

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

Virginie Marécal et al.

5 1 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.

10 Heterogeneous reactions that only apply in the stratosphere are not listed here.

1.1 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 :

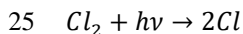
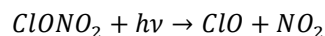
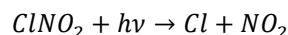
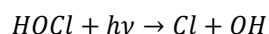
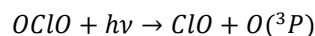
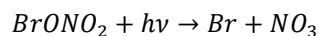
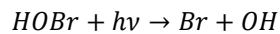
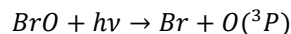
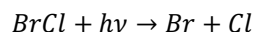


Table S1 : List of gaseous reactions for bromine and chlorine in MOCAGE except those involving halogen long-lived species since they are only of interest for stratospheric chemistry. Reactions in red colour are those that have been added to MOCAGE original scheme. The main references are JPL2015 (Burkholder 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).

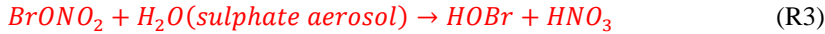
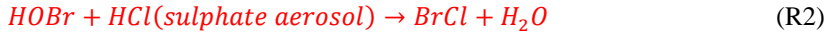
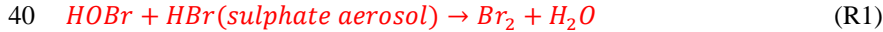
Reaction	Rate constant	Reference
$HBr + OH \rightarrow Br + H_2O$	$5.5 \cdot 10^{-12} \times e^{\frac{200}{T}}$	JPL2015
$HBr + O(^1D) \rightarrow Br + OH$	$1.5 \cdot 10^{-10}$	JPL2015
$Br + O_3 \rightarrow BrO + O_2$	$1.6 \cdot 10^{-11} \times e^{\frac{-780}{T}}$	JPL2015
$Br + HO_2 \rightarrow HBr +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

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

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

2.2 Heterogeneous reactions

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



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 ClONO₂ since their rates are much lower than those with HOBr and BrONO₂ (Roberts et al. 2009).

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

$$k = \gamma \cdot \frac{C_{rel}}{4} \cdot S_{aerosol} \quad (1)$$

50 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 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:

$$55 \quad S_{aerosol} = 4 \cdot \pi \cdot R_{eff}^2 \cdot N_{DROD} \quad (2)$$

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 (2), N_{DROD} is the number of droplets by unit of volume that is calculated from:

$$N_{DROD} = \frac{3 \cdot V_{aerosol}}{4 \cdot \pi \cdot R_{eff}^3} \quad (3)$$

$V_{aerosol}$ is the aerosol volume (per cm³ of air). For this study, it is assumed that the sulphate aerosols are composed of only two species: H₂O and H₂SO₄ in aqueous phase. The ratio of sulphuric acid to H₂O 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 with the relative humidity and temperature. It gives a higher total aerosol volume (hence also surface area) in the lower levels, favouring heterogeneous reactions.

65 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).

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