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

Electronic Supplementary Material

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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 4^{th} 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 7.5×10^4 molecules cm^{-3} on the last day and an overall maximum of about 1×10^5 molecules cm^{-3} on the 3^{rd} 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 1.2×10^5 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 5.8×10^3 molecules cm^{-3} s^{-1}, the real average forward and reverse fluxes of this equilibrium are astonishingly high with 2.1×10^9 molecules cm^{-3} 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 3.2×10^5 molecules cm^{-3} s^{-1} over sink fluxes, which total to 2.3×10^3 molecules cm^{-3} 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.

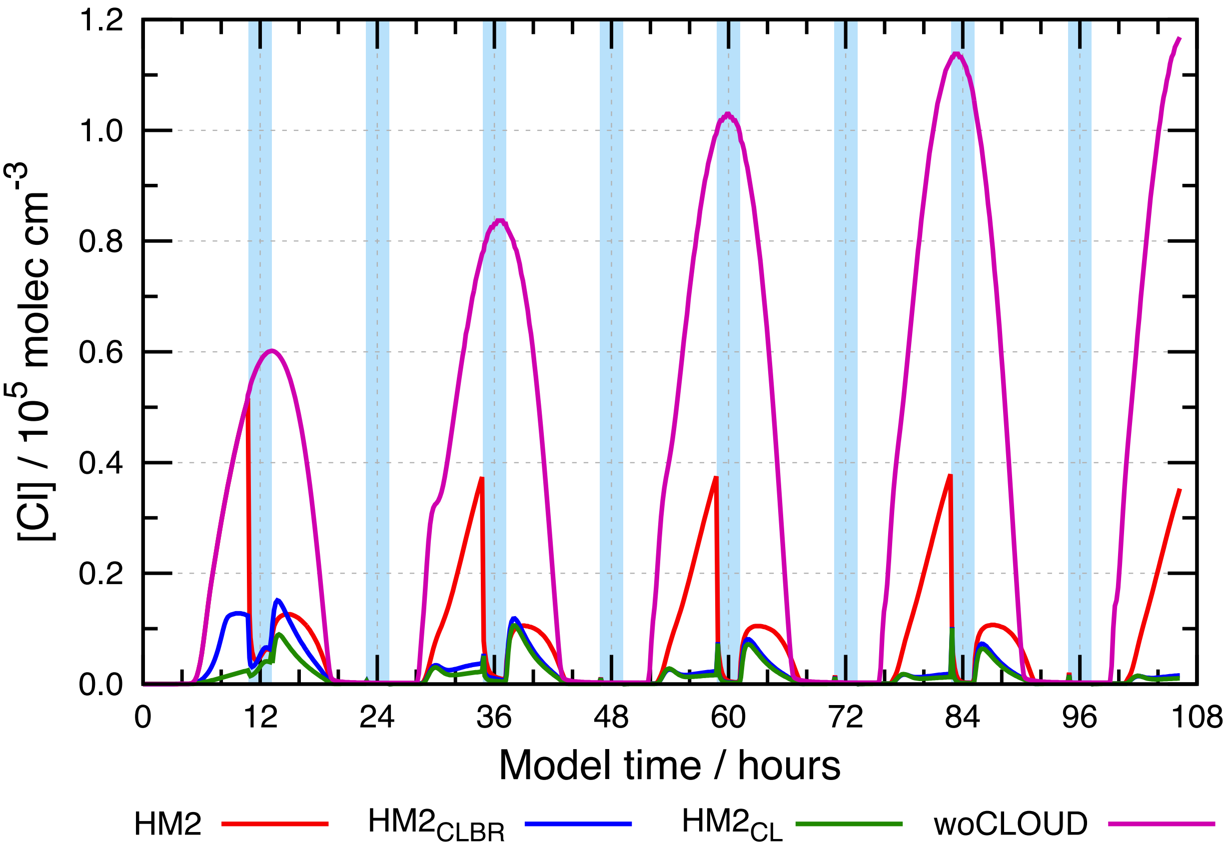


Figure S1 Modelled Cl concentration-time profiles in the gas phase over the whole modelling period of 108h for the different scenarios. Blue bars indicate in-cloud residence times of the air parcel.

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 1.7×10^4 molecules cm^{-3} s^{-1}. Photolysis is of minor importance with fluxes one order of magnitude smaller (1.1×10^3 molecules cm^{-3} s^{-1}).
Under cloud-free conditions, about two third of ClO react with HO_2 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 NO_2 to $ClNO_3$, which will then either decompose to ClO and NO_2 or photolyse to Cl and NO_3. 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).

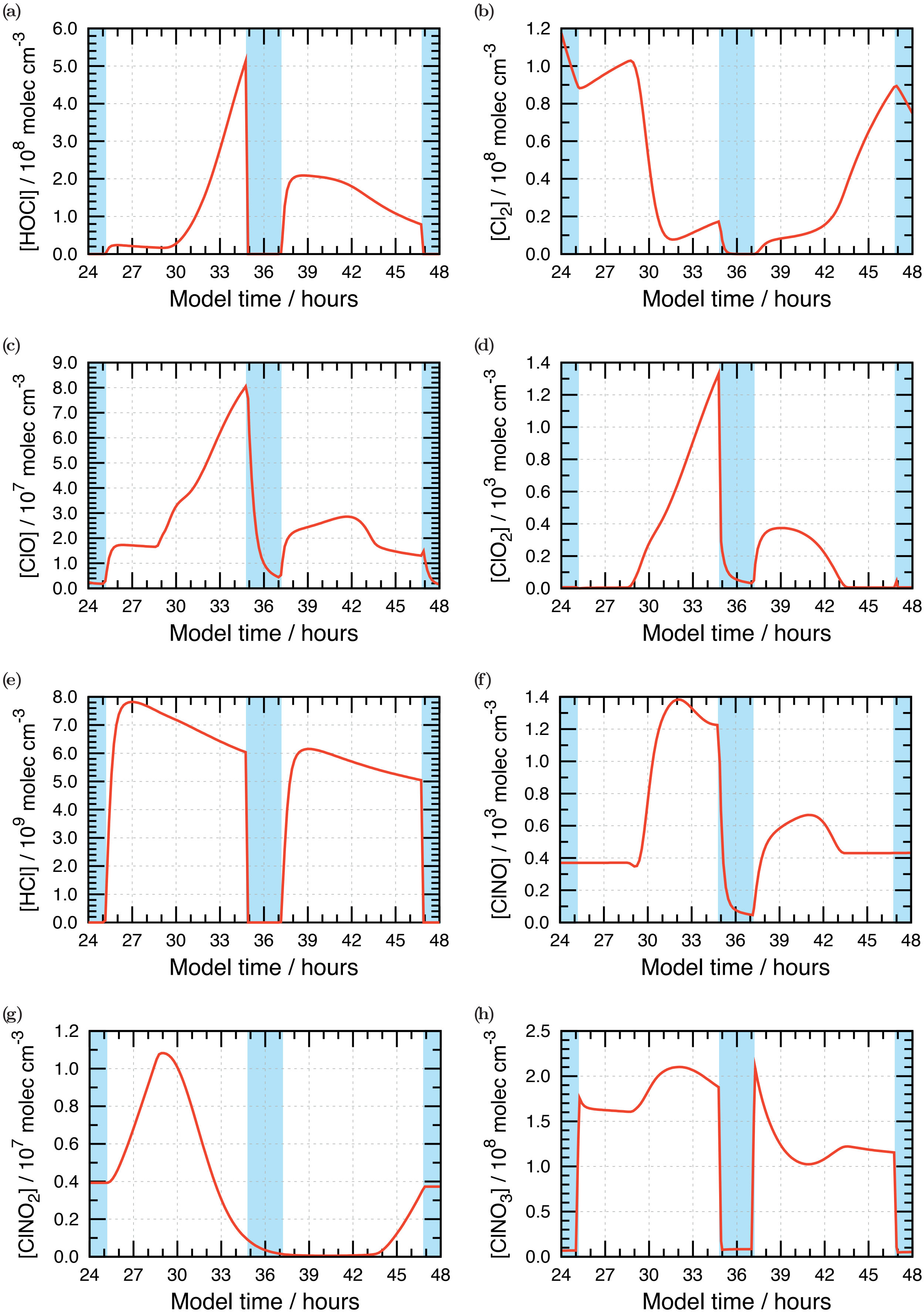


Figure S2 Modelled concentration-time profiles of selected chlorine species in the gas phase on the second model day (scenario HM2). Blue bars indicate in-cloud residence times of the air parcel.

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

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 8.8×10^3 molecules cm^{-3} s^{-1}. Photolysis as a source for $Cl_{(g)}$ is less important under in-cloud conditions. Only Cl_2 photolysis with fluxes of 2.1×10^3 molecules cm^{-3} 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 6.9×10^2 molecules cm^{-3} 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 (9.0×10^2 molecules cm^{-3} s^{-1}), while the main part of chlorine reacts with organics. In the latter reaction HCl is formed, which partitions into in the aqueous phase and accumulates there.

Under in-cloud conditions, only 24% (1.8×10^3 molecules cm^{-3} s^{-1}) of the ClO react with hydroperoxyl radicals to form hypochlorous acid. The reaction with methyl peroxyl radicals is less affected and still accounts for 13% of all losses under in-cloud conditions. A large fraction of ClO (3.8×10^3 molecules cm^{-3} 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 6.1×10^3 molecules cm^{-3} 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 8.8×10^3 molecules cm^{-3} 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.

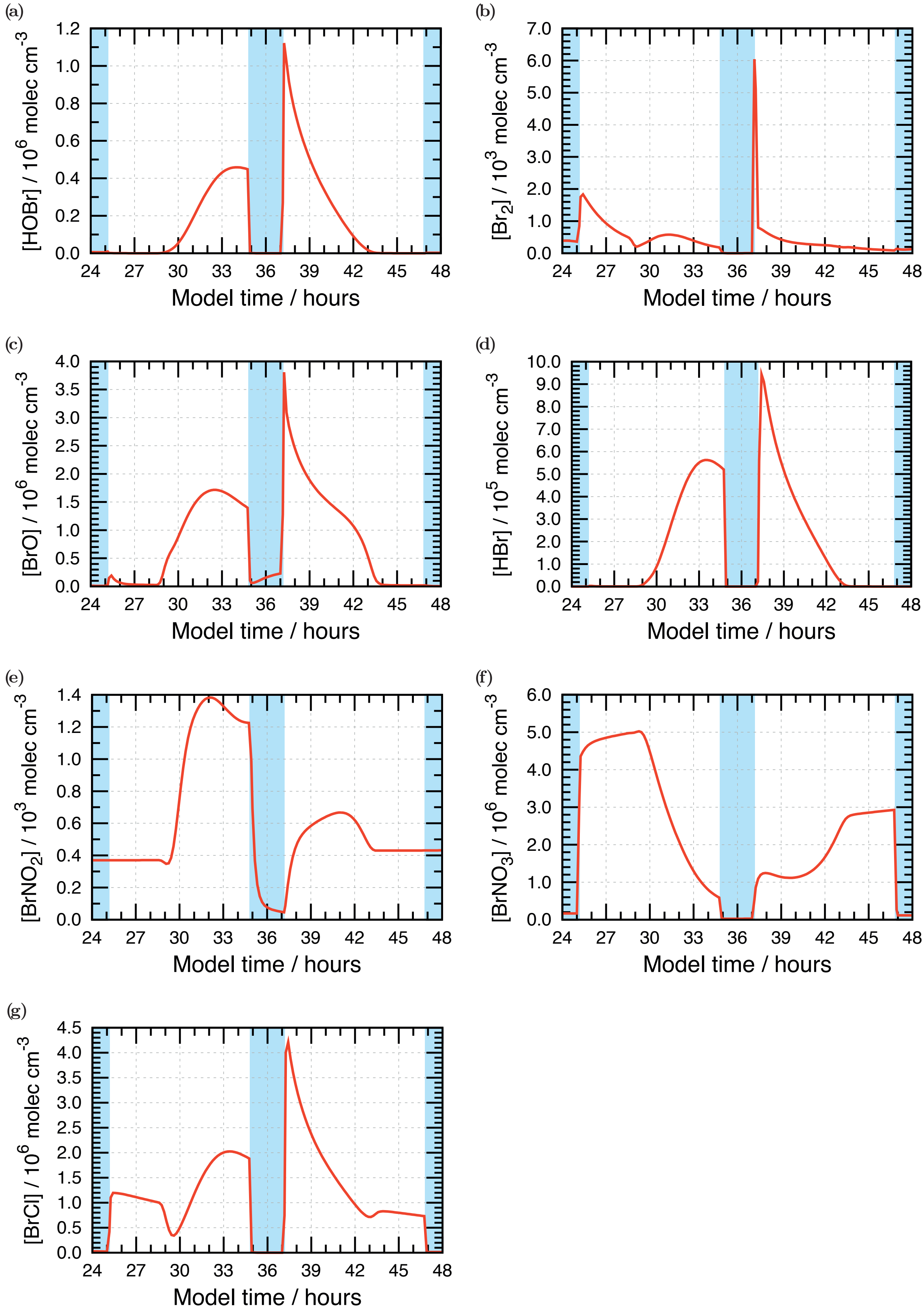


Figure S3 Modelled concentration-time profiles of selected bromine species in the gas phase on the second model day (scenario HM2). Blue bars indicate in-cloud residence times of the air parcel.

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 molecules cm^{-3} s^{-1} totalling to 6% of the sources. The largest fraction (94% of the total sources) with a flux of 219 molecules cm^{-3} 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 cm^{-3} s^{-1}]**	**Relative contribution to overall sources/sinks [%]**
P_g47	$ICl \xrightarrow{h\nu} I + Cl$	4.8×10^4	69
P_g42	$HOI \xrightarrow{h\nu} I + OH$	1.4×10^4	21
P_g36	$I_2 \xrightarrow{h\nu} 2\,I$	1.9×10^3	3
G234	$IO + IO \longrightarrow$ products	3.0×10^3	4
G254	$IO + ClO \longrightarrow$ products	1.8×10^3	3
	$I + O_3 \longrightarrow IO + O_2$	-7.7×10^4	−100
G230	$*\ I + O_3 \longrightarrow IO + O_2$	*-8.6×10^4*	
G243	$*\ IO + NO \longrightarrow I + NO_2$	*5.8×10^3*	
P_g37	$*\ IO \xrightarrow{h\nu} I + O(^3P)$	*3.4×10^3*	

The only significant loss of iodine atoms in the gas phase is the reaction with ozone with a flux of 1.0×10^5 molecules cm^{-3} s^{-1}. For the IO radicals formed, the reaction with HO_2 is the dominant sink. 7.5×10^4 molecules cm^{-3} s^{-1} or 75% of all loss fluxes are resulting from this reaction. Further fluxes are of minor importance and account for interactions with NOx (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 molecules cm^{-3} s^{-1} (6%). About 23% of the hypoiodous acid formed from the reaction of IO with HO_2 photolyse, the remaining part (5.9×10^4 molecules cm^{-3} 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%, 1.5×10^4 molecules cm^{-3} 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.

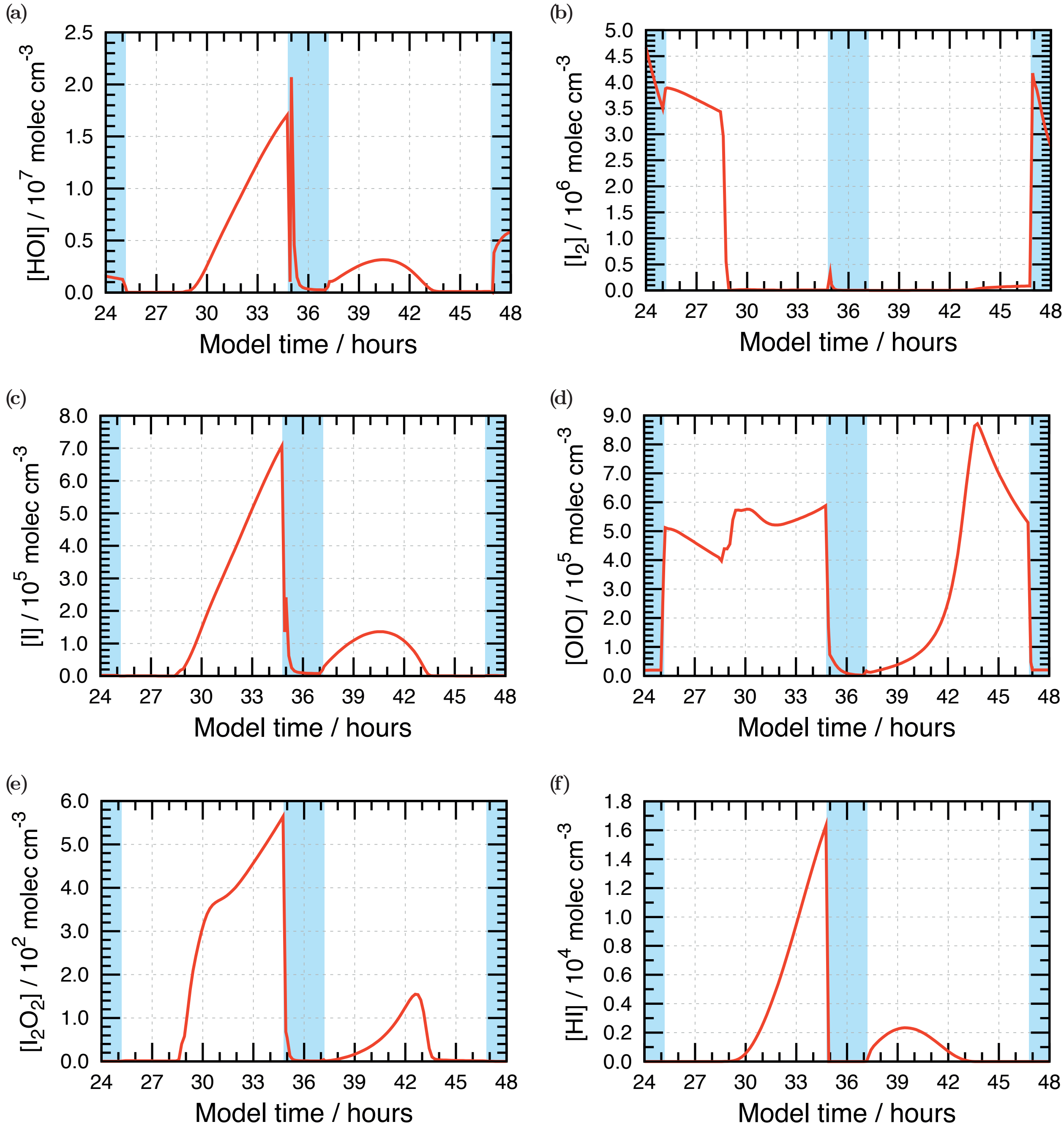


Figure S4 Modelled concentration-time profiles of selected iodine species in the gas phase on the second model day (scenario HM2). Blue bars indicate in-cloud residence times of the air parcel.

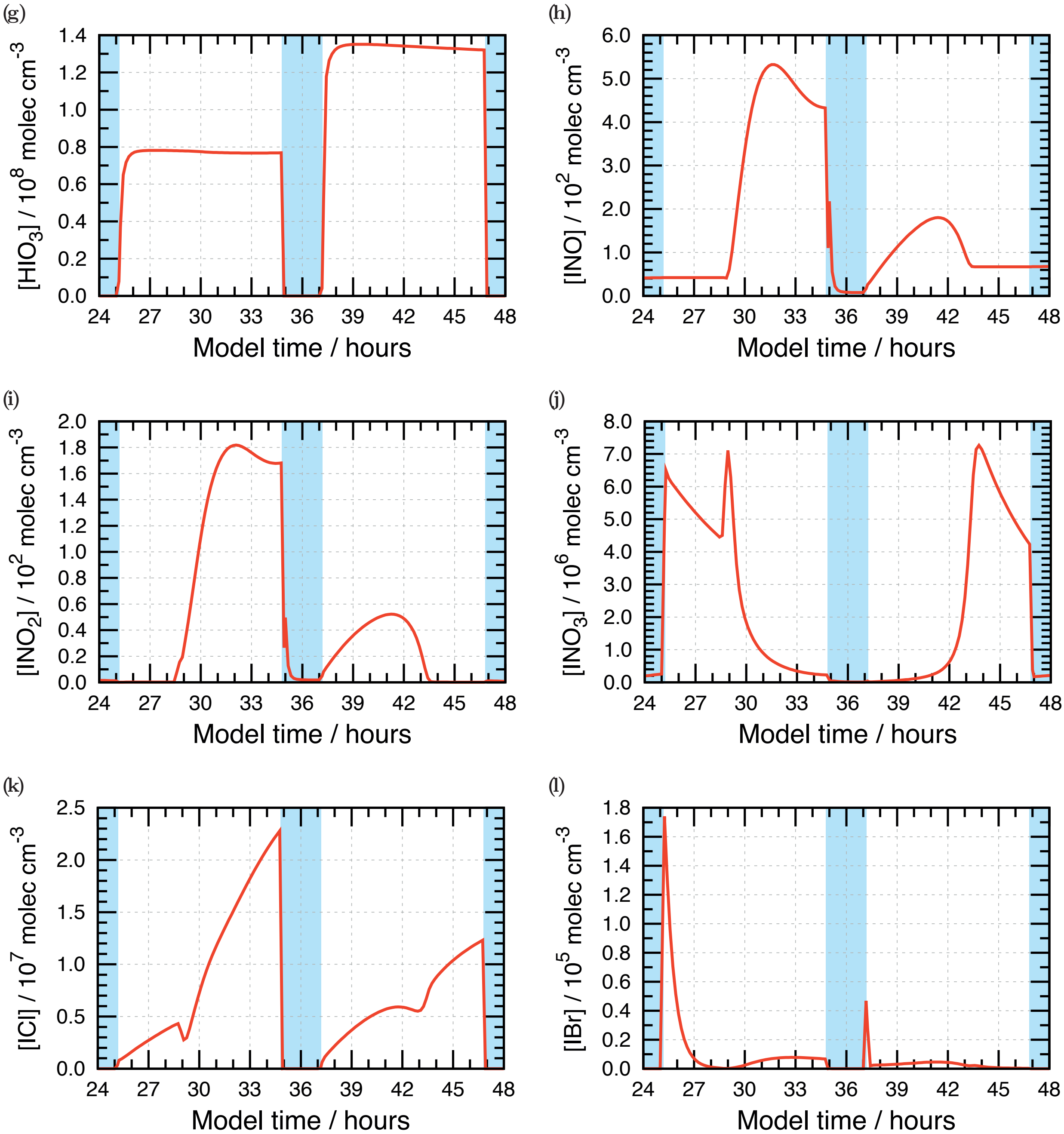
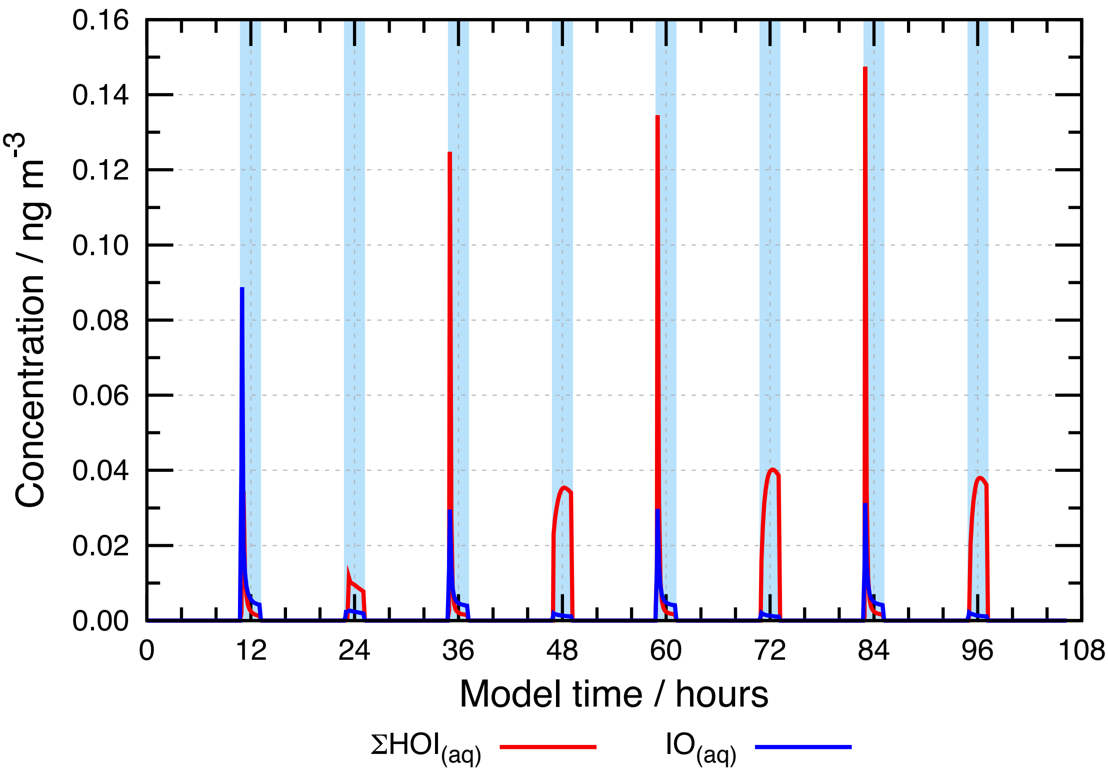


Figure S4 **(continued)** Modelled concentration-time profiles of selected bromine species in the gas phase on the second model day (scenario HM2). Blue bars indicate in-cloud residence times of the air parcel.

(a) $IO_{(aq)}$ and $\Sigma HOI_{(aq)}$



(b) $\Sigma HIO_{2\,(aq)}$ and $\Sigma HIO_{3\,(aq)}$

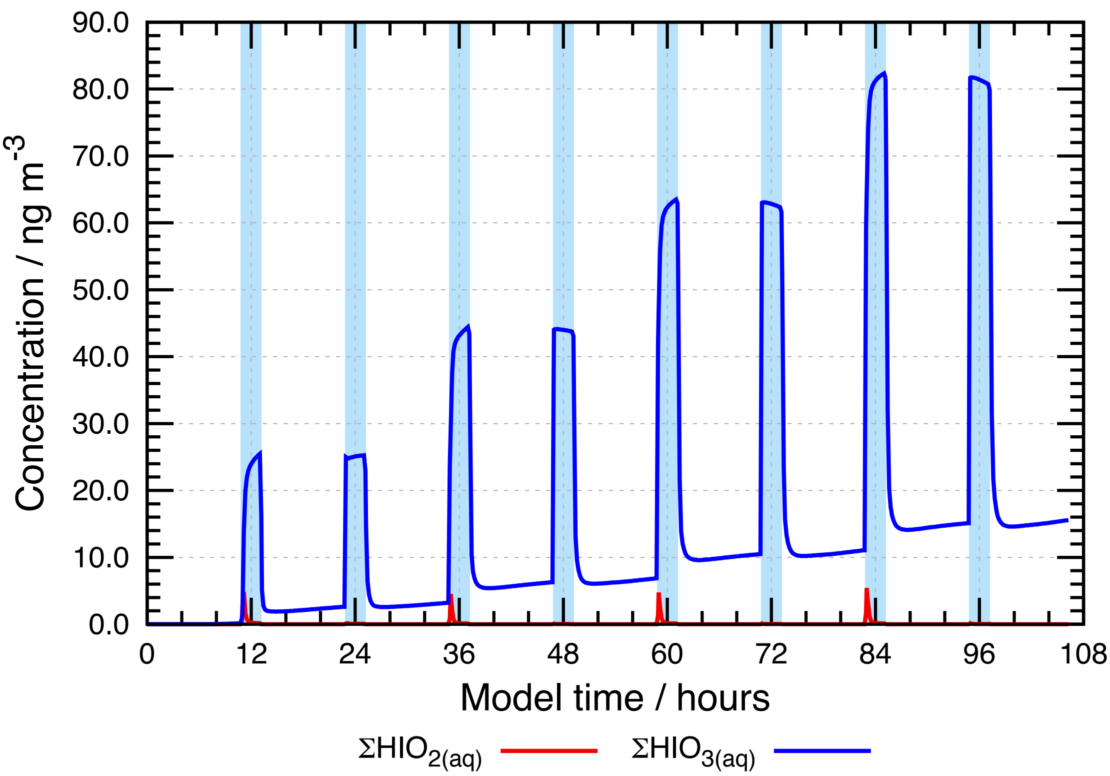


Figure S5 Modelled concentration-time profiles of selected iodine species in the aqueous phase over the whole modelling period of 108 h (scenario HM2). For HOI, HIO_2, and HIO_3 the sum of the dissociated and undissociated forms was used for the concentration-time profiles (indicated by Σ). Blue bars 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.

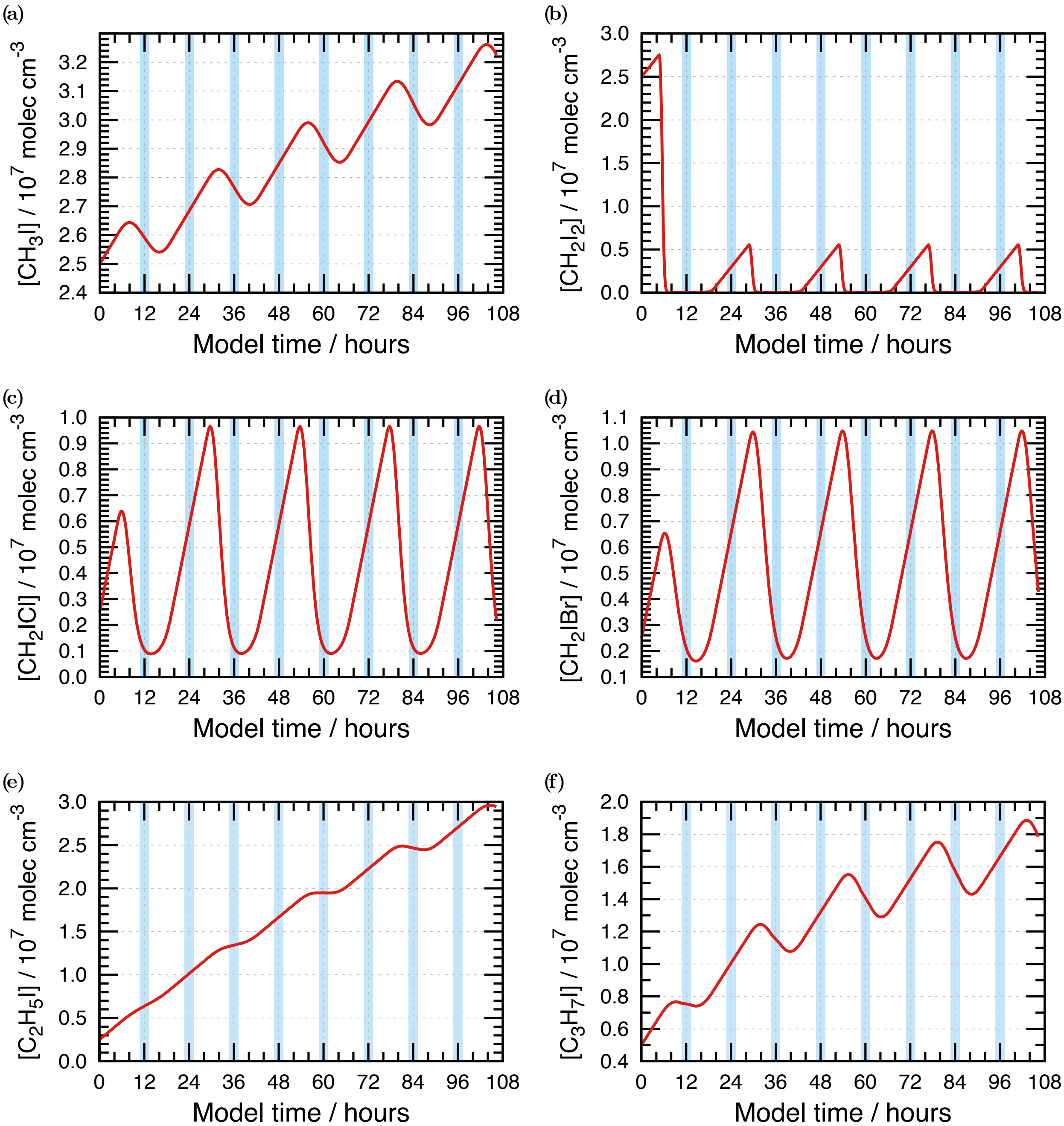


Figure S6 Modelled concentration-time profiles of the various alkyl iodides in the gas phase for the whole modelling period of 108h (scenario HM2). Blue bars indicate in-cloud residence times of the air parcel.

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 conctribute 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 $10^6\,M^{-1}\,s^{-1}$ for Cl_2^- and in the order of $10^8\,M^{-1}\,s^{-1}$ 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 $10^{-12}\,mol\,l^{-1}$) with higher reactivities than the chlorine radical di-anion and, hence, its oxidation is dominated by OH.

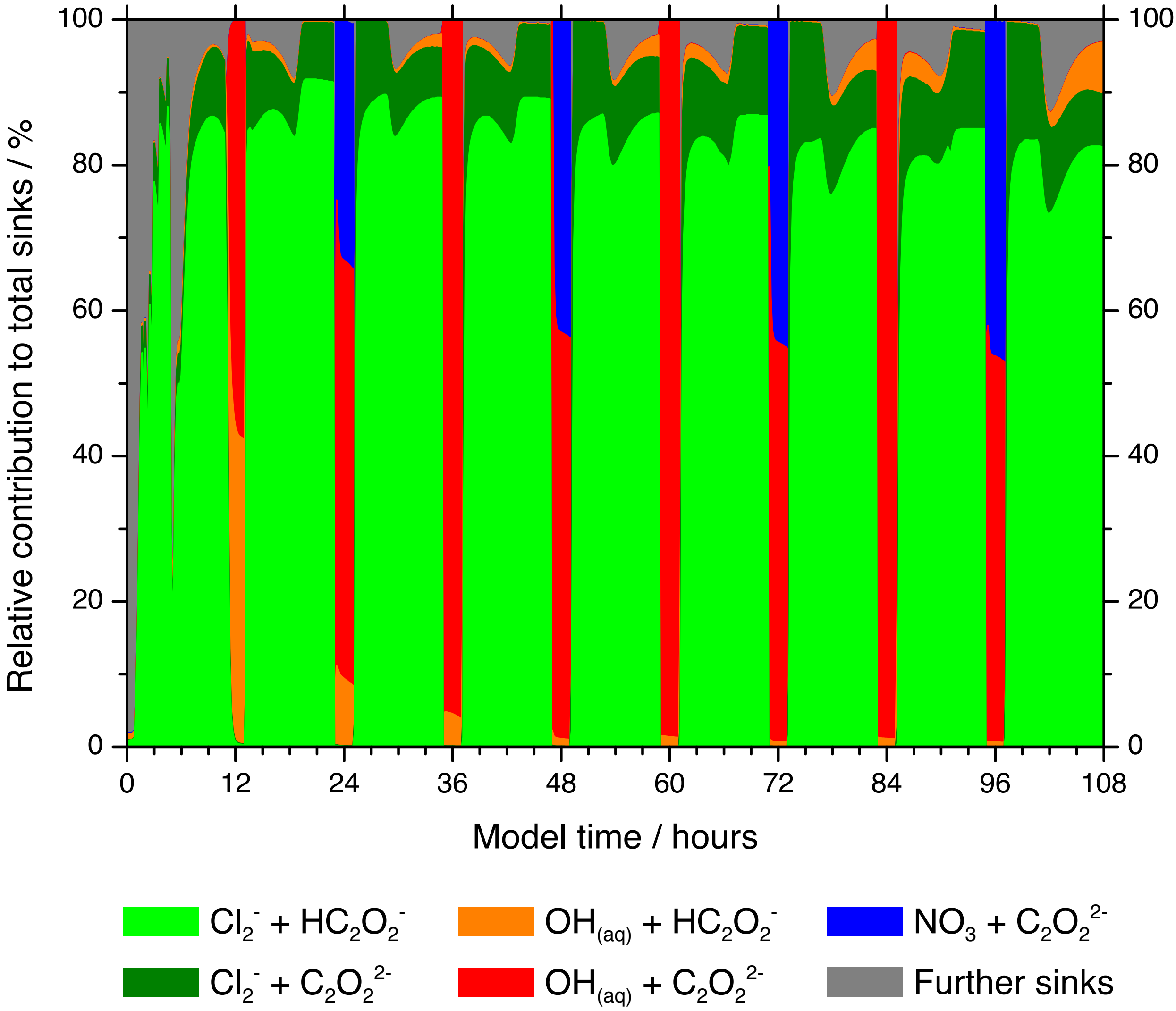


Figure S7 Modelled time-resolved contributions of the various oxidants to the aqueous phase degradation of the sum of all dissociation states of oxalic acid for the whole modelling period of 108h (scenario HM2). The respective total average sink fluxes under non-cloud, daytime in-cloud, and night-time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

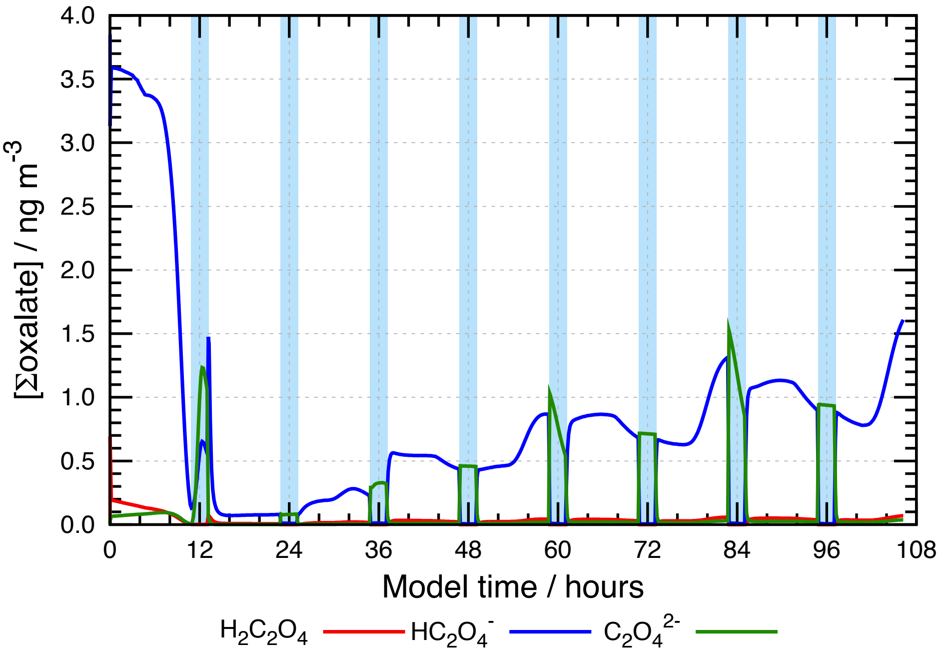


Figure S8 Modelled concentration-time profiles of the speciation of the different oxidation states of oxalic acid for the whole modelling period of 108h (scenario HM2). Blue bars indicate in-cloud residence times of the air parcel.

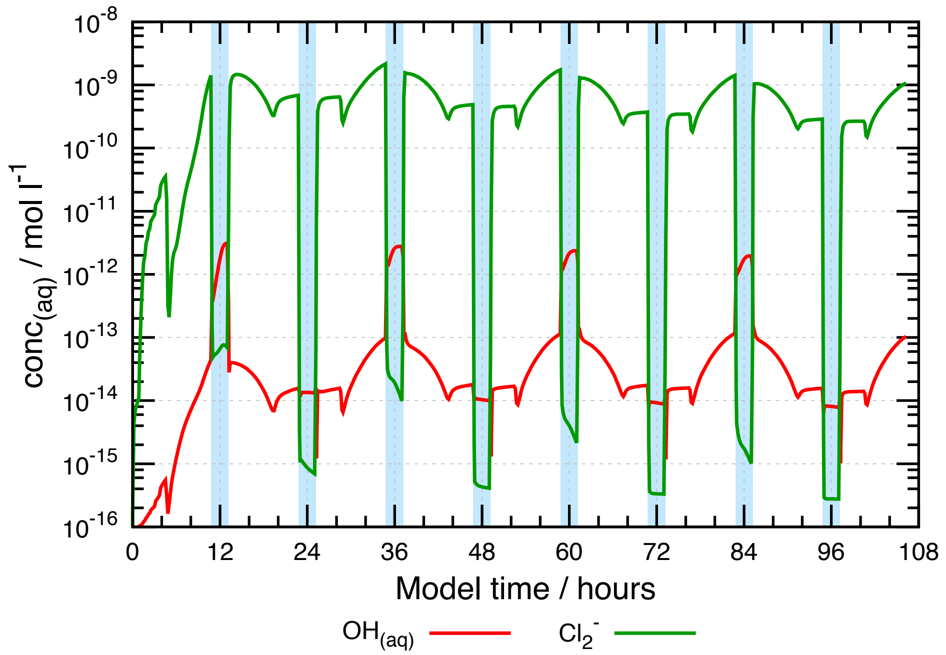


Figure S9 Modelled concentration-time profiles of $OH_{(aq)}$ and Cl_2^- for the whole modelling period of 108h (scenario HM2). Blue bars indicate in-cloud residence times of the air parcel.

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.

	∼4.5 – 7.5 × 10^6	Lowe et al. (2009)[4]
	6.5 × 10^5	this work[b]
	2.1 × 10^5	this work[c]
BrO	∼2 × 10^7	Sander and Crutzen (1996)[1]
	∼10^7	Vogt et al. (1996)[2]
	∼2 × 10^9	Sander et al. (1997)[3]
	∼4 × 10^7	Vogt et al. (1999)[2]
	∼1.2 × 10^8	von Glasow et al. (2002a)[2]
	∼4.5 × 10^7	von Glasow et al. (2002b)[5]
	∼1 – 1.2 × 10^8	Lowe et al. (2009)[4]
	2.1 × 10^7	this work[b]
	3.8 × 10^6	this work[c]
HOBr	∼6.8 × 10^8	Sander and Crutzen (1996)[1]
	∼2 × 10^8	Vogt et al. (1996)[2]
	∼5 × 10^8	Sander et al. (1997)[3]
	∼9 × 10^7	Vogt et al. (1999)[2]
	∼9.5 × 10^7	von Glasow et al. (2002a)[2]
	∼7 × 10^6	von Glasow et al. (2002b)[5]
	∼2.2 – 5 × 10^8	Lowe et al. (2009)[4]
	3.6 × 10^6	this work[b]
	1.1 × 10^6	this work[c]
Br_2	∼3.2 × 10^8	Sander and Crutzen (1996)[1]
	∼8 × 10^7	Vogt et al. (1996)[2]
	∼5 × 10^7	Vogt et al. (1999)[2]
	∼6.3 × 10^7	von Glasow et al. (2002a)[2]
	5.0 × 10^6	this work[b]
	6.0 × 10^3	this work[c]
BrCl	∼6.8 × 10^7	Sander and Crutzen (1996)[1]
	∼9 × 10^7	Vogt et al. (1996)[2]
	∼2 × 10^8	Sander et al. (1997)[3]
	∼1 × 10^8	Vogt et al. (1999)[2]
	∼1.1 × 10^8	von Glasow et al. (2002a)[2]
	∼2.8 – 4 × 10^8	Lowe et al. (2009)[4]
	1.9 × 10^7	this work[b]
	4.2 × 10^6	this work[c]
IO	∼2.2 × 10^7	Vogt et al. (1999)[2]
	∼7 × 10^7	Sander et al. (1997)[3]
	∼4 × 10^7	von Glasow et al. (2002a)[2]
	∼7.5 × 10^7	Pechtl et al. (2006)[6]
	∼2.5 × 10^7	Pechtl et al. (2006)[7]
	∼1.5 – 4.5 × 10^7	Lowe et al. (2009)[4]
	∼5 × 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]

[a]Model conditions are given in the footnotes below; [b]overall maximum concentration for the base run HM2; [c]maximum concentration on the second model day for the base run HM2
[1]polluted MBL, permanently cloud-free; [2]remote MBL, permanently cloud-free; [3]MBL in the arctic spring; [4]clean MBL, permanently cloud-free for different treatments of the microphysics; [5]remote MBL, permanently cloudy; [6]coastal MBL, permanently cloud-free; continuous alkyl iodide emissions (their scenario 1); [7]coastal MBL, permanently cloud-free; hot spot emissions of alkyl iodides/I_2 (their scenario 3); [8]open ocean, permanently cloud-free; [9]open ocean, permanently cloud-free with additional I_2 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 in the article in section 3.

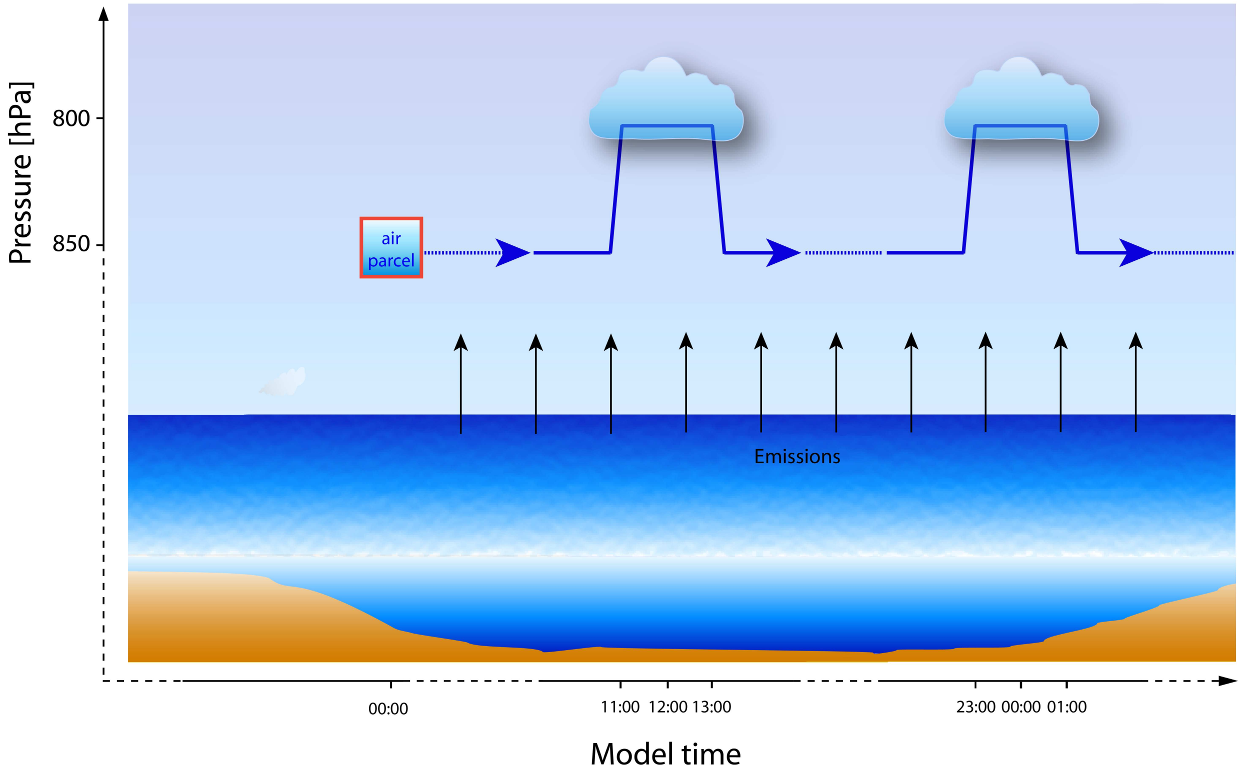


Figure S10 Schematic of the cloud scenario used in the model runs.

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 where 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 [cm^{-2} s^{-1}]	Reference
NO	2.50×10^{8}	Thompson and Zafiriou (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_3H_6	1.00×10^{8}	Plass-Dülmer et al. (1993)
ETI[d]	1.00×10^{7}	Plass-Dülmer et al. (1993)
CH_3CHO	3.60×10^{9}	Toyota et al. (2004)
C_2H_5CHO	5.47×10^{9}	Singh et al. (2003)
ISO[e]	3.20×10^{7}	Arnold et al. (2009)

[a]ETH = ethane; [b]HC3 = alkanes, alcohols, esters, and alkynes with OH rate constant (298 K, 1 atm) less than 3.4×10^{-12} cm^3 $molecules^{-1}$ s^{-1}; [c]ETE = ethylene; [d]ETI = acetylene; [e]ISO = 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_2O_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_3H_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_3CHO	5.12×10^{9}	Singh et al. (2003)
C_2H_5CHO	1.50×10^{9}	Singh et al. (2003)
CH_3OCH_3	1.10×10^{10}	Singh et al. (2003)
CH_3OH	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_3COOH	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)

[⊘]update of CAPRAM; [a]HC3 = alkanes, alcohols, esters, and alkynes with OH rate constant (298 K, 1 atm) less than 3.4×10^{-12} cm^3 $molecules^{-1}$ s^{-1}; [b]OLT = terminal alkenes; [c]ETI = acetylene; [d]ETOH = ethanol; [e]ORA1 = formic acid; [f]OP1 = methyl hydrogen peroxide; [g]PAN = peroxyacetyl nitrate and higher saturated PANs; [h]ISO = isoprene

S2.5 Additional setup of the Halogen Modul 2.0

Table S5 Emissions of halogen species

Species	Open ocean [cm^{-2} s^{-1}]	Reference
C_2Cl_4	3.2×10^6	Keene et al. (2008)
C_2HCl_3	4.0×10^6	Keene et al. (2008)
CH_3CCl_3	—	Keene et al. (2008)
$CHCl_3$	6.4×10^7	Keene et al. (2008)
CH_2Cl_2	3.2×10^7	Keene et al. (2008)
CH_3Cl	9.1×10^7	Keene et al. (2008)
$CHBr_3$	1.1×10^7	Yang et al. (2005)
CH_2Br_2	4.6×10^6	Yang et al. (2005)
CH_3Br	9.7×10^6	Yang et al. (2005)
C_3H_7I	1.0×10^7	Lowe et al. (2009)
C_2H_5I	1.0×10^7	assumed
CH_2I_2	1.5×10^7	assumed
CH_3I	6.0×10^6	Lowe et al. (2009)
CH_2ICl	2.0×10^7	Lowe et al. (2009)
CH_2IBr	2.0×10^7	Lowe et al. (2009)

Table S6 Depositions of halogen species

Species	Open ocean [s^{-1}][a]	Reference
$HCl^{\otimes}$	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)

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

Table S7 Initial concentrations of halogen species

Species	Open ocean $[cm^{-3}]$	Reference/comment
$HCl^{\oslash}$	2.5×10^{9}	Lowe et al. (2009)
C_2Cl_4	3.0×10^{8}	mean based on data presented in Zhou et al. (2005)
C_2HCl_3	1.3×10^{8}	mean based on data presented in Zhou et al. (2005)
CH_3CCl_3	—	
$CHCl_3$	2.5×10^{8}	mean based on data presented in Law et al. (2007)
CH_2Cl_2	3.3×10^{8}	mean based on data presented in Law et al. (2007)
CH_3Cl	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_2Br_2	3.1×10^{7}	mean based on data presented in Zhou et al. (2005)
CH_3Br	2.8×10^{8}	Groszko and Moore (1998)
C_3H_7I	5.0×10^{6}	assumed
C_2H_5I	2.5×10^{6}	assumed
CH_2I_2	2.5×10^{7}	assumed
CH_3I	2.5×10^{7}	Moore and Groszko (1999)
CH_2ICl	2.5×10^{6}	assumed
CH_2IBr	2.5×10^{6}	assumed

$^{\oslash}$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 refrences as described in Table S9.

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

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

Reaction	l/s^{-1}	m	n
$NO_2 \xrightarrow{h\nu} NO + O(^3P)$	1.041×10^{-2}	0.404	0.250
$O_3 \xrightarrow{h\nu} O_2 + O(^1D)$	7.531×10^{-5}	1.886	0.382
$O_3 \xrightarrow{h\nu} O_2 + O(^3P)$	5.685×10^{-4}	0.273	0.132
$HONO \xrightarrow{h\nu} OH + NO$	3.149×10^{-3}	0.430	0.263
$HNO_3 \xrightarrow{h\nu} OH + NO_2$	1.173×10^{-6}	1.385	0.271
$HNO_4 \xrightarrow{h\nu} 0.65\,HO_2 + 0.65\,NO_2 + 0.35\,OH + 0.35\,NO_3$	9.036×10^{-6}	1.262	0.327
$NO_3 \xrightarrow{h\nu} NO + O_2$	2.919×10^{-2}	0.115	0.164
$NO_3 \xrightarrow{h\nu} NO_2 + O(^3P)$	2.349×10^{-1}	0.122	0.180
$N_2O_5 \xrightarrow{h\nu} NO_3 + NO + O(^3P)$	2.071×10^{-7}	2.185	3.974
$N_2O_5 \xrightarrow{h\nu} NO_3 + NO_2$	7.083×10^{-5}	0.887	0.237
$H_2O_2 \xrightarrow{h\nu} 2\,OH$	1.189×10^{-5}	0.924	0.249
$HCHO \xrightarrow{h\nu} H_2 + CO$	7.681×10^{-5}	0.685	0.273
$HCHO \xrightarrow{h\nu,\,2\,O_2} 2\,HO_2 + CO$	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
$ALD^a \xrightarrow{h\nu, 2\,O_2} MO_2{}^b + HO_2 + CO$	1.163×10^{-5}	1.303	0.418
$CH_3CHO \xrightarrow{h\nu, 2\,O_2} MO_2 + HO_2 + CO$	1.163×10^{-5}	1.303	0.418
$C_2H_5CHO \xrightarrow{h\nu, 2\,O_2} MO_2 + HO_2 + CO$	3.546×10^{-5}	1.226	0.325
$C_3H_7CHO \xrightarrow{h\nu, 2\,O_2} MO_2 + HO_2 + CO$	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
$OP2^d \xrightarrow{h\nu, O_2} 0.47\,ALD + 0.49\,CH_3CHO + 0.02\,C_2H_5CHO + 0.02\,C_3H_7CHO + HO_2 + OH$	9.017×10^{-6}	0.870	0.244
$PAA^e \xrightarrow{h\nu} MO_2 + OH$	1.400×10^{-6}	1.059	0.265
$KET^f \xrightarrow{h\nu, 2\,O_2} ACO_3{}^g + ETHP^h$	1.029×10^{-6}	1.983	0.459
$CH_3COCH_3 \xrightarrow{h\nu, 2\,O_2} ACO_3 + ETHP$	1.029×10^{-6}	1.983	0.459
$C_2H_5COCH_3 \xrightarrow{h\nu, 2\,O_2} ACO_3 + ETHP$	1.340×10^{-6}	1.201	0.335
$CH_3COCH(CH_3)_2 \xrightarrow{h\nu, 2\,O_2} ACO_3 + ETHP$	1.029×10^{-6}	1.983	0.459
$GLY^i \xrightarrow{h\nu, 2\,O_2} 2\,CO + 2\,HO_2$	9.610×10^{-5}	0.325	0.240
$GLY \xrightarrow{h\nu} HCHO + CO$	3.026×10^{-5}	0.323	0.241
$MGLY^j \xrightarrow{h\nu, 2\,O_2} ACO_3 + CO + HO_2$	1.853×10^{-4}	0.583	0.225
$DCB^k \xrightarrow{h\nu, 2\,O_2} 0.98\,HO_2 + 0.02\,ACO_3 + TCO_3{}^l$	1.624×10^{-4}	0.244	0.267
$ONIT^m \xrightarrow{h\nu, O_2} 0.094\,ALD + 0.098\,CH_3CHO + 0.004\,C_2H_5CHO + 0.004\,C_3H_7CHO + 0.120\,KET + 0.408\,CH_3COCH_3 + 0.216\,C_2H_5COCH_3 + 0.056\,CH_3COCH(CH_3)_2 + HO_2 + NO_2$	4.615×10^{-6}	1.293	0.286
$HKET^n \xrightarrow{h\nu, 2\,O_2} HCHO + HO_2 + ACO_3$	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
$CH_2(OH)CHO \xrightarrow{h\nu, 2\,O_2} HCHO + CO + 2\,HO_2$	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).
[a]ALD = higher aldehydes; [b]MO_2 = methyl peroxyl radical; [c]OP1 = methyl hydrogen peroxide; [d]OP2 = higher organic peroxides; [e]PAA = peroxyacetic acid and higher analoges; [f]KET = ketones; [g]ACO_3 = acetyl peroxyl radical and higher saturated acyl peroxyl radicals; [h]ETHP = peroxyl radical formed from ETH; [i]GLY = glyoxal; [j]MGLY = methylglyoxal; [k]DCB = unsaturated dicarbonyls; [l]TCO3 = unsaturated acyl peroxyl radicals; [m]ONIT = organic nitrates; [n]HKET = hydroxy ketone; [o]MACR = methacrolein and other unsaturated monoaldehydes; [p]MVK = 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
$Fe(OH)^{2+} \xrightarrow{h\nu} Fe^{2+} + OH$	4.764×10^{-2}	0.829	0.291	absorption spectra from Weschler et al. (1986)/quantum yields from Benkelberg and Warneck (1995)
$Fe(OH)_2^{+} \xrightarrow{h\nu} Fe^{2+} + OH + OH^{-}$	1.343×10^{-2}	0.855	0.300	absorption spectra from Weschler et al. (1986)/quantum yields from Benkelberg and Warneck (1995)
$NO_3^{-} \xrightarrow{h\nu} NO_2 + OH + OH^{-}$	6.109×10^{-7}	1.076	0.409	absorption spectra from Graedel and Weschler (1981)/quantum yields from Zellner et al. (1990)
$NO_2^{-} \xrightarrow{h\nu} NO + OH + OH^{-}$	7.245×10^{-5}	0.480	0.303	absorption spectra from Graedel and Weschler (1981)/quantum yields from Zellner et al. (1990)
$HONO \xrightarrow{h\nu} OH + NO$	2.999×10^{-4}	0.439	0.308	Graedel and Weschler (1981)
$Fe^{3+} \xrightarrow{h\nu} Fe^{2+} + OH + H^{+}$	1.224×10^{-5}	1.467	0.248	absorption spectra from Weschler et al. (1986)/quantum yields from Benkelberg and Warneck (1995)
$Fe(SO_4)^{+} \xrightarrow{h\nu} Fe^{2+} + SO_4^{-}$	8.215×10^{-5}	0.885	0.313	Benkelberg and Warneck (1995)
$H_2O_2 \xrightarrow{h\nu} 2\,OH$	8.625×10^{-6}	1.043	0.271	absorption spectra from Graedel and Weschler (1981)/quantum yields from Zellner et al. (1990)
$Fe(C_2O_4)_2^{-} \xrightarrow{h\nu} Fe^{2+} + C_2O_4^{2-} + CO_2 + CO_2^{-}$	7.993×10^{-2}	0.625	0.279	IfT measurements
$Fe(C_2O_4)_3^{3-} \xrightarrow{h\nu} Fe^{2+} + 2\,C_2O_4^{2-} + CO_2 + CO_2^{-}$	4.659×10^{-2}	0.561	0.276	IfT measurements
$OP1^{a} \xrightarrow{h\nu} CH_3O + OH$	8.625×10^{-5}	1.043	0.271	estimated same as H_2O_2
$NO_3 \xrightarrow{h\nu} NO + O_2$	2.584×10^{-3}	0.072	0.196	Graedel and Weschler (1981)
$NO_3 \xrightarrow{h\nu} NO_2 + O(^3P)$	2.325×10^{-2}	0.072	0.196	Graedel and Weschler (1981)
$O_3 \xrightarrow{h\nu} 2\,OH + O_2$	3.652×10^{-4}	0.515	0.044	Graedel and Weschler (1981)

Photolysis reactions are parameterised with $j = l \times \cos^m \chi \times \exp\{-n \times \sec \chi\}$.
[a]OP1 = methyl hydrogen peroxide

S3.2 Phase transfer

Table S10 Henry's Law constants

	Species	$K_H(298\,\mathrm{K})$ / M atm^{-1}	$\Delta H/R$ / 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 ($K_{H,\,\mathrm{H3}} \approx K_{H,\,\mathrm{H6}}$), 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_2ClCO_3	669	-5893	estimated same as acetylperoxyl radical
H11	$CH_2ClCOOH$	5.5×10^{3}	-5890	estimated same as acetic acid
H12	$CH_3COCClO$	1.4	-7541	estimated same as methylglyoxal
H13	$COCl_2$	7.0×10^{-2}		Law et al. (2007)
H14	CHOCl	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 ($K_{H,\,\mathrm{H17}} \approx K_{H,\,\mathrm{H19}}$)
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 $\oslash$	BrCl	0.94	-5600	Bartlett and Margerum (1999)
H23	CH_2BrCO_3	669	-5893	estimated same as acetylperoxyl radical
H24	$CH_2BrCOOH$	5.5×10^{3}	-5890	estimated same as acetic acid

Table S10 (continued) Henry's Law constants

	Species	$K_H(298\,\mathrm{K})$ / M atm^{-1}	$\Delta H/R$ / K	Reference/comment
H25	$CH_3COCBrO$	1.4	-7541	estimated same as methylglyoxal
H26	$COBr_2$	7.0×10^{-2}		estimated ($K_{H,\,\mathrm{H26}} \approx K_{H,\,\mathrm{H13}}$)
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 ($K_{H,\,\mathrm{H30}} \approx K_{H,\,\mathrm{H6}}$)
H31	OIO	2.1×10^{5}	-8700	estimated same as nitric acid
H32	I_2O_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 ($K_{H,\,\mathrm{H34}} \approx K_{H,\,\mathrm{H6}}$)
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_2ICO_3	669	-5893	estimated same as acetylperoxyl radical
H41	CH_2ICOOH	5.5×10^{3}	-5890	estimated same as acetic acid
H42	COI_2	7.0×10^{-2}		estimated ($K_{H,\,\mathrm{H42}} \approx K_{H,\,\mathrm{H13}}$)
H43	CHOI	3.0×10^{3}	-7216	estimated same as formaldehyde

$^{\otimes}$already implemented in CAPRAM; $^{\oplus}$already implemented in the Halogen Module 1.0; $^{\ominus}$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 $^{\otimes}$	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 ⊖	Cl	0.05		1.82	Fuller (1986)	α estimated same as OH, [b]
H3 ⊖	ClO	0.064		1.55	Fuller (1986)	α estimated, [b]
H4 ⊖	ClO_2	0.05		1.39	Fuller (1986)	α estimated same as OH, [b]
H5 ⊘	HCl	0.1026	Schweitzer et al. (2000)	1.89	Marsh and McElroy (1985)	
H6 ⊖	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 ⊘	$ClNO_2$	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_2ClCO_3	0.019		0.94	Fuller (1986)	α estimated same as acetylperoxyl radical, [c]
H11	$CH_2ClCOOH$	0.0322		0.97	Fuller (1986)	α estimated same as acetic acid, [c]
H12	$CH_3COCClO$	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	CHOCl	0.02		1.23	Fuller (1986)	α estimated same as formaldehyde, [c]
H15 ⊗	Br_2	0.08		1.00	Schwartz (1986)	α estimated
H16 ⊖	Br	0.05		1.29	Fuller (1986)	α estimated same as OH, [b, d]
H17 ⊖	BrO	0.06	Sander and Crutzen (1996)	1.19	Fuller (1986)	[b, d]
H18 ⊖	HBr	0.0481	Schweitzer et al. (2000)	1.26	Fuller (1986)	[b, d]
H19 ⊖	HOBr	0.5	Abbatt and Waschewsky (1998)	1.16	Fuller (1986)	[b, d]
H20 ⊘	$BrNO_2$	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 ⊘	BrCl	0.33	(Katrib et al.)	1.05	Fuller (1986)	[b, d]
H23	CH_2BrCO_3	0.019		0.84	Fuller (1986)	α estimated same as acetylperoxyl radical, [c, d]
H24	$CH_2BrCOOH$	0.0322		0.84	Fuller (1986)	α estimated same as acetic acid, [c]
H25	$CH_3COCBrO$	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	CHOBr	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_2O_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_2ICO_3	0.019		0.80	Fuller (1986)	α estimated same as acetylperoxyl radical, [c, f]
H41	CH_2ICOOH	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]

$^{\otimes}$already implemented in CAPRAM; $^{\oslash}$update of CAPRAM; $^{\oplus}$already implemented in the Halogen Module 1.0; $^{\ominus}$update of the Halogen Module 1.0
[a]in 10^5 m^2 s^{-1} at 288 K; [b]correction 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 $^{\ominus}$	$Cl + O_3 \rightarrow ClO + O_2$	1.21×10^{-11}	250		*Atk07*
G2	$Cl + H_2 \xrightarrow{O_2} HCl + HO_2$	1.68×10^{-14}	2310		*Atk07*
G3	$Cl + HO_2 \rightarrow HCl + O_2$	3.40×10^{-11}			*Atk07*

Table S12 (continued) Gas phase reactions

	Reaction	k_{298} $(j_{max})^a$	E_A/R^b	Comment	Reference
G4	$Cl + HO_2 \rightarrow ClO + OH$	9.30×10^{-12}	570		*Atk07*
G5	$Cl + H_2O_2 \rightarrow HCl + HO_2$	4.10×10^{-13}	980		*Atk07*
G6	$Cl_2 + OH \rightarrow HOCl + Cl$	6.42×10^{-14}	1200		*Atk07*
P_g1 ⊖	$Cl_2 \xrightarrow{h\nu} 2\,Cl$	*(2.99×10^{-3})*		$\Phi = 1.0^{Cal/Pit66}$; see Tab. S14	*Dem97*
G7 ⊖	$ClO + O_3 \rightarrow ClO_2 + O_2$	1.13×10^{-17}	3600	upper limit	*Atk07*
G8	$ClO + O_3 \rightarrow OClO + O_2$	1.48×10^{-18}	4000	upper limit	*Atk07*
G9	$ClO + OH \rightarrow$ $0.94\,HO_2 + 0.94\,Cl + 0.06\,HCl + 0.06\,O_2$	2.00×10^{-11}	-300		*Atk07*
G10 ⊖	$ClO + HO_2 \rightarrow HOCl + O_2$	6.89×10^{-12}	-340		*Atk07*
G11	$ClO + ClO \rightarrow Cl_2 + O_2$	4.82×10^{-15}	1590		*Atk07*
G12	$ClO + ClO \rightarrow Cl + ClO_2$	8.06×10^{-15}	2450		*Atk07*
G13	$ClO + ClO \rightarrow Cl + OClO$	3.53×10^{-15}	1370		*Atk07*
G14	$ClO + ClO \xrightarrow{M} Cl_2O_2$	1.52×10^{-15}		TYP: TROE; see Tab. S13	*San06*
P_g2	$ClO \xrightarrow{h\nu} Cl + O$	*(2.64×10^{-4})*		$\Phi = 1.0^{i}$; see Tab. S14	*San06*
G15	$Cl + O_2 \xrightarrow{M} ClO_2$	5.17×10^{-14}		TYP: TROE; see Tab. S13	*San06*
G16 ⊖	$ClO_2 \xrightarrow{M} Cl + O_2$	6.23×10^{-13}	1820		*Atk07*
G17	$Cl + ClO_2 \rightarrow 0.95\,Cl_2 + 0.95\,O_2 + 0.1\,ClO$	2.42×10^{-10}			*San06*
G18	$Cl_2O_2 \xrightarrow{M} 2\,ClO$	2.87×10^{-3}		TYP: TROEXP; see Tab. S13	*Atk07*
G19	$Cl_2O_2 + O_3 \rightarrow ClO + ClO_2 + O_2$	1.00×10^{-19}		upper limit	*Atk07*
G20	$Cl_2O_2 + Cl \rightarrow Cl_2 + ClO_2$	9.45×10^{-11}	-65		*Atk07*
P_g4	$Cl_2O_2 \xrightarrow{h\nu} Cl + ClO_2$	*(1.83×10^{-3})*		$\Phi = 1.0^{i}$; see Tab. S14	*San03*
G21	$OClO + OH \rightarrow HOCl + O_2$	1.05×10^{-11}	-600		*Atk07*
G22	$Cl + OClO \rightarrow 2\,ClO$	5.66×10^{-11}	-170		*Atk07*
G23	$ClO + OClO \xrightarrow{M} Cl_2O_3$	1.08×10^{-19}		TYP: TROE; see Tab. S13	*Atk07*
P_g3	$OClO \xrightarrow{h\nu} ClO + O$	*(0.10)*		$\Phi = 1.0^{i}$; see Tab. S14	*San06*
G24	$Cl_2O_3 \xrightarrow{M} ClO + OClO$	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_g5	$Cl_2O_3 \xrightarrow{h\nu} ClO + OClO$	*(9.80×10^{-4})*		$\Phi = 1.0^i$; further products omitted; see Tab. S14	*Atk07*
G25 ⊖	$HCl + OH \rightarrow Cl + H_2O$	7.86×10^{-13}	230		*Atk07*
G26	$HOCl + OH \rightarrow ClO + H_2O$	5.60×10^{-13}	500	E_A/R estimated	*San06*
G27	$HOCl + Cl \rightarrow$ $0.76\,HCl + 0.76\,ClO + 0.24\,Cl_2 + 0.24\,OH$	1.62×10^{-12}	130	branching ratios from Vogt and Schindler (1993)	*San06*
P_g6 ⊖	$HOCl \xrightarrow{h\nu} Cl + OH$	*(3.63×10^{-4})*		$\Phi = 1.0$; see Tab. S14	*Atk07*
G28	$ClO + NO \rightarrow Cl + NO_2$	1.67×10^{-11}	-295		*Atk07*
G29	$OClO + NO \rightarrow ClO + NO_2$	3.56×10^{-13}	-350		*Atk07*
G30	$Cl + NO_3 \rightarrow ClO + NO_2$	2.40×10^{-11}			*Atk07*
G31	$ClO + NO_3 \rightarrow 0.68\,ClO_2 + 0.32\,OClO + NO_2$	4.61×10^{-13}			*Kuk94*
G32	$Cl + NO \xrightarrow{M} ClNO$	1.92×10^{-12}		TYP: SPEC2; see Tab. S13	*San06*
G33	$Cl + ClNO \rightarrow Cl_2 + NO$	8.11×10^{-11}	-100		*San06*
P_g7	$ClNO \xrightarrow{h\nu} Cl + NO$	*(5.48×10^{-4})*		see Tab. S14	*Atk07*
G34	$Cl + NO_2 \xrightarrow{M} ClNO_2$	5.80×10^{-14}		TYP: TROE; see Tab. S13	*San06*
G35	$ClNO_2 + OH \rightarrow HOCl + NO_2$	3.62×10^{-14}	1250		*Atk07*
P_g8 ⊖	$ClNO_2 \xrightarrow{h\nu} Cl + NO_2$	*(4.81×10^{-4})*		see Tab. S14	*Atk07*
G36	$ClO + NO_2 \xrightarrow{M} ClNO_3$	1.85×10^{-19}		TYP: TROEF; see Tab. S13	*Atk07*
G37	$ClNO_3 \xrightarrow{M} ClO + NO_2$	1.47×10^{-3}	11438	TYP: SPEC4	*And/Fah90*
G38	$ClNO_3 + OH \rightarrow$ $0.5\,ClO + 0.5\,HNO_3 + 0.5\,HOCl + 0.5\,NO_3$	3.97×10^{-13}	330	branching ratios from Pechtl et al. (2005)	*Atk07*
G39	$ClNO_3 + Cl \rightarrow Cl_2 + NO_3$	1.01×10^{-11}	-145		*Atk07*
P_g9	$ClNO_3 \xrightarrow{h\nu} Cl + NO_3$	*(5.16×10^{-5})*		$\Phi = 0.6 - 1.0$; see Tab. S14	*Dem97*
P_g10	$ClNO_3 \xrightarrow{h\nu} ClO + NO_2$	*(1.09×10^{-5})*		$\Phi = 0.4 - 0.0$; see Tab. S14	*Dem97*
G40 ⊖	$Cl + CH_4 \xrightarrow{O_2} HCl + MO_2$	1.03×10^{-13}	1240	*g, A*	*Atk06*
G41	$Cl + OP1 \rightarrow HCl + MO_2$	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	$Cl + MO_2 \rightarrow 0.5\,HCHO + 0.5\,ClO + 0.5\,HO_2 - 0.5\,O_2 + 0.5\,HCl + 0.5\,ORA1$	1.60×10^{-10}		branching ratios as in Pechtl et al. (2005) with revised products for H-abstraction, [A, C]	*San06*
G43	$ClO + MO_2 \xrightarrow{O_2} ClO_2 + HCHO + HO_2$	1.63×10^{-12}	238	further products omitted, [h, A]	*Atk08*
G44	$Cl + ETH \xrightarrow{O_2} HCl + ETHP$	5.93×10^{-11}	100	[g, D, E]	*Atk06*
G45	$Cl + HC3 \xrightarrow{O_2} HCl + HC3P$	1.47×10^{-10}	-13	estimated, [F, G]	
G46	$Cl + HC5 \xrightarrow{O_2} HCl + HC5P$	2.14×10^{-10}		estimated, [H, I]	
G47	$Cl + HC8 \xrightarrow{O_2} HCl + HC8P$	4.38×10^{-10}		estimated, [J, K]	
G48	$Cl + TOL \xrightarrow{O_2} HCl + TOLP$	5.15×10^{-11}		estimated, [L, M]	
G49	$Cl + HCHO \xrightarrow{O_2} HCl + CO + HO_2$	7.23×10^{-11}	34	[h]	*Atk06*
G50	$ClO + HCHO \xrightarrow{O_2} HOCl + CO + HO_2$	8.70×10^{-16}	2100	upper limit	*San06*
G51	$Cl + CH_3CHO \xrightarrow{O_2} HCl + ACO_3$	8.00×10^{-11}		[N]	*Atk06*
G52	$Cl + ALD \xrightarrow{O_2} HCl + ACO_3$	8.00×10^{-11}		estimated ($k_{G52} \approx k_{G51}$), [N, O]	
G53	$Cl + CH_3COCH_3 \xrightarrow{O_2} HCl + KETP$	2.08×10^{-11}	815		*Atk06*
G54	$Cl + KET \xrightarrow{O_2} HCl + KETP$	2.08×10^{-11}	815	estimated ($k_{G54} \approx k_{G53}$), [P, Q]	
G55	$Cl + CH_3COCH_2CH_3 \xrightarrow{O_2} HCl + KETP$	3.60×10^{-11}		[Q]	*Atk06*
G56	$Cl + HKET \xrightarrow{O_2} HCl + HO_2 + MGLY$	5.70×10^{-11}		[R, S]	*Orl99*
G57	$Cl + MGLY \xrightarrow{O_2} HCl + ACO_3$	4.80×10^{-11}		[N, S]	*Gre90*
G58	$Cl + GLY \xrightarrow{O_2} HCl + 2\,CO + HO_2$	3.80×10^{-11}		[T]	*Nik85*
G59	$Cl + CHOCH2OH \xrightarrow{O_2} HCl + ACO_3$	7.00×10^{-11}		[N]	*Nik87*
G60	$Cl + ETI \xrightarrow{O_2, M} 0.26\,CHOCl + 0.21\,Cl + 0.53\,HCl + 0.21\,GLY + 1.32\,CO + 0.79\,HO_2$	4.60×10^{-11}		TYP: TROE; see Tab. S13; [d, ,T U]	*Atk06*
G61	$Cl + ETE \xrightarrow{O_2, M} CH_2ClCH_2O_2$	8.46×10^{-11}		TYP: TROE; see Tab. S13; [g, V]	*Atk06*
G62	$CH_2ClCH_2O_2 + MO_2 \rightarrow 0.2\,CH_2ClCH_2OH + 0.8\,HCHO + 0.2\,CH_2ClCHO + 0.2\,CH_3OH + 0.4\,O_2 + 0.6\,CH_2ClCH_2O + 0.6\,HO_2$	2.00×10^{-12}		estimated ($RO_2 = MO_2$), [A]	*MCM*

Table S12 (continued) Gas phase reactions

	Reaction	k_{298} $(j_{max})^a$	E_A/R^b	Comment	Reference
G63	$CH_2ClCH_2O_2 + CH_2ClCH_2O_2 \rightarrow 1.28\,CH_2ClCH_2O + 0.36\,CH_2ClCH_2OH + 0.36\,CH_2ClCHO + O_2$	3.29×10^{-12}	-1300	branching ratio at 298 K	*Atk08*
G64	$CH_2ClCH_2O_2 + NO \rightarrow CH_2ClCH_2O + NO_2$	9.70×10^{-12}			*Atk08*
G65	$CH_2ClCH_2OH + OH \xrightarrow{O_2} CH_2ClCHO + H_2O + HO_2$	4.60×10^{-12}			*MCM*
G66	$CH_2ClCH_2O + O_2 \rightarrow CH_2ClCHO + HO_2$	9.48×10^{-15}	550		*MCM*
G67	$CH_2ClCHO + OH \xrightarrow{O_2} CH_2ClCO_3 + H_2O$	3.10×10^{-12}		[g]	*Atk08*
P_g13	$CH_2ClCHO \xrightarrow{h\nu, 2\,O_2} CH_2ClO_2 + CO + HO_2$	*(3.26×10^{-5})*		see Tab. S14	*MCM*
G68	$CH_2ClCO_3 + HO_2 \rightarrow 0.71\,CH_2ClCO_3H + 0.71\,O_2 + 0.29\,CH_2ClCOOH + 0.29\,O_3$	1.41×10^{-11}	-1040		*MCM*
G69	$CH_2ClCO_3 + MO_2 \rightarrow 0.3\,CH_2ClCOOH + HCHO + 0.7\,CH_2ClO_2 + 0.7\,CO_2 + 0.7\,HO_2 - 0.4\,O_2$	1.00×10^{-11}		estimated ($RO_2 = MO_2$), [A]	*MCM*
G70	$CH_2ClCO_3 + NO \xrightarrow{O_2} CH_2ClO_2 + CO_2 + NO_2$	2.00×10^{-11}	-270		*MCM*
G71	$CH_2ClCO_3 + NO_2 \xrightarrow{M} CH_2ClC(O)OONO_2$	1.11×10^{-11}		TYP: TROEF; see Tab. S13	*MCM*
G72	$CH_2ClC(O)OONO_2 \xrightarrow{M} CH_2ClCO_3 + NO_2$	3.48×10^{-4}		TYP: TROEXP; see Tab. S13	*MCM*
G73	$CH_2ClC(O)OONO_2 + OH \rightarrow O_2CHClC(O)OONO_2 + H_2O$	6.26×10^{-13}		[e]	*MCM*
G74	$O_2CHClC(O)OONO_2 + NO \rightarrow CHOCl + CO + O_2 + 2\,NO_2$	1.36×10^{-11}	-360	estimated	
G75	$CH_2ClCO_3H + OH \rightarrow CH_2ClCO_3 + H_2O$	4.29×10^{-12}			*MCM*
P_g14	$CH_2ClCO_3H \xrightarrow{h\nu, O_2} CH_2ClO_2 + CO_2 + OH$	*(5.79×10^{-6})*		see Tab. S14	*MCM*
G76	$CH_2ClCOOH + OH \xrightarrow{O_2} CH_2ClO_2 + CO_2 + H_2O$	3.59×10^{-12}	-190		*MCM*
G77	$Cl + C_3H_6 \xrightarrow{O_2, M} CH_3CHO_2CH_2Cl$	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	$CH_3CHO_2CH_2Cl + MO_2 \rightarrow$ $0.2\,CH_3CHOHCH_2Cl + 0.8\,HCHO +$ $0.2\,CH_3COCH_2Cl + 0.2\,CH_3OH + 0.4\,O_2 +$ $0.6\,CH_3CHOCH_2Cl + 0.6\,HO_2$	4.00×10^{-14}		estimated ($RO_2 = MO_2$), [c, A]	*MCM*
G79	$CH_3CHO_2CH_2Cl + NO \rightarrow$ $CH_3CHOCH_2Cl + NO_2$	9.04×10^{-12}	-360	further products omitted, [c]	*Atk06*
G80	$CH_3CHOHCH_2Cl + OH \xrightarrow{O_2}$ $CH_3COCH_2Cl + H_2O + HO_2$	5.09×10^{-12}	-200	products as in MCM, [c]	*Atk06*
G81	$CH_3CHOCH_2Cl + O_2 \rightarrow$ $CH_3COCH_2Cl + HO_2$	6.93×10^{-15}	230	[c]	*Atk06*
G82	$CH_3COCH_2Cl + OH \xrightarrow{O_2}$ $CH_3COCHClO_2 + H_2O$	1.05×10^{-13}	1320	[c, g]	*Atk06*
P_g11	$CH_3COCH_2Cl \xrightarrow{h\nu} 0.7\,COCl + 0.7\,ACO3 +$ $0.3\,CH_2ClCO_3 + 0.3\,MO2 - 1.3\,O_2$	*(3.83×10^{-3})*		$\Phi = 1.0^i$; see Tab. S14	*San06*
G83	$CH_3COCHClO_2 + MO_2 \rightarrow$ $0.2\,CH_3COCHClOH + 0.8\,HCHO +$ $0.2\,CH_3COCClO + 0.2\,CH_3OH - 0.2\,O_2 +$ $0.6\,ACO_3 + 0.6\,CHOCl + 0.6\,HO_2$	2.00×10^{-12}		estimated ($RO_2 = MO_2$), [c, A, N]	*MCM*
G84	$CH_3COCHClO_2 + NO \xrightarrow{O_2}$ $ACO_3 + CHOCl + NO_2$	8.00×10^{-12}		[c, N]	*Atk06*
G85	$CH_3COCHClOH + OH \xrightarrow{O_2}$ $CH_3COCClO + H_2O + HO_2$	3.00×10^{-12}		[c]	*MCM*
P_g12	$CH_3COCClO \xrightarrow{h\nu, O_2} COCl + ACO3$	*(2.78×10^{-5})*		estimated same as methylglyoxal; see Tab. S14	*MCM*
G86	$C_2Cl_4 + OH \xrightarrow{O_2} CCl_2OHCCl_2O_2$	1.60×10^{-13}	920	[g]	*Atk08*
G87	$CCl_2OHCCl_2O_2 + MO_2 \rightarrow$ $0.3\,CCl_2OHCCl_2OH + HCHO + 1.4\,COCl_2 +$ $1.4\,HO_2 - 0.4\,O_2$	9.20×10^{-14}		estimated ($RO_2 = MO_2$), [d, A]	*MCM*
G88	$CCl_2OHCCl_2O_2 + NO \xrightarrow{O_2}$ $2\,COCl_2 + HO_2 + NO_2$	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	$CCl_2OHCCl_2OH + OH \xrightarrow{O_2} 2\,COCl_2 + H_2O + HO_2$	7.18×10^{-14}		[d]	*MCM*
G90	$C_2HCl_3 + OH \xrightarrow{O_2} 0.5\,CHClOHCCl_2O_2 + 0.5\,CCl_2OHCHClO_2$	2.0×10^{-12}	-565	branching ratios as in MCM, [g]	*Atk*08
G91	$CHClOHCCl_2O_2 + MO_2 \rightarrow 0.3\,CCl_2OHCHClOH + HCHO + 0.7\,COCl_2 + 0.7\,CHOCl + 1.4\,HO_2 - 0.4\,O_2$	9.20×10^{-14}		estimated ($RO_2 = MO_2$), [d, A]	*MCM*
G92	$CHClOHCCl_2O_2 + NO \xrightarrow{O_2} COCl_2 + CHOCl + NO_2 + HO_2$	1.87×10^{-11}	-360	[d]	*MCM*
G93	$CCl_2OHCHClO_2 + MO_2 \rightarrow 0.2\,CCl_2OHCHClOH + 0.8\,HCHO + 0.2\,CCl_2OHCClO + 0.2\,CH_3OH - 0.2\,O_2 + 0.6\,COCl_2 + 0.6\,CHOCl + 1.2\,HO_2$	8.80×10^{-13}		estimated ($RO_2 = MO_2$), [d, A]	*MCM*
G94	$CCl_2OHCHClO_2 + NO \xrightarrow{O_2} COCl_2 + CHOCl + NO_2 + HO_2$	1.87×10^{-11}	-360	[d]	*MCM*
G95	$CCl_2OHCHClOH + OH \xrightarrow{O_2} CCl_2OHCClO + H_2O + HO_2$	2.85×10^{-13}			*MCM*
G96	$CCl_2OHCClO + OH \rightarrow COCl_2 + CO + Cl + H_2O$	3.59×10^{-14}			*MCM*
P_g15	$CCl_2OHCClO \xrightarrow{h\nu,O_2} COCl_2 + CO + Cl + HO_2$	*(1.99×10^{-5})*		see Tab. S14	*MCM*
G97	$CH_3CCl_3 + OH \xrightarrow{O_2} CCl_3CH_2O_2 + H_2O$	9.56×10^{-15}	1440	[g]	*Atk*08
G98	$CH_3CCl_3 + Cl \xrightarrow{O_2} CCl_3CH_2O_2 + HCl$	6.89×10^{-15}	1790	[g]	*Atk*08
G99	$CCl_3CH_2O_2 + MO_2 \rightarrow 0.2\,CCl_3CH_2OH + 0.8\,HCHO + 0.2\,CCl_3CHO + 0.2\,CH_3OH + 0.4\,O_2 + 0.6\,CCl_3CH_2O + 0.6\,HO_2$	2.00×10^{-12}		estimated ($RO_2 = MO_2$); [A]	*MCM*

Table S12 (continued) Gas phase reactions

	Reaction	k_{298} $(j_{max})^a$	E_A/R^b	Comment	Reference
G100	$CCl_3CH_2O_2 + NO \rightarrow CCl_3CH_2O + NO_2$	1.36×10^{-11}	-360		*MCM*
G101	$CCl_3CH_2O + O_2 \rightarrow CCl_3CHO + HO_2$	9.48×10^{-15}	550		*MCM*
G102	$CCl_3CH_2OH + OH \xrightarrow{O_2} CCl_3CHO + H_2O + HO_2$	2.56×10^{-12}			*MCM*
G103	$CCl_3CHO + OH \xrightarrow{O_2} CCl_3CO_3 + H_2O$	8.04×10^{-13}	240		*Atk08*
P_g16	$CCl_3CHO \xrightarrow{h\nu, 3/2\,O_2} Cl + COCl_2 + CO + HO_2$	*(1.06×10^{-4})*		$\Phi = 1.0$; see Tab. S14	*Atk08*
G104	$CCl_3CO_3 + MO_2 \xrightarrow{O_2} CCl_3O_2 + CO_2 + HCHO + HO_2 + O_2$	1.00×10^{-11}		estimated ($RO_2 = MO_2$); [A]	*MCM*
G105	$CCl_3CO_3 + NO \xrightarrow{O_2} CCl_3O_2 + CO_2 + NO_2$	2.00×10^{-11}	-270	[g]	*MCM*
G106	$CCl_3CO_3 + NO_2 \xrightarrow{M} CCl_3C(O)OONO_2$	1.11×10^{-11}		TYP: TROEF; see Tab. S13	*MCM*
G107	$CCl_3C(O)OONO_2 \xrightarrow{M} CCl_3CO_3 + NO_2$	3.48×10^{-4}		TYP: TROEXP; see Tab. S13	*MCM*
G108	$CHCl_3 + OH \xrightarrow{O_2} CCl_3O_2 + H_2O$	1.04×10^{-13}	850	[g]	*Atk08*
G109	$CHCl_3 + Cl \xrightarrow{O_2} CCl_3O_2 + HCl$	1.10×10^{-13}	920	[g]	*Atk08*
G110	$CCl_3O_2 + HO_2 \rightarrow COCl_2 + HOCl + O_2$	5.09×10^{-12}	-710		*Atk08*
G111	$CCl_3O_2 + MO_2 \rightarrow 0.3\,CCl_3OH + HCHO + 0.3\,O_2 + 0.7\,CCl_3O + 0.7\,HO_2$	6.60×10^{-12}		branching ratios from MCM, [A]	*IUPAC*
G112	$CCl_3O_2 + CCl_3O_2 \rightarrow 2\,CCl_3O + O_2$	3.95×10^{-12}	-740		*Atk08*
G113	$CCl_3O_2 + NO \rightarrow COCl_2 + Cl + NO_2$	1.81×10^{-11}	-270		*San06*
G114	$CCl_3O_2 + NO_2 \xrightarrow{M} CCl_3OONO_2$	1.41×10^{-12}		TYP: TROEF; see Tab. S13	*Atk08*
G115	$CCl_3OONO_2 \xrightarrow{M} CCl_3O_2 + NO_2$	0.26		TYP: TROEXP; see Tab. S13	*Atk08*
G116	$CCl_3OH + OH \rightarrow CCl_3O + H_2O$	3.60×10^{-14}			*MCM*
G117	$CCl_3O \xrightarrow{M} COCl_2 + Cl$	7.91×10^{6}	4600	TYP: SPEC4	*Atk08*
G118	$CH_2Cl_2 + OH \xrightarrow{O_2} CHCl_2O_2 + H_2O$	1.00×10^{-13}	860	[g]	*Atk08*
G119	$CH_2Cl_2 + Cl \xrightarrow{O_2} CHCl_2O_2 + HCl$	3.40×10^{-13}	850	[g]	*Atk08*

Table S12 (continued) Gas phase reactions

	Reaction	k_{298} $(j_{max})^a$	E_A/R^b	Comment	Reference
G120	$CHCl_2O_2 + HO_2 \rightarrow 0.3\,CHOCl + 0.3\,HOCl + 0.7\,COCl_2 + 0.7\,H_2O + O_2$	5.87×10^{-12}	-700		*Atk08*
G121	$CHCl_2O_2 + MO_2 \rightarrow 0.2\,COCl_2 + 0.2\,CH_3OH + 0.2\,CHCl_2OH + 0.8\,HCHO + 0.4\,O_2 + 0.6\,HO_2 + 0.6\,CHOCl + 0.6\,Cl$	2.00×10^{-12}		estimated ($RO_2 = MO_2$), [d, A]	*MCM*
G122	$CHCl_2O_2 + CHCl_2O_2 \rightarrow 2\,CHOCl + 2\,Cl + O_2$	7.00×10^{-12}			*Atk08*
G123	$CHCl_2O_2 + NO \rightarrow CHOCl + Cl + NO_2$	1.87×10^{-11}	-360	[d]	*MCM*
G124	$CHCl_2OH + OH \xrightarrow{O_2} COCl_2 + H_2O + HO_2$	9.34×10^{-13}			*MCM*
G125	$COCl_2 + OH \rightarrow COCl + HOCl$	5.00×10^{-15}		upper limit	*Atk08*
G126	$CH_3Cl + OH \xrightarrow{O_2} CH_2ClO_2 + H_2O$	3.62×10^{-14}	1210		*Atk08*
G127	$CH_3Cl + Cl \xrightarrow{O_2} CH_2ClO_2 + HCl$	4.85×10^{-13}	1150		*Atk08*
G128	$CH_2ClO_2 + HO_2 \rightarrow 0.3\,CH_2ClO_2H + 0.7\,CHOCl + 0.7\,H_2O + O_2$	5.01×10^{-12}	-820		*Atk08*
G129	$CH_2ClO_2 + MO_2 \rightarrow 0.2\,CH_2ClOH + 0.8\,HCHO + 0.2\,CHOCl + 0.2\,CH_3OH + 0.4\,O_2 + 0.6\,CH_2ClO + 0.6\,HO_2$	2.50×10^{-12}		branching ratios from corresponding RO_2 reaction in MCM, [A]	*IUPAC*
G130	$CH_2ClO_2 + CH_2ClO_2 \rightarrow 2\,CH_2ClO + O_2$	3.52×10^{-12}	-870		*Atk08*
G131	$CH_2ClO_2 + NO \rightarrow CH_2ClO + NO_2$	1.92×10^{-11}	-300		*San06*
G132	$CH_2ClO_2H + OH \rightarrow CH_2ClO_2 + H_2O$	3.59×10^{-12}	-190		*MCM*
G133	$CH_2ClO_2H + OH \rightarrow CHOCl + OH + H_2O$	4.14×10^{-12}			*MCM*
P_g17	$CH_2ClO_2H \xrightarrow{h\nu} CH_2ClO + OH$	*(5.79×10^{-6})*		see Tab. S14	*MCM*
G134	$CH_2ClOH + OH \xrightarrow{O_2} CHOCl + H_2O + HO_2$	1.08×10^{-12}			*MCM*
G135	$CH_2ClO + O_2 \rightarrow CHOCl + HO_2$	9.48×10^{-15}	550		*MCM*
G136	$CHOCl + OH \rightarrow COCl + H_2O$	5.00×10^{-13}		upper limit	*Atk08*
G137	$CHOCl + Cl \rightarrow HCl + COCl$	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_g18	$CHOCl \xrightarrow{h\nu,O_2} Cl + CO + HO_2$	*(2.71×10^{-7})*		$\Phi = 1.0^{Fan/Liu01}$; see Tab. S14	*Atk08*
G138	$COCl \xrightarrow{M} CO + Cl$	4.98×10^{5}	2960	TYP: SPEC4	*Atk07*
G139	$CO + Cl \xrightarrow{M} COCl$	3.33×10^{-14}		TYP: SPEC2; see Tab. S13	*Atk07*
G140 $\oplus$	$Br + O_3 \rightarrow BrO + O_2$	1.16×10^{-12}	800	better reference	*Atk07*
G141 $\ominus$	$Br + HO_2 \rightarrow HBr + O_2$	1.70×10^{-12}	450		*Atk07*
G142	$Br + H_2O_2 \rightarrow HBr + HO_2$	4.25×10^{-16}	3000		*San06*
G143	$Br_2 + OH \rightarrow HOBr + Br$	4.48×10^{-11}	-240		*Atk07*
P_g19 $\ominus$	$Br_2 \xrightarrow{h\nu} 2\,Br$	*(3.86×10^{-2})*		$\Phi = 1.0^{Fan/Liu01}$; see Tab. S14	*See/Bri64*
G144 $\ominus$	$BrO + O_3 \rightarrow 0.9\,Br + 0.1\,OBrO + 1.9\,O_2$	2.17×10^{-17}	3200	products from Atkinson et al. (2007); upper limit	*San06*
G145	$BrO + OH \rightarrow Br + HO_2$	4.16×10^{-11}	-250		*Atk07*
G146 $\ominus$	$BrO + HO_2 \rightarrow HOBr + O_2$	2.41×10^{-11}	-500	further products omitted	*Atk07*
G147	$BrO + BrO \rightarrow 1.7\,Br + 0.15\,Br_2 + O_2$	3.24×10^{-12}	-210		*Atk07*
P_g20	$BrO \xrightarrow{h\nu} Br + O(^3P)$	*(4.86×10^{-2})*		$\Phi = 1.0$; see Tab. S14	*San03*
P_g21	$OBrO \xrightarrow{h\nu} BrO + O(^3P)$	*(0.56)*		$\Phi = 1.0^{Fle05,\,i}$; see Tab. S14	*San06*
P_g22 $\ominus$	$HOBr \xrightarrow{h\nu} Br + OH$	*(2.80×10^{-3})*		$\Phi = 1.0$; see Tab. S14	*San03*
G148 $\ominus$	$HBr + OH \rightarrow Br + H_2O$	1.13×10^{-11}	-155		*Atk07*
G149	$Br + NO_2 \xrightarrow{M} BrNO_2$	1.43×10^{-12}		TYP: TROEF; see Tab. S13	*Atk07*
P_g23 $\ominus$	$BrNO_2 \xrightarrow{h\nu} Br + NO_2$	*(5.87×10^{-3})*		$\Phi = 1.0$; see Tab. S14	*Atk07*
G150	$Br + NO_3 \rightarrow BrO + NO_2$	1.60×10^{-11}			*Atk07*
G151	$BrO + NO \rightarrow Br + NO_2$	2.08×10^{-11}	-260		*Atk07*
G152	$BrO + NO_2 \xrightarrow{M} BrNO_3$	1.87×10^{-12}		TYP: TROEF; see Tab. S13	*Atk07*
G153	$BrNO_3 \rightarrow BrO + NO_2$	2.75×10^{-5}	12360		*Orl/Tyn96*
G154	$BrNO_3 + Br \rightarrow Br_2 + NO_3$	4.9×10^{-11}			*Orl/Tyn96*
P_g24	$BrNO_3 \xrightarrow{h\nu} Br + NO_3$	*(1.26×10^{-3})*		$\Phi = 0.71$; see Tab. S14	*San03*
P_g25	$BrNO_3 \xrightarrow{h\nu} BrO + NO_2$	*(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	$HBr + NO_3 \rightarrow Br + HNO_3$	1.0×10^{-16}		upper limit	*Atk07*
G156	$Br + Cl_2O_2 \rightarrow BrCl + ClO_2$	3.34×10^{-12}	170		*Atk07*
G157	$Br + OClO \rightarrow BrO + ClO$	3.44×10^{-13}	1300		*Atk07*
G158	$BrO + ClO \rightarrow Br + OClO$	6.77×10^{-12}	-430		*Atk07*
G159	$BrO + ClO \rightarrow Br + ClO_2$	6.07×10^{-12}	-220		*Atk07*
G160	$BrO + ClO \rightarrow BrCl + O_2$	1.03×10^{-12}	-170		*Atk07*
G161	$Br_2 + Cl \rightarrow BrCl + Br$	3.62×10^{-10}	-135		*Bed98*
G162	$BrCl + Br \rightarrow Br_2 + Cl$	3.32×10^{-15}			*Bau81*
G163	$Br + Cl_2 \rightarrow BrCl + Cl$	1.10×10^{-15}			*Dol/Leo87*
G164	$BrCl + Cl \rightarrow Br + Cl_2$	1.45×10^{-11}			*Cly/Cru72*
P_g26 ⊖	$BrCl \xrightarrow{h\nu} Br + Cl$	*(1.32×10^{-2})*		$\Phi = 1.0$; see Tab. S14	*Atk07*
G165	$Br + OP1 \rightarrow HBr + MO_2$	1.18×10^{-14}	1610	*A, B*	*Kon/Ben84*
G166	$BrO + MO_2 \rightarrow 0.25\,BrO_2 + 0.25\,HCHO + 0.25\,HO_2 - 0.25\,O_2 + 0.75\,HOBr + 0.75\,ORA1$	6.01×10^{-12}	-800	*A, C*	*IUPAC*
G167 ⊕	$Br + HCHO \xrightarrow{O_2} HBr + CO + HO_2$	1.16×10^{-12}	800	better reference	*San06*
G168	$BrO + HCHO \xrightarrow{O_2} HOBr + CO + HO_2$	1.50×10^{-14}			*Han99*
G169	$Br + CH_3CHO \xrightarrow{O_2} HBr + ACO_3$	3.84×10^{-12}	460	*N*	*Atk06*
G170	$Br + ALD \xrightarrow{O_2} HBr + ACO_3$	3.84×10^{-12}	460	estimated ($k_{G170} \approx k_{G169}$), *N, O*	*Atk06*
G171	$Br + ETI \xrightarrow{O_2, M} 0.17\,CHOBr + 0.09\,Br + 0.74\,HBr + 0.09\,GLY + 1.65\,CO + 0.91\,HO_2$	2.78×10^{-14}	-440	*d, ,T U*	*Atk06*
G172	$Br + ETE \xrightarrow{M, O_2} CH_2BrCH_2O_2$	2.25×10^{-13}	-277	fitted to Arrhenius expression, *g, U*	*Atk06*
G173	$CH_2BrCH_2O_2 + MO_2 \rightarrow 0.2\,CH_2BrCH_2OH + 0.8\,HCHO + 0.2\,CH_2BrCHO + 0.2\,CH_3OH + 0.4\,O_2 + 0.6\,CH_2BrCH_2O + 0.6\,HO_2$	2.00×10^{-12}		estimated ($RO_2 = MO_2$), *e A*	*MCM*
G174	$CH_2BrCH_2O_2 + CH_2BrCH_2O_2 \rightarrow 1.14\,CH_2BrCH_2O + 0.43\,CH_2BrCH_2OH + 0.43\,CH_2BrCHO + O_2$	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	$CH_2BrCH_2O_2 + NO \rightarrow CH_2BrCH_2O + NO_2$	9.70×10^{-12}		[e]	*Atk08*
G176	$CH_2BrCH_2OH + OH \xrightarrow{O_2} CH_2BrCHO + H_2O + HO_2$	4.60×10^{-12}		[e]	*MCM*
G177	$CH_2BrCH_2O + O_2 \rightarrow CH_2BrCHO + HO_2$	9.48×10^{-15}	550	[e]	*MCM*
G178	$CH_2BrCHO + OH \xrightarrow{O_2} CH_2BrCO_3 + H_2O$	3.10×10^{-12}		[e, g]	*Atk08*
P_g29	$CH_2BrCHO \xrightarrow{h\nu, 2O_2} CH_2BrO_2 + CO + HO_2$	*(3.26×10^{-5})*		estimated same as P_g13, see Tab. S14	*MCM*
G179	$CH_2BrCO_3 + HO_2 \rightarrow 0.71\,CH_2BrCO_3H + 0.71\,O_2 + 0.29\,CH_2BrCOOH + 0.29\,O_3$	1.41×10^{-11}	-1040	[e]	*MCM*
G180	$CH_2BrCO_3 + MO_2 \xrightarrow{O_2} 0.3\,CH_2BrCOOH + HCHO + 0.7\,CH_2BrO_2 + 0.7\,CO_2 + 0.7\,HO_2 - 0.4\,O_2$	1.00×10^{-11}		estimated ($RO_2 = MO_2$), [e A]	*MCM*
G181	$CH_2BrCO_3 + NO \xrightarrow{O_2} CH_2BrO_2 + CO_2 + NO_2$	2.00×10^{-11}	-270	[e]	*MCM*
G182	$CH_2BrCO_3 + NO_2 \xrightarrow{M} CH_2BrC(O)OONO_2$	1.11×10^{-11}		TYP: TROEF; see Tab. S13, [e]	*MCM*
G183	$CH_2BrC(O)OONO_2 \xrightarrow{M} CH_2BrCO_3 + NO_2$	3.48×10^{-4}		TYP: TROEXP; see Tab. S13, [e]	*MCM*
G184	$CH_2BrC(O)OONO_2 + OH \rightarrow O_2CHBrC(O)OONO_2 + H_2O$	6.26×10^{-13}		[e]	*MCM*
G185	$O_2CHBrC(O)OONO_2 + NO\,C(O)OONO_2 + NO\,CHOBr + CO + O_2 + 2\,NO_2$	1.36×10^{-11}	-360	estimated	
G186	$CH_2BrCO_3H + OH \rightarrow CH_2BrCO_3 + H_2O$	4.29×10^{-12}		[e]	*MCM*
P_g30	$CH_2BrCO_3H \xrightarrow{h\nu, O_2} CH_2BrO_2 + CO_2 + OH$	*(5.79×10^{-6})*		estimated same as P_g14, see Tab. S14	*MCM*
G187	$CH_2BrCOOH + OH \xrightarrow{O_2} CH_2BrO_2 + CO_2 + H_2O$	3.59×10^{-12}	-190	[e]	*MCM*
G188	$Br + C_3H_6 \xrightarrow{M, O_2} CH_3CHO_2CH_2Br$	3.60×10^{-12}		[g]	*Atk06*

Table S12 (continued) Gas phase reactions

	Reaction	k_{298} $(j_{max})^a$	E_A/R^b	Comment	Reference
G189	$CH_3CHO_2CH_2Br + MO_2 \rightarrow$ $0.2\,CH_3CHOHCH_2Br + 0.8\,HCHO +$ $0.2\,CH_3COCH_2Br + 0.2\,CH_3OH + 0.4\,O_2 +$ $0.6\,CH_3CHOCH_2Br + 0.6\,HO_2$	4.00×10^{-14}		estimated ($RO_2 = MO_2$), [c, A]	*MCM*
G190	$CH_3CHO_2CH_2Br + NO \rightarrow$ $CH_3CHOCH_2Br + NO_2$	9.04×10^{-12}	-360	further products omitted, [c]	*Atk06*
G191	$CH_3CHOHCH_2Br + OH \xrightarrow{O_2}$ $CH_3COCH_2Br + H_2O + HO_2$	5.09×10^{-12}	-200	further products omitted, [c]	*Atk06*
G192	$CH_3CHOCH_2Br + O_2 \rightarrow$ $CH_3COCH_2Br + HO_2$	6.93×10^{-15}	230	[c]	*Atk06*
G193	$CH_3COCH_2Br + OH \xrightarrow{O_2}$ $CH_3COCHBrO_2 + H_2O$	1.05×10^{-13}	1320	[c, g]	*Atk06*
P_g27	$CH_3COCH_2Br \xrightarrow{h\nu} 0.7\,COBr + 0.7\,ACO3 +$ $0.3\,CH_2BrCO_3 + 0.3\,MO2 - 1.3\,O_2$	*(5.87×10^{-3})*		$\Phi = 1.0^i$; see Tab. S14	*San06*
G194	$CH_3COCHBrO_2 + MO_2 \rightarrow$ $0.2\,CH_3COCHBrOH + 0.8\,HCHO +$ $0.2\,CH_3COCBrO + 0.2\,CH_3OH - 0.2\,O_2 +$ $0.6\,ACO_3 + 0.6\,CHOBr + 0.6\,HO_2$	2.00×10^{-12}		estimated ($RO_2 = MO_2$), [c, A, N]	*MCM*
G195	$CH_3COCHBrO_2 + NO \xrightarrow{O_2}$ $ACO_3 + CHOBr + NO_2$	8.00×10^{-12}		[c, N]	*Atk06*
G196	$CH_3COCHBrOH + OH \xrightarrow{O_2}$ $CH_3COCBrO + H_2O + HO_2$	3.00×10^{-12}		[c]	*MCM*
P_g28	$CH_3COCBrO \xrightarrow{h\nu,O_2} COBr + ACO3$	*(2.78×10^{-5})*		estimated same as methylglyoxal; see Tab. S14	*MCM*
G197	$CHBr_3 + OH \xrightarrow{O_2} CBr_3O_2 + H_2O$	1.80×10^{-13}	600		*San06*
G198	$CHBr_3 + Cl \xrightarrow{O_2} CBr_3O_2 + HCl$	2.80×10^{-13}	850		*San06*
P_g31	$CHBr_3 \xrightarrow{h\nu,O_2} Br + CHBr_2O_2$	*(1.77×10^{-6})*		$\Phi = 1.0^i$; see Tab. S14	*Dem97*
G199	$CBr_3O_2 + HO_2 \rightarrow COBr_2 + HOBr + O_2$	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	$CBr_3O_2 + MO_2 \rightarrow 0.3\,CBr_3OH + 0.3\,O_2 + HCHO + 0.7\,CBr_3O + 0.7\,HO_2$	6.60×10^{-12}		branching ratios from MCM, [e, A]	*MCM*
G201	$CBr_3O_2 + CBr_3O_2 \rightarrow 2\,CBr_3O + O_2$	3.95×10^{-12}	-740	[e]	*Atk08*
G202	$CBr_3O_2 + NO \rightarrow COBr_2 + Br + NO_2$	1.81×10^{-11}	-270	[e]	*San06*
G203	$CBr_3O_2 + NO_2 \xrightarrow{M} CBr_3OONO_2$	1.41×10^{-12}		TYP: TROEF; see Tab. S13; [e]	*Atk08*
G204	$CBr_3OONO_2 \xrightarrow{M} CBr_3O_2 + NO_2$	0.26		TYP: TROEXP; see Tab. S13; [e]	*Atk08*
G205	$CBr_3OH + OH \rightarrow CBr_3O + H_2O$	3.60×10^{-14}		[e]	*MCM*
G206	$CBr_3O \rightarrow COBr_2 + Br$	7.91×10^{6}	4600	[e]	*Atk08*
G207	$CH_2Br_2 + OH \xrightarrow{O_2} CHBr_2O_2 + H_2O$	1.11×10^{-13}	775		*Atk08*
G208	$CH_2Br_2 + Cl \xrightarrow{O_2} CHBr_2O_2 + HCl$	4.30×10^{-13}	800		*San06*
P_g32	$CH_2Br_2 \xrightarrow{h\nu, O_2} Br + CH_2BrO_2$	*(8.22×10^{-10})*		$\Phi = 1.0$[i]; see Tab. S14	*Atk08*
G209	$CHBr_2O_2 + HO_2 \rightarrow 0.3\,CHOBr + 0.3\,HOBr + 0.7\,COBr_2 + 0.7\,H_2O + O_2$	5.87×10^{-12}	-700	[e]	*Atk08*
G210	$CHBr_2O_2 + MO_2 \rightarrow 0.2\,CHBr_2OH + 0.8\,HCHO + 0.2\,COBr_2 + 0.2\,CH_3OH + 0.4\,O_2 + 0.6\,CHOBr + 0.6\,Br + 0.6\,HO_2$	2.00×10^{-12}		estimated ($RO_2 = MO_2$), [d, e, A]	*MCM*
G211	$CHBr_2O_2 + CHBr_2O_2 \rightarrow 2\,CHOBr + 2\,Br + O_2$	7.00×10^{-12}		[e]	*Atk08*
G212	$CHBr_2O_2 + NO \rightarrow CHOBr + Br + NO_2$	1.70×10^{-11}			*Atk08*
G213	$CHBr_2OH + OH \xrightarrow{O_2} COBr_2 + H_2O + HO_2$	9.34×10^{-13}		[e]	*MCM*
G214	$COBr_2 + OH \rightarrow COBr + HOBr$	5.00×10^{-15}		upper limit, [e]	*Atk08*
P_g33	$COBr_2 \xrightarrow{h\nu} 2\,Br + CO$	*(3.32×10^{-6})*		$\Phi = 1.0$[i]; products estimated the same as in the phosgene reaction in MCM; see Tab. S14	*San06*
G215	$CH_3Br + OH \xrightarrow{O_2} CH_2BrO_2 + H_2O$	2.88×10^{-14}	1215		*Atk08*
G216	$CH_3Br + Cl \xrightarrow{O_2} CH_2BrO_2 + HCl$	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	$CH_2BrO_2 + HO_2 \rightarrow$ $0.85\,CH_2BrO_2H + 0.15\,CHOBr + 0.15\,H_2O + O_2$	6.70×10^{-12}			*Atk08*
G218	$CH_2BrO_2 + MO_2 \rightarrow$ $0.2\,CH_2BrOH + 0.8\,HCHO + 0.2\,CHOBr +$ $0.2\,CH_3OH + 0.4\,O_2 + 0.6\,CH_2BrO + 0.6\,HO_2$	2.00×10^{-12}		estimated ($RO_2 = MO_2$), [A]	*MCM*
G219	$CH_2BrO_2 + CH_2BrO_2 \rightarrow 2\,CH_2BrO + O_2$	1.05×10^{-12}		products from Atkinson et al. (2008b)	*Vil/Les95*
G220	$CH_2BrO_2 + NO \rightarrow CH_2BrO + NO_2$	1.10×10^{-11}			*Atk08*
G221	$CH_2BrO_2H + OH \rightarrow CH_2BrO_2 + H_2O$	3.59×10^{-12}	-190		*MCM*
G222	$CH_2BrO_2H + OH \rightarrow CHOBr + OH + H_2O$	5.79×10^{-12}			*MCM*
P_g34	$CH_2BrO_2H \xrightarrow{h\nu} CH_2BrO + OH$	*5.79×10^{-6}*		see Tab. S14	*MCM*
G223	$CH_2BrOH + OH \xrightarrow{O_2} CHOBr + H_2O + HO_2$	1.06×10^{-12}			*MCM*
G224	$CH_2BrO + O_2 \rightarrow CHOBr + HO_2$	9.48×10^{-15}	550		*MCM*
G225	$CHOBr + OH \rightarrow Br + CO + H_2O$	1.16×10^{-12}			*MCM*
G226	$CHOBr + Cl \rightarrow COBr + HCl$	7.48×10^{-13}	710	[e]	*Atk08*
P_g35	$CHOBr \xrightarrow{h\nu, O_2} Br + CO + HO_2$	*(1.77×10^{-5})*		$\Phi = 1.0$[i]; see Tab. S14	*San06*
G227	$COBr \xrightarrow{M} CO + Br$	4.98×10^{5}	2960	TYP: SPEC4, [e]	*Atk07*
G228	$CO + Br \xrightarrow{M} COBr$	3.33×10^{-14}		TYP: SPEC2; see Tab. S13, [e]	*Atk07*
G229	$I + I \rightarrow I_2$	2.99×10^{-11}			*Hip73*
G230	$I + O_3 \rightarrow IO + O_2$	1.30×10^{-12}	830		*Atk07*
G231	$I_2 + OH \rightarrow I + HOI$	2.10×10^{-10}			*Atk07*
P_g36	$I_2 \xrightarrow{h\nu} 2\,I$	*(0.18)*		$\Phi = 1.0$; see Tab. S14	*Atk07*
G232	$I + HO_2 \rightarrow HI + O_2$	3.87×10^{-13}	1090		*Atk07*
G233	$IO + HO_2 \rightarrow HOI + O_2$	8.57×10^{-11}	-540		*Atk07*
G234	$IO + IO \rightarrow 0.38\,OIO + 0.485\,I_2O_2 + 0.6\,I +$ $0.135\,O_2 + 0.025\,I_2$	8.03×10^{-11}	-500	branching ratios from Sander and Kerkweg (2005)	*San06*
P_g37	$IO \xrightarrow{h\nu} I + O(^3P)$	*(2.07×10^{-3})*		$\Phi = 1.0$; see Tab. S14	*Atk07*
G235	$OIO + OH \rightarrow 0.5\,HIO_3 + 0.5\,HOI + 0.5\,O_2$	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	$OIO + OIO \rightarrow I_2O_2 + O_2$	5.00×10^{-11}		assumed	*Gla02b*
P_g38	$OIO \xrightarrow{h\nu} I + O_2$	*(3.37×10^{-2})*		$\Phi = 0.15$; upper limit; see Tab. S14	*San06*
P_g39	$OIO \xrightarrow{h\nu} IO + O(^3P)$	*(1.57×10^{-3})*		$\Phi = 0.007$; upper limit; see Tab. S14	*San06*
G237	$I_2O_2 \rightarrow 2\,IO$	20.0		assumed	*Jim03*
P_g40	$I_2O_2 \xrightarrow{h\nu} 2\,I + O_2$	*(1.83×10^{-3})*		$\Phi = 1.0^{i}$; see Tab. S14	*San03*
G238	$HI + OH \rightarrow I + H_2O$	7.00×10^{-11}	-440		*Atk07*
P_g41	$HI \xrightarrow{h\nu,O_2} I + HO_2$	*(1.58×10^{-4})*		$\Phi = 1.0$; see Tab. S14	*Atk07*
P_g42	$HOI \xrightarrow{h\nu,O_2} I + OH$	*(1.16×10^{-2})*		$\Phi = 1.0$; see Tab. S14	*Atk07*
G239	$I + NO \xrightarrow{M} INO$	9.38×10^{-14}		TYP: TROE; see Tab. S13	*Atk07*
P_g43	$INO \xrightarrow{h\nu} I + NO$	*(3.84×10^{-3})*		$\Phi = 1.0^{i}$; see Tab. S14	*San06*
G240	$I + NO_2 \xrightarrow{M} INO_2$	1.10×10^{-70}		TYP: TROEF; see Tab. S13	*Atk07*
P_g44	$INO_2 \xrightarrow{h\nu} I + NO_2$	*(3.89×10^{-3})*		$\Phi = 1.0^{i}$; see Tab. S14	*San06*
G241	$I + NO_3 \rightarrow IO + NO_2$	4.50×10^{-10}			*Cha92*
G242	$I_2 + NO_3 \rightarrow I + INO_3$	1.50×10^{-12}			*Atk07*
G243	$IO + NO \rightarrow I + NO_2$	1.96×10^{-11}	-300		*Atk07*
G244	$IO + NO_2 \xrightarrow{M} INO_3$	4.13×10^{-12}		TYP: TROEF; see Tab. S13	*Atk07*
P_g45	$INO_3 \xrightarrow{h\nu} I + NO_3$	*(5.17×10^{-2})*		$\Phi = 0.85$ (estimated same as $BrNO_3$ in Sander et al. (2006)), see Tab. S14	*San06*
P_g46	$INO_3 \xrightarrow{h\nu} IO + NO_2$	*(9.11×10^{-3})*		$\Phi = 0.15$ (estimated same as $BrNO_3$ in Sander et al. (2006)), see Tab. S14	*San06*
G245	$OIO + NO \rightarrow IO + NO_2$	6.78×10^{-12}	-542		*Atk07*
G246	$HI + NO_3 \rightarrow I + HNO_3$	2.80×10^{-15}	1830		*Atk07*
G247	$INO + INO \rightarrow I_2 + 2\,NO$	1.28×10^{-14}	2620		*Atk07*
G248	$INO_2 + INO_2 \rightarrow I_2 + 2\,NO_2$	1.73×10^{-15}	1670		*Atk07*
G249	$INO_2 \xrightarrow{M} I + NO_2$	2.4		estimated; TYP: SPEC2	*Gla02a*
G250	$INO_3 \xrightarrow{M} IO + NO_2$	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_g47	$ICl \xrightarrow{h\nu} I + CL$	*(2.77×10^{-2})*		$\Phi = 1.0$; see Tab. S14; exited atoms are treated like atoms in ground state	*Atk07*
P_g48	$IBr \xrightarrow{h\nu} I + Br$	*(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_g49	$C_3H_7I \xrightarrow{h\nu,O_2} I + CH_3CHO_2CH_3$	*(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_g50	$C_2H_5I \xrightarrow{h\nu,O_2} I + CH_3CH_2O_2$	*(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	$CH_2ICH_2O_2 + CH_2ICH_2O_2 \rightarrow 1.14\,CH_2ICH_2O + 0.43\,CH_2ICH_2OH + 0.43\,CH_2ICHO + O_2$	3.98×10^{-12}	-1250	[f]	*Atk08*
G264	$CH_2ICH_2O_2 + NO \rightarrow CH_2ICH_2O + NO_2$	9.70×10^{-12}		[e]	*Atk08*
G265	$CH_2ICH_2OH + OH \xrightarrow{O_2} CH_2ICHO + H_2O + HO_2$	4.60×10^{-12}		[e]	*MCM*
G266	$CH_2ICH_2O + O_2 \rightarrow CH_2ICHO + HO_2$	9.48×10^{-15}	550	[e]	*MCM*
G267	$CH_2ICHO + OH \xrightarrow{O_2} CH_2ICO_3 + H_2O$	3.10×10^{-12}		[e, g]	*Atk08*
P_g51	$CH_2ICHO \xrightarrow{h\nu, 2\,O_2} CH_2IO_2 + CO + HO_2$	*(3.26×10^{-5})*		estimated same as P_g13, see Tab. S14	*MCM*
G268	$CH_2ICO_3 + HO_2 \rightarrow 0.71\,CH_2ICO_3H + 0.71\,O_2 + 0.29\,CH_2ICOOH + 0.29\,O_3$	1.41×10^{-11}	-1040	[e]	*MCM*
G269	$CH_2ICO_3 + MO_2 \xrightarrow{2\,O_2} 0.3\,CH_2ICOOH + HCHO - 0.4\,O_2 + 0.7\,CH_2IO_2 + 0.7\,CO_2 + 0.7\,HO_2$	1.00×10^{-11}		estimated ($RO_2 = MO_2$), [e, A]	*MCM*
G270	$CH_2ICO_3 + NO \xrightarrow{O_2} CH_2IO_2 + CO_2 + NO_2$	2.00×10^{-11}	-270	[e]	*MCM*
G271	$CH_2ICO_3 + NO_2 \xrightarrow{M} CH_2IC(O)OONO_2$	1.11×10^{-11}		TYP: TROEF; see Tab. S13, [e]	*MCM*
G272	$CH_2IC(O)OONO_2 \xrightarrow{M} CH_2ICO_3 + NO_2$	3.48×10^{-4}		TYP: TROEXP; see Tab. S13, [e]	*MCM*
G273	$CH_2IC(O)OONO_2 + OH \rightarrow O_2CHIC(O)OONO_2 + H_2O$	6.26×10^{-13}		[e]	*MCM*
G274	$O_2CHIC(O)OONO_2 + NO \rightarrow CHOI + CO + O_2 + 2\,NO_2$	1.36×10^{-11}	-360	estimated	
G275	$CH_2ICO_3H + OH \rightarrow CH_2ICO_3 + H_2O$	4.29×10^{-12}		[e]	*MCM*
P_g52	$CH_2ICO_3H \xrightarrow{h\nu, O_2} CH_2IO_2 + CO_2 + OH$	*(5.79×10^{-6})*		estimated (wie P_g14), see Tab. S14	*MCM*
G276	$CH_2ICOOH + OH \xrightarrow{O_2} CH_2IO_2 + CO_2 + H_2O$	3.59×10^{-12}	-190	[e]	*MCM*
G277	$CH_3CHIO_2 + MO_2 \rightarrow 0.2\,CH_3CHIOH + 0.8\,HCHO + 0.2\,CH_3CIO + 0.2\,CH_3OH + 0.4\,O_2 + 0.6\,CH_3CHO + 0.6\,I + 0.6\,HO_2$	8.80×10^{-13}		estimated ($RO_2 = MO_2$), [d, e, A]	*MCM*

Table S12 (continued) Gas phase reactions

	Reaction	k_{298} $(j_{max})^a$	E_A/R^b	Comment	Reference
G278	$CH_3CHIO_2 + NO \rightarrow CH_3CHO + I + NO_2$	1.87×10^{-11}	-360	*d, e*	*MCM*
G279	$CH_3CHIOH + OH \xrightarrow{O_2} CH_3CIO + H_2O + HO_2$	2.77×10^{-12}		*e*	*MCM*
G280	$CH_3CIO + OH \xrightarrow{O_2} CIOCH_2O_2 + H_2O$	3.88×10^{-14}		*e*	*MCM*
G281	$CIOCH_2O_2 + MO_2 \rightarrow I + CO + 2\,HCHO + HO_2$	2.00×10^{-12}		*d, e, A*	*MCM*
G282	$CIOCH_2O_2 + NO \rightarrow I + CO + HCHO + NO_2$	1.36×10^{-11}	-360	*d, e*	*MCM*
G283	$CH_2I_2 + OH \xrightarrow{O_2} CHI_2O_2 + H_2O$	2.75×10^{-14}	929	estimated	
G284	$CH_2I_2 + Cl \xrightarrow{O_2} CHI_2O_2 + HCl$	4.70×10^{-13}	1135	estimated	
P_g53	$CH_2I_2 \xrightarrow{h\nu,O_2} I + CH_2IO_2$	*(1.13×10^{-2})*		$\Phi = 1.0$; see Tab. S14; exited atoms are treated like atoms in ground state	*San06*
G285	$CHI_2O_2 + HO_2 \rightarrow 0.3\,CHOI + 0.3\,HOI + 0.7\,COI_2 + 0.7\,H_2O + O_2$	5.87×10^{-12}	-700	*e*	*Atk08*
G286	$CHI_2O_2 + MO_2 \rightarrow 0.2\,CHI_2OH + 0.8\,HCHO + 0.2\,COI_2 + 0.2\,CH_3OH + 0.4\,O_2 + 0.6\,CHOI + 0.6\,I + 0.6\,HO_2$	2.00×10^{-12}		estimated ($RO_2 = MO_2$), *e, A*	*MCM*
G287	$CHI_2O_2 + CHI_2O_2 \rightarrow 2\,CHOI + 2\,I + O_2$	7.00×10^{-12}		*e*	*Atk08*
G288	$CHI_2O_2 + NO \rightarrow CHOI + I + NO_2$	1.70×10^{-11}		*h*	*Atk08*
G289	$CHI_2OH + OH \xrightarrow{O_2} COI_2 + H_2O + HO_2$	9.34×10^{-13}		*e*	*MCM*
G290	$COI_2 + OH \rightarrow COI + HOI$	5.00×10^{-15}		upper limit, *e*	*Atk08*
G291	$CH_3I + OH \xrightarrow{O_2} CH_2IO_2 + H_2O$	1.00×10^{-13}	1120		*Atk08*
G292	$CH_3I + Cl \xrightarrow{O_2} CH_2IO_2 + HCl$	1.01×10^{-12}	1000		*San06*
P_g54	$CH_3I \xrightarrow{h\nu,O_2} I + MO_2$	*(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	$CH_2IO_2 + HO_2 \rightarrow$ $0.85\,CH_2IO_2H + 0.15\,CHOI + 0.15\,H_2O + O_2$	6.70×10^{-12}		f	*Atk08*
G294	$CH_2IO_2 + MO_2 \rightarrow$ $0.2\,CH_2IOH + 0.8\,HCHO + 0.2\,CHOI +$ $0.2\,CH_3OH + 0.4\,O_2 + 0.6\,CH_2IO + 0.6\,HO_2$	2.00×10^{-12}		e, A	*MCM*
G295	$CH_2IO_2 + CH_2IO_2 \rightarrow 2\,CH_2IO + O_2$	1.05×10^{-12}		f	*Vil/Les95*, *Atk08*
G296	$CH_2IO_2 + NO \rightarrow CH_2IO + NO_2$	1.10×10^{-11}		f	*Atk08*
G297	$CH_2IO_2H + OH \rightarrow CH_2IO_2 + H_2O$	3.59×10^{-12}	-190	e	*MCM*
G298	$CH_2IO_2H + OH \rightarrow CHOI + OH + H_2O$	5.79×10^{-12}		f	*MCM*
P_g55	$CH_2IO_2H \xrightarrow{h\nu} CH_2IO + OH$	*(5.79×10^{-6})*		estimated same as P_g17, see Tab. S14	*MCM*
G299	$CH_2IOH + OH \xrightarrow{O_2} CHOI + H_2O + HO_2$	1.06×10^{-12}		f	*MCM*
G300	$CH_2IO + O_2 \rightarrow CHOI + HO_2$	9.48×10^{-15}	550	e	*MCM*
G301	$CHOI + OH \rightarrow I + CO + H_2O$	1.16×10^{-12}		f	*MCM*
G302	$CHOI + Cl \rightarrow COI + HCl$	7.48×10^{-13}	710	e	*Atk08*
P_g56	$CHOI \xrightarrow{h\nu, O_2} I + CO + HO_2$	*(2.71×10^{-7})*		estimated same as P_g18, see Tab. S14	*Atk08*
G303	$COI \xrightarrow{M} CO + I$	4.98×10^{5}	2960	TYP: SPEC4, ^{e}	*Atk07*
G304	$CO + I \xrightarrow{M} COI$	3.33×10^{-14}		TYP: SPEC2; see Tab. S13, ^{e}	*Atk07*
P_g57	$CH_2ICl \xrightarrow{h\nu, O_2} I + CH_2ClO_2$	*(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_g58	$CH_2IBr \xrightarrow{h\nu, O_2} I + CH_2BrO_2$	*(6.87 × 10^{-4})*		$\Phi = 1.0$; see Tab. S14	^{Atk08}

$^{\oplus}$already implemented in the Halogen Module 1.0; $^{\ominus}$update of the Halogen Module 1.0
^{a}in cm^3 molecules^{-1} s^{-1} (*slanted* values in parentheses represent j_{max} in s^{-1} for photolysis reactions); ^{b}in K; ^{c}estimated X = H (X = Cl, Br, I); ^{d}reactions combined; ^{e}estimated X = Cl (X = Br, I); ^{f}estimated I = Br; ^{g}immediate reaction with oxygen; ^{h}immediate hydrogen abstraction; ^{i}estimated
^{A}MO$_2$ = methyl peroxyl radical; ^{B}OP1 = methyl hydrogen peroxide; ^{C}ORA1 = formic acid; ^{D}ETH = ethane; ^{E}ETHP = peroxyl radical formed from ETH; ^{F}HC3 = alkanes, alcohols, esters, and alkynes with OH rate constant (298 K, 1 atm) less than 3.4 × 10^{-12} cm^3 molecules^{-1} s^{-1}; ^{G}HC3P = peroxyl radical formed from HC3; ^{H}HC5 = alkanes, alcohols, esters, and alkynes with OH rate constant (298 K, 1 atm) between 3.4 × 10^{-12} cm^3 molecules^{-1} s^{-1} and 6.8 × 10^{-12} cm^3 molecules^{-1} s^{-1}; ^{I}HC5P = peroxyl radical formed from HC5; ^{J}HC8 = alkanes, alcohols, esters, and alkynes with OH rate constant (298 K, 1 atm) greater than 6.8 × 10^{-12} cm^3 molecules^{-1} s^{-1}; ^{K}HC8P = peroxyl radical formed from HC8; ^{L}TOL = Toluene and less reactive aromatics; ^{M}TOLP = peroxyl radical formed from TOL; ^{N}ACO$_3$ = acetylperoxyl and higher saturated acylperoxyl radicals; ^{O}ALD = higher aldehydes; ^{P}KET = ketones; ^{Q}KETP = peroxyl radical formed from KET; ^{R}HKET = hydroxy ketone; ^{S}MGLY = methylglyoxal; ^{T}GLY = glyoxal; ^{U}ETI = acetylene; ^{V}ETE = 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	$k_0{}^a$	$k_\infty{}^a$	$F_C{}^b$
G14	$ClO + ClO \xrightarrow{M} Cl_2O_2$	TROE	$1.6 \times 10^{-32}(T/300)^{-4.5}$	$2.0 \times 10^{-12}(T/300)^{-2.4}$	
G15	$Cl + O_2 \xrightarrow{M} ClO_2$	TROE	$2.2 \times 10^{-33}(T/300)^{-3.1}$	1.8×10^{-10}	
G18	$Cl_2O_2 \xrightarrow{M} 2\,ClO$	TROEXP	$3.7 \times 10^{-7}e^{-7690/T}$	$7.9 \times 10^{15}e^{-8820/T}$	0,45
G23	$ClO + OClO \xrightarrow{M} Cl_2O_3$	TROE	$6.2 \times 10^{-32}(T/300)^{-4.7}$	2.4×10^{-11}	
G24	$Cl_2O_3 \xrightarrow{M} ClO + OClO$	TROEXP	$1.4 \times 10^{-10}e^{-3810/T}$	$2.5 \times 10^{12}e^{-4940/T}$	
G32	$Cl + NO \xrightarrow{M} ClNO$	SPEC2	$7.6 \times 10^{-32}(T/300)^{-1,8}$		
G34	$Cl + NO_2 \xrightarrow{M} ClNO_2$	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	$ClO + NO_2 \xrightarrow{M} ClNO_3$	TROEF	$1.6 \times 10^{-31}(T/300)^{-3.4}$	7.0×10^{-11}	0.4
G60	$Cl + ETI^{c} \xrightarrow{O_2, M}$ $0.26\,CHOCl + 0.21\,Cl + 0.53\,HCl +$ $0.21\,GLY^{d} + 1.32\,CO + 0.79\,HO_2$	TROE	$6.10 \times 10^{-30}(T/300)^{-3.0}$	2.0×10^{-10}	
G61	$Cl + ETE^{e} \xrightarrow{O_2,\ M} CH_2ClCH_2OO$	TROEF	$1.85 \times 10^{-29}(T/300)^{-3.3}$	6.0×10^{-10}	0.4
G71	$CH_2ClCO_3 + NO_2 \xrightarrow{M}$ $CH_2ClC(O)OONO_2$	TROEF	$2.7 \times 10^{-28}(T/300)^{-7.1}$	$1.2 \times 10^{-11}(T/300)^{-0.9}$	0.3
G72	$CH_2ClC(O)OONO_2 \xrightarrow{M}$ $CH_2ClCO_3 + NO_2$	TROEXP	$4.9 \times 10^{-3}e^{-12100/T}$	$5.4 \times 10^{16}e^{-13830/T}$	0.3
G77	$Cl + C_3H_6 \xrightarrow{O_2,\ M} CH_3CHOOCH_2Cl$	TROE	4.0×10^{-28}	2.8×10^{-10}	
G106	$CCl_3CO_3 + NO_2 \xrightarrow{M} CCl_3C(O)OONO_2$	TROEF	$2.7 \times 10^{-28}(T/300)^{-7.1}$	$1.2 \times 10^{-11}(T/300)^{-0.9}$	0.3
G107	$CCl_3C(O)OONO_2 \xrightarrow{M} CCl_3CO_3 + NO_2$	TROEXP	$4.9 \times 10^{-3}e^{-12100/T}$	$5.4 \times 10^{16}e^{-13830/T}$	0.3
G114	$CCl_3OO + NO_2 \xrightarrow{M} CCl_3OONO_2$	TROEF	$9.2 \times 10^{-29}(T/300)^{-6.0}$	$1.5 \times 10^{-12}(T/300)^{-0.7}$	0.32
G115	$CCl_3OONO_2 \xrightarrow{M} CCl_3OO + NO_2$	TROEXP	$4.3 \times 10^{-3}e^{-10235/T}$	$4.8 \times 10^{16}e^{-11820/T}$	0.32
G139	$CO + Cl \xrightarrow{M} COCl$	SPEC2	$1.3 \times 10^{-33}(T/300)^{-3.8}$		
G149	$Br + NO_2 \xrightarrow{M} BrNO_2$	TROEF	$4.2 \times 10^{-31}T/300)^{-2.4}$	2.7×10^{-11}	0.55
G152	$BrO + NO_2 \xrightarrow{M} BrNO_3$	TROEF	$4.7 \times 10^{-31}(T/300)^{-3.1}$	1.8×10^{-11}	0.4
G182	$CH_2BrCO_3 + NO_2 \xrightarrow{M}$ $CH_2BrC(O)OONO_2$	TROEF	$2.7 \times 10^{-28}(T/300)^{-7.1}$	$1.2 \times 10^{-11}(T/300)^{-0.9}$	0.3
G183	$CH_2BrC(O)OONO_2 \xrightarrow{M}$ $CH_2BrCO_3 + NO_2$	TROEXP	$4.9 \times 10^{-3}e^{-12100/T}$	$5.4 \times 10^{16}e^{-13830/T}$	0.3
G203	$CBr_3OO + NO_2 \xrightarrow{M} CBr_3OONO_2$	TROEF	$9.2 \times 10^{-29}(T/300)^{-6.0}$	$1.5 \times 10^{-12}(T/300)^{-0.7}$	0.32
G204	$CBr_3OONO_2 \xrightarrow{M} CBr_3OO + NO_2$	TROEXP	$4.3 \times 10^{-3}e^{-10235/T}$	$4.8 \times 10^{16}e^{-11820/T}$	0.32
G228	$CO + Br \xrightarrow{M} COBr$	SPEC2	$1.3 \times 10^{-33}(T/300)^{-3.8}$		
G239	$I + NO \xrightarrow{M} INO$	TROE	$1.8 \times 10^{-32}(T/300)^{-1.0}$	1.7×10^{-11}	
G240	$I + NO_2 \xrightarrow{M} INO_2$	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	$k_0{}^a$	$k_\infty{}^a$	$F_C{}^b$
G244	$IO + NO_2 \xrightarrow{M} INO_3$	TROEF	$7.7 \times 10^{-31}(T/300)^{-5.0}$	1.6×10^{-11}	0.4
G271	$CH_2ICO_3 + NO_2 \xrightarrow{M}$ $CH_2IC(O)OONO_2$	TROEF	$2.7 \times 10^{-28}(T/300)^{-7.1}$	$1.2 \times 10^{-11}(T/300)^{-0.9}$	0.3
G272	$CH_2IC(O)OONO_2 \xrightarrow{M}$ $CH_2ICO_3 + NO_2$	TROEXP	$4.9 \times 10^{-3} e^{-12100/T}$	$5.4 \times 10^{16} e^{-13830/T}$	0.3
G304	$CO + I \xrightarrow{M} COI$	SPEC2	$1.3 \times 10^{-33}(T/300)^{-3.8}$		

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

^{a}in $\frac{cm^{3n}}{molecules^n\ s}$, n = order of reaction; ^{b}if other than $F_C = 0.6$; ^{c}ETI = acetylene; ^{d}GLY = glyoxal; ^{e}ETE = ethylene

S3.4 Photolysis reactions

Table S14 Parameters for gas phase photolysis reactions

	Reaction	l/s^{-1}	m	n	Reference/comment
P_g1 $\ominus$	$Cl_2 \xrightarrow{h\nu} 2\,Cl$	3.827×10^{-3}	0.543	0.244	DeMore et al. (1997) with quantum yields from Calvert and Pitts (1966)
P_g2	$ClO \xrightarrow{h\nu} Cl + O(^3P)$	4.755×10^{-4}	1.258	0.588	Sander et al. (2006)^a
P_g3	$OClO \xrightarrow{h\nu} ClO + O(^3P)$	0.133	0.416	0.244	Sander et al. (2006)^a
P_g4	$Cl_2O_2 \xrightarrow{h\nu} Cl + ClO_2$	2.294×10^{-3}	0.745	0.223	Sander et al. (2003)^a
P_g5	$Cl_2O_3 \xrightarrow{h\nu} ClO + OClO$	1.558×10^{-3}	1.324	0.462	further products omitted, Atkinson et al. (2007)^a
P_g6 $\ominus$	$HOCl \xrightarrow{h\nu} Cl + OH$	4.615×10^{-4}	0.656	0.240	Atkinson et al. (2007)
P_g7	$ClNO \xrightarrow{h\nu} Cl + NO$	4.755×10^{-3}	0.408	0.217	Atkinson et al. (2007)
P_g8 $\ominus$	$ClNO_2 \xrightarrow{h\nu} Cl + NO_2$	6.219×10^{-4}	0.774	0.255	Atkinson et al. (2007)
P_g9	$ClNO_3 \xrightarrow{h\nu} Cl + NO_3$	6.420×10^{-5}	0.648	0.217	DeMore et al. (1997)

Table S14 (continued) Parameters for gas phase photolysis reactions

	Reaction	l/s^{-1}	m	n	Reference/comment
P_g10	$ClNO_3 \xrightarrow{h\nu} ClO + NO_2$	1.393×10^{-5}	1.052	0.243	DeMore et al. (1997)
P_g11	$CH_3COCH_2Cl \xrightarrow{h\nu} 0.7\,COCl + 0.7\,ACO_3 + 0.3\,CH_2ClCO_3 + 0.3\,MO_2 - 1.3\,O_2$	1.675×10^{-4}	1.003	0.296	Sander et al. (2006)[a, c, d]
P_g12	$CH_3COCClO \xrightarrow{h\nu,O_2} COCl + ACO_3$	1.853×10^{-4}	0.583	0.225	estimated same as methylglyoxal[c]
P_g13	$CH_2ClCHO \xrightarrow{h\nu,2\,O_2} CH_2ClO_2 + CO + HO_2$	4.642×10^{-5}	0.762	0.353	Pilling et al. (2008)
P_g14	$CH_2ClCO_3H \xrightarrow{h\nu,O_2} CH_2ClO_2 + CO_2 + OH$	7.649×10^{-6}	0.682	0.279	Pilling et al. (2008)
P_g15	$CCl_2OHCClO \xrightarrow{h\nu,O_2} COCl_2 + CO + Cl + HO_2$	2.792×10^{-5}	0.805	0.338	Pilling et al. (2008)
P_g16	$CCl_3CHO \xrightarrow{h\nu,3/2\,O_2} Cl + COCl_2 + CO + HO_2$	1.442×10^{-4}	1.027	0.302	Atkinson et al. (2008b)
P_g17	$CH_2ClO_2H \xrightarrow{h\nu} CH_2ClO + OH$	7.649×10^{-6}	0.682	0.279	Pilling et al. (2008)
P_g18	$CHOCl \xrightarrow{h\nu,O_2} Cl + CO + HO_2$	3.905×10^{-7}	1.936	0.362	Atkinson et al. (2008b) with quantum yields from Fang and Liu (2001)
P_g19 $\ominus$	$Br_2 \xrightarrow{h\nu} 2\,Br$	4.773×10^{-2}	0.193	0.213	Seery and Britton (1964) with quantum yields from Fang and Liu (2001)
P_g20	$BrO \xrightarrow{h\nu} Br + O(^3P)$	6.368×10^{-2}	0.605	0.269	Sander et al. (2003)
P_g21	$OBrO \xrightarrow{h\nu} BrO + O(^3P)$	0.688	0.144	0.198	Sander et al. (2006) with quantum yields from Fleischmann et al. (2005)
P_g22 $\ominus$	$HOBr \xrightarrow{h\nu} Br + OH$	3.464×10^{-3}	0.441	0.214	Sander et al. (2003)
P_g23 $\ominus$	$BrNO_2 \xrightarrow{h\nu} Br + NO_2$	7.443×10^{-3}	0.355	0.236	Atkinson et al. (2007)
P_g24	$BrNO_3 \xrightarrow{h\nu} Br + NO_3$	1.558×10^{-3}	0.490	0.216	Sander et al. (2003)
P_g25	$BrNO_3 \xrightarrow{h\nu} BrO + NO_2$	6.363×10^{-4}	0.492	0.215	Sander et al. (2003)
P_g26 $\ominus$	$BrCl \xrightarrow{h\nu} Br + Cl$	1.650×10^{-2}	0.297	0.224	Atkinson et al. (2007)
P_g27	$CH_3COCH_2Br \xrightarrow{h\nu} 0.7\,COBr + 0.7\,ACO_3 + 0.3\,CH_2BrCO_3 + 0.3\,MO_2 - 1.3\,O_2$	3.523×10^{-4}	0.885	0.283	Sander et al. (2006)[a, c, d]
P_g28	$CH_3COCBrO \xrightarrow{h\nu,O_2} COBr + ACO_3$	1.853×10^{-4}	0.583	0.225	estimated same as methylglyoxal[c]

Table S14 (continued) Parameters for gas phase photolysis reactions

	Reaction	l/s^{-1}	m	n	Reference/comment
P_g29	$CH_2BrCHO \xrightarrow{h\nu,2\,O_2} CH_2BrO_2 + CO + HO_2$	4.642×10^{-5}	0.762	0.353	estimated same as P_g13, Pilling et al. (2008)
P_g30	$CH_2BrCO_3H \xrightarrow{h\nu,O_2} CH_2BrO_2 + CO_2 + OH$	7.649×10^{-6}	0.682	0.279	estimated same as P_g14, Pilling et al. (2008)
P_g31	$CHBr_3 \xrightarrow{h\nu,O_2} Br + CHBr_2O_2$	2.228×10^{-6}	1.471	0.230	DeMore et al. (1997)
P_g32	$CH_2Br_2 \xrightarrow{h\nu,O_2} Br + CH_2BrO_2$	5.600×10^{-9}	2.763	1.922	Atkinson et al. (2008b)
P_g33	$COBr_2 \xrightarrow{h\nu} 2\,Br + CO$	4.377×10^{-6}	1.360	0.273	Sander et al. (2006) products estimated same as phosgene from Pilling et al. (2008)
P_g34	$CH_2BrO_2H \xrightarrow{h\nu} CH_2BrO + OH$	7.649×10^{-6}	0.682	0.279	Pilling et al. (2008)
P_g35	$CHOBr \xrightarrow{h\nu,O_2} Br + CO + HO_2$	2.547×10^{-5}	1.393	0.361	Sander et al. (2006)
P_g36	$I_2 \xrightarrow{h\nu} 2\,I$	0.217	0.125	0.185	Atkinson et al. (2007)
P_g37	$IO \xrightarrow{h\nu} I + O(^3P)$	2.640×10^{-3}	0.240	0.240	Atkinson et al. (2007)
P_g38	$OIO \xrightarrow{h\nu} I + O_2$	4.054×10^{-2}	0.119	0.185	Sander et al. (2006)
P_g39	$OIO \xrightarrow{h\nu} IO + O(^3P)$	1.894×10^{-3}	0.119	0.185	Sander et al. (2006)
P_g40	$I_2O_2 \xrightarrow{h\nu} 2\,I + O_2$	2.294×10^{-3}	0.745	0.223	estimated same as P_g4, products from von Glasow et al. (2002a)
P_g41	$HI \xrightarrow{h\nu,O_2} I + HO_2$	2.104×10^{-4}	1.123	0.281	Atkinson et al. (2007)
P_g42	$HOI \xrightarrow{h\nu,O_2} I + OH$	1.469×10^{-2}	0.342	0.236	Atkinson et al. (2007)
P_g43	$INO \xrightarrow{h\nu} I + NO$	4.849×10^{-3}	0.284	0.232	Sander et al. (2006)
P_g44	$INO_2 \xrightarrow{h\nu} I + NO_2$	5.036×10^{-3}	0.568	0.256	Sander et al. (2006)
P_g45	$INO_3 \xrightarrow{h\nu} I + NO_3$	6.599×10^{-2}	0.528	0.244	Sander et al. (2006)
P_g46	$INO_3 \xrightarrow{h\nu} IO + NO_2$	1.165×10^{-2}	0.528	0.244	Sander et al. (2006)
P_g47	$ICl \xrightarrow{h\nu} I + CL$	3.403×10^{-2}	0.179	0.207	Atkinson et al. (2007)[b]
P_g48	$IBr \xrightarrow{h\nu} I + Br$	0.1	0.149	0.197	Atkinson et al. (2007)[b]
P_g49	$C_3H_7I \xrightarrow{h\nu,O_2} I + HC3P$	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_g50	$C_2H_5I \xrightarrow{h\nu, O_2} I + ETHP$	1.386×10^{-5}	1.324	0.224	Sander et al. (2006)[b, f]
P_g51	$CH_2ICHO \xrightarrow{h\nu, 2\,O_2} CH_2IO_2 + CO + HO_2$	4.642×10^{-5}	0.762	0.353	estimated same as P_g13, Pilling et al. (2008)
P_g52	$CH_2ICO_3H \xrightarrow{h\nu, O_2} CH_2IO_2 + CO_2 + OH$	7.649×10^{-6}	0.682	0.279	estimated same as P_g14, Pilling et al. (2008)
P_g53	$CH_2I_2 \xrightarrow{h\nu, O_2} I + CH_2IO_2$	1.496×10^{-2}	0.801	0.265	Sander et al. (2006)[b]
P_g54	$CH_3I \xrightarrow{h\nu, O_2} I + MO_2$	1.206×10^{-5}	1.254	0.231	Sander et al. (2006)[b, d]
P_g55	$CH_2IO_2H \xrightarrow{h\nu} CH_2IO + OH$	7.649×10^{-6}	0.682	0.279	estimated same as P_g17, Pilling et al. (2008)
P_g56	$CHOI \xrightarrow{h\nu, O_2} I + CO + HO_2$	2.547×10^{-5}	1.393	0.361	estimated same as P_g35
P_g57	$CH_2ICl \xrightarrow{h\nu, O_2} I + CH_2ClO_2$	2.038×10^{-4}	1.057	0.238	Atkinson et al. (2008b)
P_g58	$CH_2IBr \xrightarrow{h\nu, O_2} I + CH_2BrO_2$	8.824×10^{-4}	0.976	0.250	Atkinson et al. (2008b)

Photolysis reactions are parameterised with $j = l \times \cos^m \chi \times \exp\{-n \times \sec \chi\}$.
[a]quantum yield estimated with $\Phi = 1$, [b]exited atoms are treated like atoms in ground state, [c]MO_2 = methyl peroxyl radical, [d]ACO_3 = acetyl peroxyl radical, [e]HC3P = peroxyl radical formed from alkanes, alcohols, esters, and alkynes with OH rate constant (298 K, 1 atm) less than $3.4 \times 10^{-12}\ \mathrm{cm^3\ molecules^{-1}\ s^{-1}}$, [f] ETHP = ethyl peroxyl radical

Table S15 Parameters for aqueous phase photolysis reactions

	Reaction	l/s^{-1}	m	n	Reference/comment
P_a1	$Cl_2 \xrightarrow{h\nu} 2\,Cl$	2.548×10^{-5}	0.612	0.298	Zimmerman and Strong (1957) with quantum yields from Grossweiner and Matheson (1955)
P_a2	$HOCl \xrightarrow{h\nu} Cl + OH$	2.517×10^{-5}	0.892	0.289	Zimmerman and Strong (1957)[a]
P_a3	$ClO^- \xrightarrow{h\nu,\, H_2O} Cl + OH^- + OH$	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_a4	$Cl_3^- \xrightarrow{h\nu} Cl_2 + Cl^-$	5.140×10^{-4}	0.843	0.103	Zimmerman and Strong (1957)[a]
P_a5	$Br_2 \xrightarrow{h\nu} 2\,Br$	4.501×10^{-4}	0.154	0.262	Buckles and Mills (1953)[b] with quantum yields from Grossweiner and Matheson (1955)
P_a6	$HOBr \xrightarrow{h\nu} Br + OH$	1.396×10^{-4}	0.584	0.289	Anbar and Dostrovsky (1954)[a]
P_a7	$BrO^- \xrightarrow{h\nu,\, H_2O} Br + OH^- + OH$	7.510×10^{-4}	0.548	0.300	Anbar and Dostrovsky (1954)[a]
P_a8	$BrCl \xrightarrow{h\nu} Br + Cl$	6.121×10^{-3}	0.456	0.298	Pungor et al. (1959)[a]
P_a9	$I_2 \xrightarrow{h\nu} 2\,I$	1.816×10^{-5}	0.088	0.243	Buckles and Mills (1953)[b] with quantum yields from Grossweiner and Matheson (1955)
P_a10	$ICl \xrightarrow{h\nu} I + Cl$	3.909×10^{-3}	0.130	0.239	Buckles and Mills (1953)[a, b]
P_a11	$IBr \xrightarrow{h\nu} I + Br$	7.940×10^{-3}	0.108	0.250	Buckles and Mills (1954)[a, b]

Photolysis reactions are parameterised with $j = l \times \cos^m \chi \times \exp\{-n \times \sec \chi\}$.
[a]quantum yield estimated with $\Phi = 0.1$; [b]estimated 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	$Cl + Cl \rightarrow Cl_2$	8.75×10^{7}			*Wu80*
A2	$Cl_2^- + Cl \rightarrow Cl_2 + Cl^-$	2.1×10^{9}			*Yu/Bak03*
A3 $\oslash$	$Cl_2^- + Cl_2^- \rightarrow Cl_2 + 2\,Cl^-$	1.8×10^{9}			*Jac99*
A4	$Cl^- + O_3 \rightarrow ClO^- + O_2$	3.0×10^{-3}			*Hoi85*
A5	$Cl + H_2O_2 \rightarrow H^+ + Cl^- + HO_2$	2.0×10^{9}			*Yu/Bak03*
A6 $\otimes$	$Cl_2^- + H_2O_2 \rightarrow 2\,Cl^- + H^+ + HO_2$	5×10^{4}	3340		*Jac99*
A7 $\oslash$	$Cl_2^- + H_2O \rightarrow H^+ + Cl^- + ClOH^-$	23.4		revised products from Yu and Barker (2003)	*Jac96/Bux98*
A8 $\otimes$	$Cl_2^- + HO_2 \rightarrow 2\,Cl^- + H^+ + O_2$	1.3×10^{10}			*Jac96*
A9 $\otimes$	$Cl_2^- + O_2^- \rightarrow 2\,Cl^- + O_2$	6.0×10^{9}			*Jac96*
A10	$Cl_2^- + OH \rightarrow HOCl + Cl^-$	1.0×10^{9}			*Wag86*
A11 $\otimes$	$Cl_2^- + OH^- \rightarrow 2\,Cl^- + OH$	4.0×10^{6}			*Jac96*
A12	$Cl_3^- + HO_2 \rightarrow Cl_2^- + H^+ + Cl^- + O_2$	1.0×10^{9}			*Bje81*
A13	$Cl_3^- + O_2^- \rightarrow Cl_2^- + Cl^- + O_2$	3.8×10^{9}		estimated	*Mat/Ana06*
P_a4	$Cl_3^- \xrightarrow{h\nu} Cl_2 + Cl^-$	*(4.64×10^{-4})*		$\Phi = 0.1^c$; see Tab. S15	*Zim/Str57*
A14 $\oplus$	$Cl_2 + HO_2 \rightarrow Cl_2^- + H^+ + O_2$	1.0×10^{9}			*Bje81*
A15 $\oplus$	$Cl_2 + O_2^- \rightarrow Cl_2^- + O_2$	1.0×10^{9}		estimated ($k_{A15} \approx k_{A14}$)	*Her03*
P_a1	$Cl_2 \xrightarrow{h\nu} 2\,Cl$	*(1.89×10^{-5})*		$\Phi = 0.01^{Gro/Mat55}$; see Tab. S15	*Zim/Str57*
A16	$HOCl + H_2O_2 \rightarrow H^+ + Cl^- + H_2O + O_2$	1.1×10^{4}			*Con47*
A17	$ClO^- + H_2O_2 \rightarrow Cl^- + H_2O + O_2$	1.7×10^{5}			*Con47*
A18 $\oplus$	$HOCl + HO_2 \rightarrow Cl + H_2O + O_2$	7.5×10^{6}		estimated ($k_{A18} \approx k_{A19}$)	*Her03*
A19 $\oplus$	$HOCl + O_2^- \rightarrow Cl + OH^- + O_2$	7.5×10^{6}			*Lon/Bie80*
A20	$ClO^- + O_2^- \xrightarrow{H_2O} Cl + 2\,OH^- + O_2$	2.0×10^{8}		estimated	*Mat/Ana06*
A21 $\oplus$	$HOCl + OH \rightarrow ClO + H_2O$	2.0×10^{9}		estimated ($k_{A21} \approx k_{A105}$)	*Her03*
A22	$ClO^- + OH \rightarrow ClO + OH^-$	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	$HOCl \xrightarrow{h\nu} Cl + OH$	*(1.89×10^{-5})*		$\Phi = 0.1^{c}$; see Tab. S15	*Anb/Dos54*
P_a3	$ClO^- \xrightarrow{h\nu} Cl + OH^- + OH$	*(3.17×10^{-4})*		$\Phi = 4.8155 \cdot \exp\{-0.0113\lambda\}$, fit to measurements of Herrmann (2007); see Tab. S15	*Zim/Str57*
A23 ⊗	$Cl_2^- + HSO_3^- \rightarrow 2\,Cl^- + H^+ + SO_3^-$	1.7×10^{8}	400		*Jacua96*
A24 ⊗	$Cl_2^- + SO_3^{2-} \rightarrow 2\,Cl^- + SO_3^-$	6.2×10^{7}			*Jacua96*
A25	$HOCl + SO_3^{2-} \rightarrow Cl^- + HSO_4^-$	7.6×10^{8}			*Fog89*
A26 ⊕	$HOCl + HSO_3^- \rightarrow Cl^- + H^+ + HSO_4^-$	7.6×10^{8}		estimated ($k_{A26} \approx k_{A25}$)	*Her03*
A27	$Cl^- + HSO_5^- \rightarrow HOCl + SO_4^{2-}$	1.8×10^{-3}	7352		*For60*
A28 ⊗	$Cl_2^- + CH_2OHSO_3^- \rightarrow 2\,Cl^- + CH_2OHSO_3$	5.0×10^{5}			*Bar97*
A29 ⊗	$Cl_2^- + NO_2^- \rightarrow 2\,Cl^- + NO_2$	6.0×10^{7}			*Jac96*
A30 ⊗	$Cl^- + NO_2^+ \rightarrow ClNO_2$	1.0×10^{10}			*Geo99*
A31 ⊗	$Cl_2^- + Fe^{2+} \rightarrow 2\,Cl^- + Fe^{3+}$	1.0×10^{7}	3030		*Tho/Lau73*
A32 ⊗	$Cl_2^- + Fe^{2+} \rightarrow FeCl^{2+} + Cl^-$	4.0×10^{6}	3490		*Tho/Lau73*
A33 ⊗	$Cl^- + FeO^{2+} \xrightarrow{H_2O} Fe^{3+} + ClOH^- + OH^-$	100			*Jacs98*
A34 ⊗	$Cl_2^- + Mn^{2+} \rightarrow MnCl_2^+$	2.0×10^{7}	4090		*Lau/Tho73*
A35 ⊗	$MnCl_2^+ \rightarrow Cl_2^- + Mn^{2+}$	3.0×10^{5}			*Lau/Tho73*
A36 ⊗	$MnCl_2^+ \rightarrow 2\,Cl^- + Mn^{3+}$	2.1×10^{5}			*Lau/Tho73*
A37 ⊗	$Cl_2^- + Cu^+ \rightarrow 2\,Cl^- + Cu^{2+}$	1.0×10^{8}		estimated ($k_{A37} \approx 10 \cdot k_{A31}$)	
A38	$Cl + CO_3^{2-} \rightarrow Cl^- + CO_3^-$	5.0×10^{8}			*Mer/Son95*
A39	$Cl + HCO_3^- \rightarrow Cl^- + H^+ + CO_3^-$	2.2×10^{8}			*Mer/Son95*
A40 ⊗	$Cl_2^- + CO_3^{2-} \rightarrow 2\,Cl^- + CO_3^-$	2.7×10^{6}		estimated	
A41 ⊗	$Cl_2^- + HCO_3^- \rightarrow 2\,Cl^- + H^+ + CO_3^-$	2.7×10^{6}		estimated	
A42 ⊗	$Cl_2^- + CH_3OOH \rightarrow H^+ + 2\,Cl^- + CH_3OO$	5.0×10^{4}	3340	estimated ($k_{A42} \approx k_{A6}$)	
A43	$Cl + CH_3OH \rightarrow H^+ + Cl^- + CH_2OH$	1.0×10^{9}	4089		*Wic03*
A44 ⊘	$Cl_2^- + CH_3OH \rightarrow H^+ + 2\,Cl^- + CH_2OH$	5.1×10^{4}	5533		*Jac99*
A45	$Cl + C_2H_5OH \rightarrow H^+ + Cl^- + CH_3CHOH$	1.6×10^{9}			*Par06*

Table S16 (continued) Aqueous phase irreversible reactions

	Reaction	k_{298} [a]	E_A/R [b]	Comment	Reference
A46 ⊗	$Cl_2^- + C_2H_5OH \rightarrow 2\,Cl^- + H^+ + CH_3CHOH$	1.2×10^5		better reference	*Jac99*
A47	$Cl + C_3H_7OH \rightarrow H^+ + Cl^- + C_2H_5CHOH$	2.2×10^9	2285		*Wic03*
A48	$Cl_2^- + C_3H_7OH \rightarrow 2\,Cl^- + H^+ + C_2H_5CHOH$	1.0×10^5			*Jac99*
A49	$Cl + CH_3CHOHCH_3 \rightarrow$ $H^+ + Cl^- + CH_3COHCH_3$	3.2×10^9	2766		*Wic03*
A50	$Cl_2^- + CH_3CHOHCH_3 \rightarrow$ $2\,Cl^- + H^+ + CH_3COHCH_3$	1.9×10^5			*Jac99*
A51	$Cl + CH_2(OH)_2 \rightarrow H^+ + Cl^- + CH(OH)_2$	1.4×10^9	3127	hydration calculated from K with ∼1	*Wic03*
A52 ⊗	$Cl_2^- + CH_2(OH)_2 \rightarrow 2\,Cl^- + H^+ + CH(OH)_2$	3.6×10^4	4330		*Jac99*
A53	$Cl + CH_3CHO \rightarrow H^+ + Cl^- + CH_3CO$	6.0×10^8	1928	hydration calculated from K with 1:1	*Par06*
A54	$Cl + CH_3CH(OH)_2 \rightarrow$ $H^+ + Cl^- + CH_3C(OH)_2$	6.0×10^8	1928		*Par06*
A55 ⊗	$Cl_2^- + CH_3CHO \rightarrow 2\,Cl^- + H^+ + CH_3CO$	4.0×10^4			*Jac96*
A56 ⊗	$Cl_2^- + CH_3CH(OH)_2 \rightarrow$ $H^+ + 2\,Cl^- + CH_3C(OH)_2$	4.0×10^4			*Jac96*
A57	$Cl + C_2H_5CHO \rightarrow H^+ + Cl^- + C_2H_5CO$	7.5×10^8	1566	hydration calculated from K with 1:1	*Par06*
A58	$Cl + C_2H_5CH(OH)_2 \rightarrow$ $H^+ + Cl^- + C_2H_5C(OH)_2$	7.5×10^8	1566		*Par06*
A59	$Cl + C_3H_7CHO \rightarrow H^+ + Cl^- + C_3H_7CO$	2.2×10^9	1686	hydration calculated from K with 2:1 (unhydrated/hydrated)	*Par06*
A60	$Cl + C_3H_7CH(OH)_2 \rightarrow$ $H^+ + Cl^- + C_3H_7C(OH)_2$	1.1×10^9	1686		*Par06*
A61	$Cl + CH_3COCH_3 \rightarrow H^+ + Cl^- + CH_3COCH_2$	7.8×10^7			*Wic03*
A62	$Cl_2^- + CH_3COCH_3 \rightarrow$ $2\,Cl^- + H^+ + CH_3COCH_2$	1.4×10^3			*Jac99*
A63	$Cl + HCOOH \rightarrow H^+ + Cl^- + COOH$	2.8×10^9	2405		*Wic03*
A64	$Cl + HCOO^- \rightarrow Cl^- + COOH$	4.2×10^9	1924		*Bux00*
A65 ⊗	$Cl_2^- + HCOOH \rightarrow 2\,Cl^- + H^+ + COOH$	8.0×10^4	4450		*Jac99*
A66 ⊗	$Cl_2^- + HCOO^- \rightarrow 2\,Cl^- + COOH$	1.3×10^6			*Jac99*

Table S16 (continued) Aqueous phase irreversible reactions

	Reaction	$k_{298}{}^{a}$	E_A/R^{b}	Comment	Reference
A67	$Cl + CH_3COOH \rightarrow H^+ + Cl^- + CH_2COOH$	1.0×10^8	4930		*Wic03*
A68	$Cl + CH_3COO^- \rightarrow Cl^- + CH_3 + CO_2$	3.7×10^9	1684		*Bux00*
A69 ⊗	$Cl_2^- + CH_3COOH \rightarrow$ $2\,Cl^- + H^+ + CH_2COOH$	1.5×10^3	4930		*Jac99*
A70 ⊗	$Cl_2^- + CH_3COO^- \rightarrow 2\,Cl^- + CH_3 + CO_2$	2.6×10^5	4800		*Jac99*
A71	$Cl + C_2H_5COOH \rightarrow$ $H^+ + Cl^- + CH_3CHCOOH$	1.2×10^9	5292		*Wic03*
A72	$Cl + C_2H_5COO^- \rightarrow Cl^- + CH_3CHCOO^-$	1.2×10^9	5292	estimated ($k_{A72} \approx k_{A71}$)	
A73 ⊗	$Cl_2^- + HC_2O_4^- \rightarrow 2\,Cl^- + H^+ + C_2O_4^-$	1.3×10^6		estimated (ETR)	
A74 ⊗	$Cl_2^- + C_2O_4^{2-} \rightarrow 2\,Cl^- + C_2O_4^-$	4.0×10^6		estimated (ETR)	
A75 ⊗	$Cl_2^- + CH(OH)_2CH(OH)_2 \rightarrow$ $2\,Cl^- + H^+ + C(OH)_2CH(OH)_2$	4.0×10^4			
A76 ⊗	$Cl_2^- + CH(OH)_2C(O)OH \rightarrow$ $2\,Cl^- + H^+ + C(OH)_2C(O)OH$	4.0×10^4		estimated ($k_{A76} \approx k_{A75}$)	
A77	$CH_2ClC(OH)_2O_2 \rightarrow CH_2ClCOOH + HO_2$	1.0×10^3		estimated (Cl = H)	
A78	$CH_2ClC(OH)_2O_2 \rightarrow$ $CH_2ClCOO^- + 2\,H^+ + O_2^-$	1.0×10^5		estimated (Cl = H)	
A79	$CH_3COCClO + H_2O \rightarrow$ $CH_3COCOOH + H^+ + Cl^-$	350		estimated same as acetyl chloride	*Pra01*
A80	$CHOCl \rightarrow CO + H^+ + Cl^-$	1.0×10^4			*Pra01*
A81	$CHOCl + OH^- \rightarrow HCOO^- + H^+ + Cl^-$	2.5×10^4			*Pra01*
A82	$COCl_2 + H_2O \rightarrow ClCOOH + H^+ + Cl^-$	10			*Pra01*
A83	$COCl_2 + OH^- \rightarrow ClCOOH + Cl^-$	2.8×10^4			*Pra01*
A84	$ClCOOH \rightarrow CO_2 + H^+ + Cl^-$	1.0×10^5		lower limit	*Pra01*
A85	$Br + Br \rightarrow Br_2$	1.0×10^9		estimated	*Kla/Wol85*
A86 ⊗	$Br_2^- + Br_2^- \rightarrow Br_2 + 2\,Br^-$	1.7×10^9			*Ree99*
A87	$Br^- + O_3 \rightarrow BrO^- + O_2$	210	4450		*Haa/Hoi83*
A88	$Br + HO_2 \rightarrow H^+ + Br^- + O_2$	1.6×10^8			*Wag/Str87*

Table S16 (continued) Aqueous phase irreversible reactions

	Reaction	$k_{298}{}^{a}$	E_A/R^{b}	Comment	Reference
A89	$Br + H_2O_2 \rightarrow H^+ + Br^- + HO_2$	4.0×10^{9}			*Sut65*
A90 $\oplus$	$Br_2 + HO_2 \rightarrow H^+ + Br_2^- + O_2$	1.1×10^{8}			*Sut/Dow72*
A91 $\oplus$	$Br_2 + O_2^- \rightarrow Br_2^- + O_2$	5.6×10^{9}			*Sut/Dow72*
A92	$Br_2 + H_2O_2 \rightarrow 2\,H^+ + 2\,Br^- + O_2$	1.3×10^{3}			*Wag/Str87*
A93	$Br_2^- + OH \rightarrow Br^- + HOBr$	1.0×10^{9}			*Wag/Str87*
A94 $\otimes$	$Br_2^- + OH^- \rightarrow 2\,Br^- + OH$	1.1×10^{4}			*Jac96*
A95 $\oslash$	$Br_2^- + HO_2 \rightarrow 2\,Br^- + H^+ + O_2$	4.4×10^{9}			*Mat03*
A96	$Br_2^- + HO_2 \xrightarrow{H^+} Br_2 + H_2O_2$	4.4×10^{9}			*Mat03*
A97 $\otimes$	$Br_2^- + O_2^- \rightarrow 2\,Br^- + O_2$	1.7×10^{8}			*Wag/Str87*
A98 $\otimes$	$Br_2^- + H_2O_2 \rightarrow 2\,Br^- + H^+ + HO_2$	1.0×10^{5}			*Ree97*
P_a5	$Br_2 \xrightarrow{h\nu} 2\,Br$	*(3.46×10^{-4})*		$\Phi = 0.01^{Gro/Mat55}$; ϵ estimated with measurement in CCl_4; see Tab. S15	*Buc/Mil53*
A99	$Br_3^- + HO_2 \rightarrow Br_2^- + H^+ + Br^- + O_2$	1.0×10^{7}			*Sut/Dow72*
A100	$Br_3^- + O_2^- \rightarrow Br_2^- + Br^- + O_2$	3.8×10^{9}			*Sut/Dow72*
A101 $\oplus$	$BrO + BrO \xrightarrow{H_2O} BrO_2^- + BrO^- + 2\,H^+$	2.8×10^{9}			*Kla/Wol85*
A102 $\oplus$	$BrO_2^- + BrO \rightarrow BrO_2 + BrO^-$	4.0×10^{8}			*Ami/Tre70*
A103 $\oplus$	$Br_2^- + BrO_2^- \rightarrow 2\,Br^- + BrO_2$	8.0×10^{7}			*Bux/Dai68*
A104 $\oplus$	$BrO_2^- + OH \rightarrow BrO_2 + OH^-$	1.8×10^{9}			*Bux/Dai68*
A105 $\oplus$	$HOBr + OH \rightarrow BrO + H_2O$	2.0×10^{9}			*Kla/Wol85*
A106	$BrO^- + OH \rightarrow BrO + OH^-$	4.5×10^{9}			*Bux/Dai68*
A107 $\oplus$	$HOBr + HO_2 \rightarrow Br + H_2O + O_2$	1.0×10^{9}		estimated	*Sut/Dow72*
A108 $\oplus$	$HOBr + O_2^- \rightarrow Br + OH^- + O_2$	3.5×10^{9}			*Schw/Bie86*
A109	$BrO^- + O_2^- \xrightarrow{H_2O} Br + 2\,OH^- + O_2$	2.0×10^{8}		upper limit	*Schw/Bie86*
A110	$HOBr + H_2O_2 \rightarrow H^+ + Br^- + H_2O + O_2$	3.5×10^{6}			*You50*
A111	$BrO^- + H_2O_2 \rightarrow Br^- + H_2O + O_2$	2.0×10^{5}		estimated	*Mat/Ana06*
P_a6	$HOBr \xrightarrow{h\nu} Br + OH$	*(1.05×10^{-4})*		$\Phi = 0.1^{c}$; see Tab. S15	*Anb/Dos54*

Table S16 **(continued)** Aqueous phase irreversible reactions

	Reaction	k_{298}[a]	E_A/R[b]	Comment	Reference
P_a7	$BrO^- \xrightarrow{h\nu} Br + OH^- + OH$	*(5.56×10^{-4})*		$\Phi = 0.1^c$; see Tab. S15	*Anb/Dos54*
A112 ⊗	$Br_2^- + HSO_3^- \rightarrow 2\,Br^- + H^+ + SO_3^-$	5.0×10^{7}	780		*Jac96*
A113 ⊗	$Br_2^- + SO_3^{2-} \rightarrow 2\,Br^- + SO_3^-$	3.3×10^{7}	650		*Jac96*
A114 ⊗	$Br^- + SO_4^- \rightarrow Br + SO_4^{2-}$	2.1×10^{9}			*Her97*
A115	$HOBr + SO_3^{2-} \rightarrow Br^- + HSO_4^-$	5.0×10^{9}			*Tro/Mar91*
A116 ⊕	$HOBr + HSO_3^- \rightarrow H^+ + Br^- + HSO_4^-$	5.0×10^{9}		estimated ($k_{A116} \approx k_{A115}$)	*Fog89*
A117	$Br^- + HSO_5^- \rightarrow HOBr + SO_4^{2-}$	1.0	5338		*For60*
A118 ⊗	$Br_2^- + CH_2OHSO_3^- \rightarrow 2\,Br^- + CH_2OHSO_3$	5.0×10^{4}		estimated ($k_{A118} \approx 0.1 \cdot k_{A28}$)	
A119 ⊗	$Br^- + NO_3 \rightarrow Br + NO_3^-$	3.8×10^{9}			*Zel96*
A120 ⊗	$Br_2^- + NO_2^- \rightarrow 2\,Br^- + NO_2$	1.2×10^{7}	1720		*Jac96*
A121 ⊗	$Br^- + NO_2^+ \rightarrow BrNO_2$	1.0×10^{10}			*Geo99*
A122 ⊗	$Br^- + BrNO_2 \rightarrow Br_2 + NO_2^-$	2.55×10^{4}			*Geo99*
A123 ⊗	$Br_2^- + Fe^{2+} \rightarrow 2\,Br^- + Fe^{3+}$	3.6×10^{6}	3330		*Tho/Lau73*
A124 ⊗	$MnBr_2^+ \rightarrow 2\,Br^- + Mn^{3+}$	2.2×10^{5}			*Tho/Lau73*
A125 ⊗	$Br_2^- + Mn^{2+} \rightarrow MnBr_2^+$	6.3×10^{6}	4330		*Tho/Lau73*
A126 ⊗	$MnBr_2^+ \rightarrow Br_2^- + Mn^{2+}$	3.0×10^{5}			*Tho/Lau73*
A127 ⊗	$Br_2^- + Cu^+ \rightarrow 2\,Br^- + Cu^{2+}$	3.6×10^{6}		estimated ($k_{A127} \approx k_{A123}$)	
A128	$Br + HCO_3^- \rightarrow H^+ + Br^- + CO_3^-$	1.0×10^{6}		estimated	*Mat/Ana06*
A129	$Br_2^- + CO_3^{2-} \rightarrow 2\,Br^- + CO_3^-$	1.1×10^{5}			*Hui91*
A130 ⊗	$Br_2^- + HCO_3^- \rightarrow 2\,Br^- + H^+ + CO_3^-$	1.1×10^{5}		estimated	
A131	$Br_2^- + Cl_2^- \rightarrow Br_2 + 2\,Cl^-$	4.0×10^{9}		estimated	*Mat/Ana06*
A132 ⊕	$Br^- + HOCl \xrightarrow{H^+} BrCl + H_2O$	1.3×10^{6}			*Kum/Mar87*
A133	$Br^- + ClO^- \xrightarrow{H^+} BrCl + OH^-$	3.65×10^{10}			*Kum/Mar87*
A134 ⊗	$Br^- + ClNO_2 \rightarrow BrCl + NO_2^-$	5.0×10^{6}			*Geo99*
A135 ⊗	$BrNO_2 + Cl^- \rightarrow BrCl + NO_2^-$	10			*Geo99*
P_a8	$BrCl \xrightarrow{h\nu} Br + Cl$	*(4.54×10^{-3})*		$\Phi = 0.1^c$; see Tab. S15	*Pun59*

Table S16 (continued) Aqueous phase irreversible reactions

	Reaction	k_{298}[a]	E_A/R[b]	Comment	Reference
A136 ⊗	$Br_2^- + CH_3OOH \rightarrow 2\,Br^- + H^+ + CH_3OO$	1.0×10^5		estimated ($k_{A136} \approx k_{A98}$)	
A137	$Br + CH_3OH \rightarrow H^+ + Br^- + CH_2OH$	4.1×10^4	3368		*Par*06
A138 ⊗	$Br_2^- + CH_3OH \rightarrow 2\,Br^- + H^+ + CH_2OH$	1.0×10^3			*Ree*97
A139	$Br + C_2H_5OH \rightarrow H^+ + Br^- + CH_3CHOH$	8.2×10^5	2285		*Par*06
A140 ⊗	$Br_2^- + C_2H_5OH \rightarrow 2\,Br^- + H^+ + CH_3CHOH$	3.8×10^3			*Ree*99
A141	$Br + C_3H_7OH \rightarrow H^+ + Br^- + C_2H_5CHOH$	3.8×10^5	1564		*Par*06
A142	$Br + CH_3CHOHCH_3 \rightarrow$ $H^+ + Br^- + CH_3COHCH_3$	1.8×10^6	3127		*Par*06
A143	$Br + CH_2(OH)_2 \rightarrow H^+ + Br^- + CH(OH)_2$	3.0×10^5	3608	hydration calculated from K with ~1	*Par*06
A144 ⊗	$Br_2^- + CH_2(OH)_2 \rightarrow 2\,Br^- + H^+ + CH(OH)_2$	3.0×10^3		estimated	
A145	$Br + CH_3CHO \rightarrow H^+ + Br^- + CH_3CO$	1.75×10^7	1804	hydration calculated from K with 1:1	*Par*06
A146	$Br + CH_3CH(OH_2) \rightarrow$ $H^+ + Br^- + CH_3C(OH_2)$	1.75×10^7	1804		*Par*06
A147 ⊗	$Br_2^- + CH_3CHO \rightarrow 2\,Br^- + H^+ + CH_3CO$	2.15×10^5	2526		*Par*06
A148 ⊗	$Br_2^- + CH_3CH(OH)_2 \rightarrow$ $2\,Br^- + H^+ + CH_3C(OH)_2$	2.15×10^5	2526		*Par*06
A149	$Br + C_2H_5CHO \rightarrow H^+ + Br^- + C_2H_5CO$	2.85×10^7	842	hydration calculated from K with 1:1	*Par*06
A150	$Br + C_2H_5CH(OH_2) \rightarrow$ $H^+ + Br^- + C_2H_5C(OH_2)$	2.85×10^7	842		*Par*06
A151	$Br_2^- + C_2H_5CHO \rightarrow 2\,Br^- + H^+ + C_2H_5CO$	4.95×10^5	3614		*Par*06
A152	$Br_2^- + C_2H_5CH(OH_2) \rightarrow$ $2\,Br^- + H^+ + C_2H_5C(OH_2)$	4.95×10^5	3614		*Par*06
A153	$Br + C_3H_7CHO \rightarrow H^+ + Br^- + C_3H_7CO$	6.67×10^7	1203	hydration calculated from K with 2:1	*Par*06
A154	$Br + C_3H_7CH(OH_2) \rightarrow$ $H^+ + Br^- + C_3H_7C(OH_2)$	3.33×10^7	1203	(unhydrated/hydrated)	*Par*06
A155	$Br_2^- + C_3H_7CHO \rightarrow 2\,Br^- + H^+ + C_3H_7CO$	2.6×10^5	2289		*Par*06
A156	$Br_2^- + C_3H_7CH(OH_2) \rightarrow$ $2\,Br^- + H^+ + C_3H_7C(OH_2)$	1.3×10^5	2289		*Par*06

Table S16 (continued) Aqueous phase irreversible reactions

	Reaction	k_{298}[a]	E_A/R[b]	Comment	Reference
A157	$Br + HCOOH \rightarrow H^+ + Br^- + COOH$	7.7×10^5	2288		*Par06*
A158	$Br + HCOO^- \rightarrow Br^- + COOH$	4.6×10^8			*Mer/Lin94*
A159 ⊗	$Br_2^- + HCOOH \rightarrow 2\,Br^- + H^+ + COOH$	4.0×10^3			*Ree99*
A160 ⊗	$Br_2^- + HCOO^- \rightarrow 2\,Br^- + COOH$	4.9×10^3			*Jac96*
A161 ⊗	$Br_2^- + CH_3COOH \rightarrow$ $2\,Br^- + H^+ + CH_2COOH$	10			*Ree99*
A162 ⊗	$Br_2^- + CH_3COO^- \rightarrow 2\,Br^- + CH_3 + CO_2$	100			*Jac96*
A163 ⊗	$Br_2^- + HC_2O_4^- \rightarrow 2\,Br^- + H^+ + C_2O_4^-$	3.7×10^3		estimated (ETR)	
A164 ⊗	$Br_2^- + C_2O_4^{2-} \rightarrow 2\,Br^- + C_2O_4^-$	1.1×10^4		estimated (ETR)	
A165 ⊗	$Br_2^- + CH(OH)_2CH(OH)_2 \rightarrow$ $2\,Br^- + H^+ + C(OH)_2CH(OH)_2$	500		estimated (H-abstraction)	
A166 ⊗	$Br_2^- + CH(OH)_2COOH \rightarrow$ $2\,Br^- + H^+ + C(OH)_2COOH$	500		estimated ($k_{A166} \approx k_{A165}$)	
A167	$CH_2BrC(OH)_2O_2 \rightarrow CH_2BrCOOH + HO_2$	1.0×10^3		estimated (Br = H)	
A168	$CH_2BrC(OH)_2O_2 \rightarrow$ $CH_2BrCOO^- + 2\,H^+ + O_2^-$	1.0×10^5		estimated (Br = H)	
A169	$CH_3COCBrO + H_2O \rightarrow$ $H^+ + Br^- + CH_3COCOOH$	350		estimated same as acetyl chloride	*Pra01*
A170	$CHOBr \rightarrow CO + H^+ + Br^-$	1.0×10^4		estimated ($k_{A170} \approx k_{A80}$)	*Pra01*
A171	$CHOBr + OH^- \rightarrow HCOO^- + H^+ + Br^-$	2.5×10^4		estimated ($k_{A171} \approx k_{A81}$)	*Pra01*
A172	$COBr_2 + H_2O \rightarrow BrCOOH + H^+ + Br^-$	10		estimated ($k_{A172} \approx k_{A82}$)	*Pra01*
A173	$COBr_2 + OH^- \rightarrow BrCOOH + Br^-$	2.8×10^4		estimated ($k_{A173} \approx k_{A83}$)	*Pra01*
A174	$BrCOOH \rightarrow CO_2 + H^+ + Br^-$	1.0×10^5		lower limit; estimated ($k_{A174} \approx k_{A84}$)	*Pra01*
A175	$I + I \rightarrow I_2$	1.1×10^{10}			*Bux07*
A176	$I + I_2^- \rightarrow I_3^-$	6.5×10^9			*Bux07*
A177	$I_2^- + I_2^- \rightarrow I_3^- + I^-$	2.5×10^9			*Bux07*
A178	$I^- + O_3 \xrightarrow{H^+} HOI + O_2$	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_a9	$I_2 \xrightarrow{h\nu} 2\,I$	*(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	$I_2 + HSO_3^- \xrightarrow{H_2O} 2\,H^+ + 2\,I^- + HSO_4^-$	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≅3.5 according to von Glasow et al. (2002a)	*Nag88*
A191	$I^- + HOBr \rightarrow IBr + OH^-$	5.0×10^9			*Tro/Mar91*
P_a10	$ICl \xrightarrow{h\nu} I + Cl$	*(3.08×10^{-3})*		$\Phi = 0.1^c$; ϵ estimated with measurement in CCl_4; see Tab. S15	*Buc/Mil53*
P_a11	$IBr \xrightarrow{h\nu} I + Br$	*(6.18×10^{-3})*		$\Phi = 0.1^c$; ϵ estimated with measurement in CCl_4; see Tab. S15	*Buc/Mil54*
A192	$HOI + Cl_2 \xrightarrow{H_2O} HIO_2 + 2\,H^+ + 2\,Cl^-$	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	$HIO_2 + HOCl \rightarrow IO_3^- + Cl^- + 2\,H^+$	1.5×10^3			*Len96*
A196	$IO_2^- + HOCl \rightarrow IO_3^- + Cl^- + H^+$	1.5×10^3		estimated same as A195	
A197	$HIO_2 + HOBr \rightarrow IO_3^- + Br^- + 2\,H^+$	1.0×10^6			*Chi/Sim96*

Table S16 (continued) Aqueous phase irreversible reactions

	Reaction	k_{298}[a]	E_A/R[b]	Comment	Reference
A198	$IO_2^- + HOBr \rightarrow IO_3^- + Br^- + H^+$	1.0×10^6		estimated same as A197	
A199	$CH_2IC(OH)_2O_2 \rightarrow CH_2ICOOH + HO_2$	1.0×10^3		estimated (I = H)	
A200	$CH_2IC(OH)_2O_2 \rightarrow CH_2ICOO^- + 2\,H^+ + O_2^-$	1.0×10^5		estimated (Cl = H)	
A201	$CHOI \rightarrow CO + H^+ + I^-$	1.0×10^4		estimated ($k_{A201} \approx k_{A80}$)	[Pra01]
A202	$CHOI + OH^- \rightarrow HCOO^- + H^+ + I^-$	2.5×10^4		estimated ($k_{A202} \approx k_{A81}$)	[Pra01]
A203	$COI_2 + H_2O \rightarrow ICOOH + H^+ + I^-$	10		estimated ($k_{A203} \approx k_{A82}$)	[Pra01]
A204	$COI_2 + OH^- \rightarrow ICOOH + I^-$	2.8×10^4		estimated ($k_{A204} \approx k_{A83}$)	[Pra01]
A205	$ICOOH \rightarrow CO_2 + H^+ + I^-$	1.0×10^5		lower limit; estimated ($k_{A205} \approx k_{A84}$)	[Pra01]

$^{\otimes}$already implemented in CAPRAM; $^{\oslash}$update of CAPRAM; $^{\oplus}$already implemented in the Halogen Module 1.0

[a]in $M^{-1}\,s^{-1}$; [b]in K; [c]estimation 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 ⊗	$Cl + Cl^- \rightleftharpoons Cl_2^-$	1.4×10^5	8.5×10^9		*Bux98*	6.0×10^4		*Bux98*	
E2	$Cl_2 + Cl^- \rightleftharpoons Cl_3^-$	0.18	2.0×10^4		*Ers04*	1.1×10^5		*Ers04*	
E3 ⊘ *d*	$Cl_2 + H_2O \rightleftharpoons H^+ + Cl^- + HOCl$	$1.9 \times 10^{-5} e^{-4500/T}$	0.4	8000	*Wan/Mar94*	2.1×10^4	3500	*Wan/Mar94*	*e*
E4 ⊗	$HCl \rightleftharpoons H^+ + Cl^-$	1.72×10^6	5.0×10^{11}	-6890	*Mar/Elr85*	2.9×10^5		*Gra/Wes81*	*f*
E5 ⊕	$HOCl \rightleftharpoons H^+ + ClO^-$	3.0×10^{-8}	1.5×10^3		*Atk96*	5.0×10^{10}			*g, h*
E6 ⊗	$Cl^- + OH \rightleftharpoons ClOH^-$	0.7	4.3×10^9		*Jay73*	6.1×10^9		*Jay73*	
E7	$Cl + OH^- \rightleftharpoons ClOH^-$	7.83×10^8	1.8×10^{10}		*Kla/Wol85*	23		*Kla/Wol85*	
E8 ⊗	$ClOH^- + H^+ \rightleftharpoons Cl + H_2O$	5.1×10^6	2.1×10^{10}		*Jay73*	4.1×10^3		*Jacs97*	
E9 ⊗	$ClOH^- + Cl^- \rightleftharpoons Cl_2^- + OH^-$	2.2×10^{-4}	1.0×10^4		*Gri87*	4.5×10^7		*Gri87*	
E10 ⊗	$Cl^- + SO_4^- \rightleftharpoons Cl + SO_4^{2-}$	1.2	2.52×10^8		*Bux99a*	2.1×10^8		*Bux99a*	
E11 ⊗	$Cl^- + NO_3 \rightleftharpoons Cl + NO_3^-$	3.4	3.4×10^8	4300	*Bux99b*	1.0×10^8		*Bux99b*	
E12 ⊗	$Cl^- + Fe^{3+} \rightleftharpoons FeCl^{2+}$	1.39	3.0×10^3		*Mar/Sil64*	2.16×10^3			
E13	$CH_2ClCO_3 + H_2O \rightleftharpoons CH_2ClC(OH)_2O_2$	367	1.1×10^7			3.0×10^4			*i*
E14	$CH_2ClCOOH \rightleftharpoons CH_2ClCOO^- + H^+$	1.75×10^{-5}	8.75×10^5	-46		5.0×10^{10}			*i*
E15 ⊗	$Br + Br^- \rightleftharpoons Br_2^-$	6.32×10^5	1.2×10^{10}		*Mer/Lin94*	1.9×10^4		*Mer/Lin94*	
E16	$Br_2 + Br^- \rightleftharpoons Br_3^-$	17.5	9.6×10^8		*Ers04*	5.5×10^7		*Ers04*	
E17 ⊗ ⊕	$Br_2 + H_2O \rightleftharpoons H^+ + Br^- + HOBr$	1.06×10^{-10}	1.7	7500	*Bec96*	1.6×10^{10}		*Bec96*	*d*
E18 ⊕	$HBr \rightleftharpoons H^+ + Br^-$	1.0×10^9	5.0×10^{11}		*Atk96*	5.0×10^2			*j, k, l*
E19 ⊕	$HOBr \rightleftharpoons H^+ + BrO^-$	2.0×10^{-9}	100		*Atk96*	5.0×10^{10}			*g, h*
E20 ⊗	$Br^- + OH \rightleftharpoons BrOH^-$	333	1.1×10^{10}		*Zeh/Rab72*	3.3×10^7		*Zeh/Rab72*	
E21 *d* ⊗	$Br + OH^- \rightleftharpoons BrOH^-$	3.1×10^3	1.3×10^{10}		*Kla/Wol85*	4.2×10^6		*Zeh/Rab72*	
E22 ⊗	$BrOH^- + H^+ \rightleftharpoons Br + H_2O$	1.8×10^{12}	4.4×10^{10}		*Zeh/Rab72*	2.45×10^{-2}		*Kla/Wol85*	
E23 ⊗	$BrOH^- + Br^- \rightleftharpoons Br_2^- + OH^-$	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 ⊕	$HOBr + HOBr \rightleftharpoons H^+ + Br^- + HBrO_2$	6.7×10^{-12}	2.0×10^{-5}		*Fie86*, *Fie/For86*	3.0×10^{6}		*Fie/For86*	
E25 ⊕	$HBrO_2 \rightleftharpoons H^+ + BrO_2^-$	1.3×10^{-5}	6.3×10^{5}		*Fie86*	5.0×10^{10}			*g, h*
E26 ⊕	$HOBr + HBrO_2 \rightleftharpoons 2\,H^+ + Br^- + BrO_3^-$	1.7	3.2		*Fie86*, *Fie/For86*	2.0		*Fie/For86*	
E27 ⊕	$HBrO_2 + HBrO_2 \rightleftharpoons HOBr + H^+ + BrO_3^-$	3.0×10^{11}	3.0×10^{3}		*Fie86*, *Fie/For86*	1.0×10^{-8}		*Fie/For86*	
E28 ⊕	$Br_2O_4 + H_2O \rightleftharpoons H^+ + BrO_3^- + HBrO_2$	52.6	2.2×10^{3}		*Fie86*, *Fie/For86*	42		*Fie/For86*	
E29 ⊕	$Br_2O_4 \rightleftharpoons 2\,BrO_2$	5.3×10^{-5}	7.4×10^{4}		*Fie86*, *Fie/For86*	1.4×10^{9}		*Fie/For86*	
E30	$Br^- + CO_3^- \rightleftharpoons Br + CO_3^{2-}$	0.05	1.0×10^{5}		*Mat/Ana06*	2.0×10^{6}		*Mat/Ana06*	*h, l*
E31 ⊕	$BrCl \overset{H_2O}{\rightleftharpoons} HOBr + H^+ + Cl^-$	1.8×10^{-5}	1.0×10^{5}		*Wan94*	5.6×10^{9}			*k*
E32	$BrCl^- \rightleftharpoons Br^- + Cl$	1.6×10^{-7}	1.9×10^{3}		*Don02*	1.2×10^{10}		*Don02*	
E33	$BrCl^- \rightleftharpoons Br + Cl^-$	6.1×10^{-4}	6.1×10^{4}		*Don02*	1.0×10^{8}		*Don02*	
E34	$BrCl^- + Br^- \rightleftharpoons Br_2^- + Cl^-$	1.86×10^{3}	8.0×10^{9}		*Ers04*	4.3×10^{6}		*Ers04*	
E35	$BrCl^- + Cl^- \rightleftharpoons Cl_2^- + Br^-$	2.75×10^{-8}	110		*Ers04*	4.0×10^{9}		*Ers04*	
E36 ⊕	$Br_2Cl^- \rightleftharpoons BrCl + Br^-$	5.6×10^{-5}	4.3×10^{5}		*Wan94*	7.7×10^{9}			*j, m*
E37 ⊖	$Br_2Cl^- \rightleftharpoons Br_2 + Cl^-$	0.76	3.8×10^{4}		*Wan94*	5.0×10^{4}		*Mat/Ana06*	*h, l*
E38 ⊖	$BrCl_2^- \rightleftharpoons BrCl + Cl^-$	0.17	1.7×10^{5}		*Ers04*	1.0×10^{6}		*Ers04*	
E39 ⊖	$BrCl_2^- \rightleftharpoons Br^- + Cl_2$	1.5×10^{-6}	9.0×10^{3}		*Ers04*	6.0×10^{9}		*Ers04*	
E40	$Br^- + ClOH^- \rightleftharpoons BrCl^- + OH^-$	333.3	1.0×10^{9}		*Mat/Ana06*	3.0×10^{6}		*Mat/Ana06*	*l, m*
E41	$BrOH^- + Cl^- \rightleftharpoons BrCl^- + OH^-$	9.5	1.9×10^{8}		*Mat/Ana06*	2.0×10^{7}		*Mat/Ana06*	*h, l*
E42	$CH_2BrCO_3 + H_2O \rightleftharpoons CH_2BrC(OH)_2O_2$	367	1.1×10^{7}			3.0×10^{4}			*i*
E43	$CH_2BrCOOH \rightleftharpoons CH_2BrCOO^- + H^+$	1.75×10^{-5}	8.75×10^{5}	-46		5.0×10^{10}			*i*
E44	$I + I^- \rightleftharpoons I_2^-$	1.36×10^{5}	9.1×10^{9}		*Bux07*	6.7×10^{4}		*Bux07*	

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			*j, k, l*
E47	$HOI \rightleftharpoons H^+ + IO^-$	3.16×10^{-11}	1.58		*Lid95*	5.0×10^{10}			*g, h*
E48	$HOI + H^+ + I^- \overset{H_2O}{\rightleftharpoons} I_2$	1.47×10^{12}	4.4×10^{12}		*Eig/Kus62*	3.0		*Eig/Kus62*	*j, m*
E49	$HOI + HOI \rightleftharpoons HIO_2 + H^+ + I^-$	1.25×10^{-9}	25		*Schm04*	2.0×10^{10}		*Edb87*	*j, m*
E50	$HOI + HOI \rightleftharpoons IO_2^- + 2\,H^+ + I^-$	1.25×10^{-9}	25		*Schm04*	2.0×10^{10}			*h, j, m*
E51	$HIO_2 \rightleftharpoons H^+ + IO_2^-$	2.51×10^{-2}	1.26×10^9			5.0×10^{10}			*g, h*
E52	$HIO_3 \rightleftharpoons H^+ + IO_3^-$	0.17	8.5×10^9		*Lid95*	5.0×10^{10}			*g, h*
E53	$HIO_2 + HOI \rightleftharpoons$ $IO_3^- + I^- + 2\,H^+$	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*	*l*
E55	$IO_2^- + I_2 \overset{H_2O}{\rightleftharpoons} IO_3^- + 2\,I^- + 2\,H^+$	1.3×10^{-13}	5.5×10^{-5}			4.2×10^8		*Schm00*	*l, m*
E56	$IBr + I^- \rightleftharpoons I_2 + Br^-$	4.2×10^5	2.0×10^9		*Far93*	4.74×10^3		*Far93*	*m*
E57	$HOI + H^+ + Cl^- \overset{H_2O}{\rightleftharpoons} ICl$	1.2×10^4	2.9×10^{10}		*Wan89*	2.4×10^6		*Wan89*	*j, m*
E58	$HOI + H^+ + Br^- \overset{H_2O}{\rightleftharpoons} IBr$	5.1×10^6	4.1×10^{12}		*Far93*	8.0×10^5		*Far93*	*j, m*
E59	$ICl + Cl^- \rightleftharpoons ICl_2^-$	77	4.24×10^9			5.5×10^7			*g, h*
E60	$IBr + Br^- \rightleftharpoons IBr_2^-$	290	4.93×10^6			1.7×10^5			*g, h*
E61	$ICl + Br^- \rightleftharpoons IClBr^-$	1.8×10^4	7.7×10^9			4.3×10^5			*h, l, n*
E62	$IBr + Cl^- \rightleftharpoons IClBr^-$	1.3	5.0×10^4			3.8×10^4			*h, l, n*

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	$CH_2ICO_3 + H_2O \rightleftharpoons CH_2IC(OH)_2O_2$	367	1.1×10^7			3.0×10^4			^{i}
E64	$CH_2ICOOH \rightleftharpoons CH_2ICOO^- + H^+$	1.75×10^{-5}	8.75×10^5	-46		5.0×10^{10}			^{i}

$^{\otimes}$already implemented in CAPRAM; $^{\oslash}$update of CAPRAM; $^{\oplus}$already implemented in the Halogen Module 1.0; $^{\ominus}$update of the Halogen Module 1.0 (when subscripts are present in remarks: superscripts concern only forward reaction and subscript concern only backward reaction)
^{a}in M^{m-n}, n order of reaction of forward reaction, m order of reaction of backward reaction; ^{b}in M^{-1} s^{-1}; ^{c}in K; ^{d}now implemented as equilibrium in CAPRAM; ^{e}correction of CAPRAM value; $^f k_f$ = speed of hydrogen bond breaking in water; $^g k_f$ calculated based on K; $^h k_b$ estimated; ^{i}estimated X = H (X = Cl, Br, I) ^{j}diffusion controlled; $^k k_b$ calulated based on K; $^l k_f$ estimated; ^{m}upper 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]Kläning 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).

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

k_{298} .... overall rate constant of the model species at 298 K in cm^3 $molecules^{-1}$ s^{-1}
k_i .... individual rate constant in cm^3 $molecules^{-1}$ 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_3H_8	1.40×10^{-10}	Atkinson et al. (2006)	0.029
n-C_4H_{10}	2.05×10^{-10}	Atkinson et al. (2006)	0.443
i-C_4H_{10}	1.43×10^{-10}	Atkinson et al. (2006)	0.012
$CH_3C(CH_3)_2C_2H_5$	1.71×10^{-10}	Pilling et al. (2008)	<0.001
C_2H_2	$k_0 = 6.1 \times 10^{-30}$ $\times(T/300)^{-3}[N_2]$ $k_\infty = 2.0 \times 10^{-10}$	Atkinson et al. (2006)	0.095
CH_3OH	5.5×10^{-11}	Atkinson et al. (2006)	0.007
C_2H_5OH	$8.6 \times 10^{-11} e^{45/T}$	Atkinson et al. (2006)	0.345
HC5			
i-C_5H_{12}	2.2×10^{-10}	Atkinson et al. (2008a)	0.192
n-C_6H_{14}	3.4×10^{-10}	Pilling et al. (2008)	0.109
n-C_5H_{12}	2.8×10^{-10}	Atkinson et al. (2008a)	0.108
$(CH_3)_2CHC_3H_7$	2.9×10^{-10}	Pilling et al. (2008)	0.051
$CH_3CH_2CH(CH_3)C_2H_5$	2.8×10^{-10}	Pilling et al. (2008)	0.032
$CH_3CH(CH_3)CH(CH_3)CH_3$	2.3×10^{-10}	Pilling et al. (2008)	0.020
i-C_3H_7OH	8.6×10^{-11}	Atkinson et al. (2007)	0.307
n-C_3H_7OH	$1.6 \times 10^{-11} e^{-130/T}$	Atkinson et al. (2007)	<0.001
HC8			
n-C_7H_{16}	3.9×10^{-10}	Pilling et al. (2008)	0.129
C_7H_{16}	4.95×10^{-10}	estimation with data of Atkinson et al. (2008a)	0.098
n-C_8H_{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
$C_2H_5CH(CH_3)C_3H_7$	3.11×10^{-10}	Pilling et al. (2008)	0.024
n-$C_{11}H_{24}$	6.17×10^{-10}	Pilling et al. (2008)	0.023
C_6H_{12}	3.5×10^{-10}	Pilling et al. (2008)	0.020
n-C_9H_{20}	4.8×10^{-10}	Pilling et al. (2008)	0.012
n-$C_{10}H_{22}$	5.55×10^{-10}	Pilling et al. (2008)	0.008
n-$C_{12}H_{26}$	6.74×10^{-10}	Pilling et al. (2008)	0.008
TOL			
C_6H_6	1.3×10^{-15}	Shi and Bernhard (1997)	0.100
$CH_3C_6H_6$	5.9×10^{-11}	Shi and Bernhard (1997)	0.690

^{a}in cm^3 molecules^{-1} s^{-1}, ^{b}of 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

^{a}in cm^3 molecules^{-1} s^{-1}, ^{b}covered 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 Cl_2 and Br_2 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 depencies are the temperature T and the pressure p of the ambient air:

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

$D_{i/j}$ .... 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.

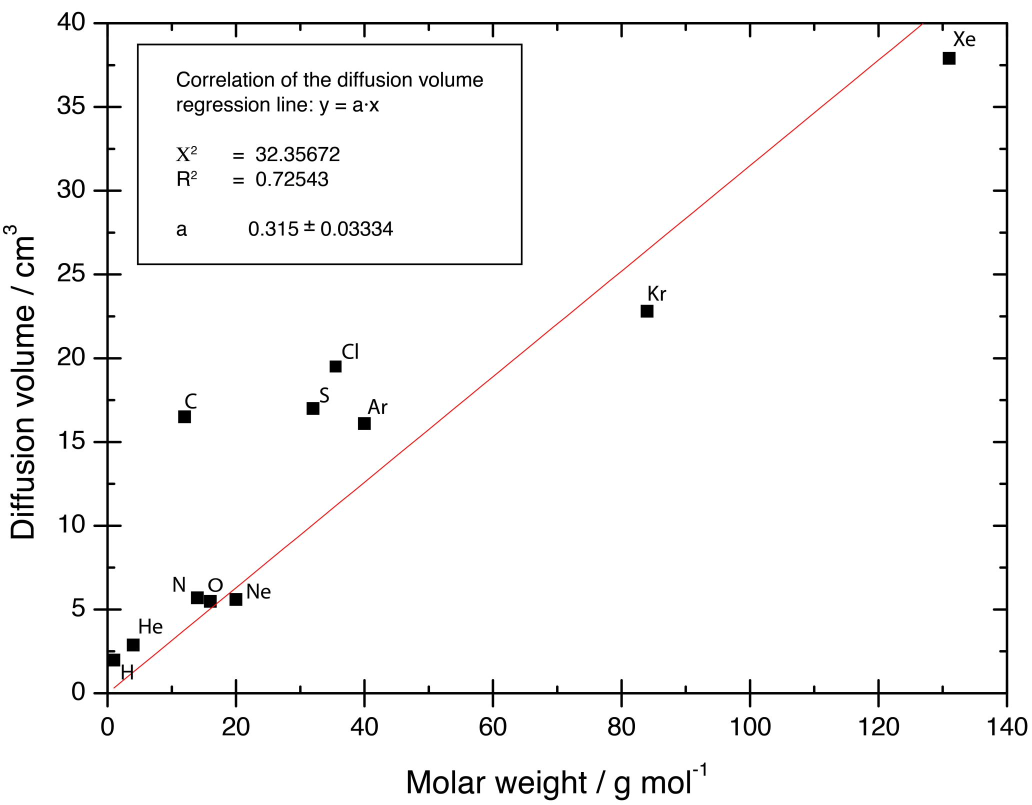


Figure S11 Estimation of diffusion volumes.

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