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

Electronic Supplementary Material  
Journal of Atmospheric Chemistry

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February 15, 2013

# Contents

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

## List of Tables

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

## List of Figures

(S1)	Modelled Cl concentration-time profiles in the gas phase over the whole modelling period of 108h for the different scenarios. . . . .	4
(S2)	Modelled concentration-time profiles of selected chlorine species in the gas phase on the second model day (scenario HM2). . . . .	5
(S3)	Modelled concentration-time profiles of selected bromine species in the gas phase on the second model day (scenario HM2). . . . .	7
(S4)	Modelled concentration-time profiles of selected iodine species in the gas phase on the second model day (scenario HM2). . . . .	10
(S5)	Modelled concentration-time profiles of selected iodine species in the aqueous phase over the whole modelling period of 108 h (scenario HM2). . . . .	12
(S6)	Modelled concentration-time profiles of the various alkyl iodides in the gas phase for the whole modelling period of 108h (scenario HM2). . . . .	13
(S7)	Modelled time-resolved contributions of the various oxidants to the aqueous phase degradation of the sum of all dissociation states of oxalic acid for the whole modelling period of 108h (scenario HM2). . . . .	14
(S8)	Modelled concentration-time profiles of the speciation of the different oxidation states of oxalic acid for the whole modelling period of 108h (scenario HM2). . . . .	15
(S9)	Modelled concentration-time profiles of $\text{OH}_{(\text{aq})}$ and $\text{Cl}_2^-$ for the whole modelling period of 108h (scenario HM2). . . . .	15
(S10)	Schematic of the cloud scenario used in the model runs. . . . .	19
(S11)	Estimation of diffusion volumes. . . . .	73

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

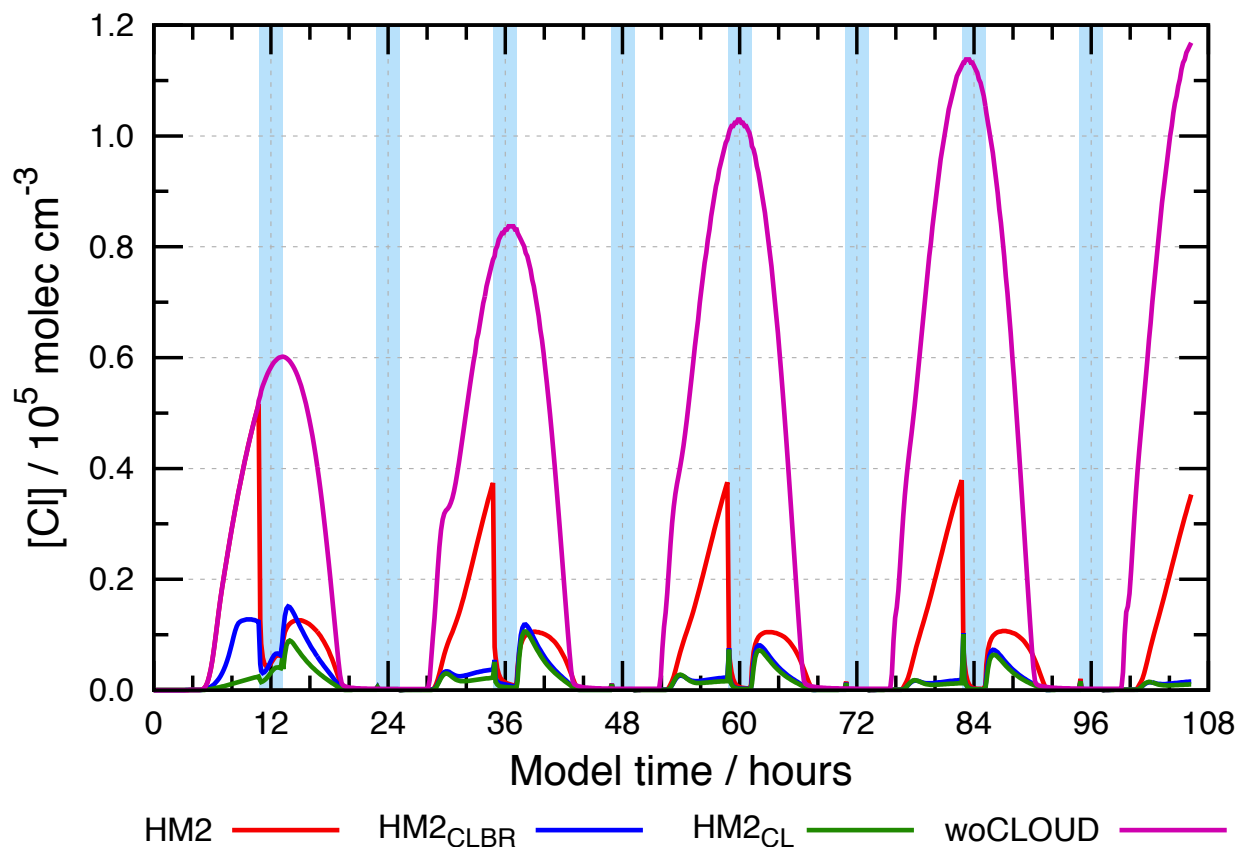
In this section, a more detailed description of the halogen chemistry is given in addition to the description in section 4 of the article. Reaction fluxes are quantified and their relative contributions to the overall sinks are given.

## S1.1 Chlorine chemistry

### *Discussion of chlorine atom concentration profiles and its reaction fluxes*

As explained in the article, the photolysis of molecular chlorine impacts the concentration-time profiles of chlorine atoms especially during morning hours. The effect of morning peaks as described in [Pechtl and von Glasow \(2007\)](#) is stronger than in this study. While the concentrations of the second model day are very similar to the ones of this study, differences arise on the third model day. In the study of [Pechtl and von Glasow \(2007\)](#), the influence of the accumulated  $\text{Cl}_2$  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<sup>th</sup> model day on, the maximum concentration starts to decrease in the model study of [Pechtl and von Glasow \(2007\)](#) using cloud-free conditions. Their base run ends with a maximum concentration of about  $7.5 \times 10^4$  molecules  $\text{cm}^{-3}$  on the last day and an overall maximum of about  $1 \times 10^5$  molecules  $\text{cm}^{-3}$  on the 3<sup>rd</sup> model day. However, in the present study the concentration rises over the whole model run for cloud-free conditions leading to maximum concentration of about  $1.2 \times 10^5$  molecules  $\text{cm}^{-3}$  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  $\text{ClO}_2$  are important non-photolysis sources for Cl atoms. The latter flux is only a net flux resulting from the fast equilibrium of Cl with  $\text{O}_2$  recombination and  $\text{ClO}_2$  destruction. While the average net flux over the whole model period is  $5.8 \times 10^3$  molecules  $\text{cm}^{-3} \text{ s}^{-1}$ , the real average forward and reverse fluxes of this equilibrium are astonishingly high with  $2.1 \times 10^9$  molecules  $\text{cm}^{-3} \text{ s}^{-1}$ , respectively. The reaction of ClO with NO is also only a backward reaction of the most important sink reaction of chlorine atoms with ozone as described later in the text. For a better evaluation of the real sinks and sources, net fluxes have been calculated. The fast re-cycling of forward and backward reactions was subtracted from each other to avoid null-cycles. Furthermore, percentages of the overall sinks and sources given in the following are derived after the elimination of all null-cycles. Most important sinks for gaseous chlorine atoms are the reactions with ozone and alkanes forming ClO and HCl, respectively. The only important gas phase loss reaction for HCl is the reaction with hydroxyl radicals, where Cl is regenerated. However, sink and source fluxes are only in the same order of magnitude during cloud periods, while during non-cloud periods production fluxes dominate with  $3.2 \times 10^5$  molecules  $\text{cm}^{-3} \text{ s}^{-1}$  over sink fluxes, which total to  $2.3 \times 10^3$  molecules  $\text{cm}^{-3} \text{ s}^{-1}$ . The ClO radicals generated during the ozone destruction by Cl atoms are either directly recycled to Cl atoms in a null-cycle (as described above) or react with  $\text{HO}_2$  radicals to hypochlorous acid as proposed by previous studies (see e.g., [von Glasow and Crutzen, 2007](#) and references therein). Most model results confirm the results of previous investigations, however, some refinements to the ozone destruction cycle have to be made as explained in the next section.



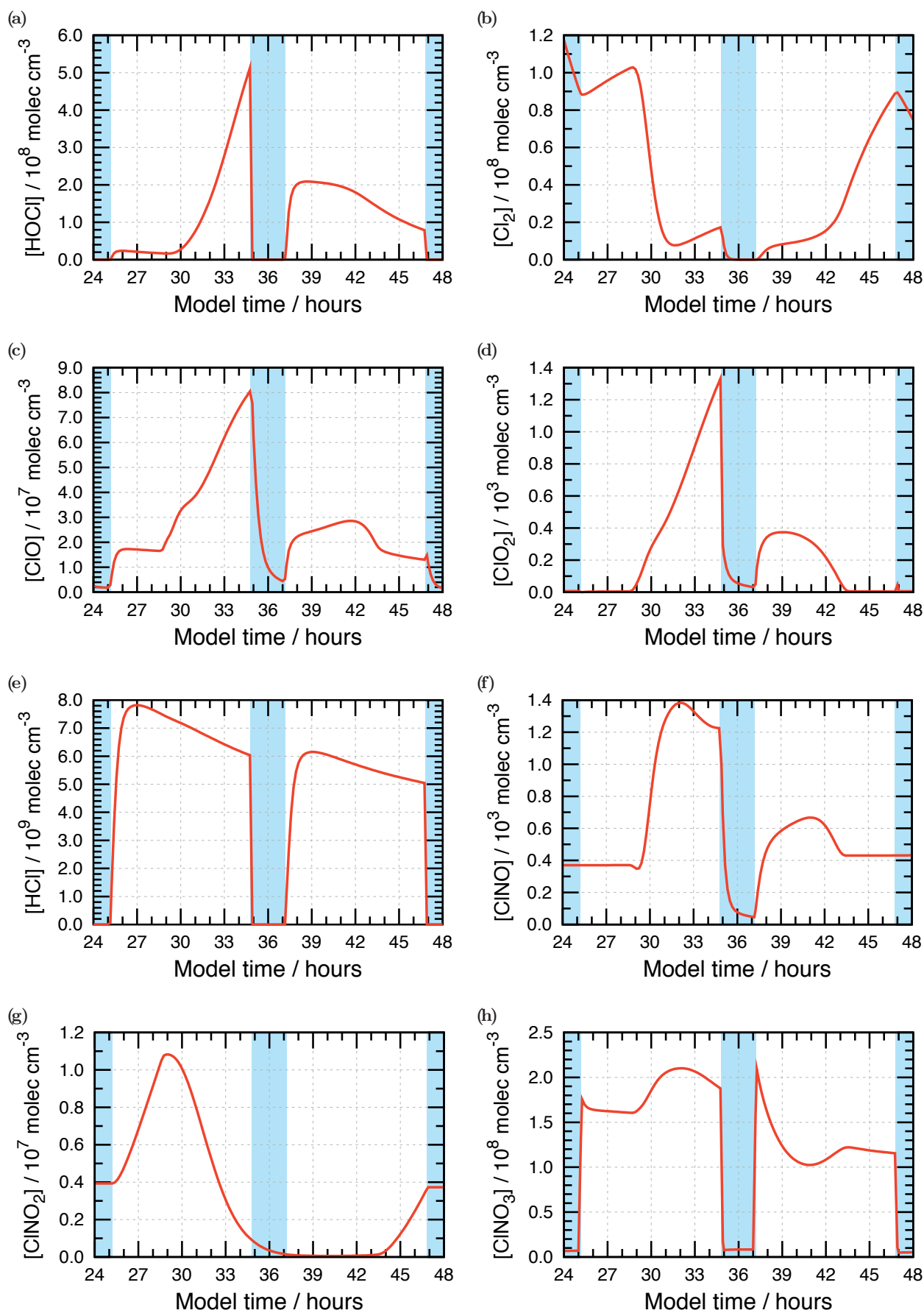
**Figure S1** Modelled Cl concentration-time profiles in the gas phase over the whole modelling period of 108h for the different scenarios. Blue bars indicate in-cloud residence times of the air parcel.

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

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

Under cloud-free conditions, about two third of ClO react with  $\text{HO}_2$  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  $\text{NO}_2$  to  $\text{ClONO}_2$ , which will then either decompose to ClO and  $\text{NO}_2$  or photolyse to Cl and  $\text{NO}_3$ . 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  $\text{Cl}^-$  (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  $\text{Cl}^-$  activation by HOI during cloud events. Thus, the main production channel for chlorine species is missing, which leads to decreased concentrations and, as a consequence, to decreased fluxes of chlorine species.

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

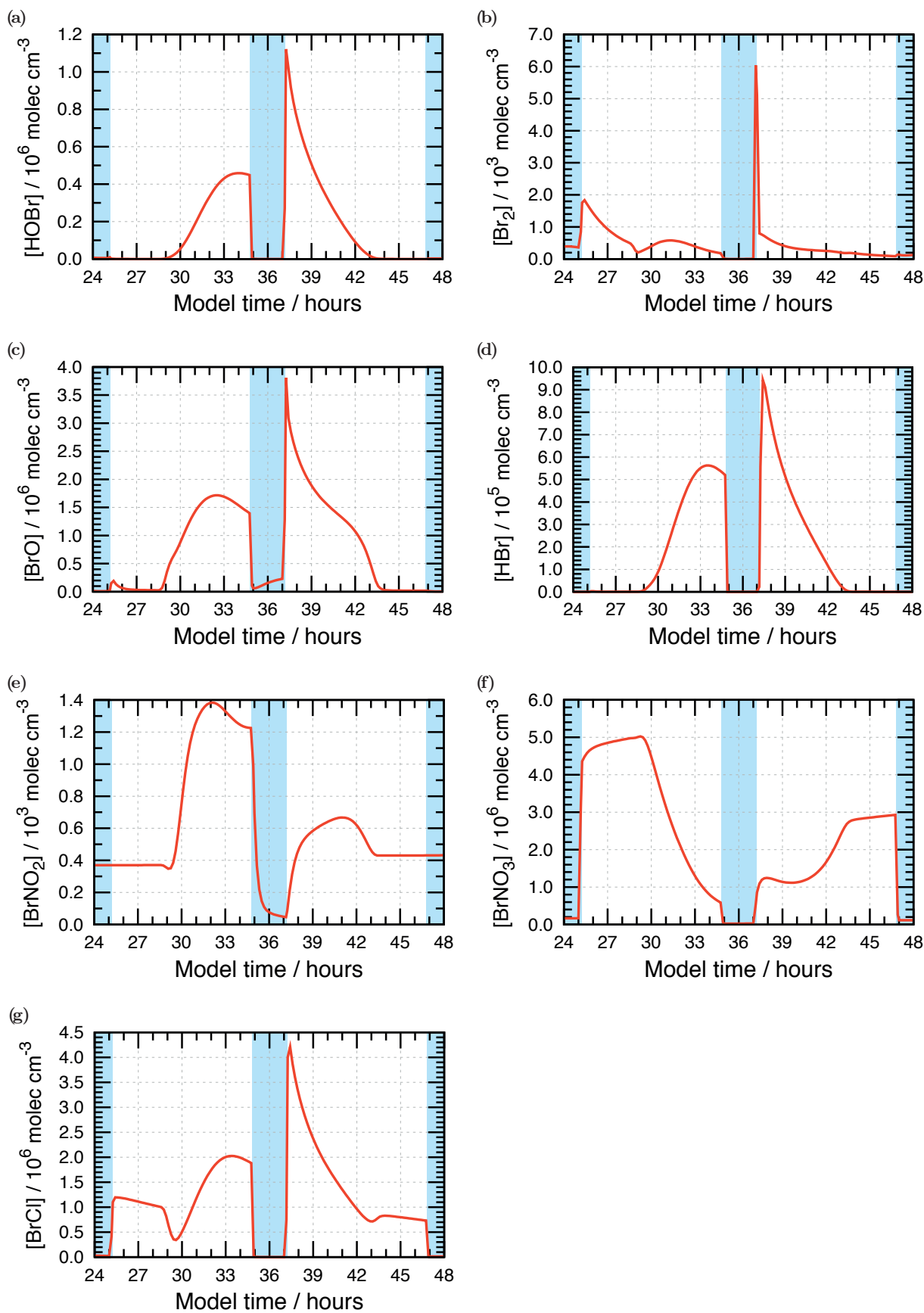
Under in-cloud conditions, the main source for Cl atoms in the gas phase is the direct release from the aqueous phase making up about 68% of the total sources with a flux of  $8.8 \times 10^3$  molecules  $\text{cm}^{-3} \text{s}^{-1}$ . Photolysis as a source for  $\text{Cl}_{(\text{g})}$  is less important under in-cloud conditions. Only  $\text{Cl}_2$  photolysis with fluxes of  $2.1 \times 10^3$  molecules  $\text{cm}^{-3} \text{s}^{-1}$  accounts for 17% to the total sources of chlorine atoms. A minor contribution results from the OH initiated oxidation of chlorinated alkanes. The decomposition of ClCO with a flux of  $6.9 \times 10^2$  molecules  $\text{cm}^{-3} \text{s}^{-1}$  amounts to 4% of the total sources. Sinks for Cl remain the same as under in-cloud conditions, yet with slightly lower absolute fluxes. In a cloud, the importance of the reaction of chlorine with ozone is dramatically reduced. After the elimination of all null-cycles, only 7% of Cl react with ozone ( $9.0 \times 10^2$  molecules  $\text{cm}^{-3} \text{s}^{-1}$ ), while the main part of chlorine reacts with organics. In the latter reaction HCl is formed, which partitions into the aqueous phase and accumulates there.

Under in-cloud conditions, only 24% ( $1.8 \times 10^3$  molecules  $\text{cm}^{-3} \text{s}^{-1}$ ) of the ClO react with hydroperoxyl radicals to form hypochlorous acid. The reaction with methyl peroxy radicals is less affected and still accounts for 13% of all losses under in-cloud conditions. A large fraction of ClO ( $3.8 \times 10^3$  molecules  $\text{cm}^{-3} \text{s}^{-1}$ ) reacts with  $\text{NO}_2$  to form  $\text{ClNO}_3$ . During the day, this makes up 38% of the total ClO sinks, while in the night-time, this is the dominant sink with 97%.  $\text{ClNO}_3$  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  $\text{ClOH}^-$  with  $\text{H}^+$ , the first originating mainly from the reaction of chloride with hydroxyl radicals and the hydrolysis of the  $\text{Cl}_2^-$  radical anion. A reaction flux of  $6.1 \times 10^3$  molecules  $\text{cm}^{-3} \text{s}^{-1}$  closes the reaction cycles by the reaction of Cl and  $\text{Cl}^-$  to  $\text{Cl}_2^-$ .

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

## **S1.2 Bromine chemistry**

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



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

## S1.3 Iodine chemistry

### S1.3.1 Inorganic iodine chemistry

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

In this paragraph, the cycles leading to the different behaviour of IBr under in-cloud conditions are explained in more detail. Under in-cloud conditions, the main source of IBr is not anymore the dissociation of the trihalide anion  $\text{IClBr}^-$  as described in section 4.1.2 of the article. This flux is now only  $14.3 \text{ molecules cm}^{-3} \text{ s}^{-1}$  totalling to 6% of the sources. The largest fraction (94% of the total sources) with a flux of  $219 \text{ molecules cm}^{-3} \text{ s}^{-1}$  originates from the iodide activation by hypobromous acid. In the only sink process for IBr, it is hydrolysed to HOI and dissociated HBr. HOI oxidises sulphur(IV) to sulphur(VI), where  $\text{I}^-$  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  $\text{BrCl}_2^-$  radical anion by the reaction with  $\text{Cl}_2$ , which dissociates to BrCl and  $\text{Cl}^-$ . 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 relative contributions to the overall sources and sinks. For a better understanding, the concentration-time profiles of the most important inorganic halogen species are shown in Fig. S4, page 10.

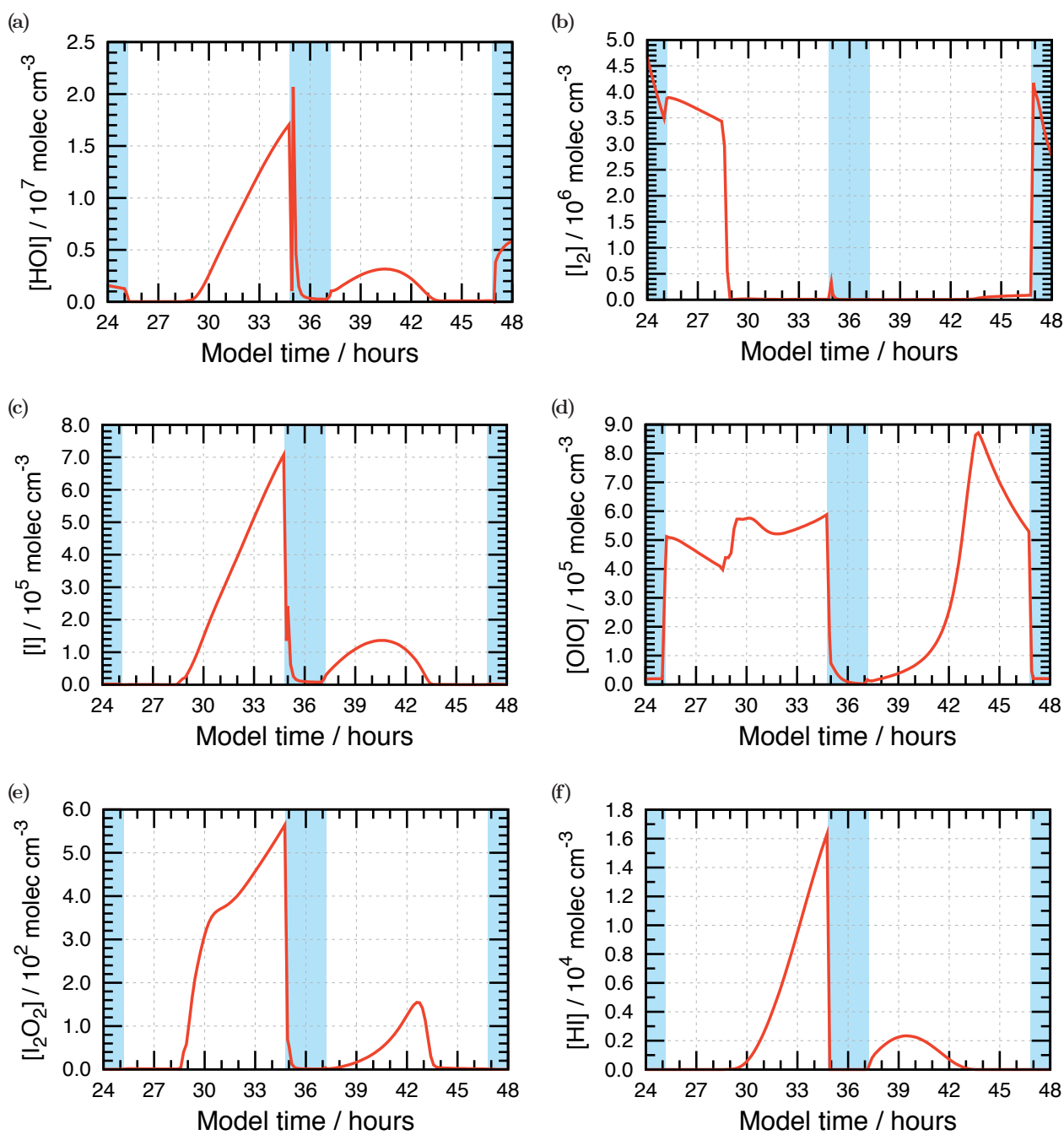
**Table S1** Most important source and sink reactions contributing to the production and destruction of I atoms. Given are the absolute chemical fluxes after the elimination of null-cycles averaged over the whole model run of 108 hours as well as their relative contributions to the overall sources/sinks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

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

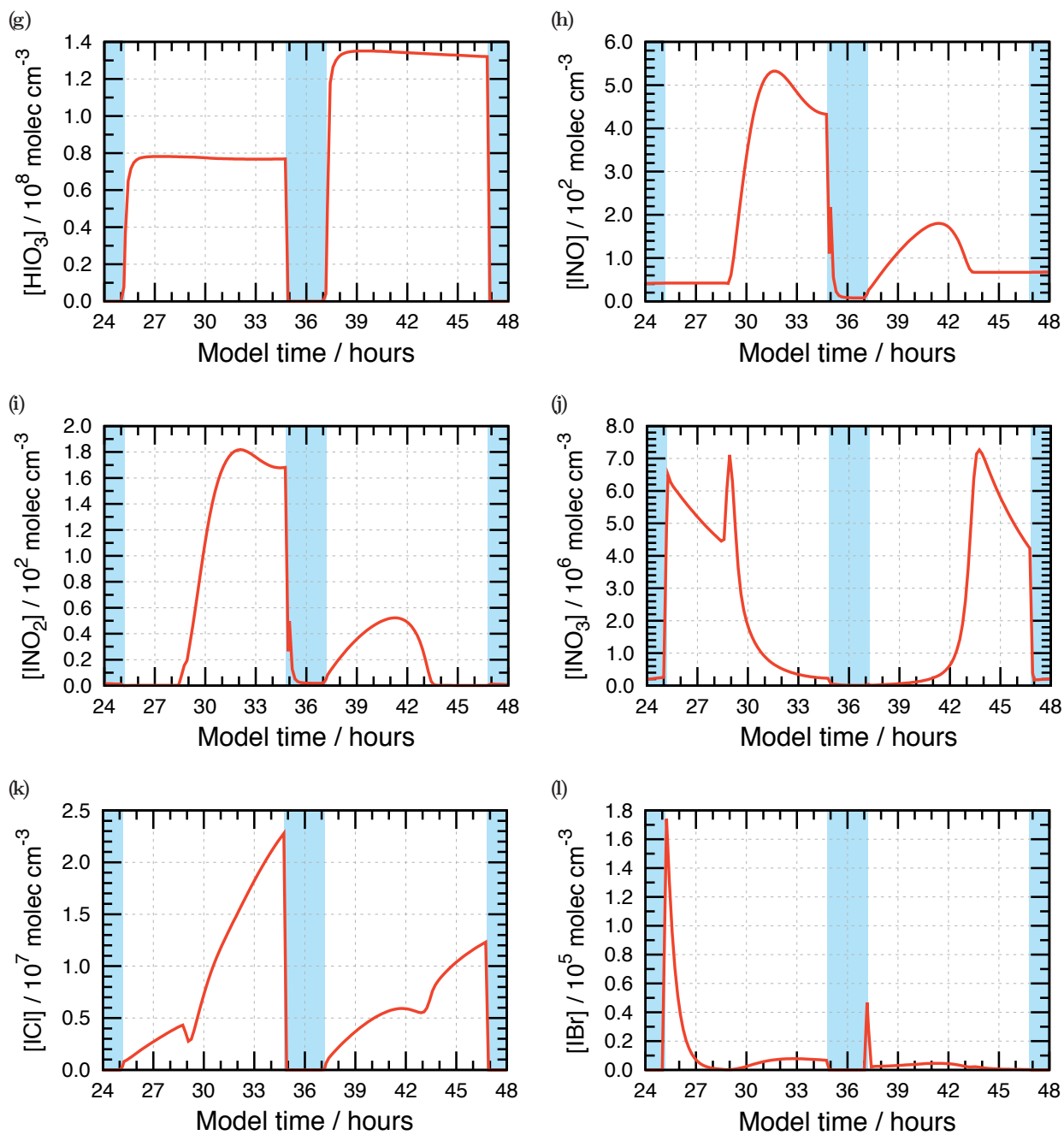
The only significant loss of iodine atoms in the gas phase is the reaction with ozone with a flux of  $1.0 \times 10^5$  molecules  $\text{cm}^{-3} \text{s}^{-1}$ . For the IO radicals formed, the reaction with  $\text{HO}_2$  is the dominant sink.  $7.5 \times 10^4$  molecules  $\text{cm}^{-3} \text{s}^{-1}$  or 75% of all loss fluxes are resulting from this reaction. Further fluxes are of minor importance and account for interactions with  $\text{NO}_x$  (7%) or trigger fast cycles between the iodine oxides IO, OIO, and  $\text{I}_2\text{O}_2$  as well as atomic and molecular iodine with fluxes in the order of  $10^3$  molecules  $\text{cm}^{-3} \text{s}^{-1}$  (6%). About 23% of the hypoiodous acid formed from the reaction of IO with  $\text{HO}_2$  photolyse, the remaining part ( $5.9 \times 10^4$  molecules  $\text{cm}^{-3} \text{s}^{-1}$ ) partitions into the aqueous phase, in which it activates chloride to  $\text{ICl}$ . 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  $\text{HO}_2$ . The main fraction of IO (84%,  $1.5 \times 10^4$  molecules  $\text{cm}^{-3} \text{s}^{-1}$ ) partitions into the aqueous phase and hence gas phase IO concentrations are decreased when a cloud is formed. In the aqueous phase, the IO radicals recombine to yield, with water, hypoiodous and iodous acid. Thus, at the beginning of the cloud period, aqueous IO concentrations show a peak and as the aqueous IO reacts further, concentrations are decreased over time as can be seen from Fig. S5a, page 12. The reaction product of the IO recombination, iodous acid, dissociates and reacts with hydrogen peroxide to form iodate, which accumulates as iodic acid. So again,  $\text{HIO}_2$  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  $\text{HIO}_2$  reacts further to  $\text{HIO}_3$  whose accumulation over time can be seen in Fig. S5b (page 12) as well.

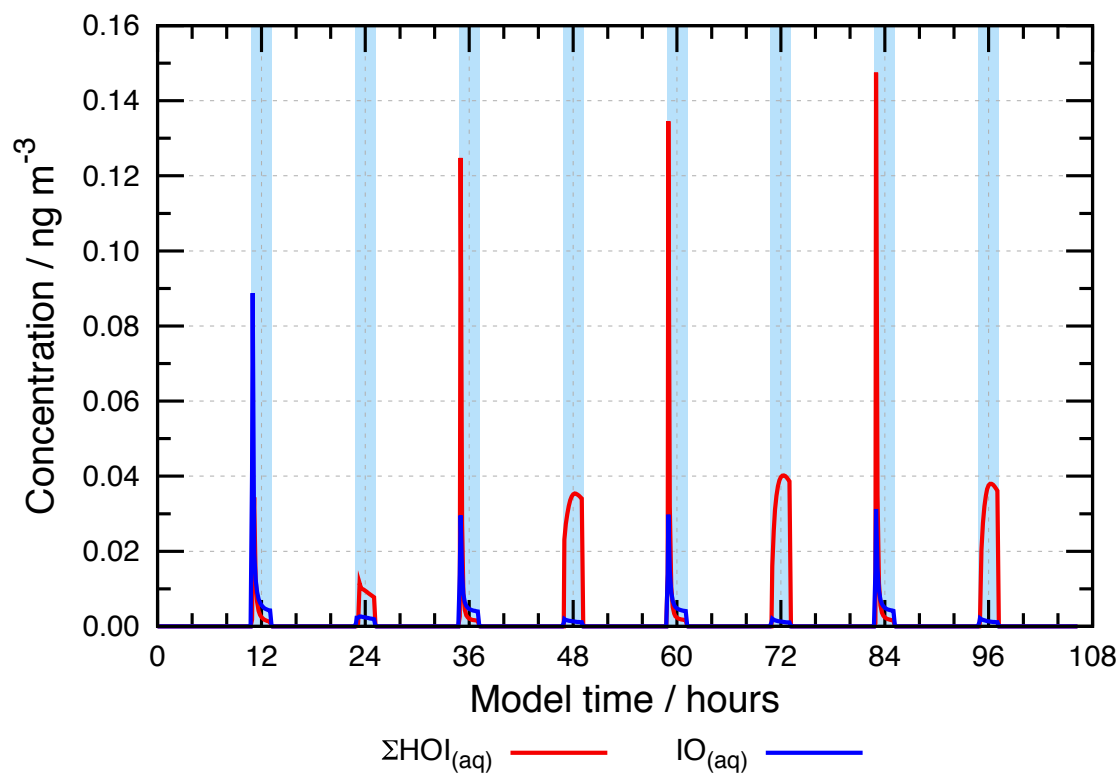


**Figure S4** Modelled concentration-time profiles of selected iodine species in the gas phase on the second model day (scenario HM2). Blue bars indicate in-cloud residence times of the air parcel.

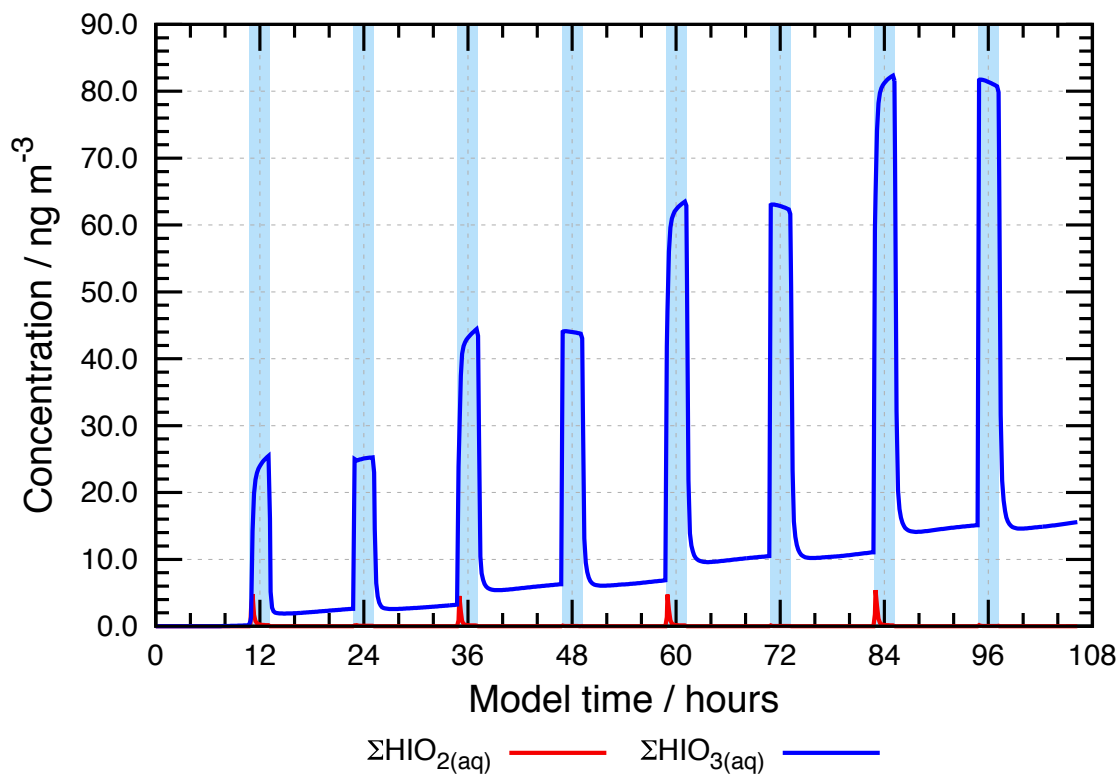


**Figure S4 (continued)** Modelled concentration-time profiles of selected bromine species in the gas phase on the second model day (scenario HM2). Blue bars indicate in-cloud residence times of the air parcel.

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



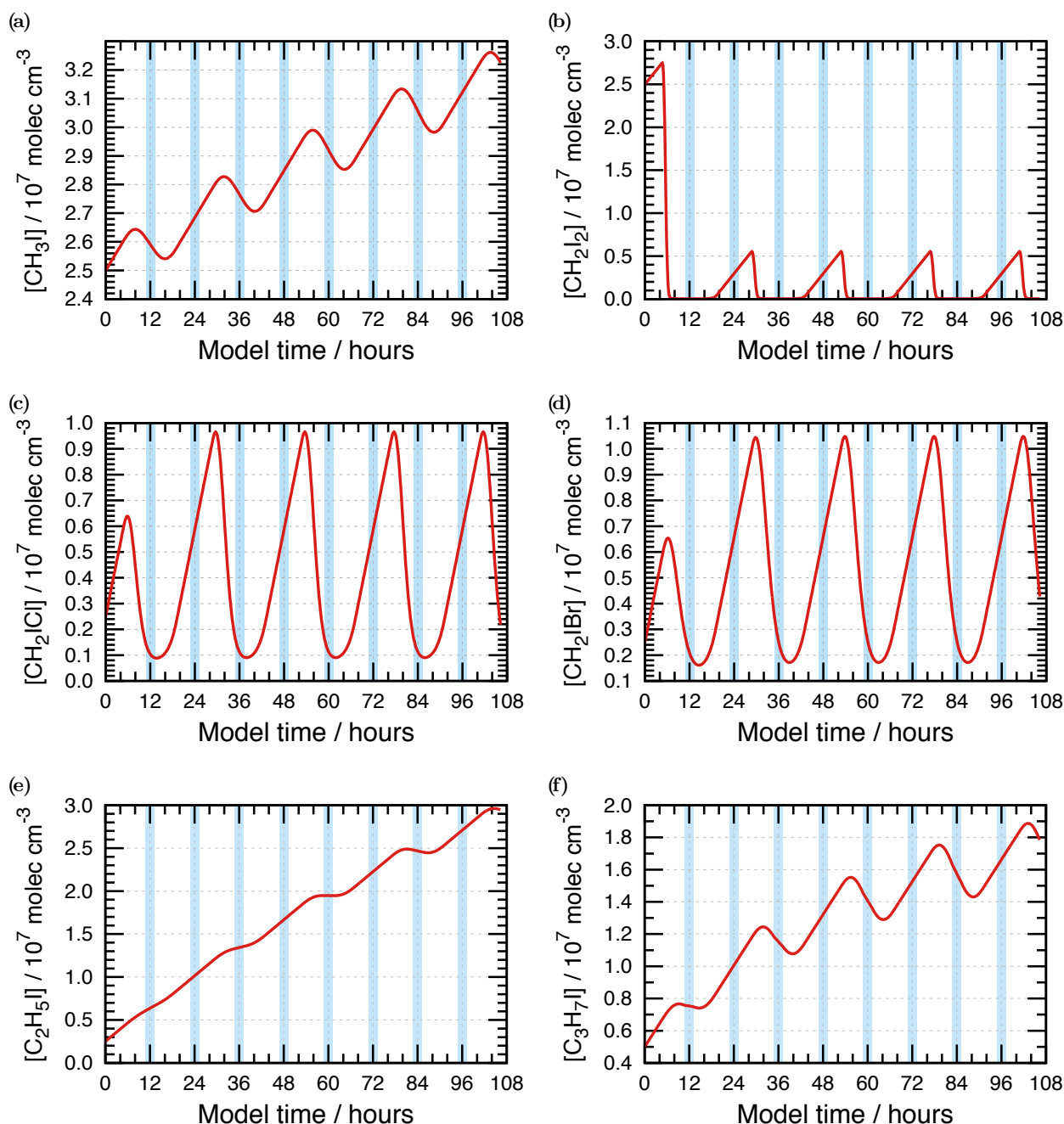
(b)  $\Sigma\text{HIO}_2_{(\text{aq})}$  and  $\Sigma\text{HIO}_3_{(\text{aq})}$



**Figure S5** Modelled concentration-time profiles of selected iodine species in the aqueous phase over the whole modelling period of 108 h (scenario HM2). For HOI, HIO<sub>2</sub>, and HIO<sub>3</sub> the sum of the dissociated and undissociated forms was used for the concentration-time profiles (indicated by  $\Sigma$ ). Blue bars indicate in-cloud residence times of the air parcel.

### S1.3.2 Organic iodine chemistry

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

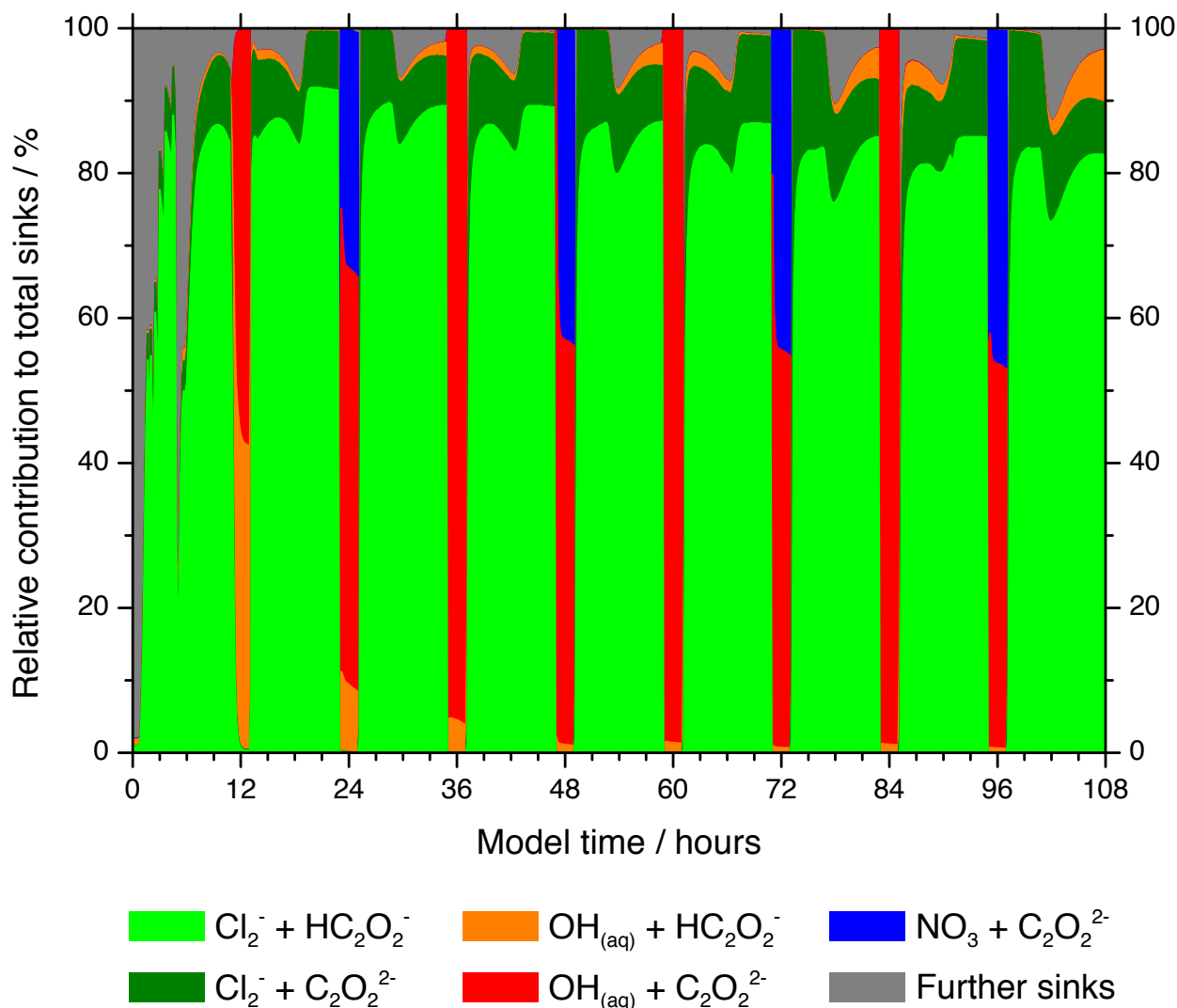


**Figure S6** Modelled concentration-time profiles of the various alkyl iodides in the gas phase for the whole modelling period of 108h (scenario HM2). Blue bars indicate in-cloud residence times of the air parcel.

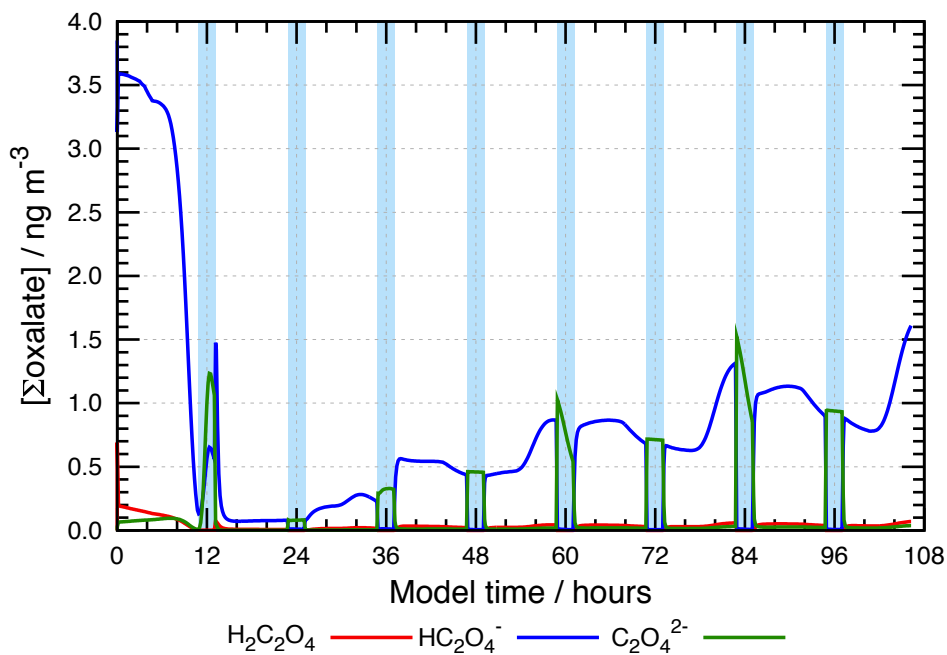
### S1.4 Influence of halogen chemistry on the aqueous phase oxalate oxidation

In this section, the oxidation of oxalate is discussed in more detail. Halogens contribute to the oxalate oxidation during non-cloud periods via electron transfer reaction of the  $\text{Cl}_2^-$  radical anion.

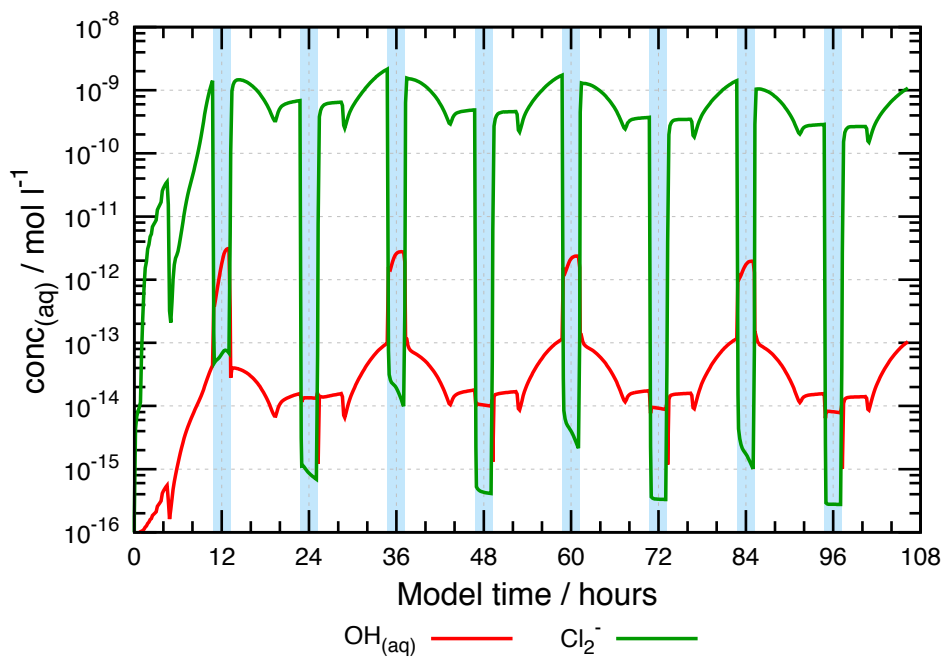
In Fig. S7 the relative contributions of all sinks are plotted over time. It can be clearly seen that under non-cloud conditions the oxidation is dominated by  $\text{Cl}_2^-$ , while under in-cloud conditions OH is the main oxidant. Only during night-time in-cloud conditions,  $\text{NO}_3$  contributes with about 40% to the total sinks. In Fig. S8 the speciation of the different dissociation states of oxalic acid is given. Under non-cloud conditions, the di-anion is the dominant form, while under in-cloud conditions the mono-anion predominantly exists. The reactivities are comparable for both forms and are in the order of  $10^6 \text{ M}^{-1} \text{ s}^{-1}$  for  $\text{Cl}_2^-$  and in the order of  $10^8 \text{ M}^{-1} \text{ s}^{-1}$  for OH. Therefore, the aqueous phase concentrations of these two species dictate the degradation process. They are given in Fig. S9. Please, note the logarithmic scale of the ordinate. The reactivity of OH is always about 2 orders of magnitude higher than that of  $\text{Cl}_2^-$ . However, during non-cloud periods the concentrations of  $\text{Cl}_2^-$  are between 4 to 5 orders of magnitude higher (in the range of  $10^9 \text{ mol l}^{-1}$ ), 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  $\text{Cl}_2^-$  in the range of  $10^{-12} \text{ mol l}^{-1}$ ) with higher reactivities than the chlorine radical di-anion and, hence, its oxidation is dominated by OH.



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



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



**Figure S9** Modelled concentration-time profiles of  $\text{OH}_{(\text{aq})}$  and  $\text{Cl}_2^-$  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 <sup>-3</sup> ]	Reference <sup>a</sup>
Cl	$\sim 1.5 \times 10^4$	Sander and Crutzen (1996) <sup>1</sup>
	$\sim 10^3$	Vogt et al. (1996) <sup>2</sup>
	$\sim 2 \times 10^4$	Sander et al. (1997) <sup>3</sup>
	$\sim 7 \times 10^3$	Vogt et al. (1999) <sup>2</sup>
	$\sim 9 \times 10^4$	Pechtl and von Glasow (2007) <sup>1</sup>
	$\sim 3 \times 10^4$	Pechtl and von Glasow (2007) <sup>2</sup>
	$\sim 1 - 2.5 \times 10^5$	Lowe et al. (2009) <sup>4</sup>
	$5.2 \times 10^4$	this work <sup>b</sup>
	$3.7 \times 10^4$	this work <sup>c</sup>
ClO	$\sim 1.4 \times 10^6$	Sander and Crutzen (1996) <sup>1</sup>
	$\sim 10^7$	Vogt et al. (1996) <sup>2</sup>
	$\sim 10^8$	Sander et al. (1997) <sup>3</sup>
	$\sim 1.2 \times 10^7$	Vogt et al. (1999) <sup>2</sup>
	$\sim 10^7 - 4.5 \times 10^8$	Lowe et al. (2009) <sup>4</sup>
	$1.3 \times 10^8$	this work <sup>b</sup>
	$8.0 \times 10^7$	this work <sup>c</sup>
HOCl	$\sim 1 \times 10^8$	Sander and Crutzen (1996) <sup>1</sup>
	$\sim 5 \times 10^7$	Vogt et al. (1996) <sup>2</sup>
	$\sim 6 \times 10^7$	Vogt et al. (1999) <sup>2</sup>
	$\sim 2.4 \times 10^9$	Pechtl and von Glasow (2007) <sup>1</sup>
	$\sim 1.2 \times 10^8$	Pechtl and von Glasow (2007) <sup>2</sup>
	$< 3 \times 10^9$	Lowe et al. (2009) <sup>4</sup>
	$7.8 \times 10^8$	this work <sup>b</sup>
$5.1 \times 10^8$	this work <sup>c</sup>	
Cl <sub>2</sub>	$\sim 9 \times 10^8$	Sander and Crutzen (1996) <sup>1</sup>
	$\sim 5 \times 10^6$	Vogt et al. (1996) <sup>2</sup>
	$\sim 8 \times 10^6$	Vogt et al. (1999) <sup>2</sup>
	$\sim 2.3 \times 10^9$	Pechtl and von Glasow (2007) <sup>1</sup>
	$\sim 7.5 \times 10^7$	Pechtl and von Glasow (2007) <sup>2</sup>
	$1.5 \times 10^8$	this work <sup>b</sup>
	$1.2 \times 10^8$	this work <sup>c</sup>
Br	$\sim 7 \times 10^5$	Sander and Crutzen (1996) <sup>1</sup>
	$\sim 3.5 \times 10^5$	Vogt et al. (1996) <sup>2</sup>
	$\sim 2 \times 10^9$	Sander et al. (1997) <sup>3</sup>
	$\sim 1.8 \times 10^6$	Vogt et al. (1999) <sup>2</sup>

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

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

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

<sup>a</sup>Model conditions are given in the footnotes below; <sup>b</sup>overall maximum concentration for the base run HM2; <sup>c</sup>maximum concentration on the second model day for the base run HM2

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

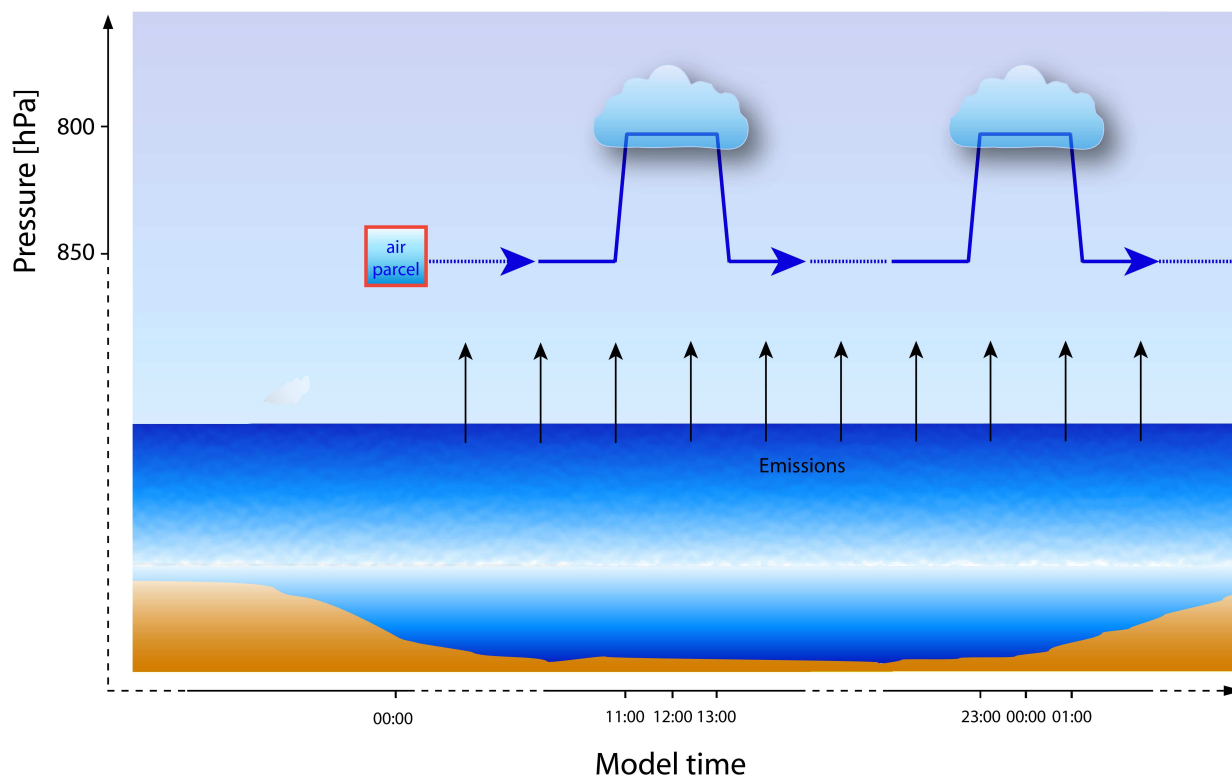
## S2 Model setup

### 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<sup>+</sup> concentration.

## S2.2 Cloud scenario

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



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

## S2.3 Calculation of photolysis rates

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

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

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

## S2.4 Changes to original setup

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

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

<sup>a</sup>ETH = ethane; <sup>b</sup>HC3 = alkanes, alcohols, esters, and alkynes with OH rate constant (298 K, 1 atm) less than  $3.4 \times 10^{-12} \text{cm}^3 \text{molecules}^{-1} \text{s}^{-1}$ ; <sup>c</sup>ETE = ethylene; <sup>d</sup>ETI = acetylene; <sup>e</sup>ISO = isoprene

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

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

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

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

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

## S2.5 Additional setup of the Halogen Modul 2.0

**Table S5** Emissions of halogen species

Species	Open ocean [ $\text{cm}^{-2} \text{s}^{-1}$ ]	Reference
$\text{C}_2\text{Cl}_4$	$3.2 \times 10^6$	Keene et al. (2008)
$\text{C}_2\text{HCl}_3$	$4.0 \times 10^6$	Keene et al. (2008)
$\text{CH}_3\text{CCl}_3$	—	Keene et al. (2008)
$\text{CHCl}_3$	$6.4 \times 10^7$	Keene et al. (2008)
$\text{CH}_2\text{Cl}_2$	$3.2 \times 10^7$	Keene et al. (2008)
$\text{CH}_3\text{Cl}$	$9.1 \times 10^7$	Keene et al. (2008)
$\text{CHBr}_3$	$1.1 \times 10^7$	Yang et al. (2005)
$\text{CH}_2\text{Br}_2$	$4.6 \times 10^6$	Yang et al. (2005)
$\text{CH}_3\text{Br}$	$9.7 \times 10^6$	Yang et al. (2005)
$\text{C}_3\text{H}_7\text{I}$	$1.0 \times 10^7$	Lowe et al. (2009)
$\text{C}_2\text{H}_5\text{I}$	$1.0 \times 10^7$	assumed
$\text{CH}_2\text{I}_2$	$1.5 \times 10^7$	assumed
$\text{CH}_3\text{I}$	$6.0 \times 10^6$	Lowe et al. (2009)
$\text{CH}_2\text{ICl}$	$2.0 \times 10^7$	Lowe et al. (2009)
$\text{CH}_2\text{IBr}$	$2.0 \times 10^7$	Lowe et al. (2009)

**Table S6** Depositions of halogen species

Species	Open ocean [ $\text{s}^{-1}$ ] <sup>a</sup>	Reference
$\text{HCl}^\otimes$	$2.0 \times 10^{-5}$	Lowe et al. (2009)
$\text{HOCl}$	$2.0 \times 10^{-6}$	Lowe et al. (2009)
$\text{HBr}$	$2.0 \times 10^{-5}$	Lowe et al. (2009)
$\text{HOBr}$	$2.0 \times 10^{-6}$	Lowe et al. (2009)
$\text{HI}$	$1.0 \times 10^{-5}$	Lowe et al. (2009)
$\text{HOI}$	$1.0 \times 10^{-5}$	Lowe et al. (2009)

**Table S6** (continued) Depositions of halogen species

Species	Open ocean [s <sup>-1</sup> ] <sup>a</sup>	Reference
INO <sub>2</sub>	1.0 × 10 <sup>-5</sup>	Lowe et al. (2009)
INO <sub>3</sub>	1.0 × 10 <sup>-5</sup>	Lowe et al. (2009)

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

**Table S7** Initial concentrations of halogen species

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

<sup>⊗</sup>update of CAPRAM

## S3 Reaction mechanism

### S3.1 Changes to Photolysis reactions in CAPRAM 3.0i

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

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

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

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

Reaction	$I/s^{-1}$	$m$	$n$
$\text{NO}_2 \xrightarrow{h\nu} \text{NO} + \text{O}(^3\text{P})$	$1.041 \times 10^{-2}$	0.404	0.250
$\text{O}_3 \xrightarrow{h\nu} \text{O}_2 + \text{O}(^1\text{D})$	$7.531 \times 10^{-5}$	1.886	0.382
$\text{O}_3 \xrightarrow{h\nu} \text{O}_2 + \text{O}(^3\text{P})$	$5.685 \times 10^{-4}$	0.273	0.132
$\text{HONO} \xrightarrow{h\nu} \text{OH} + \text{NO}$	$3.149 \times 10^{-3}$	0.430	0.263
$\text{HNO}_3 \xrightarrow{h\nu} \text{OH} + \text{NO}_2$	$1.173 \times 10^{-6}$	1.385	0.271
$\text{HNO}_4 \xrightarrow{h\nu} 0.65 \text{HO}_2 + 0.65 \text{NO}_2 + 0.35 \text{OH} + 0.35 \text{NO}_3$	$9.036 \times 10^{-6}$	1.262	0.327
$\text{NO}_3 \xrightarrow{h\nu} \text{NO} + \text{O}_2$	$2.919 \times 10^{-2}$	0.115	0.164
$\text{NO}_3 \xrightarrow{h\nu} \text{NO}_2 + \text{O}(^3\text{P})$	$2.349 \times 10^{-1}$	0.122	0.180
$\text{N}_2\text{O}_5 \xrightarrow{h\nu} \text{NO}_3 + \text{NO} + \text{O}(^3\text{P})$	$2.071 \times 10^{-7}$	2.185	3.974
$\text{N}_2\text{O}_5 \xrightarrow{h\nu} \text{NO}_3 + \text{NO}_2$	$7.083 \times 10^{-5}$	0.887	0.237
$\text{H}_2\text{O}_2 \xrightarrow{h\nu} 2 \text{OH}$	$1.189 \times 10^{-5}$	0.924	0.249
$\text{HCHO} \xrightarrow{h\nu} \text{H}_2 + \text{CO}$	$7.681 \times 10^{-5}$	0.685	0.273
$\text{HCHO} \xrightarrow{h\nu, 2\text{O}_2} 2 \text{HO}_2 + \text{CO}$	$5.681 \times 10^{-5}$	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 <sup>a</sup> $\xrightarrow{h\nu, 2O_2}$ MO <sub>2</sub> <sup>b</sup> + HO <sub>2</sub> + CO	$1.163 \times 10^{-5}$	1.303	0.418
CH <sub>3</sub> CHO $\xrightarrow{h\nu, 2O_2}$ MO <sub>2</sub> + HO <sub>2</sub> + CO	$1.163 \times 10^{-5}$	1.303	0.418
C <sub>2</sub> H <sub>5</sub> CHO $\xrightarrow{h\nu, 2O_2}$ MO <sub>2</sub> + HO <sub>2</sub> + CO	$3.546 \times 10^{-5}$	1.226	0.325
C <sub>3</sub> H <sub>7</sub> CHO $\xrightarrow{h\nu, 2O_2}$ MO <sub>2</sub> + HO <sub>2</sub> + CO	$4.476 \times 10^{-5}$	0.805	0.338
OP1 <sup>c</sup> $\xrightarrow{h\nu, O_2}$ HCHO + HO <sub>2</sub> + OH	$9.017 \times 10^{-6}$	0.870	0.244
OP2 <sup>d</sup> $\xrightarrow{h\nu, O_2}$ 0.47 ALD + 0.49 CH <sub>3</sub> CHO + 0.02 C <sub>2</sub> H <sub>5</sub> CHO + 0.02 C <sub>3</sub> H <sub>7</sub> CHO + HO <sub>2</sub> + OH	$9.017 \times 10^{-6}$	0.870	0.244
PAA <sup>e</sup> $\xrightarrow{h\nu}$ MO <sub>2</sub> + OH	$1.400 \times 10^{-6}$	1.059	0.265
KET <sup>f</sup> $\xrightarrow{h\nu, 2O_2}$ ACO <sub>3</sub> <sup>g</sup> + ETHP <sup>h</sup>	$1.029 \times 10^{-6}$	1.983	0.459
CH <sub>3</sub> COCH <sub>3</sub> $\xrightarrow{h\nu, 2O_2}$ ACO <sub>3</sub> + ETHP	$1.029 \times 10^{-6}$	1.983	0.459
C <sub>2</sub> H <sub>5</sub> COCH <sub>3</sub> $\xrightarrow{h\nu, 2O_2}$ ACO <sub>3</sub> + ETHP	$1.340 \times 10^{-6}$	1.201	0.335
CH <sub>3</sub> COCH(CH <sub>3</sub> ) <sub>2</sub> $\xrightarrow{h\nu, 2O_2}$ ACO <sub>3</sub> + ETHP	$1.029 \times 10^{-6}$	1.983	0.459
GLY <sup>i</sup> $\xrightarrow{h\nu, 2O_2}$ 2 CO + 2 HO <sub>2</sub>	$9.610 \times 10^{-5}$	0.325	0.240
GLY $\xrightarrow{h\nu}$ HCHO + CO	$3.026 \times 10^{-5}$	0.323	0.241
MGLY <sup>j</sup> $\xrightarrow{h\nu, 2O_2}$ ACO <sub>3</sub> + CO + HO <sub>2</sub>	$1.853 \times 10^{-4}$	0.583	0.225
DCB <sup>k</sup> $\xrightarrow{h\nu, 2O_2}$ 0.98 HO <sub>2</sub> + 0.02 ACO <sub>3</sub> + TCO <sub>3</sub> <sup>l</sup>	$1.624 \times 10^{-4}$	0.244	0.267
ONIT <sup>m</sup> $\xrightarrow{h\nu, O_2}$ 0.094 ALD + 0.098 CH <sub>3</sub> CHO + 0.004 C <sub>2</sub> H <sub>5</sub> CHO + 0.004 C <sub>3</sub> H <sub>7</sub> CHO + 0.120 KET + 0.408 CH <sub>3</sub> COCH <sub>3</sub> + 0.216 C <sub>2</sub> H <sub>5</sub> COCH <sub>3</sub> + 0.056 CH <sub>3</sub> COCH(CH <sub>3</sub> ) <sub>2</sub> + HO <sub>2</sub> + NO <sub>2</sub>	$4.615 \times 10^{-6}$	1.293	0.286
HKET <sup>n</sup> $\xrightarrow{h\nu, 2O_2}$ HCHO + HO <sub>2</sub> + ACO <sub>3</sub>	$3.552 \times 10^{-6}$	1.282	0.234
MACR <sup>o</sup> $\xrightarrow{h\nu, O_2}$ CO + HCHO + HO <sub>2</sub> + ACO <sub>3</sub>	$8.692 \times 10^{-6}$	0.582	0.261
MVK <sup>p</sup> $\xrightarrow{h\nu, O_2}$ CO + HCHO + HO <sub>2</sub> + ACO <sub>3</sub>	$6.990 \times 10^{-6}$	0.821	0.260
CH <sub>2</sub> (OH)CHO $\xrightarrow{h\nu, 2O_2}$ HCHO + CO + 2 HO <sub>2</sub>	$9.737 \times 10^{-6}$	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).

<sup>a</sup>ALD = higher aldehydes; <sup>b</sup>MO<sub>2</sub> = methyl peroxy radical; <sup>c</sup>OP1 = methyl hydrogen peroxide; <sup>d</sup>OP2 = higher organic peroxides; <sup>e</sup>PAA = peroxyacetic acid and higher analoges; <sup>f</sup>KET = ketones; <sup>g</sup>ACO<sub>3</sub> = acetyl peroxy radical and higher saturated acyl peroxy radicals; <sup>h</sup>ETHP = peroxy radical formed from ETH; <sup>i</sup>GLY = glyoxal; <sup>j</sup>MGLY = methylglyoxal; <sup>k</sup>DCB = unsaturated dicarbonyls; <sup>l</sup>TCO<sub>3</sub> = unsaturated acyl peroxy radicals; <sup>m</sup>ONIT = organic nitrates; <sup>n</sup>HKET = hydroxy ketone; <sup>o</sup>MACR = methacrolein and other unsaturated monoaldehydes; <sup>p</sup>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
$\text{Fe}(\text{OH})^{2+} \xrightarrow{h\nu} \text{Fe}^{2+} + \text{OH}$	$4.764 \times 10^{-2}$	0.829	0.291	absorption spectra from <a href="#">Weschler et al. (1986)</a> /quantum yields from <a href="#">Benkelberg and Warneck (1995)</a>
$\text{Fe}(\text{OH})_2^+ \xrightarrow{h\nu} \text{Fe}^{2+} + \text{OH} + \text{OH}^-$	$1.343 \times 10^{-2}$	0.855	0.300	absorption spectra from <a href="#">Weschler et al. (1986)</a> /quantum yields from <a href="#">Benkelberg and Warneck (1995)</a>
$\text{NO}_3^- \xrightarrow{h\nu} \text{NO}_2 + \text{OH} + \text{OH}^-$	$6.109 \times 10^{-7}$	1.076	0.409	absorption spectra from <a href="#">Graedel and Weschler (1981)</a> /quantum yields from <a href="#">Zellner et al. (1990)</a>
$\text{NO}_2^- \xrightarrow{h\nu} \text{NO} + \text{OH} + \text{OH}^-$	$7.245 \times 10^{-5}$	0.480	0.303	absorption spectra from <a href="#">Graedel and Weschler (1981)</a> /quantum yields from <a href="#">Zellner et al. (1990)</a>
$\text{HONO} \xrightarrow{h\nu} \text{OH} + \text{NO}$	$2.999 \times 10^{-4}$	0.439	0.308	<a href="#">Graedel and Weschler (1981)</a>
$\text{Fe}^{3+} \xrightarrow{h\nu} \text{Fe}^{2+} + \text{OH} + \text{H}^+$	$1.224 \times 10^{-5}$	1.467	0.248	absorption spectra from <a href="#">Weschler et al. (1986)</a> /quantum yields from <a href="#">Benkelberg and Warneck (1995)</a>
$\text{Fe}(\text{SO}_4)^+ \xrightarrow{h\nu} \text{Fe}^{2+} + \text{SO}_4^-$	$8.215 \times 10^{-5}$	0.885	0.313	<a href="#">Benkelberg and Warneck (1995)</a>
$\text{H}_2\text{O}_2 \xrightarrow{h\nu} 2\text{OH}$	$8.625 \times 10^{-6}$	1.043	0.271	absorption spectra from <a href="#">Graedel and Weschler (1981)</a> /quantum yields from <a href="#">Zellner et al. (1990)</a>
$\text{Fe}(\text{C}_2\text{O}_4)_2^- \xrightarrow{h\nu} \text{Fe}^{2+} + \text{C}_2\text{O}_4^{2-} + \text{CO}_2 + \text{CO}_2^-$	$7.993 \times 10^{-2}$	0.625	0.279	IfT measurements
$\text{Fe}(\text{C}_2\text{O}_4)_3^{3-} \xrightarrow{h\nu} \text{Fe}^{2+} + 2\text{C}_2\text{O}_4^{2-} + \text{CO}_2 + \text{CO}_2^-$	$4.659 \times 10^{-2}$	0.561	0.276	IfT measurements
$\text{OP1}^a \xrightarrow{h\nu} \text{CH}_3\text{O} + \text{OH}$	$8.625 \times 10^{-5}$	1.043	0.271	estimated same as $\text{H}_2\text{O}_2$
$\text{NO}_3 \xrightarrow{h\nu} \text{NO} + \text{O}_2$	$2.584 \times 10^{-3}$	0.072	0.196	<a href="#">Graedel and Weschler (1981)</a>
$\text{NO}_3 \xrightarrow{h\nu} \text{NO}_2 + \text{O}(^3\text{P})$	$2.325 \times 10^{-2}$	0.072	0.196	<a href="#">Graedel and Weschler (1981)</a>
$\text{O}_3 \xrightarrow{h\nu} 2\text{OH} + \text{O}_2$	$3.652 \times 10^{-4}$	0.515	0.044	<a href="#">Graedel and Weschler (1981)</a>

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

<sup>a</sup>OP1 = methyl hydrogen peroxide

### S3.2 Phase transfer

**Table S10** Henry's Law constants

	Species	$K_H(298\text{ K}) / \text{M atm}^{-1}$	$\Delta H/R / \text{K}$	Reference/comment
H1 $\otimes$	Cl <sub>2</sub>	$9.15 \times 10^{-2}$	-2490	Wilhelm et al. (1977)
H2 $\oplus$	Cl	0.2		Mozurkewich (1995)
H3 $\ominus$	ClO	660	-5862	estimated ( $K_{H, H3} \approx K_{H, H6}$ ), correction of Halogen Module 1.0
H4 $\oplus$	ClO <sub>2</sub>	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	$5.0 \times 10^{-2}$		upper limit, Scheer et al. (1997)
H8 $\otimes$	ClNO <sub>2</sub>	$4.6 \times 10^{-2}$		upper limit, Frenzel et al. (1998)
H9	ClNO <sub>3</sub>	$2.1 \times 10^5$	-8700	estimated same as nitric acid
H10	CH <sub>2</sub> ClCO <sub>3</sub>	669	-5893	estimated same as acetylperoxyl radical
H11	CH <sub>2</sub> ClCOOH	$5.5 \times 10^3$	-5890	estimated same as acetic acid
H12	CH <sub>3</sub> COCClO	1.4	-7541	estimated same as methylglyoxal
H13	COCl <sub>2</sub>	$7.0 \times 10^{-2}$		Law et al. (2007)
H14	CHOC1	$3.0 \times 10^3$	-7216	estimated same as formaldehyde
H15 $\otimes$	Br <sub>2</sub>	0.76	-4100	Law et al. (2007)
H16 $\oplus$	Br	1.2		Mozurkewich (1995)
H17 $\oplus$	BrO	93	-5862	estimated ( $K_{H, H17} \approx K_{H, H19}$ )
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 <sub>2</sub>	0.3		Frenzel et al. (1998)
H21	BrNO <sub>3</sub>	$2.1 \times 10^5$	-8700	estimated same as nitric acid
H22 $\ominus$	BrCl	0.94	-5600	Bartlett and Margerum (1999)
H23	CH <sub>2</sub> BrCO <sub>3</sub>	669	-5893	estimated same as acetylperoxyl radical
H24	CH <sub>2</sub> BrCOOH	$5.5 \times 10^3$	-5890	estimated same as acetic acid

**Table S10** (continued) Henry's Law constants

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

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

**Table S11** Mass accommodation coefficients and gas phase diffusion coefficients

	Species	$\alpha$	Reference	$D_g^a$	Reference	Comment
H1	Cl <sub>2</sub>	0.08		1.28	Schwartz (1986)	$\alpha$ estimated

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

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

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

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

⊗already implemented in CAPRAM; ⊙update of CAPRAM; ⊕already implemented in the Halogen Module 1.0; ⊖update of the Halogen Module 1.0  
<sup>a</sup>in  $10^5 \text{ m}^2 \text{ s}^{-1}$  at 288 K; <sup>b</sup>correction of  $D_g$  in the Halogen Module 1.0; <sup>c</sup> $D_g$  calculated with the FSG method (Fuller, 1986); <sup>d</sup> $v_{Br}$  estimated with 34.8; <sup>e</sup> $v_{I_2}$  estimated with 77.3; <sup>f</sup> $v_I$  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 <sup>⊖</sup>	$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	$1.21 \times 10^{-11}$	250		Atk07
G2	$\text{Cl} + \text{H}_2 \xrightarrow{\text{O}_2} \text{HCl} + \text{HO}_2$	$1.68 \times 10^{-14}$	2310		Atk07
G3	$\text{Cl} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_2$	$3.40 \times 10^{-11}$			Atk07

**Table S12 (continued)** Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	$E_A/R^b$	Comment	Reference
G4	$\text{Cl} + \text{HO}_2 \rightarrow \text{ClO} + \text{OH}$	$9.30 \times 10^{-12}$	570		Atk07
G5	$\text{Cl} + \text{H}_2\text{O}_2 \rightarrow \text{HCl} + \text{HO}_2$	$4.10 \times 10^{-13}$	980		Atk07
G6	$\text{Cl}_2 + \text{OH} \rightarrow \text{HOCl} + \text{Cl}$	$6.42 \times 10^{-14}$	1200		Atk07
P <sub>g</sub> 1 <sup>⊖</sup>	$\text{Cl}_2 \xrightarrow{h\nu} 2 \text{Cl}$	$(2.99 \times 10^{-3})$		$\Phi = 1.0^{\text{Cal/Pit66}}$ ; see Tab. S14	Dem97
G7 <sup>⊖</sup>	$\text{ClO} + \text{O}_3 \rightarrow \text{ClO}_2 + \text{O}_2$	$1.13 \times 10^{-17}$	3600	upper limit	Atk07
G8	$\text{ClO} + \text{O}_3 \rightarrow \text{OCIO} + \text{O}_2$	$1.48 \times 10^{-18}$	4000	upper limit	Atk07
G9	$\text{ClO} + \text{OH} \rightarrow$ $0.94 \text{HO}_2 + 0.94 \text{Cl} + 0.06 \text{HCl} + 0.06 \text{O}_2$	$2.00 \times 10^{-11}$	-300		Atk07
G10 <sup>⊖</sup>	$\text{ClO} + \text{HO}_2 \rightarrow \text{HOCl} + \text{O}_2$	$6.89 \times 10^{-12}$	-340		Atk07
G11	$\text{ClO} + \text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2$	$4.82 \times 10^{-15}$	1590		Atk07
G12	$\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{ClO}_2$	$8.06 \times 10^{-15}$	2450		Atk07
G13	$\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{OCIO}$	$3.53 \times 10^{-15}$	1370		Atk07
G14	$\text{ClO} + \text{ClO} \xrightarrow{\text{M}} \text{Cl}_2\text{O}_2$	$1.52 \times 10^{-15}$		TYP: TROE; see Tab. S13	San06
P <sub>g</sub> 2	$\text{ClO} \xrightarrow{h\nu} \text{Cl} + \text{O}$	$(2.64 \times 10^{-4})$		$\Phi = 1.0^i$ ; see Tab. S14	San06
G15	$\text{Cl} + \text{O}_2 \xrightarrow{\text{M}} \text{ClO}_2$	$5.17 \times 10^{-14}$		TYP: TROE; see Tab. S13	San06
G16 <sup>⊖</sup>	$\text{ClO}_2 \xrightarrow{\text{M}} \text{Cl} + \text{O}_2$	$6.23 \times 10^{-13}$	1820		Atk07
G17	$\text{Cl} + \text{ClO}_2 \rightarrow 0.95 \text{Cl}_2 + 0.95 \text{O}_2 + 0.1 \text{ClO}$	$2.42 \times 10^{-10}$			San06
G18	$\text{Cl}_2\text{O}_2 \xrightarrow{\text{M}} 2 \text{ClO}$	$2.87 \times 10^{-3}$		TYP: TROEXP; see Tab. S13	Atk07
G19	$\text{Cl}_2\text{O}_2 + \text{O}_3 \rightarrow \text{ClO} + \text{ClO}_2 + \text{O}_2$	$1.00 \times 10^{-19}$		upper limit	Atk07
G20	$\text{Cl}_2\text{O}_2 + \text{Cl} \rightarrow \text{Cl}_2 + \text{ClO}_2$	$9.45 \times 10^{-11}$	-65		Atk07
P <sub>g</sub> 4	$\text{Cl}_2\text{O}_2 \xrightarrow{h\nu} \text{Cl} + \text{ClO}_2$	$(1.83 \times 10^{-3})$		$\Phi = 1.0^i$ ; see Tab. S14	San03
G21	$\text{OCIO} + \text{OH} \rightarrow \text{HOCl} + \text{O}_2$	$1.05 \times 10^{-11}$	-600		Atk07
G22	$\text{Cl} + \text{OCIO} \rightarrow 2 \text{ClO}$	$5.66 \times 10^{-11}$	-170		Atk07
G23	$\text{ClO} + \text{OCIO} \xrightarrow{\text{M}} \text{Cl}_2\text{O}_3$	$1.08 \times 10^{-19}$		TYP: TROE; see Tab. S13	Atk07
P <sub>g</sub> 3	$\text{OCIO} \xrightarrow{h\nu} \text{ClO} + \text{O}$	$(0.10)$		$\Phi = 1.0^i$ ; see Tab. S14	San06
G24	$\text{Cl}_2\text{O}_3 \xrightarrow{\text{M}} \text{ClO} + \text{OCIO}$	$6.17 \times 10^{-2}$		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 <sub>g</sub> 5	$\text{Cl}_2\text{O}_3 \xrightarrow{h\nu} \text{ClO} + \text{OCIO}$	$(9.80 \times 10^{-4})$		$\Phi = 1.0^i$ ; further products omitted; see Tab. S14	Atk07
G25 <sup>⊖</sup>	$\text{HCl} + \text{OH} \rightarrow \text{Cl} + \text{H}_2\text{O}$	$7.86 \times 10^{-13}$	230		Atk07
G26	$\text{HOCl} + \text{OH} \rightarrow \text{ClO} + \text{H}_2\text{O}$	$5.60 \times 10^{-13}$	500	$E_A/R$ estimated	San06
G27	$\text{HOCl} + \text{Cl} \rightarrow$ $0.76 \text{HCl} + 0.76 \text{ClO} + 0.24 \text{Cl}_2 + 0.24 \text{OH}$	$1.62 \times 10^{-12}$	130	branching ratios from Vogt and Schindler (1993)	San06
P <sub>g</sub> 6 <sup>⊖</sup>	$\text{HOCl} \xrightarrow{h\nu} \text{Cl} + \text{OH}$	$(3.63 \times 10^{-4})$		$\Phi = 1.0$ ; see Tab. S14	Atk07
G28	$\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$	$1.67 \times 10^{-11}$	-295		Atk07
G29	$\text{OCIO} + \text{NO} \rightarrow \text{ClO} + \text{NO}_2$	$3.56 \times 10^{-13}$	-350		Atk07
G30	$\text{Cl} + \text{NO}_3 \rightarrow \text{ClO} + \text{NO}_2$	$2.40 \times 10^{-11}$			Atk07
G31	$\text{ClO} + \text{NO}_3 \rightarrow 0.68 \text{ClO}_2 + 0.32 \text{OCIO} + \text{NO}_2$	$4.61 \times 10^{-13}$			Kuk94
G32	$\text{Cl} + \text{NO} \xrightarrow{\text{M}} \text{ClNO}$	$1.92 \times 10^{-12}$		TYP: SPEC2; see Tab. S13	San06
G33	$\text{Cl} + \text{ClNO} \rightarrow \text{Cl}_2 + \text{NO}$	$8.11 \times 10^{-11}$	-100		San06
P <sub>g</sub> 7	$\text{ClNO} \xrightarrow{h\nu} \text{Cl} + \text{NO}$	$(5.48 \times 10^{-4})$		see Tab. S14	Atk07
G34	$\text{Cl} + \text{NO}_2 \xrightarrow{\text{M}} \text{ClNO}_2$	$5.80 \times 10^{-14}$		TYP: TROE; see Tab. S13	San06
G35	$\text{ClNO}_2 + \text{OH} \rightarrow \text{HOCl} + \text{NO}_2$	$3.62 \times 10^{-14}$	1250		Atk07
P <sub>g</sub> 8 <sup>⊖</sup>	$\text{ClNO}_2 \xrightarrow{h\nu} \text{Cl} + \text{NO}_2$	$(4.81 \times 10^{-4})$		see Tab. S14	Atk07
G36	$\text{ClO} + \text{NO}_2 \xrightarrow{\text{M}} \text{ClNO}_3$	$1.85 \times 10^{-19}$		TYP: TROEF; see Tab. S13	Atk07
G37	$\text{ClNO}_3 \xrightarrow{\text{M}} \text{ClO} + \text{NO}_2$	$1.47 \times 10^{-3}$	11438	TYP: SPEC4	And/Fah90
G38	$\text{ClNO}_3 + \text{OH} \rightarrow$ $0.5 \text{ClO} + 0.5 \text{HNO}_3 + 0.5 \text{HOCl} + 0.5 \text{NO}_3$	$3.97 \times 10^{-13}$	330	branching ratios from Pechtl et al. (2005)	Atk07
G39	$\text{ClNO}_3 + \text{Cl} \rightarrow \text{Cl}_2 + \text{NO}_3$	$1.01 \times 10^{-11}$	-145		Atk07
P <sub>g</sub> 9	$\text{ClNO}_3 \xrightarrow{h\nu} \text{Cl} + \text{NO}_3$	$(5.16 \times 10^{-5})$		$\Phi = 0.6 - 1.0$ ; see Tab. S14	Dem97
P <sub>g</sub> 10	$\text{ClNO}_3 \xrightarrow{h\nu} \text{ClO} + \text{NO}_2$	$(1.09 \times 10^{-5})$		$\Phi = 0.4 - 0.0$ ; see Tab. S14	Dem97
G40 <sup>⊖</sup>	$\text{Cl} + \text{CH}_4 \xrightarrow{\text{O}_2} \text{HCl} + \text{MO}_2$	$1.03 \times 10^{-13}$	1240	<i>g, A</i>	Atk06
G41	$\text{Cl} + \text{OP1} \rightarrow \text{HCl} + \text{MO}_2$	$5.70 \times 10^{-11}$		<i>A, B</i>	San06

**Table S12 (continued)** Gas phase reactions

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

**Table S12 (continued)** Gas phase reactions

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

**Table S12 (continued)** Gas phase reactions

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

**Table S12 (continued)** Gas phase reactions

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

**Table S12 (continued)** Gas phase reactions

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

**Table S12 (continued)** Gas phase reactions

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

**Table S12 (continued)** Gas phase reactions

	Reaction	$k_{298} (j_{max})^a$	$E_A/R^b$	Comment	Reference
P <sub>g</sub> 18	CHOC1 $\xrightarrow{h\nu, O_2}$ Cl + CO + HO <sub>2</sub>	$(2.71 \times 10^{-7})$		$\Phi = 1.0^{Fan/Liu01}$ ; see Tab. S14	Atk08
G138	COCl $\xrightarrow{M}$ CO + Cl	$4.98 \times 10^5$	2960	TYP: SPEC4	Atk07
G139	CO + Cl $\xrightarrow{M}$ COCl	$3.33 \times 10^{-14}$		TYP: SPEC2; see Tab. S13	Atk07
G140 <sup>⊕</sup>	Br + O <sub>3</sub> → BrO + O <sub>2</sub>	$1.16 \times 10^{-12}$	800	better reference	Atk07
G141 <sup>⊖</sup>	Br + HO <sub>2</sub> → HBr + O <sub>2</sub>	$1.70 \times 10^{-12}$	450		Atk07
G142	Br + H <sub>2</sub> O <sub>2</sub> → HBr + HO <sub>2</sub>	$4.25 \times 10^{-16}$	3000		San06
G143	Br <sub>2</sub> + OH → HOBr + Br	$4.48 \times 10^{-11}$	-240		Atk07
P <sub>g</sub> 19 <sup>⊖</sup>	Br <sub>2</sub> $\xrightarrow{h\nu}$ 2 Br	$(3.86 \times 10^{-2})$		$\Phi = 1.0^{Fan/Liu01}$ ; see Tab. S14	See/Bri64
G144 <sup>⊖</sup>	BrO + O <sub>3</sub> → 0.9 Br + 0.1 OBrO + 1.9 O <sub>2</sub>	$2.17 \times 10^{-17}$	3200	products from Atkinson et al. (2007); upper limit	San06
G145	BrO + OH → Br + HO <sub>2</sub>	$4.16 \times 10^{-11}$	-250		Atk07
G146 <sup>⊖</sup>	BrO + HO <sub>2</sub> → HOBr + O <sub>2</sub>	$2.41 \times 10^{-11}$	-500	further products omitted	Atk07
G147	BrO + BrO → 1.7 Br + 0.15 Br <sub>2</sub> + O <sub>2</sub>	$3.24 \times 10^{-12}$	-210		Atk07
P <sub>g</sub> 20	BrO $\xrightarrow{h\nu}$ Br + O( <sup>3</sup> P)	$(4.86 \times 10^{-2})$		$\Phi = 1.0$ ; see Tab. S14	San03
P <sub>g</sub> 21	OBrO $\xrightarrow{h\nu}$ BrO + O( <sup>3</sup> P)	$(0.56)$		$\Phi = 1.0^{Fle05, i}$ ; see Tab. S14	San06
P <sub>g</sub> 22 <sup>⊖</sup>	HOBr $\xrightarrow{h\nu}$ Br + OH	$(2.80 \times 10^{-3})$		$\Phi = 1.0$ ; see Tab. S14	San03
G148 <sup>⊖</sup>	HBr + OH → Br + H <sub>2</sub> O	$1.13 \times 10^{-11}$	-155		Atk07
G149	Br + NO <sub>2</sub> $\xrightarrow{M}$ BrNO <sub>2</sub>	$1.43 \times 10^{-12}$		TYP: TROEF; see Tab. S13	Atk07
P <sub>g</sub> 23 <sup>⊖</sup>	BrNO <sub>2</sub> $\xrightarrow{h\nu}$ Br + NO <sub>2</sub>	$(5.87 \times 10^{-3})$		$\Phi = 1.0$ ; see Tab. S14	Atk07
G150	Br + NO <sub>3</sub> → BrO + NO <sub>2</sub>	$1.60 \times 10^{-11}$			Atk07
G151	BrO + NO → Br + NO <sub>2</sub>	$2.08 \times 10^{-11}$	-260		Atk07
G152	BrO + NO <sub>2</sub> $\xrightarrow{M}$ BrNO <sub>3</sub>	$1.87 \times 10^{-12}$		TYP: TROEF; see Tab. S13	Atk07
G153	BrNO <sub>3</sub> → BrO + NO <sub>2</sub>	$2.75 \times 10^{-5}$	12360		Orl/Tyn96
G154	BrNO <sub>3</sub> + Br → Br <sub>2</sub> + NO <sub>3</sub>	$4.9 \times 10^{-11}$			Orl/Tyn96
P <sub>g</sub> 24	BrNO <sub>3</sub> $\xrightarrow{h\nu}$ Br + NO <sub>3</sub>	$(1.26 \times 10^{-3})$		$\Phi = 0.71$ ; see Tab. S14	San03
P <sub>g</sub> 25	BrNO <sub>3</sub> $\xrightarrow{h\nu}$ BrO + NO <sub>2</sub>	$(5.13 \times 10^{-4})$		$\Phi = 0.29$ ; see Tab. S14	San03

**Table S12 (continued)** Gas phase reactions

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

**Table S12 (continued)** Gas phase reactions

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

**Table S12 (continued)** Gas phase reactions

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

**Table S12 (continued)** Gas phase reactions

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

**Table S12 (continued)** Gas phase reactions

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

**Table S12 (continued)** Gas phase reactions

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

**Table S12 (continued)** Gas phase reactions

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

**Table S12 (continued)** Gas phase reactions

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

**Table S12 (continued)** Gas phase reactions

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

**Table S12 (continued)** Gas phase reactions

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

**Table S12 (continued)** Gas phase reactions

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

<sup>⊕</sup>already implemented in the Halogen Module 1.0; <sup>⊖</sup>update of the Halogen Module 1.0

<sup>a</sup>in  $\text{cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  (*slanted* values in parentheses represent  $j_{max}$  in  $\text{s}^{-1}$  for photolysis reactions); <sup>b</sup>in K; <sup>c</sup>estimated X = H (X = Cl, Br, I); <sup>d</sup>reactions combined; <sup>e</sup>estimated X = Cl (X = Br, I); <sup>f</sup>estimated I = Br; <sup>g</sup>immediate reaction with oxygen; <sup>h</sup>immediate hydrogen abstraction; <sup>i</sup>estimated  
<sup>A</sup>MO<sub>2</sub> = methyl peroxy radical; <sup>B</sup>OP1 = methyl hydrogen peroxide; <sup>C</sup>ORA1 = formic acid; <sup>D</sup>ETH = ethane; <sup>E</sup>ETHP = peroxy radical formed from ETH; <sup>F</sup>HC3 = alkanes, alcohols, esters, and alkynes with OH rate constant (298 K, 1 atm) less than  $3.4 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ; <sup>G</sup>HC3P = peroxy radical formed from HC3; <sup>H</sup>HC5 = alkanes, alcohols, esters, and alkynes with OH rate constant (298 K, 1 atm) between  $3.4 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$  and  $6.8 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ; <sup>I</sup>HC5P = peroxy radical formed from HC5; <sup>J</sup>HC8 = alkanes, alcohols, esters, and alkynes with OH rate constant (298 K, 1 atm) greater than  $6.8 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ ; <sup>K</sup>HC8P = peroxy radical formed from HC8; <sup>L</sup>TOL = Toluene and less reactive aromatics; <sup>M</sup>TOLP = peroxy radical formed from TOL; <sup>N</sup>ACO<sub>3</sub> = acetylperoxy and higher saturated acylperoxy radicals; <sup>O</sup>ALD = higher aldehydes; <sup>P</sup>KET = ketones; <sup>Q</sup>KETP = peroxy radical formed from KET; <sup>R</sup>HKET = hydroxy ketone; <sup>S</sup>MGLY = methylglyoxal; <sup>T</sup>GLY = glyoxal; <sup>U</sup>ETI = acetylene; <sup>V</sup>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	$\text{ClO} + \text{ClO} \xrightarrow{\text{M}} \text{Cl}_2\text{O}_2$	TROE	$1.6 \times 10^{-32} (T/300)^{-4.5}$	$2.0 \times 10^{-12} (T/300)^{-2.4}$	
G15	$\text{Cl} + \text{O}_2 \xrightarrow{\text{M}} \text{ClO}_2$	TROE	$2.2 \times 10^{-33} (T/300)^{-3.1}$	$1.8 \times 10^{-10}$	
G18	$\text{Cl}_2\text{O}_2 \xrightarrow{\text{M}} 2 \text{ClO}$	TROEXP	$3.7 \times 10^{-7} e^{-7690/T}$	$7.9 \times 10^{15} e^{-8820/T}$	0,45
G23	$\text{ClO} + \text{OCLO} \xrightarrow{\text{M}} \text{Cl}_2\text{O}_3$	TROE	$6.2 \times 10^{-32} (T/300)^{-4.7}$	$2.4 \times 10^{-11}$	
G24	$\text{Cl}_2\text{O}_3 \xrightarrow{\text{M}} \text{ClO} + \text{OCLO}$	TROEXP	$1.4 \times 10^{-10} e^{-3810/T}$	$2.5 \times 10^{12} e^{-4940/T}$	
G32	$\text{Cl} + \text{NO} \xrightarrow{\text{M}} \text{ClNO}$	SPEC2	$7.6 \times 10^{-32} (T/300)^{-1.8}$		
G34	$\text{Cl} + \text{NO}_2 \xrightarrow{\text{M}} \text{ClNO}_2$	TROE	$1.8 \times 10^{-31} (T/300)^{-2}$	$1.0 \times 10^{-10} (T/300)^{-1}$	

**Table S13 (continued)** Parameters for pressure dependent reactions

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

**Table S13 (continued)** Parameters for pressure dependent reactions

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

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

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

### S3.4 Photolysis reactions

**Table S14** Parameters for gas phase photolysis reactions

	Reaction	$I/s^{-1}$	$m$	$n$	Reference/comment
P <sub>g1</sub> <sup>⊖</sup>	$\text{Cl}_2 \xrightarrow{h\nu} 2\text{Cl}$	$3.827 \times 10^{-3}$	0.543	0.244	DeMore et al. (1997) with quantum yields from Calvert and Pitts (1966)
P <sub>g2</sub>	$\text{ClO} \xrightarrow{h\nu} \text{Cl} + \text{O}(^3\text{P})$	$4.755 \times 10^{-4}$	1.258	0.588	Sander et al. (2006) <sup>a</sup>
P <sub>g3</sub>	$\text{OCIO} \xrightarrow{h\nu} \text{ClO} + \text{O}(^3\text{P})$	0.133	0.416	0.244	Sander et al. (2006) <sup>a</sup>
P <sub>g4</sub>	$\text{Cl}_2\text{O}_2 \xrightarrow{h\nu} \text{Cl} + \text{ClO}_2$	$2.294 \times 10^{-3}$	0.745	0.223	Sander et al. (2003) <sup>a</sup>
P <sub>g5</sub>	$\text{Cl}_2\text{O}_3 \xrightarrow{h\nu} \text{ClO} + \text{OCIO}$	$1.558 \times 10^{-3}$	1.324	0.462	further products omitted, Atkinson et al. (2007) <sup>a</sup>
P <sub>g6</sub> <sup>⊖</sup>	$\text{HOCl} \xrightarrow{h\nu} \text{Cl} + \text{OH}$	$4.615 \times 10^{-4}$	0.656	0.240	Atkinson et al. (2007)
P <sub>g7</sub>	$\text{ClNO} \xrightarrow{h\nu} \text{Cl} + \text{NO}$	$4.755 \times 10^{-3}$	0.408	0.217	Atkinson et al. (2007)
P <sub>g8</sub> <sup>⊖</sup>	$\text{ClNO}_2 \xrightarrow{h\nu} \text{Cl} + \text{NO}_2$	$6.219 \times 10^{-4}$	0.774	0.255	Atkinson et al. (2007)
P <sub>g9</sub>	$\text{ClNO}_3 \xrightarrow{h\nu} \text{Cl} + \text{NO}_3$	$6.420 \times 10^{-5}$	0.648	0.217	DeMore et al. (1997)

**Table S14 (continued)** Parameters for gas phase photolysis reactions

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

**Table S14 (continued)** Parameters for gas phase photolysis reactions

	Reaction	$I/s^{-1}$	$m$	$n$	Reference/comment
P <sub>g</sub> 29	CH <sub>2</sub> BrCHO $\xrightarrow{h\nu, 2O_2}$ CH <sub>2</sub> BrO <sub>2</sub> + CO + HO <sub>2</sub>	$4.642 \times 10^{-5}$	0.762	0.353	estimated same as P <sub>g</sub> 13, Pilling et al. (2008)
P <sub>g</sub> 30	CH <sub>2</sub> BrCO <sub>3</sub> H $\xrightarrow{h\nu, O_2}$ CH <sub>2</sub> BrO <sub>2</sub> + CO <sub>2</sub> + OH	$7.649 \times 10^{-6}$	0.682	0.279	estimated same as P <sub>g</sub> 14, Pilling et al. (2008)
P <sub>g</sub> 31	CHBr <sub>3</sub> $\xrightarrow{h\nu, O_2}$ Br + CHBr <sub>2</sub> O <sub>2</sub>	$2.228 \times 10^{-6}$	1.471	0.230	DeMore et al. (1997)
P <sub>g</sub> 32	CH <sub>2</sub> Br <sub>2</sub> $\xrightarrow{h\nu, O_2}$ Br + CH <sub>2</sub> BrO <sub>2</sub>	$5.600 \times 10^{-9}$	2.763	1.922	Atkinson et al. (2008b)
P <sub>g</sub> 33	COBr <sub>2</sub> $\xrightarrow{h\nu}$ 2 Br + CO	$4.377 \times 10^{-6}$	1.360	0.273	Sander et al. (2006) products estimated same as phosgene from Pilling et al. (2008)
P <sub>g</sub> 34	CH <sub>2</sub> BrO <sub>2</sub> H $\xrightarrow{h\nu}$ CH <sub>2</sub> BrO + OH	$7.649 \times 10^{-6}$	0.682	0.279	Pilling et al. (2008)
P <sub>g</sub> 35	CHOBr $\xrightarrow{h\nu, O_2}$ Br + CO + HO <sub>2</sub>	$2.547 \times 10^{-5}$	1.393	0.361	Sander et al. (2006)
P <sub>g</sub> 36	I <sub>2</sub> $\xrightarrow{h\nu}$ 2I	0.217	0.125	0.185	Atkinson et al. (2007)
P <sub>g</sub> 37	IO $\xrightarrow{h\nu}$ I + O( <sup>3</sup> P)	$2.640 \times 10^{-3}$	0.240	0.240	Atkinson et al. (2007)
P <sub>g</sub> 38	OIO $\xrightarrow{h\nu}$ I + O <sub>2</sub>	$4.054 \times 10^{-2}$	0.119	0.185	Sander et al. (2006)
P <sub>g</sub> 39	OIO $\xrightarrow{h\nu}$ IO + O( <sup>3</sup> P)	$1.894 \times 10^{-3}$	0.119	0.185	Sander et al. (2006)
P <sub>g</sub> 40	I <sub>2</sub> O <sub>2</sub> $\xrightarrow{h\nu}$ 2I + O <sub>2</sub>	$2.294 \times 10^{-3}$	0.745	0.223	estimated same as P <sub>g</sub> 4, products from von Glasow et al. (2002a)
P <sub>g</sub> 41	HI $\xrightarrow{h\nu, O_2}$ I + HO <sub>2</sub>	$2.104 \times 10^{-4}$	1.123	0.281	Atkinson et al. (2007)
P <sub>g</sub> 42	HOI $\xrightarrow{h\nu, O_2}$ I + OH	$1.469 \times 10^{-2}$	0.342	0.236	Atkinson et al. (2007)
P <sub>g</sub> 43	INO $\xrightarrow{h\nu}$ I + NO	$4.849 \times 10^{-3}$	0.284	0.232	Sander et al. (2006)
P <sub>g</sub> 44	INO <sub>2</sub> $\xrightarrow{h\nu}$ I + NO <sub>2</sub>	$5.036 \times 10^{-3}$	0.568	0.256	Sander et al. (2006)
P <sub>g</sub> 45	INO <sub>3</sub> $\xrightarrow{h\nu}$ I + NO <sub>3</sub>	$6.599 \times 10^{-2}$	0.528	0.244	Sander et al. (2006)
P <sub>g</sub> 46	INO <sub>3</sub> $\xrightarrow{h\nu}$ IO + NO <sub>2</sub>	$1.165 \times 10^{-2}$	0.528	0.244	Sander et al. (2006)
P <sub>g</sub> 47	ICl $\xrightarrow{h\nu}$ I + Cl	$3.403 \times 10^{-2}$	0.179	0.207	Atkinson et al. (2007) <sup>b</sup>
P <sub>g</sub> 48	IBr $\xrightarrow{h\nu}$ I + Br	0.1	0.149	0.197	Atkinson et al. (2007) <sup>b</sup>
P <sub>g</sub> 49	C <sub>3</sub> H <sub>7</sub> I $\xrightarrow{h\nu, O_2}$ I + HC3P	$3.731 \times 10^{-5}$	1.292	0.217	Sander et al. (2006) <sup>b, e</sup>

**Table S14 (continued)** Parameters for gas phase photolysis reactions

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

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

<sup>a</sup>quantum yield estimated with  $\Phi = 1$ , <sup>b</sup>excited atoms are treated like atoms in ground state, <sup>c</sup>MO<sub>2</sub> = methyl peroxy radical, <sup>d</sup>ACO<sub>3</sub> = acetyl peroxy radical, <sup>e</sup>HC3P = peroxy radical formed from alkanes, alcohols, esters, and alkynes with OH rate constant (298 K, 1 atm) less than  $3.4 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ , <sup>f</sup> EHP = ethyl peroxy radical

**Table S15** Parameters for aqueous phase photolysis reactions

	Reaction	$l/s^{-1}$	$m$	$n$	Reference/comment
P <sub>a</sub> 1	$Cl_2 \xrightarrow{h\nu} 2Cl$	$2.548 \times 10^{-5}$	0.612	0.298	Zimmerman and Strong (1957) with quantum yields from Grossweiner and Matheson (1955)
P <sub>a</sub> 2	$HOCl \xrightarrow{h\nu} Cl + OH$	$2.517 \times 10^{-5}$	0.892	0.289	Zimmerman and Strong (1957) <sup>a</sup>
P <sub>a</sub> 3	$ClO^- \xrightarrow{h\nu, H_2O} Cl + OH^- + OH$	$4.205 \times 10^{-4}$	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 <sub>a</sub> 4	$Cl_3^- \xrightarrow{h\nu} Cl_2 + Cl^-$	$5.140 \times 10^{-4}$	0.843	0.103	Zimmerman and Strong (1957) <sup>a</sup>
P <sub>a</sub> 5	$Br_2 \xrightarrow{h\nu} 2 Br$	$4.501 \times 10^{-4}$	0.154	0.262	Buckles and Mills (1953) <sup>b</sup> with quantum yields from Grossweiner and Matheson (1955)
P <sub>a</sub> 6	$HOBr \xrightarrow{h\nu} Br + OH$	$1.396 \times 10^{-4}$	0.584	0.289	Anbar and Dostrovsky (1954) <sup>a</sup>
P <sub>a</sub> 7	$BrO^- \xrightarrow{h\nu, H_2O} Br + OH^- + OH$	$7.510 \times 10^{-4}$	0.548	0.300	Anbar and Dostrovsky (1954) <sup>a</sup>
P <sub>a</sub> 8	$BrCl \xrightarrow{h\nu} Br + Cl$	$6.121 \times 10^{-3}$	0.456	0.298	Pungor et al. (1959) <sup>a</sup>
P <sub>a</sub> 9	$I_2 \xrightarrow{h\nu} 2 I$	$1.816 \times 10^{-5}$	0.088	0.243	Buckles and Mills (1953) <sup>b</sup> with quantum yields from Grossweiner and Matheson (1955)
P <sub>a</sub> 10	$ICl \xrightarrow{h\nu} I + Cl$	$3.909 \times 10^{-3}$	0.130	0.239	Buckles and Mills (1953) <sup>a, b</sup>
P <sub>a</sub> 11	$IBr \xrightarrow{h\nu} I + Br$	$7.940 \times 10^{-3}$	0.108	0.250	Buckles and Mills (1954) <sup>a, b</sup>

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

<sup>a</sup>quantum yield estimated with  $\Phi = 0.1$ ; <sup>b</sup>estimated with measurement of the extinction coefficient  $\epsilon$  in the solvent carbon tetrachloride (CCl<sub>4</sub>)

### S3.5 Aqueous phase chemistry

**Table S16** Aqueous phase irreversible reactions

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

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

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

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

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

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

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

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

	Reaction	$k_{298}^a$	$E_A/R^b$	Comment	Reference
A89	$\text{Br} + \text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{Br}^- + \text{HO}_2$	$4.0 \times 10^9$			<i>Sut65</i>
A90 $\oplus$	$\text{Br}_2 + \text{HO}_2 \rightarrow \text{H}^+ + \text{Br}_2^- + \text{O}_2$	$1.1 \times 10^8$			<i>Sut/Dow72</i>
A91 $\oplus$	$\text{Br}_2 + \text{O}_2^- \rightarrow \text{Br}_2^- + \text{O}_2$	$5.6 \times 10^9$			<i>Sut/Dow72</i>
A92	$\text{Br}_2 + \text{H}_2\text{O}_2 \rightarrow 2\text{H}^+ + 2\text{Br}^- + \text{O}_2$	$1.3 \times 10^3$			<i>Wag/Str87</i>
A93	$\text{Br}_2^- + \text{OH} \rightarrow \text{Br}^- + \text{HOBr}$	$1.0 \times 10^9$			<i>Wag/Str87</i>
A94 $\otimes$	$\text{Br}_2^- + \text{OH}^- \rightarrow 2\text{Br}^- + \text{OH}$	$1.1 \times 10^4$			<i>Jac96</i>
A95 $\circ$	$\text{Br}_2^- + \text{HO}_2 \rightarrow 2\text{Br}^- + \text{H}^+ + \text{O}_2$	$4.4 \times 10^9$			<i>Mat03</i>
A96	$\text{Br}_2^- + \text{HO}_2 \xrightarrow{\text{H}^+} \text{Br}_2 + \text{H}_2\text{O}_2$	$4.4 \times 10^9$			<i>Mat03</i>
A97 $\otimes$	$\text{Br}_2^- + \text{O}_2^- \rightarrow 2\text{Br}^- + \text{O}_2$	$1.7 \times 10^8$			<i>Wag/Str87</i>
A98 $\otimes$	$\text{Br}_2^- + \text{H}_2\text{O}_2 \rightarrow 2\text{Br}^- + \text{H}^+ + \text{HO}_2$	$1.0 \times 10^5$			<i>Ree97</i>
P <sub>a</sub> 5	$\text{Br}_2 \xrightarrow{h\nu} 2\text{Br}$	$(3.46 \times 10^{-4})$		$\Phi = 0.01^{\text{Gro/Mat55}}$ ; $\epsilon$ estimated with measurement in $\text{CCl}_4$ ; see Tab. S15	<i>Buc/Mil53</i>
A99	$\text{Br}_3^- + \text{HO}_2 \rightarrow \text{Br}_2^- + \text{H}^+ + \text{Br}^- + \text{O}_2$	$1.0 \times 10^7$			<i>Sut/Dow72</i>
A100	$\text{Br}_3^- + \text{O}_2^- \rightarrow \text{Br}_2^- + \text{Br}^- + \text{O}_2$	$3.8 \times 10^9$			<i>Sut/Dow72</i>
A101 $\oplus$	$\text{BrO} + \text{BrO} \xrightarrow{\text{H}_2\text{O}} \text{BrO}_2^- + \text{BrO}^- + 2\text{H}^+$	$2.8 \times 10^9$			<i>Kla/Wol85</i>
A102 $\oplus$	$\text{BrO}_2^- + \text{BrO} \rightarrow \text{BrO}_2 + \text{BrO}^-$	$4.0 \times 10^8$			<i>Ami/Tre70</i>
A103 $\oplus$	$\text{Br}_2^- + \text{BrO}_2^- \rightarrow 2\text{Br}^- + \text{BrO}_2$	$8.0 \times 10^7$			<i>Bux/Dai68</i>
A104 $\oplus$	$\text{BrO}_2^- + \text{OH} \rightarrow \text{BrO}_2 + \text{OH}^-$	$1.8 \times 10^9$			<i>Bux/Dai68</i>
A105 $\oplus$	$\text{HOBr} + \text{OH} \rightarrow \text{BrO} + \text{H}_2\text{O}$	$2.0 \times 10^9$			<i>Kla/Wol85</i>
A106	$\text{BrO}^- + \text{OH} \rightarrow \text{BrO} + \text{OH}^-$	$4.5 \times 10^9$			<i>Bux/Dai68</i>
A107 $\oplus$	$\text{HOBr} + \text{HO}_2 \rightarrow \text{Br} + \text{H}_2\text{O} + \text{O}_2$	$1.0 \times 10^9$		estimated	<i>Sut/Dow72</i>
A108 $\oplus$	$\text{HOBr} + \text{O}_2^- \rightarrow \text{Br} + \text{OH}^- + \text{O}_2$	$3.5 \times 10^9$			<i>Schw/Bie86</i>
A109	$\text{BrO}^- + \text{O}_2^- \xrightarrow{\text{H}_2\text{O}} \text{Br} + 2\text{OH}^- + \text{O}_2$	$2.0 \times 10^8$		upper limit	<i>Schw/Bie86</i>
A110	$\text{HOBr} + \text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{Br}^- + \text{H}_2\text{O} + \text{O}_2$	$3.5 \times 10^6$			<i>You50</i>
A111	$\text{BrO}^- + \text{H}_2\text{O}_2 \rightarrow \text{Br}^- + \text{H}_2\text{O} + \text{O}_2$	$2.0 \times 10^5$		estimated	<i>Mat/Ana06</i>
P <sub>a</sub> 6	$\text{HOBr} \xrightarrow{h\nu} \text{Br} + \text{OH}$	$(1.05 \times 10^{-4})$		$\Phi = 0.1^c$ ; see Tab. S15	<i>Anb/Dos54</i>

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

	Reaction	$k_{298}^a$	$E_A/R^b$	Comment	Reference
P <sub>a</sub> 7	$\text{BrO}^- \xrightarrow{h\nu} \text{Br} + \text{OH}^- + \text{OH}$	$(5.56 \times 10^{-4})$		$\Phi = 0.1^c$ ; see Tab. S15	Anb/Dos54
A112 ⊗	$\text{Br}_2^- + \text{HSO}_3^- \rightarrow 2\text{Br}^- + \text{H}^+ + \text{SO}_3^-$	$5.0 \times 10^7$	780		Jac96
A113 ⊗	$\text{Br}_2^- + \text{SO}_3^{2-} \rightarrow 2\text{Br}^- + \text{SO}_3^-$	$3.3 \times 10^7$	650		Jac96
A114 ⊗	$\text{Br}^- + \text{SO}_4^- \rightarrow \text{Br} + \text{SO}_4^{2-}$	$2.1 \times 10^9$			Her97
A115	$\text{HOBr} + \text{SO}_3^{2-} \rightarrow \text{Br}^- + \text{HSO}_4^-$	$5.0 \times 10^9$			Tro/Mar91
A116 ⊕	$\text{HOBr} + \text{HSO}_3^- \rightarrow \text{H}^+ + \text{Br}^- + \text{HSO}_4^-$	$5.0 \times 10^9$		estimated ( $k_{\text{A116}} \approx k_{\text{A115}}$ )	Fog89
A117	$\text{Br}^- + \text{HSO}_5^- \rightarrow \text{HOBr} + \text{SO}_4^{2-}$	1.0	5338		For60
A118 ⊗	$\text{Br}_2^- + \text{CH}_2\text{OHHSO}_3^- \rightarrow 2\text{Br}^- + \text{CH}_2\text{OHHSO}_3$	$5.0 \times 10^4$		estimated ( $k_{\text{A118}} \approx 0.1 \cdot k_{\text{A28}}$ )	
A119 ⊗	$\text{Br}^- + \text{NO}_3 \rightarrow \text{Br} + \text{NO}_3^-$	$3.8 \times 10^9$			Zel96
A120 ⊗	$\text{Br}_2^- + \text{NO}_2^- \rightarrow 2\text{Br}^- + \text{NO}_2$	$1.2 \times 10^7$	1720		Jac96
A121 ⊗	$\text{Br}^- + \text{NO}_2^+ \rightarrow \text{BrNO}_2$	$1.0 \times 10^{10}$			Geo99
A122 ⊗	$\text{Br}^- + \text{BrNO}_2 \rightarrow \text{Br}_2 + \text{NO}_2^-$	$2.55 \times 10^4$			Geo99
A123 ⊗	$\text{Br}_2^- + \text{Fe}^{2+} \rightarrow 2\text{Br}^- + \text{Fe}^{3+}$	$3.6 \times 10^6$	3330		Tho/Lau73
A124 ⊗	$\text{MnBr}_2^+ \rightarrow 2\text{Br}^- + \text{Mn}^{3+}$	$2.2 \times 10^5$			Tho/Lau73
A125 ⊗	$\text{Br}_2^- + \text{Mn}^{2+} \rightarrow \text{MnBr}_2^+$	$6.3 \times 10^6$	4330		Tho/Lau73
A126 ⊗	$\text{MnBr}_2^+ \rightarrow \text{Br}_2^- + \text{Mn}^{2+}$	$3.0 \times 10^5$			Tho/Lau73
A127 ⊗	$\text{Br}_2^- + \text{Cu}^+ \rightarrow 2\text{Br}^- + \text{Cu}^{2+}$	$3.6 \times 10^6$		estimated ( $k_{\text{A127}} \approx k_{\text{A123}}$ )	
A128	$\text{Br} + \text{HCO}_3^- \rightarrow \text{H}^+ + \text{Br}^- + \text{CO}_3^-$	$1.0 \times 10^6$		estimated	Mat/Ana06
A129	$\text{Br}_2^- + \text{CO}_3^{2-} \rightarrow 2\text{Br}^- + \text{CO}_3^-$	$1.1 \times 10^5$			Hui91
A130 ⊗	$\text{Br}_2^- + \text{HCO}_3^- \rightarrow 2\text{Br}^- + \text{H}^+ + \text{CO}_3^-$	$1.1 \times 10^5$		estimated	
A131	$\text{Br}_2^- + \text{Cl}_2^- \rightarrow \text{Br}_2 + 2\text{Cl}^-$	$4.0 \times 10^9$		estimated	Mat/Ana06
A132 ⊕	$\text{Br}^- + \text{HOCl} \xrightarrow{\text{H}^+} \text{BrCl} + \text{H}_2\text{O}$	$1.3 \times 10^6$			Kum/Mar87
A133	$\text{Br}^- + \text{ClO}^- \xrightarrow{\text{H}^+} \text{BrCl} + \text{OH}^-$	$3.65 \times 10^{10}$			Kum/Mar87
A134 ⊗	$\text{Br}^- + \text{ClNO}_2 \rightarrow \text{BrCl} + \text{NO}_2^-$	$5.0 \times 10^6$			Geo99
A135 ⊗	$\text{BrNO}_2 + \text{Cl}^- \rightarrow \text{BrCl} + \text{NO}_2^-$	10			Geo99
P <sub>a</sub> 8	$\text{BrCl} \xrightarrow{h\nu} \text{Br} + \text{Cl}$	$(4.54 \times 10^{-3})$		$\Phi = 0.1^c$ ; see Tab. S15	Pun59

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

	Reaction	$k_{298}^a$	$E_A/R^b$	Comment	Reference
A136	$\text{Br}_2^- + \text{CH}_3\text{OOH} \rightarrow 2\text{Br}^- + \text{H}^+ + \text{CH}_3\text{OO}$	$1.0 \times 10^5$		estimated ( $k_{\text{A136}} \approx k_{\text{A98}}$ )	
A137	$\text{Br} + \text{CH}_3\text{OH} \rightarrow \text{H}^+ + \text{Br}^- + \text{CH}_2\text{OH}$	$4.1 \times 10^4$	3368		Par06
A138	$\text{Br}_2^- + \text{CH}_3\text{OH} \rightarrow 2\text{Br}^- + \text{H}^+ + \text{CH}_2\text{OH}$	$1.0 \times 10^3$			Rec97
A139	$\text{Br} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{H}^+ + \text{Br}^- + \text{CH}_3\text{CHOH}$	$8.2 \times 10^5$	2285		Par06
A140	$\text{Br}_2^- + \text{C}_2\text{H}_5\text{OH} \rightarrow 2\text{Br}^- + \text{H}^+ + \text{CH}_3\text{CHOH}$	$3.8 \times 10^3$			Rec99
A141	$\text{Br} + \text{C}_3\text{H}_7\text{OH} \rightarrow \text{H}^+ + \text{Br}^- + \text{C}_2\text{H}_5\text{CHOH}$	$3.8 \times 10^5$	1564		Par06
A142	$\text{Br} + \text{CH}_3\text{CHOHCH}_3 \rightarrow$ $\text{H}^+ + \text{Br}^- + \text{CH}_3\text{COHCH}_3$	$1.8 \times 10^6$	3127		Par06
A143	$\text{Br} + \text{CH}_2(\text{OH})_2 \rightarrow \text{H}^+ + \text{Br}^- + \text{CH}(\text{OH})_2$	$3.0 \times 10^5$	3608	hydration calculated from $K$ with $\sim 1$	Par06
A144	$\text{Br}_2^- + \text{CH}_2(\text{OH})_2 \rightarrow 2\text{Br}^- + \text{H}^+ + \text{CH}(\text{OH})_2$	$3.0 \times 10^3$		estimated	
A145	$\text{Br} + \text{CH}_3\text{CHO} \rightarrow \text{H}^+ + \text{Br}^- + \text{CH}_3\text{CO}$	$1.75 \times 10^7$	1804		Par06
A146	$\text{Br} + \text{CH}_3\text{CH}(\text{OH}_2) \rightarrow$ $\text{H}^+ + \text{Br}^- + \text{CH}_3\text{C}(\text{OH}_2)$	$1.75 \times 10^7$	1804	hydration calculated from $K$ with 1:1	Par06
A147	$\text{Br}_2^- + \text{CH}_3\text{CHO} \rightarrow 2\text{Br}^- + \text{H}^+ + \text{CH}_3\text{CO}$	$2.15 \times 10^5$	2526		Par06
A148	$\text{Br}_2^- + \text{CH}_3\text{CH}(\text{OH})_2 \rightarrow$ $2\text{Br}^- + \text{H}^+ + \text{CH}_3\text{C}(\text{OH})_2$	$2.15 \times 10^5$	2526		Par06
A149	$\text{Br} + \text{C}_2\text{H}_5\text{CHO} \rightarrow \text{H}^+ + \text{Br}^- + \text{C}_2\text{H}_5\text{CO}$	$2.85 \times 10^7$	842		Par06
A150	$\text{Br} + \text{C}_2\text{H}_5\text{CH}(\text{OH}_2) \rightarrow$ $\text{H}^+ + \text{Br}^- + \text{C}_2\text{H}_5\text{C}(\text{OH}_2)$	$2.85 \times 10^7$	842	hydration calculated from $K$ with 1:1	Par06
A151	$\text{Br}_2^- + \text{C}_2\text{H}_5\text{CHO} \rightarrow 2\text{Br}^- + \text{H}^+ + \text{C}_2\text{H}_5\text{CO}$	$4.95 \times 10^5$	3614		Par06
A152	$\text{Br}_2^- + \text{C}_2\text{H}_5\text{CH}(\text{OH}_2) \rightarrow$ $2\text{Br}^- + \text{H}^+ + \text{C}_2\text{H}_5\text{C}(\text{OH}_2)$	$4.95 \times 10^5$	3614		Par06
A153	$\text{Br} + \text{C}_3\text{H}_7\text{CHO} \rightarrow \text{H}^+ + \text{Br}^- + \text{C}_3\text{H}_7\text{CO}$	$6.67 \times 10^7$	1203	hydration calculated from $K$ with 2:1	Par06
A154	$\text{Br} + \text{C}_3\text{H}_7\text{CH}(\text{OH}_2) \rightarrow$ $\text{H}^+ + \text{Br}^- + \text{C}_3\text{H}_7\text{C}(\text{OH}_2)$	$3.33 \times 10^7$	1203	(unhydrated/hydrated)	Par06
A155	$\text{Br}_2^- + \text{C}_3\text{H}_7\text{CHO} \rightarrow 2\text{Br}^- + \text{H}^+ + \text{C}_3\text{H}_7\text{CO}$	$2.6 \times 10^5$	2289		Par06
A156	$\text{Br}_2^- + \text{C}_3\text{H}_7\text{CH}(\text{OH}_2) \rightarrow$ $2\text{Br}^- + \text{H}^+ + \text{C}_3\text{H}_7\text{C}(\text{OH}_2)$	$1.3 \times 10^5$	2289		Par06

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

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

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

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

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

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

<sup>⊗</sup>already implemented in CAPRAM; <sup>⊙</sup>update of CAPRAM; <sup>⊕</sup>already implemented in the Halogen Module 1.0

<sup>a</sup>in  $\text{M}^{-1} \text{s}^{-1}$ ; <sup>b</sup>in K; <sup>c</sup>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 $\otimes$	$\text{Cl} + \text{Cl}^- \rightleftharpoons \text{Cl}_2^-$	$1.4 \times 10^5$	$8.5 \times 10^9$		<i>Bux98</i>	$6.0 \times 10^4$		<i>Bux98</i>	
E2	$\text{Cl}_2 + \text{Cl}^- \rightleftharpoons \text{Cl}_3^-$	0.18	$2.0 \times 10^4$		<i>Ers04</i>	$1.1 \times 10^5$		<i>Ers04</i>	
E3 $\otimes$ <sub>d</sub>	$\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons$ $\text{H}^+ + \text{Cl}^- + \text{HOCl}$	$1.9 \times 10^{-5} e^{-4500/T}$	0.4	8000	<i>Wan/Mar94</i>	$2.1 \times 10^4$	3500	<i>Wan/Mar94</i>	<i>e</i>
E4 $\otimes$	$\text{HCl} \rightleftharpoons \text{H}^+ + \text{Cl}^-$	$1.72 \times 10^6$	$5.0 \times 10^{11}$	-6890	<i>Mar/Elr85</i>	$2.9 \times 10^5$		<i>Gra/Wes81</i>	<i>f</i>
E5 $\oplus$	$\text{HOCl} \rightleftharpoons \text{H}^+ + \text{ClO}^-$	$3.0 \times 10^{-8}$	$1.5 \times 10^3$		<i>Atk96</i>	$5.0 \times 10^{10}$			<i>g, h</i>
E6 $\otimes$	$\text{Cl}^- + \text{OH} \rightleftharpoons \text{ClOH}^-$	0.7	$4.3 \times 10^9$		<i>Jay73</i>	$6.1 \times 10^9$		<i>Jay73</i>	
E7	$\text{Cl} + \text{OH}^- \rightleftharpoons \text{ClOH}^-$	$7.83 \times 10^8$	$1.8 \times 10^{10}$		<i>Kla/Wol85</i>	23		<i>Kla/Wol85</i>	
E8 $\otimes$	$\text{ClOH}^- + \text{H}^+ \rightleftharpoons \text{Cl} + \text{H}_2\text{O}$	$5.1 \times 10^6$	$2.1 \times 10^{10}$		<i>Jay73</i>	$4.1 \times 10^3$		<i>Jacs97</i>	
E9 $\otimes$	$\text{ClOH}^- + \text{Cl}^- \rightleftharpoons \text{Cl}_2^- + \text{OH}^-$	$2.2 \times 10^{-4}$	$1.0 \times 10^4$		<i>Gri87</i>	$4.5 \times 10^7$		<i>Gri87</i>	
E10 $\otimes$	$\text{Cl}^- + \text{SO}_4^- \rightleftharpoons \text{Cl} + \text{SO}_4^{2-}$	1.2	$2.52 \times 10^8$		<i>Bux99a</i>	$2.1 \times 10^8$		<i>Bux99a</i>	
E11 $\otimes$	$\text{Cl}^- + \text{NO}_3 \rightleftharpoons \text{Cl} + \text{NO}_3^-$	3.4	$3.4 \times 10^8$	4300	<i>Bux99b</i>	$1.0 \times 10^8$		<i>Bux99b</i>	
E12 $\otimes$	$\text{Cl}^- + \text{Fe}^{3+} \rightleftharpoons \text{FeCl}^{2+}$	1.39	$3.0 \times 10^3$		<i>Mar/Sil64</i>	$2.16 \times 10^3$			
E13	$\text{CH}_2\text{ClCO}_3 + \text{H}_2\text{O} \rightleftharpoons$ $\text{CH}_2\text{ClC}(\text{OH})_2\text{O}_2$	367	$1.1 \times 10^7$			$3.0 \times 10^4$			<i>i</i>
E14	$\text{CH}_2\text{ClCOOH} \rightleftharpoons$ $\text{CH}_2\text{ClCOO}^- + \text{H}^+$	$1.75 \times 10^{-5}$	$8.75 \times 10^5$	-46		$5.0 \times 10^{10}$			<i>i</i>
E15 $\otimes$	$\text{Br} + \text{Br}^- \rightleftharpoons \text{Br}_2^-$	$6.32 \times 10^5$	$1.2 \times 10^{10}$		<i>Mer/Lin94</i>	$1.9 \times 10^4$		<i>Mer/Lin94</i>	
E16	$\text{Br}_2 + \text{Br}^- \rightleftharpoons \text{Br}_3^-$	17.5	$9.6 \times 10^8$		<i>Ers04</i>	$5.5 \times 10^7$		<i>Ers04</i>	
E17 $\otimes$ $\oplus$	$\text{Br}_2 + \text{H}_2\text{O} \rightleftharpoons$ $\text{H}^+ + \text{Br}^- + \text{HOBr}$	$1.06 \times 10^{-10}$	1.7	7500	<i>Bec96</i>	$1.6 \times 10^{10}$		<i>Bec96</i>	<i>d</i>
E18 $\oplus$	$\text{HBr} \rightleftharpoons \text{H}^+ + \text{Br}^-$	$1.0 \times 10^9$	$5.0 \times 10^{11}$		<i>Atk96</i>	$5.0 \times 10^2$			<i>j, k, l</i>
E19 $\oplus$	$\text{HOBr} \rightleftharpoons \text{H}^+ + \text{BrO}^-$	$2.0 \times 10^{-9}$	100		<i>Atk96</i>	$5.0 \times 10^{10}$			<i>g, h</i>
E20 $\otimes$	$\text{Br}^- + \text{OH} \rightleftharpoons \text{BrOH}^-$	333	$1.1 \times 10^{10}$		<i>Zeh/Rab72</i>	$3.3 \times 10^7$		<i>Zeh/Rab72</i>	
E21 $\otimes$ <sub>d</sub>	$\text{Br} + \text{OH}^- \rightleftharpoons \text{BrOH}^-$	$3.1 \times 10^3$	$1.3 \times 10^{10}$		<i>Kla/Wol85</i>	$4.2 \times 10^6$		<i>Zeh/Rab72</i>	
E22 $\otimes$	$\text{BrOH}^- + \text{H}^+ \rightleftharpoons \text{Br} + \text{H}_2\text{O}$	$1.8 \times 10^{12}$	$4.4 \times 10^{10}$		<i>Zeh/Rab72</i>	$2.45 \times 10^{-2}$		<i>Kla/Wol85</i>	
E23 $\otimes$	$\text{BrOH}^- + \text{Br}^- \rightleftharpoons \text{Br}_2^- + \text{OH}^-$	70	$1.9 \times 10^8$		<i>Zeh/Rab72</i>	$2.7 \times 10^6$		<i>Vio81</i>	

**Table S17 (continued)** Aqueous phase equilibria

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

**Table S17 (continued)** Aqueous phase equilibria

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

**Table S17 (continued)** Aqueous phase equilibria

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

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

<sup>a</sup>in  $\text{M}^{\text{m}-\text{n}}$ , n order of reaction of forward reaction, m order of reaction of backward reaction; <sup>b</sup>in  $\text{M}^{-1} \text{s}^{-1}$ ; <sup>c</sup>in K; <sup>d</sup>now implemented as equilibrium in CAPRAM; <sup>e</sup>correction of CAPRAM value; <sup>f</sup> $k_f$  = speed of hydrogen bond breaking in water; <sup>g</sup> $k_f$  calculated based on  $K$ ; <sup>h</sup> $k_b$  estimated; <sup>i</sup>estimated X = H (X = Cl, Br, I) <sup>j</sup>diffusion controlled; <sup>k</sup> $k_b$  calculated based on  $K$ ; <sup>l</sup> $k_f$  estimated; <sup>m</sup>upper limit; <sup>n</sup> $K$  estimated

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

## S4 Estimation of rate constants of reactions with lumped species

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

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

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

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

$x_i$  . . . . . fraction of the individual species to the overall model species

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

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

Reactant	$k^a$	Reference	Fraction <sup>b</sup>
<b>HC3</b>			
C <sub>3</sub> H <sub>8</sub>	$1.40 \times 10^{-10}$	Atkinson et al. (2006)	0.029
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	$2.05 \times 10^{-10}$	Atkinson et al. (2006)	0.443
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	$1.43 \times 10^{-10}$	Atkinson et al. (2006)	0.012
CH <sub>3</sub> C(CH <sub>3</sub> ) <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	$1.71 \times 10^{-10}$	Pilling et al. (2008)	<0.001
C <sub>2</sub> H <sub>2</sub>	$k_0 = 6.1 \times 10^{-30}$ $\times (T/300)^{-3} [\text{N}_2]$ $k_\infty = 2.0 \times 10^{-10}$	Atkinson et al. (2006)	0.095
CH <sub>3</sub> OH	$5.5 \times 10^{-11}$	Atkinson et al. (2006)	0.007
C <sub>2</sub> H <sub>5</sub> OH	$8.6 \times 10^{-11} e^{45/T}$	Atkinson et al. (2006)	0.345
<b>HC5</b>			
<i>i</i> -C <sub>5</sub> H <sub>12</sub>	$2.2 \times 10^{-10}$	Atkinson et al. (2008a)	0.192
<i>n</i> -C <sub>6</sub> H <sub>14</sub>	$3.4 \times 10^{-10}$	Pilling et al. (2008)	0.109
<i>n</i> -C <sub>5</sub> H <sub>12</sub>	$2.8 \times 10^{-10}$	Atkinson et al. (2008a)	0.108
(CH <sub>3</sub> ) <sub>2</sub> CHC <sub>3</sub> H <sub>7</sub>	$2.9 \times 10^{-10}$	Pilling et al. (2008)	0.051
CH <sub>3</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub>	$2.8 \times 10^{-10}$	Pilling et al. (2008)	0.032
CH <sub>3</sub> CH(CH <sub>3</sub> )CH(CH <sub>3</sub> )CH <sub>3</sub>	$2.3 \times 10^{-10}$	Pilling et al. (2008)	0.020
<i>i</i> -C <sub>3</sub> H <sub>7</sub> OH	$8.6 \times 10^{-11}$	Atkinson et al. (2007)	0.307
<i>n</i> -C <sub>3</sub> H <sub>7</sub> OH	$1.6 \times 10^{-11} e^{-130/T}$	Atkinson et al. (2007)	<0.001
<b>HC8</b>			
<i>n</i> -C <sub>7</sub> H <sub>16</sub>	$3.9 \times 10^{-10}$	Pilling et al. (2008)	0.129
C <sub>7</sub> H <sub>16</sub>	$4.95 \times 10^{-10}$	estimation with data of Atkinson et al. (2008a)	0.098
<i>n</i> -C <sub>8</sub> H <sub>18</sub>	$4.6 \times 10^{-10}$	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 <sup>b</sup>
C <sub>2</sub> H <sub>5</sub> CH(CH <sub>3</sub> )C <sub>3</sub> H <sub>7</sub>	$3.11 \times 10^{-10}$	Pilling et al. (2008)	0.024
<i>n</i> -C <sub>11</sub> H <sub>24</sub>	$6.17 \times 10^{-10}$	Pilling et al. (2008)	0.023
C <sub>6</sub> H <sub>12</sub>	$3.5 \times 10^{-10}$	Pilling et al. (2008)	0.020
<i>n</i> -C <sub>9</sub> H <sub>20</sub>	$4.8 \times 10^{-10}$	Pilling et al. (2008)	0.012
<i>n</i> -C <sub>10</sub> H <sub>22</sub>	$5.55 \times 10^{-10}$	Pilling et al. (2008)	0.008
<i>n</i> -C <sub>12</sub> H <sub>26</sub>	$6.74 \times 10^{-10}$	Pilling et al. (2008)	0.008
<b>TOL</b>			
C <sub>6</sub> H <sub>6</sub>	$1.3 \times 10^{-15}$	Shi and Bernhard (1997)	0.100
CH <sub>3</sub> C <sub>6</sub> H <sub>6</sub>	$5.9 \times 10^{-11}$	Shi and Bernhard (1997)	0.690

<sup>a</sup>in cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup>, <sup>b</sup>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 <sup>b</sup>
HC3	$1.41 \times 10^{-10} e^{13/T}$	0.93
HC5	$2.14 \times 10^{-10}$	0.82
HC8	$4.38 \times 10^{-10}$	0.33
TOL	$5.15 \times 10^{-11}$	0.79

<sup>a</sup>in cm<sup>3</sup> molecules<sup>-1</sup> s<sup>-1</sup>, <sup>b</sup>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<sub>2</sub> and Br<sub>2</sub> by Schwartz (1986) and the one of HCl by Marsh and McElroy (1985).

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

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

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

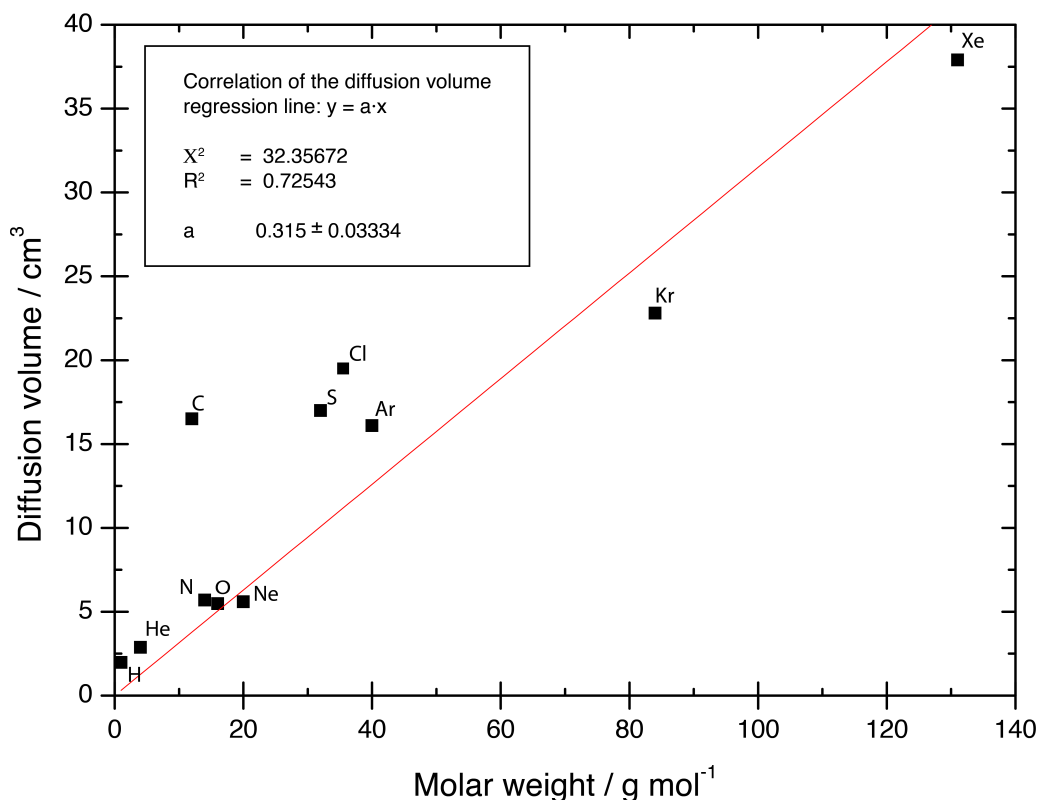
The FSG method provides values for the diffusion volumes of compounds containing C, N, S, O, H, and Cl atoms. Diffusion volumes of molecules can be calculated by summing up the individual diffusion volumes of atoms part of that molecule. Furthermore, the method provides values for diffusion volumes of simple molecules such as  $\text{Cl}_2$  and  $\text{Br}_2$ .

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  $\text{Br}_2$  with whom it is possible to estimate the diffusion volume of Br atoms. Therefore, the diffusion volume of  $\text{Br}_2$  was scaled by the ratio of the diffusion volumes of atomic and molecular chlorine  $\text{Cl}_2/\text{Cl}$  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  $40 \text{ cm}^3$  could be calculated for I atoms.



**Figure S11** Estimation of diffusion volumes.

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