + \text{COOH}$	4.6×10^8			Mer/Lin94
A159 \otimes	$\text{Br}_2^- + \text{HCOOH} \rightarrow 2\text{Br}^- + \text{H}^+ + \text{COOH}$	4.0×10^3			Ree99
A160 \otimes	$\text{Br}_2^- + \text{HCOO}^- \rightarrow 2\text{Br}^- + \text{COOH}$	4.9×10^3			Jac96
A161 \otimes	$\text{Br}_2^- + \text{CH}_3\text{COOH} \rightarrow$ $2\text{Br}^- + \text{H}^+ + \text{CH}_2\text{COOH}$	10			Ree99
A162 \otimes	$\text{Br}_2^- + \text{CH}_3\text{COO}^- \rightarrow 2\text{Br}^- + \text{CH}_3 + \text{CO}_2$	100			Jac96
A163 \otimes	$\text{Br}_2^- + \text{HC}_2\text{O}_4^- \rightarrow 2\text{Br}^- + \text{H}^+ + \text{C}_2\text{O}_4^-$	3.7×10^3		estimated (ETR)	
A164 \otimes	$\text{Br}_2^- + \text{C}_2\text{O}_4^{2-} \rightarrow 2\text{Br}^- + \text{C}_2\text{O}_4^-$	1.1×10^4		estimated (ETR)	
A165 \otimes	$\text{Br}_2^- + \text{CH}(\text{OH})_2\text{CH}(\text{OH})_2 \rightarrow$ $2\text{Br}^- + \text{H}^+ + \text{C}(\text{OH})_2\text{CH}(\text{OH})_2$	500		estimated (H-abstraction)	
A166 \otimes	$\text{Br}_2^- + \text{CH}(\text{OH})_2\text{COOH} \rightarrow$ $2\text{Br}^- + \text{H}^+ + \text{C}(\text{OH})_2\text{COOH}$	500		estimated ($k_{\text{A166}} \approx k_{\text{A165}}$)	
A167	$\text{CH}_2\text{BrC}(\text{OH})_2\text{O}_2 \rightarrow \text{CH}_2\text{BrCOOH} + \text{HO}_2$	1.0×10^3		estimated (Br = H)	
A168	$\text{CH}_2\text{BrC}(\text{OH})_2\text{O}_2 \rightarrow$ $\text{CH}_2\text{BrCOO}^- + 2\text{H}^+ + \text{O}_2^-$	1.0×10^5		estimated (Br = H)	
A169	$\text{CH}_3\text{COCBrO} + \text{H}_2\text{O} \rightarrow$ $\text{H}^+ + \text{Br}^- + \text{CH}_3\text{COCO}^-\text{OH}$	350		estimated same as acetyl chloride	Pra01
A170	$\text{CHOBr} \rightarrow \text{CO} + \text{H}^+ + \text{Br}^-$	1.0×10^4		estimated ($k_{\text{A170}} \approx k_{\text{A80}}$)	Pra01
A171	$\text{CHOBr} + \text{OH}^- \rightarrow \text{HCOO}^- + \text{H}^+ + \text{Br}^-$	2.5×10^4		estimated ($k_{\text{A171}} \approx k_{\text{A81}}$)	Pra01
A172	$\text{COBr}_2 + \text{H}_2\text{O} \rightarrow \text{BrCOOH} + \text{H}^+ + \text{Br}^-$	10		estimated ($k_{\text{A172}} \approx k_{\text{A82}}$)	Pra01
A173	$\text{COBr}_2 + \text{OH}^- \rightarrow \text{BrCOOH} + \text{Br}^-$	2.8×10^4		estimated ($k_{\text{A173}} \approx k_{\text{A83}}$)	Pra01
A174	$\text{BrCOOH} \rightarrow \text{CO}_2 + \text{H}^+ + \text{Br}^-$	1.0×10^5		lower limit; estimated ($k_{\text{A174}} \approx k_{\text{A84}}$)	Pra01
A175	$\text{I} + \text{I} \rightarrow \text{I}_2$	1.1×10^{10}			Bux07
A176	$\text{I} + \text{I}_2^- \rightarrow \text{I}_3^-$	6.5×10^9			Bux07
A177	$\text{I}_2^- + \text{I}_2^- \rightarrow \text{I}_3^- + \text{I}^-$	2.5×10^9			Bux07
A178	$\text{I}^- + \text{O}_3 \xrightarrow{\text{H}^+} \text{HOI} + \text{O}_2$	2.17×10^9	8790		Mag97

Table S16 (continued) Aqueous phase irreversible reactions

	Reaction	k_{298}^a	E_A/R^b	Comment	Reference
A179	$I_2 + HO_2 \rightarrow I_2^- + H^+ + O_2$	6.0×10^9		estimated ($k_{A179} \approx k_{A180}$)	Bux07
A180	$I_2 + O_2^- \rightarrow I_2^- + O_2$	6.0×10^9			Bux07
P _a 9	$I_2 \xrightarrow{h\nu} 2I$	(1.42×10^{-5})		$\Phi = 0.01^{Gro/Mat55}$; ϵ estimated with measurement in CCl ₄ ; see Tab. S15	Buc/Mil53
A181	$I_3^- + HO_2 \rightarrow I_2^- + H^+ + I^- + O_2$	2.5×10^8		estimated ($k_{A181} \approx k_{A182}$)	Bux07
A182	$I_3^- + O_2^- \rightarrow I_2^- + I^- + O_2$	2.5×10^8			Bux07
A183	$HIO_2 + H_2O_2 \rightarrow H^+ + IO_3^- + H_2O$	60			Fur87
A184	$IO_2^- + H_2O_2 \rightarrow IO_3^- + H_2O$	60		estimated same as A183	
A185	$IO + IO \xrightarrow{H_2O} HOI + HIO_2$	1.5×10^9			Bux86
A186	$I_2 + HSO_3^- \xrightarrow{H_2O} 2H^+ + 2I^- + HSO_4^-$	1.0×10^6			Ols/Eps91
A187	$HOI + SO_3^{2-} \rightarrow I^- + HSO_4^-$	5.0×10^9		estimated ($k_{A187} \approx k_{A115}$)	Pec07
A188	$HOI + HSO_3^- \rightarrow H^+ + I^- + HSO_4^-$	5.0×10^9		estimated ($k_{A188} \approx k_{A187}$)	Pec07
A189	$I^- + ICl \rightarrow I_2 + Cl^-$	1.1×10^9			Mar86
A190	$I^- + HOCl \xrightarrow{H^+} ICl + H_2O$	3.5×10^{11}		changed into reaction of third order at pH \cong 3.5 according to von Glasow et al. (2002a)	Nag88
A191	$I^- + HOBr \rightarrow IBr + OH^-$	5.0×10^9			Tro/Mar91
P _a 10	$ICl \xrightarrow{h\nu} I + Cl$	(3.08×10^{-3})		$\Phi = 0.1^c$; ϵ estimated with measurement in CCl ₄ ; see Tab. S15	Buc/Mil53
P _a 11	$IBr \xrightarrow{h\nu} I + Br$	(6.18×10^{-3})		$\Phi = 0.1^c$; ϵ estimated with measurement in CCl ₄ ; see Tab. S15	Buc/Mil54
A192	$HOI + Cl_2 \xrightarrow{H_2O} HIO_2 + 2H^+ + 2Cl^-$	1.0×10^6			Len96
A193	$HOI + HOCl \rightarrow HIO_2 + H^+ + Cl^-$	5.0×10^5			Cit/Eps88
A194	$HOI + HOBr \rightarrow HIO_2 + H^+ + Br^-$	1.0×10^6			Chi/Sim96
A195	$HIO_2 + HOCl \rightarrow IO_3^- + Cl^- + 2H^+$	1.5×10^3			Len96
A196	$IO_2^- + HOCl \rightarrow IO_3^- + Cl^- + H^+$	1.5×10^3		estimated same as A195	
A197	$HIO_2 + HOBr \rightarrow IO_3^- + Br^- + 2H^+$	1.0×10^6			Chi/Sim96

Table S16 (continued) Aqueous phase irreversible reactions

	Reaction	k_{298}^a	E_A/R^b	Comment	Reference
A198	$\text{IO}_2^- + \text{HOBr} \rightarrow \text{IO}_3^- + \text{Br}^- + \text{H}^+$	1.0×10^6		estimated same as A197	
A199	$\text{CH}_2\text{IC(OH)}_2\text{O}_2 \rightarrow \text{CH}_2\text{ICOOH} + \text{HO}_2$	1.0×10^3		estimated (I = H)	
A200	$\text{CH}_2\text{IC(OH)}_2\text{O}_2 \rightarrow \text{CH}_2\text{ICOO}^- + 2\text{H}^+ + \text{O}_2^-$	1.0×10^5		estimated (Cl = H)	
A201	$\text{CHOI} \rightarrow \text{CO} + \text{H}^+ + \text{I}^-$	1.0×10^4		estimated ($k_{\text{A201}} \approx k_{\text{A80}}$)	<i>Pra01</i>
A202	$\text{CHOI} + \text{OH}^- \rightarrow \text{HCOO}^- + \text{H}^+ + \text{I}^-$	2.5×10^4		estimated ($k_{\text{A202}} \approx k_{\text{A81}}$)	<i>Pra01</i>
A203	$\text{COI}_2 + \text{H}_2\text{O} \rightarrow \text{ICOOH} + \text{H}^+ + \text{I}^-$	10		estimated ($k_{\text{A203}} \approx k_{\text{A82}}$)	<i>Pra01</i>
A204	$\text{COI}_2 + \text{OH}^- \rightarrow \text{ICOOH} + \text{I}^-$	2.8×10^4		estimated ($k_{\text{A204}} \approx k_{\text{A83}}$)	<i>Pra01</i>
A205	$\text{ICOOH} \rightarrow \text{CO}_2 + \text{H}^+ + \text{I}^-$	1.0×10^5		lower limit; estimated ($k_{\text{A205}} \approx k_{\text{A84}}$)	<i>Pra01</i>

[⊗]already implemented in CAPRAM; [⊙]update of CAPRAM; [⊕]already implemented in the Halogen Module 1.0

^ain $\text{M}^{-1} \text{s}^{-1}$; ^bin K; ^cestimation according to [Herrmann \(2007\)](#)

^{Wu80}[Wu et al. \(1980\)](#); ^{Yu/Bak03}[Yu and Barker \(2003\)](#); ^{Jac99}[Jacobi et al. \(1999\)](#); ^{Hoi85}[Hoigné et al. \(1985\)](#); ^{Jac96}[Jabobi \(1996\)](#); ^{Bux98}[Buxton et al. \(1998\)](#); ^{Wag86}[Wagner et al. \(1986\)](#); ^{Bje81}[Bjergbakke et al. \(1981\)](#); ^{Mat/Ana06}[Matthew and Anastasio \(2006\)](#); ^{Zim/Str57}[Zimmerman and Strong \(1957\)](#); ^{Her03}[Herrmann \(2003\)](#); ^{Gro/Mat55}[Grossweiner and Matheson \(1955\)](#); ^{Con47}[Connick \(1947\)](#); ^{Lon/Bie80}[Long and Bielsky \(1980\)](#); ^{Bux/Sub72}[Buxton and Subhani \(1972\)](#); ^{Anb/Dos54}[Anbar and Dostrovsky \(1954\)](#); ^{Jacua96}[Jacobi et al. \(1996\)](#); ^{Fog89}[Fogelman et al. \(1989\)](#); ^{For60}[Fortnum et al. \(1960\)](#); ^{Bar97}[Barlow et al. \(1997\)](#); ^{Zel96}[Zellner et al. \(1996\)](#); ^{Geo99}George, C. (pers. comm., 1999); ^{Tho/Lau73}[Thornton and Laurence \(1973\)](#); ^{Jacs98}[Jacobsen et al. \(1998\)](#); ^{Lau/Tho73}[Laurence and Thornton \(1973\)](#); ^{Mer/Son95}[Mertens and von Sonntag \(1995\)](#); ^{Pra01}[Prager et al. \(2001\)](#); ^{Wic03}[Wicktor et al. \(2003\)](#); ^{Par06}[Parajuli \(2006\)](#); ^{Bux00}[Buxton et al. \(2000\)](#); ^{Kla/Wol85}[Kläning and Wolff \(1985\)](#); ^{Ree99}[Reese et al. \(1999\)](#); ^{Haa/Hoi83}[Haag and Hoigné \(1983\)](#); ^{Wag/Str87}[Wagner and Strehlow \(1987\)](#); ^{Sut65}[Sutton et al. \(1965\)](#); ^{Sut/DOW72}[Sutton and Downes \(1972\)](#); ^{Mat03}[Matthew et al. \(2003\)](#); ^{Ree97}[Reese \(1997\)](#); ^{Buc/Mil53}[Buckles and Mills \(1953\)](#); ^{Ami/Tre70}[Amichai and Treinin \(1970\)](#); ^{Bux/Dai68}[Buxton and Dainton \(1968\)](#); ^{Schw/Bie86}[Schwarz and Bielski \(1986\)](#); ^{You50}[Young \(1950\)](#); ^{Her97}[Herrmann et al. \(1997\)](#); ^{Tro/Mar91}[Troy and Margerum \(1991\)](#); ^{Gla02}[von Glasow et al. \(2002a\)](#); ^{Pun59}[Pungor et al. \(1959\)](#); ^{Hui91}[Huie et al. \(1991\)](#); ^{Kum/Mar87}[Kumar and Margerum \(1987\)](#); ^{Mer/Lin94}[Merényi and Lind \(1994\)](#); ^{Bux07}[Buxton and Mulazzani \(2007\)](#); ^{Mag97}[Magi et al. \(1997\)](#); ^{Fur87}[Furrow \(1987\)](#); ^{Bux86}[Buxton et al. \(1986\)](#); ^{Chi/Sim96}[Chinake and Simoyi \(1996\)](#); ^{Schm00}[Schmitz \(2000\)](#); ^{Ols/Eps91}[Olsen and Epstein \(1991\)](#); ^{Pec07}[Pechtl et al. \(2007\)](#); ^{Mar86}[Margerum et al. \(1986\)](#); ^{Nag88}[Nagy et al. \(1988\)](#); ^{Buc/Mil54}[Buckles and Mills \(1954\)](#); ^{Len96}[Lengyel et al. \(1996\)](#); ^{Cit/Eps88}[Citri and Epstein \(1988\)](#)

Table S17 Aqueous phase equilibria

	Reaction	K^a	$k_{f,298}^b$	E_A/R^c	Reference	$k_{b,298}^b$	E_A/R^c	Reference	Comm.
E1 \otimes	$\text{Cl} + \text{Cl}^- \rightleftharpoons \text{Cl}_2^-$	1.4×10^5	8.5×10^9		Bux98	6.0×10^4		Bux98	
E2	$\text{Cl}_2 + \text{Cl}^- \rightleftharpoons \text{Cl}_3^-$	0.18	2.0×10^4		Ers04	1.1×10^5		Ers04	
E3 \otimes_d	$\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{Cl}^- + \text{HOCl}$	$1.9 \times 10^{-5} \text{e}^{-4500/T}$	0.4	8000	Wan/Mar94	2.1×10^4	3500	Wan/Mar94	e
E4 \otimes	$\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$	1.72×10^6	5.0×10^{11}	-6890	Mar/Elr85	2.9×10^5		Gra/Wes81	f
E5 \oplus	$\text{HOCl} \rightleftharpoons \text{H}^+ + \text{ClO}^-$	3.0×10^{-8}	1.5×10^3		Atk96	5.0×10^{10}			g, h
E6 \otimes	$\text{Cl}^- + \text{OH} \rightleftharpoons \text{ClOH}^-$	0.7	4.3×10^9		Jay73	6.1×10^9		Jay73	
E7	$\text{Cl} + \text{OH}^- \rightleftharpoons \text{ClOH}^-$	7.83×10^8	1.8×10^{10}		Kla/Wol85	23		Kla/Wol85	
E8 \otimes	$\text{ClOH}^- + \text{H}^+ \rightleftharpoons \text{Cl} + \text{H}_2\text{O}$	5.1×10^6	2.1×10^{10}		Jay73	4.1×10^3		Jacs97	
E9 \otimes	$\text{ClOH}^- + \text{Cl}^- \rightleftharpoons \text{Cl}_2^- + \text{OH}^-$	2.2×10^{-4}	1.0×10^4		Gri87	4.5×10^7		Gri87	
E10 \otimes	$\text{Cl}^- + \text{SO}_4^- \rightleftharpoons \text{Cl} + \text{SO}_4^{2-}$	1.2	2.52×10^8		Bux99a	2.1×10^8		Bux99a	
E11 \otimes	$\text{Cl}^- + \text{NO}_3 \rightleftharpoons \text{Cl} + \text{NO}_3^-$	3.4	3.4×10^8	4300	Bux99b	1.0×10^8		Bux99b	
E12 \otimes	$\text{Cl}^- + \text{Fe}^{3+} \rightleftharpoons \text{FeCl}^{2+}$	1.39	3.0×10^3		Mar/Sil64	2.16×10^3			
E13	$\text{CH}_2\text{ClCO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2\text{ClC(OH)}_2\text{O}_2$	367	1.1×10^7			3.0×10^4			i
E14	$\text{CH}_2\text{ClCOOH} \rightleftharpoons \text{CH}_2\text{ClCOO}^- + \text{H}^+$	1.75×10^{-5}	8.75×10^5	-46		5.0×10^{10}			i
E15 \otimes	$\text{Br} + \text{Br}^- \rightleftharpoons \text{Br}_2^-$	6.32×10^5	1.2×10^{10}		Mer/Lin94	1.9×10^4		Mer/Lin94	
E16	$\text{Br}_2 + \text{Br}^- \rightleftharpoons \text{Br}_3^-$	17.5	9.6×10^8		Ers04	5.5×10^7		Ers04	
E17 \otimes_\oplus	$\text{Br}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{Br}^- + \text{HOBr}$	1.06×10^{-10}	1.7	7500	Bec96	1.6×10^{10}		Bec96	d
E18 \oplus	$\text{HBr} \rightleftharpoons \text{H}^+ + \text{Br}^-$	1.0×10^9	5.0×10^{11}		Atk96	5.0×10^2			j, k, l
E19 \oplus	$\text{HOBr} \rightleftharpoons \text{H}^+ + \text{BrO}^-$	2.0×10^{-9}	100		Atk96	5.0×10^{10}			g, h
E20 \otimes	$\text{Br}^- + \text{OH} \rightleftharpoons \text{BrOH}^-$	333	1.1×10^{10}		Zeh/Rab72	3.3×10^7		Zeh/Rab72	
E21 d_\otimes	$\text{Br} + \text{OH}^- \rightleftharpoons \text{BrOH}^-$	3.1×10^3	1.3×10^{10}		Kla/Wol85	4.2×10^6		Zeh/Rab72	
E22 \otimes	$\text{BrOH}^- + \text{H}^+ \rightleftharpoons \text{Br} + \text{H}_2\text{O}$	1.8×10^{12}	4.4×10^{10}		Zeh/Rab72	2.45×10^{-2}		Kla/Wol85	
E23 \otimes	$\text{BrOH}^- + \text{Br}^- \rightleftharpoons \text{Br}_2^- + \text{OH}^-$	70	1.9×10^8		Zeh/Rab72	2.7×10^6		Vio81	

Table S17 (continued) Aqueous phase equilibria

	Reaction	K^a	$k_{f,298}^a$	E_A/R^b	Reference	$k_{b,298}^a$	E_A/R^b	Reference	Comm.
E24 \oplus	$\text{HOBr} + \text{HOBr} \rightleftharpoons \text{H}^+ + \text{Br}^- + \text{HBrO}_2$	6.7×10^{-12}	2.0×10^{-5}		<i>Fie86,</i> <i>Fie/For86</i>	3.0×10^6		<i>Fie/For86</i>	
E25 \oplus	$\text{HBrO}_2 \rightleftharpoons \text{H}^+ + \text{BrO}_2^-$	1.3×10^{-5}	6.3×10^5		<i>Fie86</i>	5.0×10^{10}			<i>g, h</i>
E26 \oplus	$\text{HOBr} + \text{HBrO}_2 \rightleftharpoons 2\text{H}^+ + \text{Br}^- + \text{BrO}_3^-$	1.7	3.2		<i>Fie86,</i> <i>Fie/For86</i>	2.0		<i>Fie/For86</i>	
E27 \oplus	$\text{HBrO}_2 + \text{HBrO}_2 \rightleftharpoons \text{HOBr} + \text{H}^+ + \text{BrO}_3^-$	3.0×10^{11}	3.0×10^3		<i>Fie86,</i> <i>Fie/For86</i>	1.0×10^{-8}		<i>Fie/For86</i>	
E28 \oplus	$\text{Br}_2\text{O}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{BrO}_3^- + \text{HBrO}_2$	52.6	2.2×10^3		<i>Fie86,</i> <i>Fie/For86</i>	42		<i>Fie/For86</i>	
E29 \oplus	$\text{Br}_2\text{O}_4 \rightleftharpoons 2\text{BrO}_2$	5.3×10^{-5}	7.4×10^4		<i>Fie86,</i> <i>Fie/For86</i>	1.4×10^9		<i>Fie/For86</i>	
E30	$\text{Br}^- + \text{CO}_3^{2-} \rightleftharpoons \text{Br} + \text{CO}_3^{2-}$	0.05	1.0×10^5		<i>Mat/Ana06</i>	2.0×10^6		<i>Mat/Ana06</i>	<i>h, l</i>
E31 \oplus	$\text{BrCl} \xrightleftharpoons{\text{H}_2\text{O}} \text{HOBr} + \text{H}^+ + \text{Cl}^-$	1.8×10^{-5}	1.0×10^5		<i>Wan94</i>	5.6×10^9			<i>k</i>
E32	$\text{BrCl}^- \rightleftharpoons \text{Br}^- + \text{Cl}$	1.6×10^{-7}	1.9×10^3		<i>Don02</i>	1.2×10^{10}		<i>Don02</i>	
E33	$\text{BrCl}^- \rightleftharpoons \text{Br} + \text{Cl}^-$	6.1×10^{-4}	6.1×10^4		<i>Don02</i>	1.0×10^8		<i>Don02</i>	
E34	$\text{BrCl}^- + \text{Br}^- \rightleftharpoons \text{Br}_2^- + \text{Cl}^-$	1.86×10^3	8.0×10^9		<i>Ers04</i>	4.3×10^6		<i>Ers04</i>	
E35	$\text{BrCl}^- + \text{Cl}^- \rightleftharpoons \text{Cl}_2^- + \text{Br}^-$	2.75×10^{-8}	110		<i>Ers04</i>	4.0×10^9		<i>Ers04</i>	
E36 \oplus	$\text{Br}_2\text{Cl}^- \rightleftharpoons \text{BrCl} + \text{Br}^-$	5.6×10^{-5}	4.3×10^5		<i>Wan94</i>	7.7×10^9			<i>j, m</i>
E37 \ominus	$\text{Br}_2\text{Cl}^- \rightleftharpoons \text{Br}_2 + \text{Cl}^-$	0.76	3.8×10^4		<i>Wan94</i>	5.0×10^4		<i>Mat/Ana06</i>	<i>h, l</i>
E38 \ominus	$\text{BrCl}_2^- \rightleftharpoons \text{BrCl} + \text{Cl}^-$	0.17	1.7×10^5		<i>Ers04</i>	1.0×10^6		<i>Ers04</i>	
E39 \ominus	$\text{BrCl}_2^- \rightleftharpoons \text{Br}^- + \text{Cl}_2$	1.5×10^{-6}	9.0×10^3		<i>Ers04</i>	6.0×10^9		<i>Ers04</i>	
E40	$\text{Br}^- + \text{ClOH}^- \rightleftharpoons \text{BrCl}^- + \text{OH}^-$	333.3	1.0×10^9		<i>Mat/Ana06</i>	3.0×10^6		<i>Mat/Ana06</i>	<i>l, m</i>
E41	$\text{BrOH}^- + \text{Cl}^- \rightleftharpoons \text{BrCl}^- + \text{OH}^-$	9.5	1.9×10^8		<i>Mat/Ana06</i>	2.0×10^7		<i>Mat/Ana06</i>	<i>h, l</i>
E42	$\text{CH}_2\text{BrCO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2\text{BrC}(\text{OH})_2\text{O}_2$	367	1.1×10^7			3.0×10^4			<i>i</i>
E43	$\text{CH}_2\text{BrCOOH} \rightleftharpoons \text{CH}_2\text{BrCOO}^- + \text{H}^+$	1.75×10^{-5}	8.75×10^5	-46		5.0×10^{10}			<i>i</i>
E44	$\text{I} + \text{I}^- \rightleftharpoons \text{I}_2^-$	1.36×10^5	9.1×10^9		<i>Bux07</i>	6.7×10^4		<i>Bux07</i>	

Table S17 (continued) Aqueous phase equilibria

	Reaction	K^a	$k_{f,298}^a$	E_A/R^b	Reference	$k_{b,298}^a$	E_A/R^b	Reference	Comm.
E45	$I_2 + I^- \rightleftharpoons I_3^-$	713	6.2×10^9		Bux07	8.7×10^6		Bux07	
E46	$HI \rightleftharpoons H^+ + I^-$	3.2×10^9	5.0×10^{11}		Schw00	156			<i>j, k, l</i>
E47	$HOI \rightleftharpoons H^+ + IO^-$	3.16×10^{-11}	1.58		Lid95	5.0×10^{10}			<i>g, h</i>
E48	$HOI + H^+ + I^- \xrightleftharpoons{H_2O} I_2$	1.47×10^{12}	4.4×10^{12}		Eig/Kus62	3.0		Eig/Kus62	<i>j, m</i>
E49	$HOI + HOI \rightleftharpoons HIO_2 + H^+ + I^-$	1.25×10^{-9}	25		Schm04	2.0×10^{10}		Edb87	<i>j, m</i>
E50	$HOI + HOI \rightleftharpoons IO_2^- + 2H^+ + I^-$	1.25×10^{-9}	25		Schm04	2.0×10^{10}			<i>h, j, m</i>
E51	$HIO_2 \rightleftharpoons H^+ + IO_2^-$	2.51×10^{-2}	1.26×10^9			5.0×10^{10}			<i>g, h</i>
E52	$HIO_3 \rightleftharpoons H^+ + IO_3^-$	0.17	8.5×10^9		Lid95	5.0×10^{10}			<i>g, h</i>
E53	$HIO_2 + HOI \rightleftharpoons IO_3^- + I^- + 2H^+$	0.2	2.4×10^2		Fur87	1.2×10^3		Schm00	
E54	$IO_2^- + HOI \rightleftharpoons IO_3^- + I^- + H^+$	0.2	2.4×10^2			1.2×10^3		Schm00	<i>l</i>
E55	$IO_2^- + I_2 \xrightleftharpoons{H_2O} IO_3^- + 2I^- + 2H^+$	1.3×10^{-13}	5.5×10^{-5}			4.2×10^8		Schm00	<i>l, m</i>
E56	$IBr + I^- \rightleftharpoons I_2 + Br^-$	4.2×10^5	2.0×10^9		Far93	4.74×10^3		Far93	<i>m</i>
E57	$HOI + H^+ + Cl^- \xrightleftharpoons{H_2O} ICl$	1.2×10^4	2.9×10^{10}		Wan89	2.4×10^6		Wan89	<i>j, m</i>
E58	$HOI + H^+ + Br^- \xrightleftharpoons{H_2O} IBr$	5.1×10^6	4.1×10^{12}		Far93	8.0×10^5		Far93	<i>j, m</i>
E59	$ICl + Cl^- \rightleftharpoons ICl_2^-$	77	4.24×10^9			5.5×10^7			<i>g, h</i>
E60	$IBr + Br^- \rightleftharpoons IBr_2^-$	290	4.93×10^6			1.7×10^5			<i>g, h</i>
E61	$ICl + Br^- \rightleftharpoons IClBr^-$	1.8×10^4	7.7×10^9			4.3×10^5			<i>h, l, n</i>
E62	$IBr + Cl^- \rightleftharpoons IClBr^-$	1.3	5.0×10^4			3.8×10^4			<i>h, l, n</i>

Table S17 (continued) Aqueous phase equilibria

	Reaction	K^a	$k_{f,298}^a$	E_A/R^b	Reference	$k_{b,298}^a$	E_A/R^b	Reference	Comm.
E63	$\text{CH}_2\text{ICO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2\text{IC(OH)}_2\text{O}_2$	367	1.1×10^7			3.0×10^4			<i>i</i>
E64	$\text{CH}_2\text{ICOOH} \rightleftharpoons \text{CH}_2\text{ICOO}^- + \text{H}^+$	1.75×10^{-5}	8.75×10^5	-46		5.0×10^{10}			<i>i</i>

[⊗]already implemented in CAPRAM; [⊙]update of CAPRAM; [⊕]already implemented in the Halogen Module 1.0; [⊖]update of the Halogen Module 1.0 (when subscripts are present in remarks: superscripts concern only forward reaction and subscript concern only backward reaction)

^ain $\text{M}^{\text{m}-\text{n}}$, n order of reaction of forward reaction, m order of reaction of backward reaction; ^bin $\text{M}^{-1} \text{s}^{-1}$; ^cin K; ^dnow implemented as equilibrium in CAPRAM; ^ecorrection of CAPRAM value; ^f k_f = speed of hydrogen bond breaking in water; ^g k_f calculated based on K ; ^h k_b estimated; ⁱestimated X = H (X = Cl, Br, I) ^jdiffusion controlled; ^k k_b calculated based on K ; ^l k_f estimated; ^mupper limit; ⁿ K estimated

^{Bux98}Buxton et al. (1998); ^{Ers04}Ershov (2004); ^{Wan/Mar94}Wang and Margerum (1994); ^{Mar/Elr85}Marsh and McElroy (1985); ^{Gra/Wes81}Graedel and Weschler (1981); ^{Atk96}ATKINS, 1996; ^{Jay73}Jayson et al. (1973); ^{Kla/Wol85}Klänning and Wolff (1985); ^{Jacs97}Jacobsen et al. (1997); ^{Gri87}Grigor'ev et al. (1987); ^{Bux99a}Buxton et al. (1999a); ^{Bux99b}Buxton et al. (1999b); ^{Mar/Sil64}Martell and Sillen (1964); ^{Mer/Lin94}Merényi and Lind (1994); ^{Bec96}Beckwith et al. (1996); ^{Zeh/Rab72}Zehavi and Rabani (1972); ^{Vio81}Fornier de Violet (1981); ^{Fie86}FIELD, 1986; ^{Fie/For86}Field and Försterling (1986); ^{Mat/Ana06}Matthew and Anastasio (2006); ^{Wan94}Wang et al. (1994); ^{Don02}Donati (2002); ^{Bux07}Buxton and Mulazzani (2007); ^{Eig/Kus62}Eigen and Kustin (1962); ^{Schw00}Schweitzer et al. (2000); ^{Lid95}Lide et al. (1995); ^{Schm04}Schmitz (2004); ^{Edb87}Edblom et al. (1987); ^{Schm00}Schmitz (2000); ^{Far93}Faria et al. (1993); ^{Wan89}Wang et al. (1989); ^{Tro91}Troy et al. (1991); ^{Tro/Mar91}Troy and Margerum (1991)

S4 Estimation of rate constants of reactions with lumped species

For reactions of chlorine with lumped model species, rate constants had to be synthesised from the individual rate constants of the real species. The overall rate constants were calculated by scaling the individual rate constants based on their fraction of the model species (Equation 1). The size of the fractions was determined according to the emission rates used in RACM as described in Middleton et al. (1990).

$$k_{298} = \frac{\sum_i x_i k_i}{\sum_i x_i} \quad (1)$$

k_{298} overall rate constant of the model species at 298 K in $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$

k_i individual rate constant in $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$

x_i fraction of the individual species to the overall model species

Table S18 shows the kinetic data of the individual species used to synthesise the overall rate constant to the model species. Information is also given about the fractions of the individual species of the model species. In Table S19, the synthesised rate constants are shown as well as the percentages of those species that were covered by kinetic data.

Table S18 Kinetic data used for synthesising rate constants of the reactions of chlorine with the lumped model species HC3, HC5, HC8 and TOL

Reactant	k^a	Reference	Fraction ^b
HC3			
C ₃ H ₈	1.40×10^{-10}	Atkinson et al. (2006)	0.029
<i>n</i> -C ₄ H ₁₀	2.05×10^{-10}	Atkinson et al. (2006)	0.443
<i>i</i> -C ₄ H ₁₀	1.43×10^{-10}	Atkinson et al. (2006)	0.012
CH ₃ C(CH ₃) ₂ C ₂ H ₅	1.71×10^{-10}	Pilling et al. (2008)	<0.001
C ₂ H ₂	$k_0 = 6.1 \times 10^{-30}$ $\times (T/300)^{-3} [\text{N}_2]$ $k_\infty = 2.0 \times 10^{-10}$	Atkinson et al. (2006)	0.095
CH ₃ OH	5.5×10^{-11}	Atkinson et al. (2006)	0.007
C ₂ H ₅ OH	$8.6 \times 10^{-11} \text{e}^{45/T}$	Atkinson et al. (2006)	0.345
HC5			
<i>i</i> -C ₅ H ₁₂	2.2×10^{-10}	Atkinson et al. (2008a)	0.192
<i>n</i> -C ₆ H ₁₄	3.4×10^{-10}	Pilling et al. (2008)	0.109
<i>n</i> -C ₅ H ₁₂	2.8×10^{-10}	Atkinson et al. (2008a)	0.108
(CH ₃) ₂ CHC ₃ H ₇	2.9×10^{-10}	Pilling et al. (2008)	0.051
CH ₃ CH ₂ CH(CH ₃)C ₂ H ₅	2.8×10^{-10}	Pilling et al. (2008)	0.032
CH ₃ CH(CH ₃)CH(CH ₃)CH ₃	2.3×10^{-10}	Pilling et al. (2008)	0.020
<i>i</i> -C ₃ H ₇ OH	8.6×10^{-11}	Atkinson et al. (2007)	0.307
<i>n</i> -C ₃ H ₇ OH	$1.6 \times 10^{-11} \text{e}^{-130/T}$	Atkinson et al. (2007)	<0.001
HC8			
<i>n</i> -C ₇ H ₁₆	3.9×10^{-10}	Pilling et al. (2008)	0.129
C ₇ H ₁₆	4.95×10^{-10}	estimation with data of Atkinson et al. (2008a)	0.098
<i>n</i> -C ₈ H ₁₈	4.6×10^{-10}	Pilling et al. (2008)	0.028

Table S18 (continued) Kinetic data used for synthesising rate constants of the reactions of chlorine with the lumped model species HC3, HC5, HC8 and TOL

Reactant	k^a	Reference	Fraction ^b
C ₂ H ₅ CH(CH ₃)C ₃ H ₇	3.11×10^{-10}	Pilling et al. (2008)	0.024
<i>n</i> -C ₁₁ H ₂₄	6.17×10^{-10}	Pilling et al. (2008)	0.023
C ₆ H ₁₂	3.5×10^{-10}	Pilling et al. (2008)	0.020
<i>n</i> -C ₉ H ₂₀	4.8×10^{-10}	Pilling et al. (2008)	0.012
<i>n</i> -C ₁₀ H ₂₂	5.55×10^{-10}	Pilling et al. (2008)	0.008
<i>n</i> -C ₁₂ H ₂₆	6.74×10^{-10}	Pilling et al. (2008)	0.008
TOL			
C ₆ H ₆	1.3×10^{-15}	Shi and Bernhard (1997)	0.100
CH ₃ C ₆ H ₆	5.9×10^{-11}	Shi and Bernhard (1997)	0.690

^ain cm³ molecules⁻¹ s⁻¹, ^bof the individual compounds to the overall model species

Table S19 Overall rate constants of the reactions of chlorine with the model species HC3, HC5, HC8 and TOL

Reactant	k^a	Fraction ^b
HC3	$1.41 \times 10^{-10} e^{13/T}$	0.93
HC5	2.14×10^{-10}	0.82
HC8	4.38×10^{-10}	0.33
TOL	5.15×10^{-11}	0.79

^ain cm³ molecules⁻¹ s⁻¹, ^bcovered by kinetic data

S5 Estimation of gas phase diffusion coefficients

Data for gas phase diffusion coefficients D_g are very restricted. The only known values for halogen compounds are those of Cl₂ and Br₂ by Schwartz (1986) and the one of HCl by Marsh and McElroy (1985).

All other data had to be estimated. Therefore, the Fuller-Schettler-Giddings (FSG) method was used, which calculates the gas phase diffusion coefficient D_g as a function of the molecular weight of the compound considered (M_i) and the air (M_j) as well as the diffusion volumes ($v_{i/j}$) of those species. Further dependencies are the temperature T and the pressure p of the ambient air:

$$D_{ij} = 0.0101 \frac{T^{1.75} \left(\frac{1}{M_i} + \frac{1}{M_j} \right)^{1/2}}{p \left[(\sum v_i)^{1/3} + (\sum v_j)^{1/3} \right]^2} \quad (2)$$

$D_{i/j}$ Gas phase diffusion coefficients of the halogen species i in the medium j (air)
 $M_{i/j}$ Molar masses of the halogen species i and the medium j
 $v_{i/j}$ Diffusion volumes of the halogen species i and the medium j
 T Temperature
 p Pressure

The FSG method provides values for the diffusion volumes of compounds containing C, N, S, O, H, and Cl atoms. Diffusion volumes of molecules can be calculated by summing up the individual diffusion volumes of atoms part of that molecule. Furthermore, the method provides values for diffusion volumes of simple molecules such as Cl_2 and Br_2 .

The FSG method allows for the immediate calculation of the gas phase diffusion coefficients of chlorine containing species. For bromine containing species, the diffusion volume of Br atoms is missing. However, the methods provides a value for Br_2 with whom it is possible to estimate the diffusion volume of Br atoms. Therefore, the diffusion volume of Br_2 was scaled by the ratio of the diffusion volumes of atomic and molecular chlorine Cl_2/Cl to derive a value of 34.8 for v_{Br} .

No data was available for the diffusion coefficients of iodine species. Therefore, a new estimation approach had to be used. Figure S11 shows a good correlation between the diffusion volume and the molar mass. For the linear regression only atoms have been used since the scattering increases when considering molecules. The regression line has been forced through the origin for physical reasons leading to

$$D_g = (0.315 \pm 0.033) \cdot M_i.$$

With this regression a atomic diffusion volume of 40 cm^3 could be calculated for I atoms.

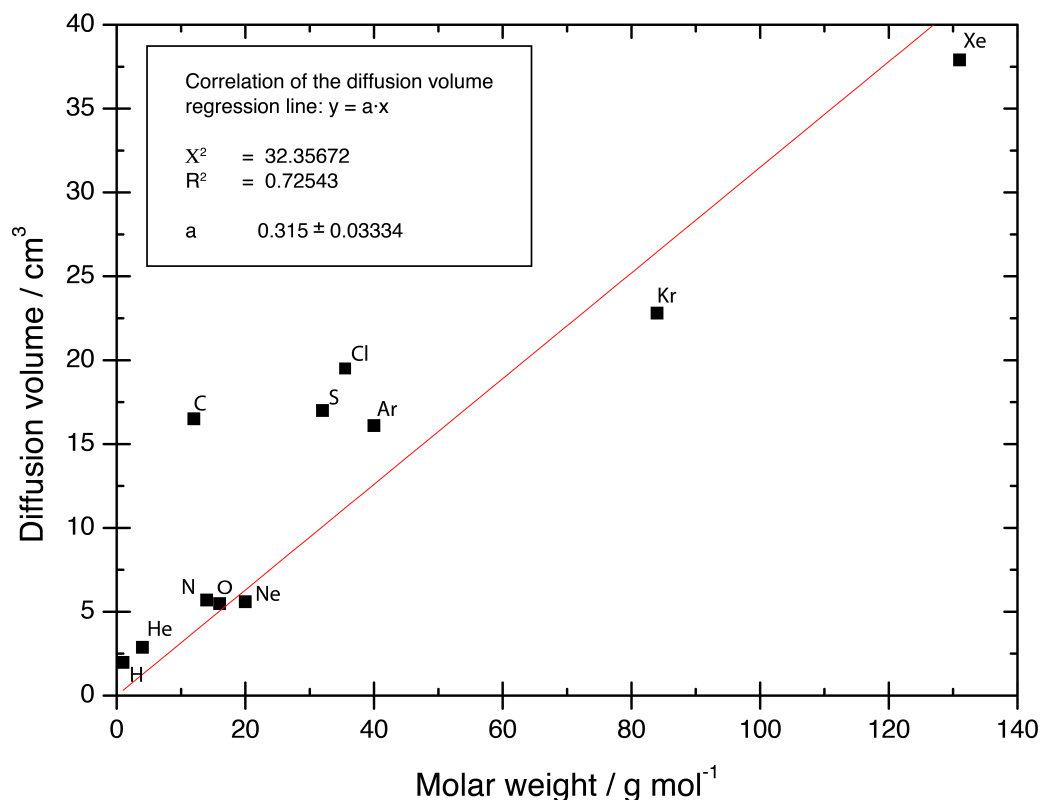


Figure S11 Estimation of diffusion volumes.

References

- J. P. D. Abbatt and G. C. G. Waschewsky. Heterogeneous interactions of HOBr, HNO₃, O₃, and NO₂ with deliquescent NaCl aerosols at room temperature. *Journal of Physical Chemistry A*, 102(21): 3719 – 3725, 1998. ISSN 1089-5639.
- O. Amichai and A. Treinin. On Oxybromine Radicals. *Journal of Physical Chemistry*, 74(20):3670, 1970. ISSN 0022-3654.
- M. Anbar and I. Dostrovsky. Ultra-violet absorption spectra of some organic hypohalites. *Journal of the Chemical Society*, pages 1105 – 1108, 1954. doi: 10.1039/JR9540001105.
- L. C. Anderson and D. W. Fahey. Studies with ClONO₂ – Thermal Dissociation Rate And Catalytic Conversion to NO Using an NO/O₃ Chemiluminescence Detector. *Journal of Physical Chemistry*, 94(2):644 – 652, 1990. ISSN 0022-3654.
- S. R. Arnold, D. V. Spracklen, J. Williams, N. Yassaa, J. Sciare, B. Bonsang, V. Gros, I. Peeken, A. C. Lewis, S. Alvain, and C. Moulin. Evaluation of the global oceanic isoprene source and its impacts on marine organic carbon aerosol. *Atmospheric Chemistry and Physics*, 9(4):1253 – 1262, 2009. ISSN 1680-7316.
- R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, and J. Troe. 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.
- R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, and J. Troe. Evaluated kinetic and photochemical data for atmospheric chemistry: Volume III – gas phase reactions of inorganic halogens. *Atmospheric Chemistry and Physics*, 7(4):981 – 1191, 2007. ISSN 1680-7316.
- R. Atkinson, M. Ammann, R. A. Cox, J. Crowley, R. Hynes, M. E. Jenkin, M. J. Rossi, J. Troe, T. Wallington, T. L. Baulch, and J. A. Kerr. IUPAC Subcommittee for Gas Kinetic Data Evaluation, 2008a. URL <http://www.iupac-kinetic.ch.cam.ac.uk/>.
- R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, J. Troe, and T. J. Wallington. Evaluated kinetic and photochemical data for atmospheric chemistry: Volume IV — gas phase reactions of organic halogen species. *Atmospheric Chemistry and Physics*, 8(15):4141 – 4496, 2008b. ISSN 1680-7316.
- S. Barlow, G. V. Buxton, S. A. Murray, and G. A. Salmon. Free radical-induced oxidation of hydroxymethanesulfonate in aqueous solution. Part 1 and Part 2. A pulse radiolysis study of the reactions of OH• and SO₄•⁻. *Journal of the Chemical Society – Faraday Transactions*, 93(20):3637 – 3645, 1997. ISSN 0956-5000.
- W. B. Bartlett and D. W. Margerum. 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. ISSN 0013-936x.
- D. L. Baulch, J. Duxbury, S. J. Grant, and D. C. Montague. Evaluated kinetic data for high-temperature reactions, Volume 4 – Homogeneous gas phase reactions of halogen-containing and cyanide-containing species. *Journal of Physical and Chemical Reference Data*, 10(Suppl. 1):1 – 721, 1981. ISSN 0047-2689.

- R. C. Beckwith, T. X. Wang, and D. W. Margerum. Equilibrium and kinetics of bromine hydrolysis. *Inorganic Chemistry*, 35(4):995 – 1000, 1996. ISSN 0020-1669.
- Y. Bedjanian, G. LeBras, and G. Poulet. Rate constants for the reactions $I + OClO$, $I + ClO$, $Cl + I_2$, and $Cl + IO$ and heat of formation of IO radicals. *Journal of Physical Chemistry*, 100(37):15130 – 15136, 1996. ISSN 0022-3654.
- Y. Bedjanian, G. LeBras, and G. Poulet. Kinetic study of the $Br + IO$, $I + BrO$ and $Br + I_2$ reactions. Heat of formation of the BrO radical. *CHEMICAL PHYSICS LETTERS*, 266(1-2):233 – 238, 1997. ISSN 0009-2614.
- Y. Bedjanian, G. Laverdet, and G. Le Bras. Low-pressure study of the reaction of Cl atoms with isoprene. *Journal of Physical Chemistry A*, 102(6):953 – 959, 1998. ISSN 1089-5639.
- H. J. Benkelberg and P. Warneck. Photodecomposition of Iron(III) Hydroxo and Sulfato Complexes in Aqueous Solution – Wavelength Dependence of OH and SO_4^- Quantum Yields. *JOURNAL OF PHYSICAL CHEMISTRY*, 99(14):5214 – 5221, APR 6 1995. ISSN 0022-3654.
- E. Bjergbakke, S. Navaratnam, B. J. Parsons, and A. J. Swallow. Reactions between HO_2 and Chlorine in Aqueous Solution. *Journal of the American Chemical Society*, 103(19):5926 – 5928, 1981. ISSN 0002-7863.
- P. Brimblecombe and S. L. Clegg. Erratum. *Journal of Atmospheric Chemistry*, 8(1):95, 1989. ISSN 0167-0662. doi: 10.1007/BF00053818.
- W. J. Broadgate, P. S. Liss, and S. A. Penkett. Seasonal emissions of isoprene and other reactive hydrocarbon gases from the ocean. *Geophysical Research Letters*, 24(21):2675 – 2678, NOV 1 1997. ISSN 0094-8276.
- R. E. Buckles and J. F. Mills. Solutions of Halogens in Highly Acidic, Polar Solvents. *Journal of the American Chemical Society*, 75(3):552 – 555, 1953. ISSN 0002-7863.
- R. E. Buckles and J. F. Mills. Dissociation of Quaternary Ammonium Polyhalides in Tetrafluoroacetic Acid. *Journal of the American Chemical Society*, 76(23):6021 – 6022, 1954. ISSN 0002-7863.
- G. V. Buxton and F. S. Dainton. Radiolysis of Aqueous Solutions of Oxybromine Compounds – Spectra and Reactions of BrO and BrO_2 . *Proceedings of the Royal Society of London Series A – Mathematical and Physical Sciences*, 304(1479):427, 1968.
- G. V. Buxton and Q. G. Mulazzani. On the hydrolysis of iodine in alkaline solution: A radiation chemical study. *Radiation Physics and Chemistry*, 76(6):932 – 940, JUN 2007. ISSN 0969-806X. doi: {10.1016/j.radphyschem.2006.06.009}.
- G. V. Buxton and M. S. Subhani. Radiation-Chemistry and Photochemistry of Oxychlorine Ions. Part 1. Radiolysis of Aqueous-Solutions of Hypochlorite and Chlorite Ions. *Journal of the Chemical Society – Faraday Transactions I*, 68:947 – 957, 1972. ISSN 0300-9599.
- G. V. Buxton, C. Kilner, and R. M. Sellers. Pulse radiolysis of HOI and IO^- in aqueous solution, formation and characterization of I^{II} . In *6th Symposium on Radiation Chemistry*, pages 155 – 159, 1986.

- G. V. Buxton, M. Bydder, and G. A. Salmon. Reactivity of chlorine atoms in aqueous solution. Part 1. The equilibrium $\text{Cl}\bullet + \text{Cl}^- \rightleftharpoons \text{Cl}_2\bullet^-$. *Journal of the Chemical Society – Faraday Transactions*, 94(5): 653 – 657, 1998. ISSN 0956-5000.
- G. V. Buxton, M. Bydder, and G. A. Salmon. The reactivity of chlorine atoms in aqueous solution - Part II. The equilibrium $\text{SO}_4^{\bullet-} + \text{Cl}^- \rightleftharpoons \text{Cl}\bullet + \text{SO}_4^{2-}$. *Physical Chemistry Chemical Physics*, 1(2): 269 – 273, 1999a. ISSN 1463-9076.
- G. V. Buxton, G. A. Salmon, and J. Q. Wang. The equilibrium $\text{NO}_3^{\bullet} + \text{Cl}^- \rightleftharpoons \text{NO}_3^- + \text{Cl}\bullet$: A laser flash photolysis and pulse radiolysis study of the reactivity of NO_3^{\bullet} with chloride ion in aqueous solution. *Physical Chemistry Chemical Physics*, 1(15):3589 – 3593, 1999b. ISSN 1463-9076.
- G. V. Buxton, M. Bydder, G. A. Salmon, and J. E. Williams. The reactivity of chlorine atoms in aqueous solution. Part III. The reactions of Cl-center dot with solutes. *Physical Chemistry Chemical Physics*, 2(2):237 – 245, 2000. ISSN 1463-9076.
- J. G. Calvert and J. N. Pitts. *Photochemistry*. Wiley, New York, 1966.
- R. M. Chambers, A. C. Heard, and R. P. Wayne. Inorganic Gas-Phase Reactions of the Nitrate Radical – $\text{I}_2 + \text{NO}_3$ and $\text{I} + \text{NO}_3$. *JOURNAL OF PHYSICAL CHEMISTRY*, 96(8):3321–3331, APR 16 1992. ISSN 0022-3654.
- C. R. Chinake and R. H. Simoyi. Kinetics and mechanism of the complex bromate-iodine reaction. *Journal of Physical Chemistry*, 100(5):1643 – 1656, 1996. ISSN 0022-3654.
- O. Citri and I. R. Epstein. Mechanistic Study of a Coupled Chemical Oscillator: The Bromate-Chlorite-Iodide Reaction. *Journal of Physical Chemistry*, 92(7):1865 – 1871, 1988. ISSN 0022-3654.
- M. A. A. Clyne and H. W. Cruse. Atomic Resonance Fluorescence Spectrometry for Rate Constants of Rapid Bimolecular Reactions. 2. Reactions $\text{Cl} + \text{BrCl}$, $\text{Cl} + \text{ICl}$, $\text{Br} + \text{IBr}$, $\text{Br} + \text{ICl}$. *Journal of the Chemical Society – Faraday Transactions II*, 68:1377, 1972. ISSN 0300-9238.
- R. E. Connick. The interaction of hydrogen peroxide and hypochlorous acid in acidic solutions containing chloride ion. *Journal of the American Chemical Society*, 69(6):1509 – 1514, 1947. ISSN 0002-7863.
- L. Deguillaume, M. Leriche, A. Monod, and N. Chaumerliac. The role of transition metal ions on HOx radicals in clouds: a numerical evaluation of its impact on multiphase chemistry. *ATMOSPHERIC CHEMISTRY AND PHYSICS*, 4:95 – 110, JAN 26 2004. ISSN 1680-7324.
- W. B. DeMore, S. P. Sander, D. M. Golden, R. F. Hampson, M. J. Kurylo, C. J. Howard, A. R. Ravishankara, C. E. Kolb, and M. J. Molina. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*. JPL Evaluation No. 12, Jet Propulsion Laboratory, Pasadena, CA, 1997.
- D. A. Dolson and S. R. Leone. A Reinvestigation of the Laser-Initiated Cl_2/HBr Chain Reaction – Absolute Rate Constants and the $V = 2/V = 1$ Ratio from $\text{Cl} + \text{HBr} \rightarrow \text{HCl(v)} + \text{Br}$. *Journal of Physical Chemistry*, 91(13):3543 – 3550, 1987. ISSN 0022-3654.
- A. Donati. *Spectroscopic and kinetic investigations of halogen-containing radicals in the tropospheric aqueous phase*. PhD thesis, Universität Leipzig, 2002.
- E. C. Edblom, L. Gyorgyi, M. Orban, and I. R. Epstein. Systematic Design of Chemical Oscillators. 41. A Mechanism for Dynamic Behavior in the Landolt Reaction with Ferrocyanide. *Journal of the American Chemical Society*, 109(16):4876 – 4880, 1987. ISSN 0002-7863.

- M. Eigen and K. Kustin. Kinetics of Halogen Hydrolysis. *Journal of the American Chemical Society*, 84(8):1355 – 1361, 1962. ISSN 0002-7863.
- B. G. Ershov. Kinetics, mechanism and intermediates of some radiation – induced reactions in aqueous solutions. *Uspekhi Khimii*, 73(1):107 – 120, 2004. ISSN 0042-1308.
- W. H. Fang and R. Z. Liu. Ab initio studies of dissociation pathways on the ground- and excited-state potential energy surfaces for formyl chloride (HClCO). *Journal of Chemical Physics*, 115(22):10431 – 10437, 2001. ISSN 0021-9606.
- R. D. Faria, I. Lengyel, I. R. Epstein, and K. Kustin. Combined Mechanism Explaining Nonlinear Dynamics in Bromine(III) and Bromine(V) Oxidations of Iodine Ion. *Journal of Physical Chemistry*, 97(6):1164–1171, 1993. ISSN 0022-3654.
- R. J. Field and H. D. Försterling. On the Oxybromine Chemistry Rate Constants with Cerium Ions in the Field-Koros-Noyes Mechanism of the Belousow-Zhabotinskii Reaction – The Equilibrium $\text{HBrO}_3^- + \text{BrO}_3^- + \text{H}^+ \rightleftharpoons 2\text{BrO}_2 + \text{H}_2\text{O}$. *Journal of Physical Chemistry*, 90(21):5400 – 5407, 1986. ISSN 0022-3654.
- O. C. Fleischmann, J. Meyer-Arnek, J. P. Burrows, and J. Orphal. The visible absorption spectrum of OBrO, investigated by Fourier transform spectroscopy. *Journal of Physical Chemistry A*, 109(23): 5093 – 5103, 2005. ISSN 1089-5639. doi: {10.1021/jp044911x}.
- K. D. Fogelman, D. M. Walker, and D. W. Margerum. Non-Metal Redox Kinetics: Hypochlorite and Hypochlorous Acid Reactions with Sulfite. *Inorganic Chemistry*, 28(6):986 – 993, 1989. ISSN 0020-1669.
- P. Fornier de Violet. Polyhalide anions as intermediates in chemistry. *Review Chemical Intermediates* 4, pages 121 – 169, 1981.
- D. H. Fortnum, C. J. Battaglia, S. R. Cohen, and J. O. Edwards. The Kinetics of the Oxidation of Halide Ions by Monosubstituted Peroxides. *Journal of the American Chemical Society*, 82(4):778 – 782, 1960. ISSN 0002-7863.
- A. Frenzel, V. Scheer, R. Sikorski, C. George, W. Behnke, and C. Zetzsch. Heterogeneous Interconversion Reactions of BrNO_2 , ClNO_2 , Br_2 , and Cl_2 . *Journal of Physical Chemistry A*, 102(8):1329 – 1337, 1998. ISSN 1089-5639.
- E. N. Fuller. A New Method for Prediction of Binary Gas-Phase Diffusion Coefficients. *Industrial and Engineering Chemistry*, 1986.
- S. Furrow. Reactions of Iodine Intermediates in Iodate Hydrogen Peroxide Oscillators. *Journal of Physical Chemistry*, 91(8):2129 – 2135, 1987. ISSN 0022-3654.
- T. E. Graedel and C. J. Weschler. Chemistry within Aqueous Atmospheric Aerosols and Raindrops. *Reviews of Geophysics*, 19(4):505 – 539, 1981. ISSN 8755-1209.
- M. Green, G. Yarwood, and H. Niki. FTIR Study of the Cl-Atom Initiated Oxidation of Methylglyoxal. *International Journal of Chemical Kinetics*, 22(7):689 – 699, 1990. ISSN 0538-8066.
- A. E. Grigor'ev, I. E. Makarov, and A. K. Pikaev. Formation of Cl_2^- in the bulk solution during the radiolysis of concentrated aqueous solutions of chloride. *High Energy Chemistry*, 21:99 – 102, 1987.

- L. I. Grossweiner and M. S. Matheson. Short-Lived Species from the Photolysis of Aqueous Alkali Halide and Halogen Solutions. *Journal of Chemical Physics*, 23(12):2443 – 2444, 1955. ISSN 0021-9606.
- W. Groszko and R. M. Moore. Ocean-atmosphere exchange of methyl bromide: NW Atlantic and Pacific Ocean studies. *Journal of Geophysical Research – Atmospheres*, 103(D13):16737 – 16741, 1998. ISSN 0747-7309.
- W. R. Haag and J. Hoigné. Ozonation of Bromide-Containing Waters – Kinetics of Formation of Hypobromous Acid and Bromate. *Environmental Science & Technology*, 17(5):261 – 267, 1983. ISSN 0013-936X.
- J. C. Hansen, Y. Li, J. S. Francisco, and Z. Li. On the Mechanism of the $\text{BrO} + \text{CH}_2\text{O}$ Reaction. *Journal of Physical Chemistry A*, 103(42):8543 – 8546, 1999. ISSN 1089-5639.
- D. R. Hanson, A. R. Ravishankara, and E. R. Lovejoy. Reaction of BrONO_2 with H_2O on submicron sulfuric acid aerosol and the implications for the lower stratosphere. *Journal of Geophysical Research – Atmospheres*, 101(D4):9063 – 9069, 1996. ISSN 0148-0227.
- H. Herrmann. Kinetics of aqueous phase reactions relevant for atmospheric chemistry. *Chemical Reviews*, 103(12):4691 – 4716, 2003. ISSN 0009-2665. doi: {10.1021/cr020658q}.
- H. Herrmann. On the photolysis of simple anions and neutral molecules as sources of O^-/OH , SO_x^- and Cl in aqueous solution. *PHYSICAL CHEMISTRY CHEMICAL PHYSICS*, 9(30):3935 – 3964, 2007. ISSN 1463-9076. doi: {10.1039/b618565g}.
- H. Herrmann, H.-W. Jacobi, A. Reese, and R. Zellner. Laboratory studies of small radicals and radical anions of interest for tropospheric aqueous phase chemistry: The reactivity of SO_4^- , in P. M. Borrell, P. Borrell, T. Cvitaö, K. Kelly and W. Seiler (eds). *Proceedings of EUROTRAC Symposium '96: Transport and Transformation of Pollutants in the Troposphere*, 1:407 – 411, 1997. Computational Mechanics Publications, Southampton, UK.
- H. Hippler, K. Luther, and J. Troe. Study on Recombination of Iodine Atoms in highly compressed Gases and in Fluids. *BERICHTE DER BUNSEN-GESELLSCHAFT – PHYSICAL CHEMISTRY CHEMICAL PHYSICS*, 77(12):1104 – 1114, 1973. ISSN 0005-9021.
- J. Hoigné, H. Bader, W. R. Haag, and J. Staehelin. Rate constants of reactions of ozone with organic and inorganic compounds in water – III Inorganic compounds and radicals. *Water Research*, 19(8): 993 – 1004, 1985. ISSN 0043-1354.
- R. E. Huie, C. L. Clifton, and P. Neta. Electron Transfer Reaction Rates and Equilibria of the Carbonate and Sulfate Radical Anions. *Radiation Physics and Chemistry*, 38(5):477 – 481, 1991.
- T. Huthwelker, T. Peter, B. P. Luo, S. L. Clegg, K. S. Carslaw, and P. Brimblecombe. Solubility of HOCl in Water and Aqueous H_2SO_4 to Stratospheric Temperatures. *Journal of Atmospheric Chemistry*, 21(1):81 – 95, 1995. ISSN 0167-7764.
- H.-W. Jacobi. *Kinetische Untersuchungen und Modellrechnungen zur troposphärischen Chemie von Radikalanionen und Ozon in wäßriger Phase*. PhD thesis, Universität-GH-Essen, Germany, 1996.
- H. W. Jacobi, H. Herrmann, and R. Zellner. Kinetic investigation of the Cl_2^- radical in the aqueous phase, in Ph. Mirabel (ed). *Air Pollution Research Report*, 57(Homogenous and heterogenous chemical Processes in the Troposphere):172 – 176, 1996. Office for official Publications of the European Communities, Luxembourg.

- H. W. Jacobi, F. Wicktor, H. Herrmann, and R. Zellner. A laser flash photolysis kinetic study of reactions of the Cl_2^- radical anion with oxygenated hydrocarbons in aqueous solution. *International Journal of Chemical Kinetics*, 31(3):169 – 181, 1999. ISSN 0538-8066.
- F. Jacobsen, J. Holcman, and K. Sehested. Manganese(II)-Superoxide Complex in Aqueous Solution. *Journal of Physical Chemistry A*, 101:1324 – 1328, 1997.
- F. Jacobsen, J. Holcman, and K. Sehested. 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.
- G. G. Jayson, B. J. Parsons, and A. J. Swallow. Some Simple, Highly Reactive, Inorganic Chlorine 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, 1973. ISSN 0300-9599.
- M. E. Jenkin, S. M. Saunders, and M. J. Pilling. The tropospheric degradation of volatile organic compounds: A protocol for mechanism development. *Atmospheric Environment*, 31(1):81 – 104, JAN 1997. ISSN 1352-2310.
- J. L. Jimenez, R. Bahreini, D. R. Cocker, H. Zhuang, V. Varutbangkul, R. Flagan, J. Seinfeld, C. D. O'Dowd, and T. Hoffmann. New particle formation from photooxidation of diiodomethane (CH_2I_2). *Journal of Geophysical Research – Atmospheres*, 108(D10), 2003. ISSN 0148-0227. doi: 10.1029/2002JD002452.
- C. E. Jones, K. E. Hornsby, R. Sommariva, R. M. Dunk, R. von Glasow, G. McFiggans, and L. J. Carpenter. Quantifying the contribution of marine organic gases to atmospheric iodine. *Geophysical Research Letters*, 37, SEP 18 2010. ISSN 0094-8276. doi: {10.1029/2010GL043990}.
- W. Keene, M. Khalil, D. Erickson, A. McCulloch, T. Graedel, J. Lobert, M. Aucott, S.-L. Gong, D. Harper, G. Kleiman, P. Midgley, R. Moore, C. Seuzaret, W. Sturges, C. Benkovitz, V. Koropalov, B. L.A., and Y.-F. Li. RCEI: Reactive Chlorine Emission Inventory, AUG 2008. URL <http://www.eurochlor.org/rcei>.
- U. K. Kläning and T. Wolff. Laser Flash-Photolysis of HClO , ClO^- , HBrO , and 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.
- O. Kondo and S. W. Benson. Kinetics and Equilibria in the System $\text{Br} + \text{CH}_3\text{OOH} \rightleftharpoons \text{HBr} + \text{CH}_3\text{OO}$ – an Upper Limit for the Heat of Formation of the Methylperoxy Radical. *Journal of Physical Chemistry*, 88(26):6675 – 6680, 1984. ISSN 0022-3654.
- A. Kukui, T. P. W. Jungkamp, and R. N. Schindler. Determination of the Product Branching Ratio in the Reaction of NO_3 with OCL at 300 K. *BERICHTE DER BUNSEN-GESELLSCHAFT – PHYSICAL CHEMISTRY CHEMICAL PHYSICS*, 98(12):1619 – 1621, 1994. ISSN 0005-9021.
- K. Kumar and D. W. Margerum. Kinetics and Mechanism of General-Acid-Assisted Oxidation of Bromide by Hypochlorite and Hypochlorous Acid. *Inorganic Chemistry*, 26(16):2706 – 2711, 1987. ISSN 0020-1669.
- G. S. Laurence and A. T. Thornton. Kinetics of oxidation of transition-metal ions by halogen radical-anions. III. 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.

- K. S. Law, W. T. Sturges (Lead Authors), D. R. Blake, N. J. Blake, J. B. Burkholder, J. H. Butler, R. A. Cox, P. H. Haynes, M. K. W. Ko, K. Kreher, C. Mari, K. Pfeilsticker, J. M. C. Plane, R. J. Salawitch, C. Schiller, B.-M. Sinnhuber, R. von Glasow, N. J. Warwick, D. J. Wuebbles, and S. A. Yvon-Lewis. *Scientific Assessment of Ozone Depletion*, chapter 2: Halogenated Very Short Live Substances. Global Ozone Research and Monitoring Project – Report No. 50. World Meteorological Organization, Genf, Schweiz, 2007.
- I. Lengyel, J. Li, K. Kustin, and I. R. Epstein. Rate constants for reactions between iodine- and chlorine-containing species: A detailed mechanism of the chlorine dioxide/chlorite-iodide reaction. *Journal of the American Chemical Society*, 118(15):3708 – 3719, 1996. ISSN 0002-7863.
- D. R. Lide, H. P. R. Frederickse, M. Bass, L. Brewer, F. J. DiSalvo, R. J. Donnelly, B. L. Karger, W. C. Lineberger, D. A. Palmer, D. Seyferth, and J. H. Westbrook, editors. *CRC Handbook of Chemistry and Physics*. CRC Press, 76th edition, 1995.
- C. A. Long and B. H. J. Bielsky. Rate of Reaction of Superoxide Radical with Chloride-Containing Species. *Journal of Physical Chemistry*, 84(5):555 – 557, 1980. ISSN 0022-3654.
- D. Lowe, D. Topping, and G. McFiggans. Modelling multi-phase halogen chemistry in the remote marine boundary layer: investigation of the influence of aerosol size resolution on predicted gas- and condensed-phase chemistry. *Atmospheric Chemistry and Physics*, 9(14):4559 – 4573, 2009. ISSN 1680-7316.
- S. Madronich and S. Flocke. Theoretical estimation of biologically effective UV radiation at the Earth's surface. In C. Zerefos, editor, *Solar Ultraviolet Radiation - Modeling, Measurements and Effects*. NATO ASI Series Vol. I52, Springer-Verlag, Berlin, 1997.
- L. Magi, F. Schweitzer, C. Pallares, S. Cherif, P. Mirabel, and C. George. Investigation of the uptake rate of ozone and methyl hydroperoxide by water surfaces. *Journal of Physical Chemistry A*, 101(27):4943 – 4949, 1997. ISSN 1089-5639.
- W. G. Mallard, R. F. Hampson, F. Westley, J. T. Herron, and F. D. H. NIST Chemical Kinetics Database: Version 17 – 2Q98, 1998.
- D. W. Margerum, P. N. Dickson, J. C. Nagy, K. Kumar, C. P. Bowers, and K. D. Fogelman. Kinetics of the Iodine Monochloride Reaction with Iodide Measured by the Pulsed-Accelerated-Flow Method. *Inorganic Chemistry*, 25(27):4900 – 4904, 1986. ISSN 0020-1669.
- A. R. W. Marsh and W. J. McElroy. The Dissociation Constant and Henry Law Constant of HCl in Aqueous Solution. *Atmospheric Environment*, 19(7):1075 – 1080, 1985. ISSN 1352-2310.
- A. E. Martell and L. G. Sillen. Stability Constants of Metal Ion Complexes, Section I⁻ Inorganic Ligands, 2nd edition. *Chemical Society (London)*, (17):400, 1964.
- S. Matsunaga, M. Mochida, T. Saito, and K. Kawamura. In situ measurement of isoprene in the marine air and surface seawater from the western North Pacific. *Atmospheric Environment*, 36(39 – 40):6051 – 6057, DEC 2002. ISSN 1352-2310.
- B. M. Matthew and C. Anastasio. Supplementary material for ACP manuscripts "A chemical probe technique for the determination of reactive halogen species in aqueous solution: Part 1 and 2". *Atmospheric Chemistry and Physics*, 6(9):2423 – 2437, 2006. ISSN 1680-7316.

- B. M. Matthew, I. George, and C. Anastasio. Hydroperoxyl radical (HO_2^\bullet) oxidizes dibromide radical anion ($\text{Br}_2^{\bullet 2-}$) to bromine (Br_2) in aqueous solution: Implications for the formation of Br_2 in the marine boundary layer. *Geophysical Research Letters*, 30(24), 2003. ISSN 0094-8276. doi: 10.1029/2003GL018572.
- S. Mertens and C. von Sonntag. Photolysis ($\lambda = 254\text{ nm}$) of tetrachloroethene in aqueous solutions. *Journal of Photochemistry and Photobiology A*, 85:1 – 9, 1995.
- G. Merényi and J. Lind. 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.
- P. Middleton, W. R. Stockwell, and W. P. L. Carter. Aggregation and Analysis of Volatile Organic Compound Emissions for Regional Modeling. *Atmospheric Environment Part A – General Topics*, 24(5):1107 – 1133, 1990. ISSN 0004-6981.
- R. M. Moore and W. Groszko. Methyl iodide distribution in the ocean and fluxes to the atmosphere. *Journal of Geophysical Research – Oceans*, 104(C5):11163 – 11171, 1999. ISSN 0148-0227.
- R. M. Moore, W. Groszko, and S. J. Niven. Ocean-atmosphere exchange of methyl chloride: Results from NW Atlantic and Pacific Ocean studies. *Journal of Geophysical Research – Oceans*, 101(C12): 28529 – 28538, 1996.
- M. Mozurkewich. Possible Role of NO_3 in the Nighttime Chemistry of a Cloud – Comment. *Journal of Geophysical Research – Atmospheres*, 91(D13):14569 – 14570, 1986.
- M. Mozurkewich. Mechanisms for the Release of Halogens from Sea-Salt Particles by Free Radical Reactions. *Journal of Geophysical Research – Atmospheres*, 100(D7):14199 – 14207, 1995. ISSN 0148-0227.
- J. C. Nagy, K. Kumar, and D. W. Margerum. Non-Metal Redox Kinetics: Oxidation of Iodide by Hypochlorous Acid and by Nitrogen Trichloride Measured by the Pulsed-Accelerated-Flow Method. *Inorganic Chemistry*, 27(16):2773 – 2780, 1988. ISSN 0020-1669.
- H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach. An FTIR Study of the Cl-Atom-Initiated Reaction of glyoxal. *International Journal of Chemical Kinetics*, 17(5):547 – 558, 1985. ISSN 0538-8066.
- H. Niki, P. D. Maker, C. M. Savage, and M. D. Hurley. Fourier-Transform Infrared Study of the Kinetics and Mechanisms for the Cl-Atom- and HO-Radical-Initiated Oxidation of Glycolaldehyde. *Journal of Physical Chemistry*, 91(8):2174 – 2178, 1987. ISSN 0022-3654.
- R. J. Olsen and I. R. Epstein. Bifurcation Analysis of Chemical Reaction Mechanisms. 1. Steady-State Bifurcation Structure. *Journal of Chemical Physics*, 94(4):3083 – 3095, 1991. ISSN 0021-9606.
- J. J. Orlando and G. S. Tyndall. Rate coefficients for the thermal decomposition of BrONO_2 and the heat of formation of BrONO_2 . *Journal of Physical Chemistry*, 100(50):19398 – 19405, 1996. ISSN 0022-3654.
- J. J. Orlando, G. S. Tyndall, J. M. Fracheboud, E. G. Estupinan, S. Haberkorn, and A. Zimmer. The rate and mechanism of the gas-phase oxidation of hydroxyacetone. *Atmospheric Environment*, 33(10):1621 – 1629, 1999. ISSN 1352-2310.

- D. A. Palmer, R. W. Ramette, and R. E. Mesmer. The Hydrolysis of Iodine – Equilibria at High Temperatures. *Journal of Nuclear Materials*, 130:280 – 286, 1985. ISSN 0022-3115.
- K. Parajuli. *Laser based kinetic investigations of halogen radicals in aqueous solution*. PhD thesis, Universität Leipzig, Germany, 2006.
- S. Pechtl and R. von Glasow. Reactive chlorine in the marine boundary layer in the outflow of polluted continental air: A model study. *Geophysical Research Letters*, 34(11), JUN 15 2007. ISSN 0094-8276. doi: {10.1029/2007GL029761}.
- S. Pechtl, E. R. Lovejoy, J. B. Burkholder, and R. von Glasow. Modeling the possible role of iodine oxides in atmospheric new particle formation. *Atmospheric Chemistry and Physics Discussions*, 5(5): 9907 – 9952, 2005. ISSN 1680-7367.
- S. Pechtl, E. R. Lovejoy, J. B. Burkholder, and R. von Glasow. Modeling the possible role of iodine oxides in atmospheric new particle formation. *Atmospheric Chemistry and Physics*, 6:505 – 523, 2006. ISSN 1680-7324.
- S. Pechtl, G. Schmitz, and R. von Glasow. Modelling iodide-iodate speciation in atmospheric aerosol: Contributions of inorganic and organic iodine chemistry. *Atmospheric Chemistry and Physics*, 7:1381 – 1393, 2007. ISSN 1680-7316.
- M. Pilling, A. Rickard, S. Pascoe, C. Boss, S. Saunders, M. E. Jenkin, N. Carslaw, and D. Derwent. Master Chemical Mechanism, Version 3.1, Aug 2008. URL <http://mcm.leeds.ac.uk/MCM/>.
- C. Plass-Dülmer, A. Khedim, R. Koppmann, F. J. Johnen, J. Rudolph, and H. Kuosa. Emissions of light nonmethane hydrocarbons from the Atlantic into the atmosphere. *Global Biogeochemical Cycles*, 7(1):211 – 228, MAR 1993. ISSN 0886-6236.
- L. Prager, P. Dowideit, H. Langguth, H. P. Schuchmann, and C. von Sonntag. Hydrolytic removal of the chlorinated products from the oxidative free-radical-induced degradation of chloroethylenes: acid chlorides and chlorinated acetic acids. *Journal of the Chemical Society – Perkin Transactions 2*, (9): 1641 – 1647, 2001. ISSN 1472-779X. doi: 10.1039/b101687n.
- E. Pungor, K. Burger, and E. Schulek. Interhaloid Complexes in Aqueous Solution. *Journal of Inorganic & Nuclear Chemistry*, 11(1):56 – 61, 1959. ISSN 0022-1902.
- A. Reese. *UV/VIS-spektrometrische und kinetische Untersuchungen von Radikalen und Radikalanionen in wäßriger Lösung*. PhD thesis, Universität Essen, Germany, 1997.
- A. Reese, H. Herrmann, and R. Zellner. Kinetic and Spectroscopic Investigations of the Br_2^- Radical in Aqueous Solution, in: Proceedings of the EUROTRAC-2 '98 symposium, eds: P. M. Borrell and P. Borrell. WIT press, Southampton, pages 714 – 718, 1999.
- Röth, E. P. A Fast Algorithm to Calculate the Photonflux in Optically Dense Media for Use in Photochemical Models. *Berichte der Bunsen-Gesellschaft – Physical Chemistry Chemical Physics*, 96(3):417 – 420, MAR 1992. ISSN 0005-9021.
- R. Sander and P. J. Crutzen. Model study indicating halogen activation and ozone destruction in polluted air masses transported to the sea. *Journal of Geophysical Research – Atmospheres*, 101(D4): 9121 – 9138, 1996. ISSN 0148-0227.

- R. Sander and A. Kerkweg. *The Chemical Mechanism of MECCA*. Air Chemistry Department, Max-Planck Institute of Chemistry, Mainz, Germany, 2005.
- R. Sander, R. Vogt, G. W. Harris, and P. J. Crutzen. Modeling the chemistry ozone, halogen compounds, and hydrocarbons in the arctic troposphere during spring. *Tellus Series B – Chemical and Physical Meteorology*, 49(5):522 – 532, NOV 1997. ISSN 0280-6509.
- S. P. Sander, R. R. Friedl, D. M. Golden, M. J. Kurylo, R. E. Huie, V. L. Orkin, G. K. Moortgat, A. R. Ravishankara, C. E. Kolb, M. Molina, J., and B. J. Finlayson-Pitts. *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies*. JPL Evaluation No. 14, Jet Propulsion Laboratory, Pasadena, CA, 2003.
- S. P. Sander, R. R. Friedl, D. M. Golden, M. J. Kurylo, G. K. Moortgat, P. H. Wine, A. R. Ravishankara, C. E. Kolb, M. J. Molina, B. J. Finlayson-Pitts, R. E. Huie, and V. L. Orkin. *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies*. JPL Evaluation No. 15, Jet Propulsion Laboratory, Pasadena, CA, 2006.
- S. M. Saunders, M. E. Jenkin, R. G. Derwent, and M. J. Pilling. 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*, 3:161 – 180, FEB 12 2003. ISSN 1680-7324.
- V. Scheer, A. Frenzel, W. Behnke, C. Zetzsch, L. Magi, C. George, and P. Mirabel. Uptake of Nitrosyl Chloride (NOCl) by Aqueous Solutions. *Journal of Physical Chemistry A*, 101(49):9359 – 9366, 1997. ISSN 1089-5639.
- G. Schmitz. Kinetics of the Dushman reaction at low I^- concentrations. *Physical Chemistry Chemical Physics*, 2(18):4041 – 4044, 2000. ISSN 1463-9076.
- G. Schmitz. Inorganic reactions of iodine(+1) in acidic solutions. *International Journal of Chemical Kinetics*, 36(9):480 – 493, 2004. ISSN 0538-8066. doi: 10.1002/kin.20020.
- S. E. Schwartz. *Mass transport considerations pertinent to aqueous phase reactions of gases in liquid water clouds*. Chemistry of Multiphase Atmospheric Systems, 1986.
- H. A. Schwarz and B. H. J. Bielski. Reactions of HO_2 and O_2^- with Iodine and Bromine and the I_2^- and I Atom Reduction Potentials. *Journal of Physical Chemistry*, 90(7):1445 – 1448, 1986. ISSN 0022-3654.
- F. Schweitzer, L. Magi, P. Mirabel, and C. George. Uptake rate measurements of methanesulfonic acid and glyoxal by aqueous droplets. *Journal of Physical Chemistry A*, 102(3):593 – 600, 1998. ISSN 1089-5639.
- F. Schweitzer, P. Mirabel, and C. George. Uptake of hydrogen halides by water droplets. *Journal of Physical Chemistry A*, 104(1):72 – 76, 2000. ISSN 1089-5639.
- D. J. Seery and D. Britton. The Continuous Absorption Spectra of Chlorine, Bromine, Bromine Chloride, Iodine Chloride, and Iodine Bromide. *Journal of Physical Chemistry*, 68(8):2263 – 2266, 1964. ISSN 0022-3654.
- J. C. Shi and M. J. Bernhard. Kinetic studies of Cl-atom reactions with selected aromatic compounds using the photochemical reactor-FTIR spectroscopy technique. *International Journal of Chemical Kinetics*, 29(5):349 – 358, 1997. ISSN 0538-8066.

- H. B. Singh, A. Tabazadeh, M. J. Evans, B. D. Field, D. J. Jacob, G. Sachse, J. H. Crawford, R. Shetter, and W. H. Brune. Oxygenated volatile organic chemicals in the oceans: Inferences and implications based on atmospheric observations and air-sea exchange models. *Geophysical Research Letters*, 30 (16), AUG 28 2003. ISSN 0094-8276. doi: {10.1029/2003GL017933}.
- H. C. Sutton and M. T. Downes. Reactions of HO₂ radical in aqueous solution with bromine and related compounds. *Journal of the Chemical Society – Faraday Transactions I*, 68(8):1498, ISSN = 0300-9599,, 1972.
- H. E. Sutton, G. E. Adams, J. W. Boag, and B. D. Michael. Radical yields and kinetics in the pulse radiolysis of potassium bromide solutions, In International Symposium on Pulse Radiolysis, EBERT, M., KEENE, J. P., AND SWALLOW, A. J. (eds). *Academic Press, Manchester, England*, pages 61 – 81, 1965.
- A. M. Thompson and O. C. Zafiriou. Air-sea fluxes of transient atmospheric species. *Journal of Geophysical Research – Oceans and Atmospheres*, 88(NC11):6696 – 6708, 1983. ISSN 0148-0227.
- A. T. Thornton and G. S. Laurence. Kinetics of oxidation of transition-metal ions by halogen radical-anions. I. 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.
- Y. Toyota, K. Kanaya, M. Takahashi, and H. Akimoto. A box model study on photochemical interactions between VOCs and reactive halogen species in the marine boundary layer. *Atmospheric Chemistry and Physics*, 4:1961 – 1987, SEP 30 2004. ISSN 1680-7324.
- R. C. Troy and D. W. Margerum. Nonmetal Redox Kinetics – Hypobromite and Hypobromous Acid Reactions with Iodide and with Sulfite and the Hydrolysis of Bromosulfate. *Inorganic Chemistry*, 30 (18):3538 – 3543, 1991. ISSN 0020-1669.
- R. C. Troy, M. D. Kelley, J. C. Nagy, and D. W. Margerum. Nonmetal Redox Kinetics – Iodine Monobromide Reaction with Iodide Ion and the Hydrolysis of IBr. *Inorganic Chemistry*, 30(25):4838 – 4845, 1991. ISSN 0020-1669.
- E. Villenave and R. Lesclaux. The UV absorption spectra of CH₂Br and CH₂BrO₂ and the reaction kinetics of CH₂BrO₂ with itself and with HO₂ at 298 K. 236(4 – 5):376 – 384, 1995. ISSN 0009-2614. doi: 10.1016/0009-2614(95)00253-Z.
- R. Vogt and R. N. Schindler. Eine gaskinetische Studie zur Reaktion von HOCl mit F-, Cl- und H-Atomen bei Raumtemperatur. *BERICHTE DER BUNSEN-GESELLSCHAFT – PHYSICAL CHEMISTRY CHEMICAL PHYSICS*, 97(6):819 – 829, 1993. ISSN 0005-9021.
- R. Vogt, P. J. Crutzen, and R. Sander. A mechanism for halogen release from sea-salt aerosol in the remote marine boundary layer. *NATURE*, 383(6598):327 – 330, 1996. ISSN 0028-0836.
- R. Vogt, R. Sander, R. von Glasow, and P. J. Crutzen. Iodine chemistry and its role in halogen activation and ozone loss in the marine boundary layer: A model study. *Journal of Atmospheric Chemistry*, 32(3):375 – 395, 1999. ISSN 0167-7764.
- R. von Glasow and P. J. Crutzen. Tropospheric Halogen Chemistry. In D. H. Heinrich and K. K. Turekian, editors, *Treatise on Geochemistry*, pages 1 – 67, Oxford, 2007. Pergamon. ISBN 978-0-08-043751-4. doi: 10.1016/B0-08-043751-6/04141-4.

- R. von Glasow, R. Sander, A. Bott, and P. J. Crutzen. Modeling halogen chemistry in the marine boundary layer – 1. Cloud-free MBL. *Journal of Geophysical Research – Atmospheres*, 107(D17), 2002a. ISSN 0747-7309. doi: 10.1029/2001JD000942.
- R. von Glasow, R. Sander, A. Bott, and P. J. Crutzen. Modeling halogen chemistry in the marine boundary layer – 2. Interactions with sulfur and the cloud-covered MBL. *Journal of Geophysical Research – Atmospheres*, 107(D17), SEP 2002b. ISSN 0747-7309. doi: {10.1029/2001JD000943}.
- I. Wagner and H. Strehlow. 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.
- I. Wagner, J. Karthäuser, and H. Strehlow. On the decay of the dichloride anion Cl_2^- in aqueous solution. *BERICHTE DER BUNSEN-GESELLSCHAFT – PHYSICAL CHEMISTRY CHEMICAL PHYSICS*, 90(10):861 – 867, 1986. ISSN 0005-9021.
- T. X. Wang and D. W. Margerum. Kinetics of Reversible Chlorine Hydrolysis: Temperature Dependence and General-Acid/Base-Assisted Mechanisms. *Inorganic Chemistry*, 33(6):1050 – 1055, 1994. ISSN 0020-1669.
- T. X. Wang, M. D. Kelley, J. N. Cooper, R. C. Beckwith, and D. W. Margerum. Equilibrium, Kinetic, and UV-Spectral Characteristics of Aqueous Bromine Chloride, Bromine, and Chlorine Species. *Inorganic Chemistry*, 33(25):5872 – 5878, 1994. ISSN 0020-1669.
- Y. L. Wang, J. C. Nagy, and D. W. Margerum. Kinetics of Hydrolysis of Iodine Monochloride Measured by the Pulsed-Accelerated-Flow Method. *Journal of the American Chemical Society*, 111(20):7838 – 7844, 1989. ISSN 0002-7863.
- P. Warneck. Multi-phase chemistry of C-2 and C-3 organic compounds in the marine atmosphere. *Journal of Atmospheric Chemistry*, 51(2):119 – 159, JUN 2005. ISSN 0167-7764. doi: {10.1007/s10874-005-5984-7}.
- C. J. Weschler, M. L. Mandich, and T. E. Graedel. Speciation, Photosensitivity, and Reactions of Transition Metal Ions in Atmospheric Droplets. *JOURNAL OF GEOPHYSICAL RESEARCH-ATMOSPHERES*, 91(D4):5189 – 5204, APR 20 1986.
- F. Wicktor, A. Donati, H. Herrmann, and R. Zellner. Laser based spectroscopic and kinetic investigations of reactions of the Cl atom with oxygenated hydrocarbons in aqueous solution. *Physical Chemistry Chemical Physics*, 5(12):2562 – 2572, 2003. ISSN 1463-9076. doi: 10.1039/b212666d.
- E. Wilhelm, R. Battino, and R. J. Wilcock. Low-Pressure Solubility of Gases in Liquid Water. *Chemical Reviews*, 77(2):219 – 262, 1977. ISSN 0009-2665.
- D. Wu, D. Wong, and B. DiBartolo. EVOLUTION OF Cl_2^- IN AQUEOUS NaCl SOLUTIONS. *Journal of Photochemistry*, 14(4):303 – 310, 1980. ISSN 0047-2670.
- X. Yang, R. A. Cox, N. J. Warwick, J. A. Pyle, G. D. Carver, F. M. O'Connor, and N. H. Savage. Tropospheric bromine chemistry and its impacts on ozone: A model study. *Journal of Geophysical Research – Atmospheres*, 110(D23), 2005. ISSN 0148-0227. doi: {10.1029/2005JD006244}.
- Y. Yokouchi, H. J. Li, T. Machida, S. Aoki, and H. Akimoto. Isoprene in the marine boundary layer (Southeast Asian Sea, eastern Indian Ocean, and Southern Ocean): Comparison with dimethyl sulfide

- and bromoform. *Journal of Geophysical Research – Atmospheres*, 104(D7):8067 – 8076, APR 20 1999. ISSN 0747-7309.
- H. A. Young. The Reduction of Bromic Acid by Hydrobromic Acid in the Prescence of Hydrogen Peroxide. *Journal of the American Chemical Society*, 72(7):3310 – 3312, 1950. ISSN 0002-7863.
- X.-Y. Yu and J. R. Barker. Hydrogen Peroxide Photolysis in Acidic Aqueous Solutions Containing Chloride Ions. I. Chemical Mechanism. *Journal of Physical Chemistry A*, 107(9):1313 – 1324, 2003. ISSN 1089-5639. Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109-1055, and Department of Atmospheric, Oceanic, and Space Sciences, The University of Michigan, Ann Arbor, Michigan 48109-2143.
- D. Zehavi and J. Rabani. Oxidation of Aqueous Bromide Ions by Hydroxyl Radicals – Pulse Radiolytic Investigation. *Journal of Physical Chemistry*, 76(3):312 – 319, 1972. ISSN 0022-3654.
- R. Zellner, M. Exner, and H. Herrmann. Absolute OH Quantum Yields in the Laser Photolysis of Nitrate, Nitrite and Dissolved H₂O₂ at 308 and 351 nm in the Temperature Range 278 – 353 K. *Journal of Atmospheric Chemistry*, 10(4):411 – 425, MAY 1990. ISSN 0167-7764.
- R. Zellner, H. Herrmann, M. Exner, H.-W. Jacobi, G. Raabe, and A. Reese. Formation and Reactions of Oxidants in the Aqueous Phase, in P. Warneck (ed), Heterogeneous and Liquid Phase Processes. *Springer Verlag, Berlin*, pages 146 – 152, 1996.
- Y. Zhou, R. K. Varner, R. S. Russo, O. W. Wingenter, K. B. Haase, R. Talbot, and B. C. Sive. Coastal water source of short-lived halocarbons in New England. *Journal of Geophysical Research – Atmospheres*, 110(D21), 2005. ISSN 0148-0227. doi: {10.1029/2004JD005603}.
- G. Zimmerman and F. C. Strong. Equilibria and spectra of aqueous chlorine solutions. *Journal of the American Chemical Society*, 79(9):2063 – 2066, 1957. doi: 10.1021/ja01566a011.