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Supplement of

Halogen chemistry in volcanic plumes: a 1D framework based on MOCAGE 1D (version R1.18.1) preparing 3D global chemistry modelling

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S1 Halogen chemical mechanism in MOCAGE

The halogen reactions used in MOCAGE-1D model are detailed in this section. They come from the stratospheric scheme REPROBUS (Lefèvre et al., 1994) completed with additional reactions (noted in red colour) to represent tropospheric halogen gaseous and the heterogeneous reactions relevant for the bromine explosion cycle. For the gaseous reactions, those involving halogen long-lived species are not given here since they are only of interest for stratospheric chemistry. Heterogeneous reactions that only apply in the stratosphere are not listed here.

S1.1 Photolysis

Photolysis rates over the wavelength range 121-750 nm are taken into account using a multi-entry look-up table computed off-line with the TUV software version 4.6 (Madronich, 1987). Photolysis rates depend on month (including monthly aerosol climatologies), solar zenith angle, ozone column above each cell from C-IFS-MOCAGE at every timestep, altitude and surface albedo in the UV. The photolysis reactions represented in MOCAGE are :

$$BrCl + h\nu \rightarrow Br + Cl$$
$$BrO + h\nu \rightarrow Br + O(^3P)$$
$$HOBr + h\nu \rightarrow Br + OH$$
$$BrONO_2 + h\nu \rightarrow Br + NO_3$$
$$\textcolor{red}{Br_2 + h\nu \rightarrow 2Br}$$
$$OClO + h\nu \rightarrow ClO + O(^3P)$$
$$HOCl + h\nu \rightarrow Cl + OH$$
$$ClNO_2 + h\nu \rightarrow Cl + NO_2$$
$$ClONO_2 + h\nu \rightarrow ClO + NO_2$$
$$Cl_2 + h\nu \rightarrow 2Cl$$
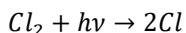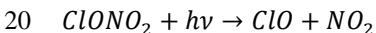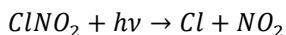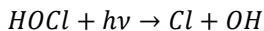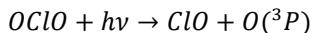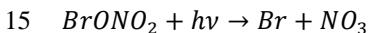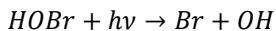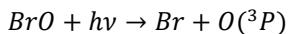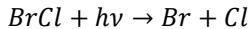
S1.2 Gaseous reactions

Table S1 : List of gaseous reactions for bromine and chlorine in MOCAGE except those involving halogen long-lived species since they are only of interest for stratospheric chemistry. Reactions in red colour are those that have been added to MOCAGE original scheme. The main references are JPL2015 (Burkholder et al. 2015) and IUPAC (http://iupac.pole-ether.fr: Atkinson et al., 2004, 2006, 2007, 2008; Crowley et al., 2010; Ammann et al., 2013).

Reaction	Rate constant	Reference
$HBr + OH \rightarrow Br + H_2O$	$5.5\ 10^{-12} \times e^{\frac{200}{T}}$	JPL2015
$HBr + O(^1D) \rightarrow Br + OH$	$1.5\ 10^{-10}$	JPL2015
$Br + O_3 \rightarrow BrO + O_2$	$1.6\ 10^{-11} \times e^{\frac{-780}{T}}$	JPL2015
$Br + HO_2 \rightarrow HBr + O_2$	$4.8\ 10^{-12} \times e^{\frac{-310}{T}}$	JPL2015
$BrO + HO_2 \rightarrow HOBr + O_2$	$4.5\ 10^{-12} \times e^{\frac{460}{T}}$	JPL2015
$BrO + OH \rightarrow Br + HO_2$	$1.7\ 10^{-11} \times e^{\frac{250}{T}}$	JPL2015
$BrO + NO_2 \rightarrow BrONO_2$	$\dfrac{k_0}{1 + \frac{k_0}{k_\infty}} \times 0.6^{\left(1 + \left(log_{10}(\frac{k_0}{k_\infty})\right)^2\right)^{-1}}$ $k_0 = 5.4 \times 10^{-31} \left(\frac{T}{300}\right)^{-3.1} [M]$ $k_\infty = 6.5 \times 10^{-12} \left(\frac{T}{300}\right)^{-2.9}$	JPL2015
$BrO + NO \rightarrow Br + NO_2$	$8.8\ 10^{-12} \times e^{\frac{260}{T}}$	JPL2015
$BrO + BrO \rightarrow 2Br + O_2$	$1.5\ 10^{-12} \times e^{\frac{230}{T}}$	JPL2015
$BrO + BrO \rightarrow Br_2 + O_2$	$2.8\ 10^{-14} \times e^{\frac{860}{T}}$	JPL2015
$BrO + O(^3P) \rightarrow Br + O_2$	$1.9\ 10^{-11} \times e^{\frac{230}{T}}$	JPL2015
$HOBr + O(^3P) \rightarrow BrO + OH$	$1.2\ 10^{-10} \times e^{\frac{-430}{T}}$	JPL2015
$BrONO_2 \rightarrow BrO + NO_2$	$2.8\ 10^{13} \times e^{\frac{-12360}{T}}$	Orlando and Tyndall (1996)
$Br_2 + OH \rightarrow HOBr + Br$	$1.9\ 10^{-11} \times e^{\frac{240}{T}}$	IUPAC
$Br + HCHO \rightarrow HBr + HO_2 + CO$	$1.7\ 10^{-11} \times e^{\frac{-800}{T}}$	JPL2015
$Br + CH_3OOH \rightarrow HBr + CH_3O_2$	$2.66\ 10^{-12} \times e^{\frac{-1610}{T}}$	von Glasow et al. (2004)

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Reaction	Rate	Reference
$BrO + CH_3O_2 \rightarrow 0.72HOBr + 0.28Br + 0.28HO_2 + HCHO$	$5.7\ 10^{-12}$	von Glasow et al. (2004)
$BrO + ClO \rightarrow Br + OClO$	$9.5\ 10^{-13} \times e^{\frac{550}{T}}$	JPL2015
$BrO + ClO \rightarrow Br + Cl + O_2$	$2.3\ 10^{-12} \times e^{\frac{260}{T}}$	JPL2015
$BrO + ClO \rightarrow BrCl + O_2$	$4.1\ 10^{-13} \times e^{\frac{290}{T}}$	JPL2015
$HCl + OH \rightarrow Cl + H_2O$	$1.8\ 10^{-12} \times e^{\frac{-250}{T}}$	JPL2015
$Cl + O_3 \rightarrow ClO + O_2$	$2.3\ 10^{-11} \times e^{\frac{-200}{T}}$	JPL2015
$Cl + HO_2 \rightarrow HCl + O_2$	$1.4\ 10^{-11} \times e^{\frac{270}{T}}$	JPL2015
$Cl + HO_2 \rightarrow ClO + OH$	$3.6\ 10^{-11} \times e^{\frac{-375}{T}}$	JPL2015
$Cl + H_2O_2 \rightarrow HCl + HO_2$	$1.1\ 10^{-11} \times e^{\frac{-980}{T}}$	IUPAC
$Cl + H_2 \rightarrow HCl + H$	$3.05\ 10^{-11} \times e^{\frac{-2270}{T}}$	JPL2015
$Cl + NO_2 \rightarrow ClNO_2$	$\frac{k_O}{1+\frac{k_O}{k_\infty}} \times 0.6^{\left(1+\left(log_{10}\left(\frac{k_0}{k_\infty}\right)\right)^2\right)^{-1}}$ $k_0 = 1.8 \times 10^{-31}\left(\frac{T}{300}\right)^{-2.0}[M]$ $k_\infty = 1.0 \times 10^{-10}\left(\frac{T}{300}\right)^{-1.0}$	JPL2015
$ClO + O(^3P) \rightarrow Cl + O_2$	$2.8\ 10^{-11} \times e^{\frac{85}{T}}$	JPL2015
$ClO + NO \rightarrow Cl + NO_2$	$6.4\ 10^{-12} \times e^{\frac{290}{T}}$	JPL2015
$ClO + NO_2 \rightarrow ClONO_2$	$\frac{k_O}{1+\frac{k_O}{k_\infty}} \times 0.6^{\left(1+\left(log_{10}\left(\frac{k_0}{k_\infty}\right)\right)^2\right)^{-1}}$ $k_0 = 1.8 \times 10^{-31}\left(\frac{T}{300}\right)^{-3.4}[M]$ $k_\infty = 1.5 \times 10^{-11}\left(\frac{T}{300}\right)^{-1.9}$	JPL2015
$ClO + OH \rightarrow Cl + HO_2$	$7.4\ 10^{-12} \times e^{\frac{270}{T}}$	JPL2015
$ClO + OH \rightarrow HCl + O_2$	$6.0\ 10^{-13} \times e^{\frac{230}{T}}$	JPL2015
$ClO + HO_2 \rightarrow HOCl + O_2$	$2.6\ 10^{-12} \times e^{\frac{290}{T}}$	JPL2015

Reaction	Rate	Reference
$ClO + ClO \rightarrow Cl_2O_2$	$\dfrac{k_0}{1 + \dfrac{k_0}{k_\infty}} \times 0.6^{\left(1 + \left(log_{10}\left(\frac{k_0}{k_\infty}\right)\right)^2\right)^{-1}}$ $k_0 = 1.9 \times 10^{-32} \left(\dfrac{T}{300}\right)^{-3.6} [M]$ $k_\infty = 3.7 \times 10^{-12} \left(\dfrac{T}{300}\right)^{-1.6}$	JPL2015
$Cl_2O_2 \rightarrow 2ClO$	$\left(\dfrac{1}{A_{eq}}\right) \times e^{\left(\frac{-B_{eq}}{T}\right)} \times k_{ClO+ClO}$ $A_{eq} = 2.16 \times 10^{-27}$ $B_{eq} = 8537$ $k_{ClO+ClO}$	JPL2015
$ClO + ClO \rightarrow Cl_2 + O_2$	$1.0 \ 10^{-12} \times e^{\frac{-1590}{T}}$	JPL2015
$ClO + ClO \rightarrow OClO + Cl$	$3.5 \ 10^{-13} \times e^{\frac{-1370}{T}}$	JPL2015
$HOCl + OH \rightarrow ClO + H_2O$	$3.0 \ 10^{-12} \times e^{\frac{-500}{T}}$	JPL2015
$HOCl + O(^3P) \rightarrow ClO + OH$	$1.7 \ 10^{-13}$	JPL2015
$HOCl + Cl \rightarrow Cl_2 + OH$	$3.4 \ 10^{-12} \times e^{\frac{-130}{T}}$	JPL2015
$ClONO_2 + O(^3P) \rightarrow ClO + NO_3$	$3.6 \ 10^{-12} \times e^{\frac{-840}{T}}$	JPL2015
$Cl + HCHO \rightarrow HCl + HO_2 + CO$	$8.1 \ 10^{-11} \times e^{\frac{-30}{T}}$	JPL2015
$Cl + CH_4 \rightarrow HCl + CH_3$	$7.1 \ 10^{-12} \times e^{\frac{-1270}{T}}$	JPL2015
$Cl + C_2H_6 \rightarrow HCl + C_2H_5O_2$	$7.05 \ 10^{-11} \times e^{\frac{-60}{T}}$	IUPAC
$Cl + CH_3O_2 + 0.5O_2$ $\rightarrow 0.5ClO + 0.5HCl$ $+ 0.5HCHO + 0.5HO_2$ $+ 0.5CO + 0.5H_2O$	$1.6 \ 10^{-10}$	IUPAC (reaction chanel 1)
$ClO + CH_3O_2 \rightarrow Cl + CH_3O + O_2$	$1.8 \ 10^{-12} \times e^{\frac{-600}{T}}$	JPL2015

S1.3 Heterogeneous reactions

35   The three following halogen heterogeneous reactions have been included in MOCAGE-1D as they play an important role in the bromine explosion process.

$$HOBr + HBr(sulphate\ aerosol) \rightarrow Br_2 + H_2O \qquad \text{(R1)}$$
$$HOBr + HCl(sulphate\ aerosol) \rightarrow BrCl + H_2O \qquad \text{(R2)}$$
$$BrONO_2 + H_2O(sulphate\ aerosol) \rightarrow HOBr + HNO_3 \qquad \text{(R3)}$$
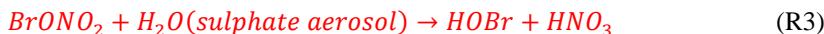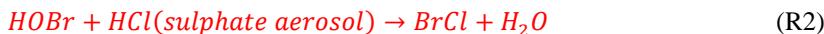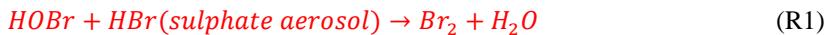
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The notation "$HBr(sulphate\ aerosol)$" (resp. "$HCl(sulphate\ aerosol)$") means that HOBr reacts heterogeneously with HBr (resp. HCl) in the volcanic sulphate aerosols. Note that, as in Jourdain et al. (2016), we do not include in MOCAGE heterogeneous reactions with HOCl and ClONO$_2$ since their rates are much lower than those with HOBr and BrONO$_2$ (Roberts et al. 2009).

45   The general expression for the heterogeneous rate constant is given by:

$$k = \gamma \cdot \frac{C_{rel}}{4} \cdot S_{aerosol} \qquad \text{(S1)}$$

Where the γ parameter is the uptake coefficient that is defined for each heterogeneous reaction. We use the same γ values as in Roberts et al. (2009) and Jourdain et al. (2016): 0.2 for (R1) and (R2) and 0.8 for (R3). C_{rel} is the average velocity of the gaseous species (cm s^{-1}) described by the following equation. $C_{rel} = \sqrt{\frac{8RT}{\pi M}}$ with R gas constant, T is the temperature and M is

50   the molar weight. $S_{aerosol}$ is the surface area (aerosols surface.cm^{-3} of air) of the aerosols.

The aerosols are assumed to have a spherical shape with a surface given by:

$$S_{aerosol} = 4 \cdot \pi \cdot R_{eff}^2 \cdot N_{DROP} \qquad \text{(S2)}$$

where R_{eff} is the effective aerosol radius (mean surface area-weighted radius) in cm. R_{eff} represents the total surface area of the aerosol size distribution. In (S2), N_{DROP} is the number of droplets by unit of volume that is calculated from:

55    $$N_{DROP} = \frac{3 \cdot V_{aerosol}}{4 \cdot \pi \cdot R_{eff}^3} \qquad \text{(S3)}$$

$V_{aerosol}$ is the aerosol volume (per cm^3 of air). For this study, it is assumed that the sulphate aerosols are composed of only two species: H$_2$O and H$_2$SO$_4$ in aqueous phase. The ratio of sulphuric acid to H$_2$O inside the aerosol droplet is the sulphuric acid weight fraction W_S. $V_{aerosol}$ is calculated from the sulphuric acid concentrations, W_S and $\rho_{aerosol}$ the density of aerosols. As in Jourdain et al. (2016), we use the method presented in Tabazadeh et al. (1997) to determine W_S and $\rho_{aerosol}$ which vary

60   with the relative humidity and temperature. It gives a higher total aerosol volume (hence also surface area) in the lower levels, favouring heterogeneous reactions.

Since reactions (R1) and (R2) are competing, we apply branching ratios following the approach used in Roberts et al. (2009), Jourdain et al. (2016) and Surl et al. (2021).

5

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