

Supplementary online material

**Bromine and iodine in a global chemistry-climate  
model: Description, very short-lived oceanic  
sources and evaluation**

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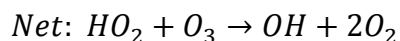
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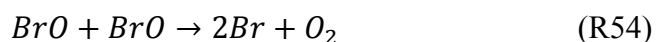
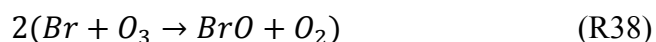
## Chemistry of VSL halogen species in CAM-Chem

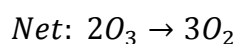
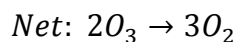
An introduction to the tropospheric halogen chemistry scheme in CAM-Chem is given in Section 3 of the main text. That section also describes the breakdown of very short-lived (VSL) halocarbons into their products. Here we focus on the main gas phase reactions involving reactive bromine and iodine in the model, in particular those which are relevant for tropospheric ozone ( $O_3$ ) depletion. We will also briefly summarise other processes of importance for the troposphere, following the review by von Glasow and Crutzen (2007). The bimolecular, termolecular and photolytic reactions involving halogen species in the model are summarised in Tables 1, 2 and 3, respectively. Information on heterogeneous reactions, Henry's Law constants and dry deposition velocities of halogen species is included in Tables 4, 5 and 6, respectively. In the following, X represents Cl, Br or I. If two halogen species are present in the same reaction then we use X and Y to design both of them.

In addition to the photochemical breakdown of halocarbons, halogen radicals (X, Y) can be formed in the troposphere by the photolysis of dihalogens ( $X_2$  or  $XY$ ) or other inorganic halogen species like HOX (Table 3). They react with  $O_3$  producing halogen oxides (XO). If these oxides photolyse, both  $O_3$  and the halogen radical X are formed again; however they can also undergo chemical reactions that lead to net  $O_3$  destruction. One of the main  $O_3$  destruction paths includes the reaction of XO with  $HO_2$ , which is also responsible for reducing the  $HO_x$  ( $HO_2/OH$ ) ratio:

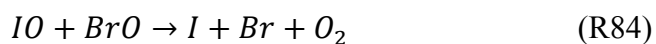
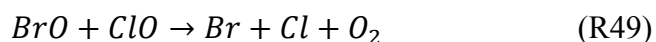


BrO and IO self-reactions are also of importance for tropospheric ozone destruction:





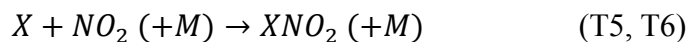
When two halogen oxides are present in the troposphere, cross reactions such as



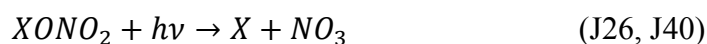
can make  $\text{O}_3$  destruction very efficient. Photochemical box model calculations of observations in coastal Antarctica (Saiz-Lopez et al., 2007) and the tropical Atlantic Ocean (Read et al., 2008) have shown that the effect of IO and BrO together is greater than the sum of their individual contributions, because the reaction  $\text{IO} + \text{BrO}$  increases the rate at which the halogen oxides are converted back to I and Br atoms. Other reaction paths for the  $\text{BrO} + \text{ClO}$  reaction produce  $\text{OClO}$  (R48) and  $\text{BrCl}$  (R50), while an additional channel of the  $\text{IO} + \text{BrO}$  reaction yields  $\text{OIO}$  (R85).

In very clean air ( $\text{NO}_x < 30$  ppt), the gas-phase chemistry of IO is dominated by the reactions of IO with itself to form  $\text{I}_2\text{O}_2$  and  $\text{OIO} + \text{I}$ ,  $\text{IO} + \text{OIO}$  to form  $\text{I}_2\text{O}_3$ , and  $\text{OIO} + \text{OIO}$  to form  $\text{I}_2\text{O}_4$  (Table 1). These reactions proceed rapidly in the gas phase, with rate coefficients of  $\sim 10^{10}$ – $10^{11}$ . In the current version of CAM-Chem we do not include the formation of gas phase  $\text{I}_2\text{O}_5$  through oxidation of  $\text{I}_2\text{O}_4$  by  $\text{O}_3$ . We also assume that, with the only exception of the very rapid thermal decomposition of  $\text{I}_2\text{O}_2$  (R73 and R74),  $\text{I}_2\text{O}_x$  ( $x=2, 3, 4$ ) do not undergo photolysis or other reactions which would reduce them to IO or OIO. Hence, the rapid conversion of IO and OIO into higher order iodine oxides limits the atmospheric lifetime of both radicals in the model. 1-D model calculations strongly suggest that the photolysis of  $\text{I}_2\text{O}_2$ ,  $\text{I}_2\text{O}_3$ ,  $\text{I}_2\text{O}_4$  and  $\text{I}_2\text{O}_5$  would be required to explain the vertical distribution of IO in the Antarctic boundary layer (Saiz-Lopez et al., 2008). However further laboratory work on the photochemistry of these species is needed.

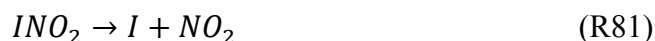
The formation of halogen nitrates and nitrites can be important in semi-polluted environments:



Depending on conditions, these species can either photolyse



thermally decompose



undergo oxidation (see Table 1) or react on surfaces (Table 4). Some of these reactions can also lead to O<sub>3</sub> depletion.

Sea salt is also an important source of reactive bromine and iodine in the troposphere. Typical diameters of sea salt particles are > 0.1 μm, which limits their relevance to the marine boundary layer due to fast removal by sedimentation and wet scavenging. In CAM-Chem, the heterogeneous recycling of halogens on sea salt aerosols is treated as follows. The uptake and subsequent hydrolysis of XONO<sub>2</sub>, HOX and XNO<sub>2</sub> on marine aerosols produces HOX, which equilibrates between gas and aqueous phase according to its Henry's law solubility. The processing of aqueous HOX to Br<sub>2</sub>, BrCl, IBr, ICl and Cl<sub>2</sub> via reaction with Br<sup>-</sup>, Cl<sup>-</sup> and I<sup>-</sup> takes only between 10 and 15 min on fresh sea-salt aerosols (McFiggans et al., 2000). Since di-halogen molecules are insoluble they are rapidly released to the gas phase. As a consequence, uptake of inorganic bromine and iodine species onto aerosols is the rate-limiting step of the process (McFiggans et al., 2000). Aged sea-salt aerosols become depleted in Br<sup>-</sup> and Cl<sup>-</sup> thus slowing down the halogen recycling on aerosols (e.g. Fickert et al., 1999; von Glasow et al., 2002). Additionally, aged particles become progressively acidified by uptake of HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and SO<sub>2</sub>, which in turn increases the rate of processing. In CAM-Chem we do not explicitly treat the aqueous phase chemistry in the bulk of the sea salt aerosols. Instead, we assume that the limiting step for halogen recycling on sea salt aerosols is the first-

order rate of uptake computed for a number of gaseous species using the free molecular transfer regime approximation (see Table 4). CAM-Chem simulations indicate that heterogeneous processing of bromine on sea-salt aerosol is needed to reproduce the observed BrO in the marine boundary layer, but the full description of all the processes which release halogens from sea-salt aerosols is out of the scope of this paper. Note that the photochemical processing of bromocarbons provides the main source of mid- and upper tropospheric reactive bromine due to their longer lifetimes relative to those of most inorganic bromine species, as already pointed out by Yang et al. (2005) and Warwick et al. (2006).

The halogen species removed in CAM-Chem by washout and scavenging in clouds are listed in Table 5 together with the corresponding Henry Law's coefficients. In addition, dry deposition to the surface occurs from the lowermost level of the model for the following reactive halogen species: HCl, HBr, HOCl, ClONO<sub>2</sub>, HOBr, BrONO<sub>2</sub>, HI, I<sub>2</sub>O<sub>2</sub>, HOI, IONO<sub>2</sub>, INO<sub>2</sub> (see Table 6 of the Supplementary Material). The deposition flux of each gaseous species is calculated as the product of the deposition velocity and the concentration.

**Table 1.** Halogen chemistry scheme in CAM-Chem. Bimolecular and thermal decomposition reactions.

Reactions		Rate Constants ( $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ )	Notes
R1.	$\text{CH}_3\text{Cl} + \text{Cl} \rightarrow \text{HO}_2 + \text{CO} + 2\text{HCl}$	$3.20 \times 10^{-11} e^{(-1250/T)}$	1
R2.	$\text{CH}_3\text{Cl} + \text{OH} \rightarrow \text{Cl} + \text{H}_2\text{O} + \text{HO}_2$	$2.40 \times 10^{-12} e^{(-1250/T)}$	2
R3.	$\text{CH}_3\text{CCl}_3 + \text{OH} \rightarrow \text{H}_2\text{O} + 3\text{Cl}$	$1.60 \times 10^{-12} e^{(-1520/T)}$	1
R4.	$\text{HCFC22} + \text{OH} \rightarrow \text{Cl} + \text{H}_2\text{O} + \text{CF}_2\text{O}$	$4.00 \times 10^{-12} e^{(-1400/T)}$	1
R5.	$\text{CH}_3\text{Br} + \text{OH} \rightarrow \text{Br} + \text{H}_2\text{O} + \text{HO}_2$	$2.35 \times 10^{-12} e^{(-1300/T)}$	2
R6.	$\text{CH}_2\text{BrCl} + \text{OH} \rightarrow \text{Br} + \text{Cl}$	$2.40 \times 10^{-12} e^{(-920/T)}$	2
R7.	$\text{CH}_2\text{Br}_2 + \text{OH} \rightarrow 2\text{Br}$	$2.00 \times 10^{-12} e^{(-840/T)}$	2
R8.	$\text{CHBr}_3 + \text{OH} \rightarrow 3\text{Br}$	$1.35 \times 10^{-12} e^{(-600/T)}$	2
R9.	$\text{CHBrCl}_2 + \text{OH} \rightarrow \text{Br} + 2\text{Cl}$	$9.00 \times 10^{-13} e^{(-600/T)}$	3
R10.	$\text{CHBr}_2\text{Cl} + \text{OH} \rightarrow 2\text{Br} + \text{Cl}$	$9.00 \times 10^{-13} e^{(-600/T)}$	3
R11.	$\text{OH} + \text{CH}_3\text{I} \rightarrow \text{CH}_2\text{I} + \text{H}_2\text{O}$	$2.9 \times 10^{-12} e^{(-1100/T)}$	2
R12.	$\text{OH} + \text{CF}_3\text{I} \rightarrow \text{HOI} + \text{CF}_3$	$2.5 \times 10^{-11} e^{(-2070/T)}$	2
R13.	$\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$	$2.30 \times 10^{-11} e^{(-200/T)}$	1
R14.	$\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$	$3.70 \times 10^{-11} e^{(-2300/T)}$	1
R15.	$\text{Cl} + \text{H}_2\text{O}_2 \rightarrow \text{HCl} + \text{HO}_2$	$1.10 \times 10^{-11} e^{(-980/T)}$	1
R16.	$\text{Cl} + \text{HO}_2 \rightarrow \text{HCl} + \text{O}_2$	$1.80 \times 10^{-11} e^{(170/T)}$	1
R17.	$\text{Cl} + \text{HO}_2 \rightarrow \text{OH} + \text{ClO}$	$4.10 \times 10^{-11} e^{(-450/T)}$	1
R18.	$\text{Cl} + \text{HCHO} \rightarrow \text{HCl} + \text{HO}_2 + \text{CO}$	$8.10 \times 10^{-11} e^{(-30/T)}$	1
R19.	$\text{Cl} + \text{CH}_4 \rightarrow \text{CH}_3\text{O}_2 + \text{HCl}$	$9.60 \times 10^{-12} e^{(-1360/T)}$	1
R20.	$\text{ClO} + \text{O}(^3\text{P}) \rightarrow \text{Cl} + \text{O}_2$	$3.00 \times 10^{-11} e^{(+70/T)}$	1
R21.	$\text{ClO} + \text{OH} \rightarrow \text{Cl} + \text{HO}_2$	$7.40 \times 10^{-12} e^{(270/T)}$	1
R22.	$\text{ClO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2$	$6.0 \times 10^{-13} e^{(230/T)}$	1
R23.	$\text{ClO} + \text{HO}_2 \rightarrow \text{O}_2 + \text{HOCl}$	$2.7 \times 10^{-12} e^{(220/T)}$	1
R24.	$\text{ClO} + \text{NO} \rightarrow \text{NO}_2 + \text{Cl}$	$6.40 \times 10^{-12} e^{(290/T)}$	1
R25.	$\text{ClO} + \text{ClO} \rightarrow 2\text{Cl} + \text{O}_2$	$3.00 \times 10^{-11} e^{(-2450/T)}$	1
R26.	$\text{ClO} + \text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2$	$1.00 \times 10^{-12} e^{(-1590/T)}$	1
R27.	$\text{ClO} + \text{ClO} \rightarrow \text{Cl} + \text{OClO}$	$3.50 \times 10^{-13} e^{(-1370/T)}$	1
R28.	$\text{HCl} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{Cl}$	$2.60 \times 10^{-12} e^{(-350/T)}$	1
R29.	$\text{HCl} + \text{O}(^3\text{P}) \rightarrow \text{Cl} + \text{OH}$	$1.00 \times 10^{-11} e^{(-3300/T)}$	1
R30.	$\text{HOCl} + \text{O}(^3\text{P}) \rightarrow \text{ClO} + \text{OH}$	$1.70 \times 10^{-13}$	1
R31.	$\text{HOCl} + \text{Cl} \rightarrow \text{HCl} + \text{ClO}$	$2.50 \times 10^{-12} e^{(-130/T)}$	1
R32.	$\text{HOCl} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{ClO}$	$3.00 \times 10^{-12} e^{(-500/T)}$	1
R33.	$\text{ClONO}_2 + \text{O}(^3\text{P}) \rightarrow \text{ClO} + \text{NO}_3$	$2.90 \times 10^{-12} e^{(-800/T)}$	1
R34.	$\text{ClONO}_2 + \text{OH} \rightarrow \text{HOCl} + \text{NO}_3$	$1.20 \times 10^{-12} e^{(-330/T)}$	1
R35.	$\text{ClONO}_2 + \text{Cl} \rightarrow \text{Cl}_2 + \text{NO}_3$	$6.50 \times 10^{-12} e^{(135/T)}$	1
R36.	$\text{ClNO}_2 + \text{OH} \rightarrow \text{HOCl} + \text{NO}_2$	$2.40 \times 10^{-12} e^{(-1250/T)}$	1
R37.	$\text{Cl}_2 + \text{OH} \rightarrow \text{HOCl} + \text{Cl}$	$1.4 \times 10^{-12} e^{(-900/T)}$	1
R38.	$\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2$	$1.7 \times 10^{-11} e^{(-800/T)}$	1
R39.	$\text{Br} + \text{HO}_2 \rightarrow \text{HBr} + \text{O}_2$	$1.5 \times 10^{-11} e^{(-600/T)}$	1
R40.	$\text{Br} + \text{HCHO} \rightarrow \text{HBr} + \text{HO}_2 + \text{CO}$	$1.7 \times 10^{-11} e^{(-800/T)}$	2
R41.	$\text{Br} + \text{CH}_3\text{CHO} \rightarrow \text{HBr} + \text{CH}_3\text{CO}_3$	$1.3 \times 10^{-11} e^{(-360/T)}$	11
R42.	$\text{Br} + \text{NO}_3 \rightarrow \text{BrO} + \text{NO}_2$	$1.6 \times 10^{-11}$	2
R43.	$\text{Br} + \text{OH} \rightarrow \text{HOBr}$	$4.2 \times 10^{-11}$	11

R44.	$\text{BrO} + \text{O}({}^3\text{P}) \rightarrow \text{Br} + \text{O}_2$	$1.9 \times 10^{-11} e^{(230/T)}$	1
R45.	$\text{BrO} + \text{OH} \rightarrow \text{Br} + \text{HO}_2$	$7.5 \times 10^{-11}$	1
R46.	$\text{BrO} + \text{HO}_2 \rightarrow \text{HOBr} + \text{O}_2$	$3.4 \times 10^{-12} e^{(540/T)}$	1
R47.	$\text{BrO} + \text{NO} \rightarrow \text{Br} + \text{NO}_2$	$8.8 \times 10^{-12} e^{(260/T)}$	2
R48.	$\text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{OCIO}$	$9.5 \times 10^{-13} e^{(550/T)}$	2
R49.	$\text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{Cl} + \text{O}_2$	$2.3 \times 10^{-12} e^{(260/T)}$	2
R50.	$\text{BrO} + \text{ClO} \rightarrow \text{BrCl} + \text{O}_2$	$4.1 \times 10^{-13} e^{(290/T)}$	2
R51.	$\text{BrO} + \text{CH}_3\text{O}_2 \rightarrow \text{Br} + \text{HCHO} + \text{HO}_2$	$1.6 \times 10^{-12}$	4
R52.	$\text{BrO} + \text{CH}_3\text{O}_2 \rightarrow \text{HOBr} + \text{HCHO}$	$4.1 \times 10^{-12}$	4
R53.	$\text{BrO} + \text{CH}_3\text{CO}_3 \rightarrow \text{Br} + \text{CH}_3\text{O}_2$	$1.7 \times 10^{-12}$	11
R54.	$\text{BrO} + \text{BrO} \rightarrow 2\text{Br} + \text{O}_2$	$1.5 \times 10^{-12} e^{(230/T)}$	2
R55.	$\text{HBr} + \text{OH} \rightarrow \text{Br} + \text{H}_2\text{O}$	$5.5 \times 10^{-12} e^{(200/T)}$	2
R56.	$\text{HBr} + \text{O}({}^3\text{P}) \rightarrow \text{OH} + \text{Br}$	$5.8 \times 10^{-12} e^{(-1500/T)}$	1
R57.	$\text{HBr} + \text{O}({}^1\text{D}) \rightarrow 0.2\text{O} + 0.2\text{HBr} + 0.8\text{OH} + 0.8\text{Br}$	$1.5 \times 10^{-10}$	2
R58.	$\text{Br}_2 + \text{OH} \rightarrow \text{HOBr} + \text{Br}$	$2.1 \times 10^{-11} e^{(240/T)}$	1
R59.	$\text{BrONO}_2 + \text{O}({}^3\text{P}) \rightarrow \text{BrO} + \text{NO}_3$	$1.91 \times 10^{-11} e^{(215/T)}$	1
R60.	$\text{BrONO}_2 + \text{Br} \rightarrow \text{Br}_2 + \text{NO}_3$	$1.78 \times 10^{-11} e^{(365/T)}$	5
R61.	$\text{BrONO}_2 + \text{Cl} \rightarrow \text{BrCl} + \text{NO}_3$	$6.28 \times 10^{-11} e^{(215/T)}$	5
R62.	$\text{BrO} + \text{DMS} \rightarrow \text{Br} + \text{DMSO}$	$1.4 \times 10^{-14} e^{(950/T)}$	2
R63.	$\text{I}_2 + \text{O}_3 \rightarrow \text{IO} + \text{I} + \text{O}_2$	$3.8 \times 10^{-18}$	5
R64.	$\text{I}_2 + \text{O}_3 \rightarrow \text{OIO} + \text{IO}$	$3.8 \times 10^{-18}$	5
R65.	$\text{I} + \text{O}_3 \rightarrow \text{IO} + \text{O}_2$	$2.1 \times 10^{-11} e^{(-830/T)}$	6
R66.	$\text{I} + \text{HO}_2 \rightarrow \text{HI} + \text{O}_2$	$1.5 \times 10^{-11} e^{(-1090/T)}$	2
R67.	$\text{IO} + \text{NO} \rightarrow \text{I} + \text{NO}_2$	$7.15 \times 10^{-12} e^{(300/T)}$	6
R68.	$\text{IO} + \text{HO}_2 \rightarrow \text{HOI} + \text{O}_2$	$1.4 \times 10^{-11} e^{(540/T)}$	6
R69.	$\text{IO} + \text{IO} \rightarrow \text{OIO} + \text{I}$	$1.6 \times 10^{-11} e^{(180/T)}$	6
R70.	$\text{IO} + \text{IO} \rightarrow \text{I}_2\text{O}_2$	$3.7 \times 10^{-11} e^{(180/T)}$	6
R71.	$\text{IO} + \text{OIO} \rightarrow \text{I}_2\text{O}_3$	$5.0 \times 10^{-11}$	7
R72.	$\text{OIO} + \text{OIO} \rightarrow \text{I}_2\text{O}_4$	$1.5 \times 10^{-10}$	7
R73.	$\text{I}_2\text{O}_2 \rightarrow \text{OIO} + \text{I}$	$2.5 \times 10^{14} e^{(-9770/T)}$	8
R74.	$\text{I}_2\text{O}_2 \rightarrow \text{IO} + \text{IO}$	$1 \times 10^{12} e^{(-9770/T)}$	8
R75.	$\text{I}_2 + \text{OH} \rightarrow \text{HOI} + \text{I}$	$1.8 \times 10^{-10}$	2
R76.	$\text{I}_2 + \text{NO}_3 \rightarrow \text{I} + \text{INO}_2$	$1.5 \times 10^{-12}$	6
R77.	$\text{I} + \text{NO}_3 \rightarrow \text{IO} + \text{NO}_2$	$4.5 \times 10^{-10}$	9
R78.	$\text{OH} + \text{HI} \rightarrow \text{I} + \text{H}_2\text{O}$	$3.0 \times 10^{-11}$	2
R79.	$\text{HOI} + \text{OH} \rightarrow \text{IO} + \text{H}_2\text{O}$	$2.0 \times 10^{-13}$	10
R80.	$\text{IO} + \text{DMS} \rightarrow \text{DMSO} + \text{I}$	$1.2 \times 10^{-14}$	2
R81.	$\text{INO}_2 \rightarrow \text{I} + \text{NO}_2$	$(2.4 / 0.005) \times 2.07 \times 10^{15} e^{(-11859/T)}$	10
R82.	$\text{INO} + \text{INO} \rightarrow \text{I}_2 + 2\text{NO}$	$8.4 \times 10^{-11} e^{(-2620/T)}$	2
R83.	$\text{INO}_2 + \text{INO}_2 \rightarrow \text{I}_2 + 2\text{NO}_2$	$2.9 \times 10^{-11} e^{(-2600/T)}$	2
R84.	$\text{IO} + \text{BrO} \rightarrow \text{Br} + \text{I} + \text{O}_2$	$0.30 \times 10^{-11} e^{(510/T)}$	6
R85.	$\text{IO} + \text{BrO} \rightarrow \text{Br} + \text{OIO}$	$1.20 \times 10^{-11} e^{(510/T)}$	6
R86.	$\text{I} + \text{BrO} \rightarrow \text{IO} + \text{Br}$	$1.2 \times 10^{-11}$	2
R87.	$\text{IO} + \text{ClO} \rightarrow \text{I} + \text{OCIO}$	$5.1 \times 10^{-12} e^{(280/T)}$	2

<sup>1</sup> JPL 02-25 (Sander et al., 2003); <sup>2</sup> JPL 06-02 (Sander et al., 2006); <sup>3</sup> estimated (see main text of the paper); <sup>4</sup> Aranda et al. (1997); <sup>5</sup> NIST (2010); <sup>6</sup> Atkinson et al. (2007b); <sup>7</sup> Gómez Martín et al. (2007); <sup>8</sup> calculated using RRKM theory; <sup>9</sup> Chambers et al. (1992); <sup>10</sup> McFiggans et al. (2000); <sup>11</sup> Estimated.

**Table 2.** Halogen chemistry scheme in CAM-Chem. Termolecular reactions.

Termolecular reactions	$k = (k_0 [M] / (1 + k_0 [M] / k_\infty)) \times F_c^n$ $n = \{1 + (\log_{10}(k_0 [M] / k_\infty))^2\}^{-1}$ $F_c = 0.6$
T1. ClO + NO <sub>2</sub> (+ M) → ClONO <sub>2</sub> (+ M)	$k_0 = 1.8 \times 10^{-31} \times (T / 300)^{-3.4}$ $k_\infty = 1.5 \times 10^{-11} \times (T / 300)^{-1.9}$
T2. Cl + NO <sub>2</sub> (+ M) → ClNO <sub>2</sub> (+ M)	$k_0 = 1.8 \times 10^{-31} \times (T / 300)^{-2}$ $k_\infty = 1.0 \times 10^{-10} \times (T / 300)^{-1}$
T3. ClO + ClO (+ M) → Cl <sub>2</sub> O <sub>2</sub> (+ M)	$k_0 = 1.6 \times 10^{-32} \times (T / 300)^{-4.5}$ $k_\infty = 2.0 \times 10^{-12} \times (T / 300)^{-2.4}$
T4. BrO + NO <sub>2</sub> (+ M) → BrONO <sub>2</sub> (+ M)	$k_0 = 5.2 \times 10^{-31} \times (T / 300)^{-3.2}$ $k_\infty = 6.9 \times 10^{-12} \times (T / 300)^{-2.9}$
T5. Br + NO <sub>2</sub> (+ M) → BrNO <sub>2</sub> (+ M)	$k_0 = 4.2 \times 10^{-31} \times (T / 300)^{-2.4}$ $k_\infty = 2.7 \times 10^{-11}$
T6. I + NO <sub>2</sub> (+ M) → INO <sub>2</sub> (+ M)	$k_0 = 3 \times 10^{-31} \times (T / 300)^{-1}$ $k_\infty = 6.6 \times 10^{-11}$
T7. IO + NO <sub>2</sub> (+ M) → IONO <sub>2</sub> (+ M)	$k_0 = 6.5 \times 10^{-31} \times (T / 300)^{-3.5}$ $k_\infty = 7.6 \times 10^{-12} \times (T / 300)^{-1.5}$
T8. I + NO (+ M) → INO (+ M)	$k_0 = 1.8 \times 10^{-32} \times (T / 300)^{-1}$ $k_\infty = 1.7 \times 10^{-11}$
T9. Cl <sub>2</sub> O <sub>2</sub> + M → ClO + ClO + M	$K_{T9} = K_{T3} / [9.3 \times 10^{-28} \times e^{(8835/T)}]$

$k_0$  is given in cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>

$k_\infty$  is given in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>

All expressions taken from JPL 06-02 (Sander et al., 2006).



**Table 3.** Photochemical reactions for halogen species in CAM-Chem.

Photochemical reactions of halogen species	
J1.	$\text{CH}_3\text{Cl} + h\nu \rightarrow \text{Cl} + \text{CH}_3\text{O}_2$
J2.	$\text{CCl}_4 + h\nu \rightarrow 4\text{Cl}$
J3.	$\text{CH}_3\text{CCl}_3 + h\nu \rightarrow 3\text{Cl}$
J4.	$\text{CFC11} + h\nu \rightarrow 3\text{Cl}$
J5.	$\text{CFC12} + h\nu \rightarrow 2\text{Cl}$
J6.	$\text{CFC113} + h\nu \rightarrow 3\text{Cl}$
J7.	$\text{HCFC22} + h\nu \rightarrow \text{Cl}$
J8.	$\text{Cl}_2 + h\nu \rightarrow 2\text{Cl}$
J9.	$\text{OCIO} + h\nu \rightarrow \text{O} + \text{ClO}$
J10.	$\text{Cl}_2\text{O}_2 + h\nu \rightarrow 2\text{Cl}$
J11.	$\text{HOCl} + h\nu \rightarrow \text{OH} + \text{Cl}$
J12.	$\text{HCl} + h\nu \rightarrow \text{H} + \text{Cl}$
J13.	$\text{ClONO}_2 + h\nu \rightarrow \text{Cl} + \text{NO}_3$
J14.	$\text{ClONO}_2 + h\nu \rightarrow \text{ClO} + \text{NO}_2$
J15.	$\text{CH}_3\text{Br} + h\nu \rightarrow \text{Br} + \text{CH}_3\text{O}_2$
J16.	$\text{CF}_3\text{Br} + h\nu \rightarrow \text{Br}$
J17.	$\text{CF}_2\text{ClBr} + h\nu \rightarrow \text{Br} + \text{Cl}$
J18.	$\text{CHBr}_3 + h\nu \rightarrow 3\text{Br}$
J19.	$\text{CH}_2\text{Br}_2 + h\nu \rightarrow 2\text{Br}$
J20.	$\text{CH}_2\text{BrCl} + h\nu \rightarrow \text{Br} + \text{Cl}$
J21.	$\text{CHBr}_2\text{Cl} + h\nu \rightarrow 2\text{Br} + \text{Cl}$
J22.	$\text{CHBrCl}_2 + h\nu \rightarrow \text{Br} + 2\text{Cl}$
J23.	$\text{BrCl} + h\nu \rightarrow \text{Br} + \text{Cl}$
J24.	$\text{BrO} + h\nu \rightarrow \text{Br} + \text{O}$
J25.	$\text{HOBr} + h\nu \rightarrow \text{Br} + \text{OH}$
J26.	$\text{BrONO}_2 + h\nu \rightarrow \text{Br} + \text{NO}_3$
J27.	$\text{BrONO}_2 + h\nu \rightarrow \text{BrO} + \text{NO}_2$
J28.	$\text{BrNO}_2 + h\nu \rightarrow \text{Br} + \text{NO}_2$
J29.	$\text{BrNO}_2 + h\nu \rightarrow \text{BrO} + \text{NO}$
J30.	$\text{CH}_3\text{I} + h\nu \rightarrow \text{CH}_3 + \text{I}$
J31.	$\text{CH}_2\text{I}_2 + h\nu \rightarrow \text{CH}_2 + 2\text{I}$
J32.	$\text{CH}_2\text{IBr} + h\nu \rightarrow \text{CH}_2\text{Br} + \text{I}$
J33.	$\text{CH}_2\text{ICl} + h\nu \rightarrow \text{CH}_2\text{Cl} + \text{I}$
J34.	$\text{I}_2 + h\nu \rightarrow 2\text{I}$
J35.	$\text{IO} + h\nu \rightarrow \text{I} + \text{O}$
J36.	$\text{OIO} + h\nu \rightarrow \text{I} + \text{O}_2$
J37.	$\text{INO} + h\nu \rightarrow \text{I} + \text{NO}$
J38.	$\text{INO}_2 + h\nu \rightarrow \text{I} + \text{NO}_2$
J39.	$\text{INO}_2 + h\nu \rightarrow \text{IO} + \text{NO}$
J40.	$\text{IONO}_2 + h\nu \rightarrow \text{I} + \text{NO}_3$
J41.	$\text{HOI} + h\nu \rightarrow \text{I} + \text{OH}$
J42.	$\text{IBr} + h\nu \rightarrow \text{I} + \text{Br}$
J43.	$\text{ICl} + h\nu \rightarrow \text{I} + \text{Cl}$

Photolysis rates are computed online from absorption cross-sections and quantum yields reported in Atkinson et al. (2000, 2007a) and JPL 06-02 (Sander et al., 2006), and the actinic flux calculation in CAM-Chem.

**Table 4.** Heterogeneous reactions involving halogens in CAM-Chem.

Reactions		Comments
Sulfate aerosol reactions		
H1.	$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3$	*
H2.	$\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HNO}_3$	*
H3.	$\text{BrONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOBr} + \text{HNO}_3$	*
H4.	$\text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3$	*
H5.	$\text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$	*
H6.	$\text{HOBr} + \text{HCl} \rightarrow \text{BrCl} + \text{H}_2\text{O}$	*
Nitric acid tri-hydrate reactions		
H7.	$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3$	*
H8.	$\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HNO}_3$	*
H9.	$\text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3$	*
H10.	$\text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$	*
H11.	$\text{BrONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOBr} + \text{HNO}_3$	*
Water-ice aerosol reactions		
H12.	$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3$	*
H13.	$\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HNO}_3$	*
H14.	$\text{BrONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOBr} + \text{HNO}_3$	*
H15.	$\text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3$	*
H16.	$\text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$	*
H17.	$\text{HOBr} + \text{HCl} \rightarrow \text{BrCl} + \text{H}_2\text{O}$	*
Sea-salt aerosol reactions		
HSS0.	$\text{BrONO}_2 \rightarrow 0.65 \text{ Br}_2 + 0.35 \text{ BrCl}$	$\gamma = 0.08$
HSS1.	$\text{BrNO}_2 \rightarrow 0.65 \text{ Br}_2 + 0.35 \text{ BrCl}$	$\gamma = 0.04$
HSS2.	$\text{HOBr} \rightarrow 0.65 \text{ Br}_2 + 0.35 \text{ BrCl}$	$\gamma = 0.1$
HSS3.	$\text{ClONO}_2 \rightarrow \text{Cl}_2$	$\gamma = 0.02$
HSS4.	$\text{ClNO}_2 \rightarrow \text{Cl}_2$	$\gamma = 0.02$
HSS5.	$\text{HOCl} \rightarrow \text{Cl}_2$	$\gamma = 0.1$
HSS6.	$\text{IONO}_2 \rightarrow 0.5 \text{ IBr} + 0.5 \text{ ICl}$	$\gamma = 0.01$
HSS7.	$\text{INO}_2 \rightarrow 0.5 \text{ IBr} + 0.5 \text{ ICl}$	$\gamma = 0.02$
HSS8.	$\text{HOI} \rightarrow 0.5 \text{ IBr} + 0.5 \text{ ICl}$	$\gamma = 0.06$

(\*) As in Table A4 from Auxiliary Material in Kinnison et al. (2007)

Following McFiggans et al. (2000) we applied the free molecular transfer approximation for the uptake of gas-phase halogen species on sea-salt aerosols. That is, the transfer coefficient ( $s^{-1}$ ) is given by

$$K = \frac{\gamma}{4} \langle c \rangle A$$

where  $\gamma$  is the uptake coefficient,  $\langle c \rangle$  is the root-mean-square molecular speed, and  $A$  is the total available sea-salt surface area density ( $\text{cm}^2/\text{cm}^3$ ).  $\langle c \rangle$  is given by:

$$\langle c \rangle = 100 \sqrt{\frac{8 R T}{\pi M}}$$

with  $R = 8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $T$  is the temperature and  $M$  the molecular mass of the species (in  $\text{Kg mol}^{-1}$ ). The factor 100 converts to  $\text{cm s}^{-1}$ .

**Table 5.** Henry's Law constants for relevant halogen species in CAM-Chem.

Species	$k_0$ (M atm <sup>-1</sup> )	c (K)	Reference
ClONO <sub>2</sub>	$1.0 \times 10^6$		1, a
BrONO <sub>2</sub>	$1.0 \times 10^6$		1, a
HCl	$1.9 \times 10^1$	9000	1, b
HOCl	$9.3 \times 10^2$		1, b
HOBr	$1.9 \times 10^3$		1, c
HBr	$7.2 \times 10^{-1}$	6100	1, b
BrCl	$7.0 \times 10^{-2}$	4000	3
IBr	$2.4 \times 10^1$		1
ICl	$1.1 \times 10^2$		1
BrNO <sub>2</sub>	$3.0 \times 10^{-1}$		1
ClNO <sub>2</sub>	$4.0 \times 10^{-2}$		1, c
HI	$2.5 \times 10^1$	9800	3
HOI	$4.5 \times 10^2$		2

Temperature dependent Henry's law constants are calculated as:

$$k_H = k_0 \times \exp \left[ c \left( \frac{1}{T} - \frac{1}{T_0} \right) \right]$$

where

$$\begin{aligned} k_0 &= \text{value of } k_H \text{ at standard conditions} \\ T_0 &= 298.15 \text{ K} \end{aligned}$$

<sup>1</sup> Sander (1999)

<sup>a</sup> Virtually infinite solubility is represented in the model using a very large but arbitrary number.

<sup>b</sup> Other values are also reported in the corresponding reference.

<sup>c</sup> Within the range of values given in the corresponding reference.

<sup>2</sup> Chemical mechanism of MECCA (Sander et al., 2011).

<sup>3</sup> Estimated.

**Table 6.** Dry deposition velocities of relevant halogen species in CAM-Chem.

<b>Species</b>	<b>Deposition velocity (cm s<sup>-1</sup>)</b>
HCl, HBr	2.00
HOCl, ClONO <sub>2</sub>	1.00
HOBr	1.60
BrONO <sub>2</sub>	0.50
HI	1.00
I <sub>2</sub> O <sub>2</sub>	1.00
HOI, IONO <sub>2</sub> , INO <sub>2</sub>	0.75

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