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Submitted on 28 Oct 2013

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Detailed modeling of the atmospheric degradation mechanism
of very-short lived brominated species

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Atmospheric Environment.

Abstract

Detailed chemical reaction schemes for the atmospheric degradations of the very short-lived species (VSLS) bromoform (CHBr\textsubscript{3}) and dibromomethane (CH\textsubscript{2}Br\textsubscript{2}) have been established. These degradation schemes have been implemented in the meteorological/tracer transport model CATT-BRAMS used in the present case as pseudo one-dimensional model with chemistry of CH\textsubscript{4}, CO, HO\textsubscript{x}, NO\textsubscript{x}, NO\textsubscript{y} and O\textsubscript{x}. They include the main possible reactions of the intermediate brominated peroxy radicals RO\textsubscript{2} (with R = CH\textsubscript{2}Br, CHBr\textsubscript{2} and CBr\textsubscript{3}) for which the most likely reaction pathways with HO\textsubscript{2} have been found using \textit{ab initio} computational calculations. The full degradation schemes have been run for two well-defined realistic scenarios, “clean” atmosphere and “moderately” NO\textsubscript{y}-polluted atmosphere, as representative of a tropical coastal region where these VSLS natural emissions are expected to be important. The Henry’s law constants of the brominated organics products have been estimated by using the Bond Contribution Method (BCM; Meylan and Howard, 1991) or the Molecular Connectivity Index (MCI; Nirmalakhandan and Speece, 1988). Using these constants, the least soluble species formed from the VSLS degradation are found to be CBr\textsubscript{2}O,
CHBrO, CBr$_3$O$_2$NO$_2$, CHBr$_2$O$_2$NO$_2$, BrO, BrONO$_2$ and HOBr, which leads those to be potentially transported into the tropical tropopause layer (TTL) in case of deep convection and contribute to stratospheric bromine additionally to the original substances. For bromoform and dibromomethane degradation, the moderate NO$_x$ pollution increases the production of the least soluble species and thus approximately doubles the bromine quantity potentially able to reach the TTL (from 22.5% to 43% for CHBr$_3$ and from 8.8% to 20.2% for CH$_2$Br$_2$). The influence of the reactions of the RO$_2$ radicals with HO$_2$, CH$_3$O$_2$ and NO$_2$ on the nature and abundance of the stable intermediate and end-products has been tested for CHBr$_3$ degradation. As a result, the reactions of the RO$_2$ radicals with NO$_2$ have no impact. Taking into account the reaction between RO$_2$ and CH$_3$O$_2$ and modifying the branching ratios of the reaction between RO$_2$ and HO$_2$ lead to a small impact on the bromoform degradation by slightly decreasing (by 10%) the bromine quantity potentially able to reach the TTL. As a final point, in contrast to CHBr$_3$, CH$_2$Br$_2$ degradation produces negligible quantities of organics species and the effects of pollution increase only the inorganic species production. By taking into account the results of these tests, new simplified degradation schemes for CHBr$_3$ and CH$_2$Br$_2$ are proposed.
1. Introduction

Until the beginning of the 21st century, stratospheric ozone depletion has been exclusively explained by reactions of active halogen gases with ozone. The active halogen gases originated from long-lived species such as chlorofluorocarbons (CFCs) for chlorine, and halons and CH$_3$Br for bromine. Recent measurements of total stratospheric inorganic bromine, Br$_y$ (Dorf et al., 2008), and their comparison with the measurements of bromine derived from halons and CH$_3$Br showed significant discrepancies (Montzka and Reimann et al., 2011). Actually bromine-containing long-lived species are not the single source of stratospheric inorganic bromine as very short-lived species (VSLS) also contribute (Ko and Poulet et al., 2003; Law and Sturges et al., 2007; Montzka and Reimann et al., 2011). These VSLS are substances with atmospheric lifetime shorter than six months, which is generally too short to reach the stratosphere. However, they may enter the tropical tropopause layer (TTL) into the tropical region by deep convection, and then the stratosphere by slow radiative ascent for air having reached at least the level of zero radiative heating (LZRH, ~15.5 km or 360 K). Convection can lift VSLS, in the form of their source gases (SGs) or their low solubility product gases (PGs) within a few hours from the boundary layer into the TTL. In the tropics, VSLS are mainly emitted by natural marine sources from warm tropical oceans (Hense and Quack, 2009). Bromoform (CHBr$_3$) and dibromomethane (CH$_2$Br$_2$) are the most abundant brominated short-lived SGs, with a global mean lifetime of 26 days and 120 days, respectively (Ko and Poulet et al., 2003). Research is now focused on the contribution of VSLS to stratospheric bromine by using modeling calculations (Kerkweg et al., 2008; Brioude et al., 2010; Pisso et al., 2010; Aschmann et al., 2009; Hossaini et al., 2010), balloon-borne measurements (Dorf et al., 2008) and satellite measurements (Sinnhuber et al., 2005). This contribution is found to be largely uncertain, varying from less than 1 part per trillion volume (pptv) mixing ratios up to more than 8 pptv. Most models use simple degradation schemes for the VSLS, which do not consider the intermediates organic PGs as particular species with their own physical properties (e.g., solubility) and reactivity toward other atmospheric species. Only one detailed chemical scheme for degradation of CHBr$_3$ and CH$_2$Br$_2$ has been proposed, by Hossaini et al. (2010). They used a chemistry reaction scheme in the three dimensional (3D) TOMCAT/SLIMCAT global chemistry transport model and concluded on the small influence of the organic products on the global scale. Nevertheless, neither study considered all the possible degradation pathways.
The aim of this paper is firstly to propose a full degradation scheme of bromoform and dibromomethane and to implement it in a meteorological/tracer transport model (CATT-BRAMS; Freitas et al., 2009) used as a pseudo one dimensional model with the atmospheric chemistry of CH$_4$, CO, HO$_x$, NO$_x$, NO$_y$ and O$_x$. The computations are made under high sunlight conditions as those prevailing in the tropical regions.

The atmospheric removal of CHBr$_3$ and CH$_2$Br$_2$ is mainly initiated via reaction with OH radical and photolysis. In the presence of molecular oxygen, the first step (either OH- or Cl-oxidation reaction, or photolysis) leads to the formation of organic brominated peroxy radicals RO$_2$ (with R = CH$_3$Br, CHBr$_2$ or CBr$_3$). The chemistry of peroxy radicals closely depends on the conditions of pollution and in particular on the level of nitrogen oxides (NO$_x$). In regions with high NO$_x$ levels, the chemistry of RO$_2$ radicals is essentially governed by the reactions with NO, which lead to the exclusive formation of the alkoxy radical (RO) and NO$_2$ for bromine and small size compounds (Mc Givern et al., 2004; Wallington et al., 1997).

However, it is also interesting to study the importance of the reactions between RO$_2$ and NO$_2$, giving alkyl peroxy nitrates (RO$_2$NO$_2$), compared to the RO$_2$ + NO reactions. Indeed, species such as CH$_3$O$_2$NO$_2$ are rather unstable, but the substitution of one or more H atoms by halogen atoms leads to much longer thermal lifetimes (Kirchner et al., 1998, Köppenkastrop et al., 1991). Consequently, halogenated alkyl peroxy nitrates might be temporary reservoirs for peroxy radicals. In regions with low NO$_x$ levels (less than few tens of pptv) such as the marine atmosphere, the degradation of peroxy radicals also involves the cross reactions RO$_2$ + HO$_2$ and RO$_2$ + R’O$_2$, where R’O$_2$ represents the most abundant atmospheric organic peroxy radicals, i.e. mainly CH$_3$O$_2$, C$_2$H$_5$O$_2$ and CH$_3$C(O)O$_2$. In particular CH$_3$O$_2$ can reach concentrations as high as HO$_2$ concentrations (Villenave and Lesclaux, 1996) so that the RO$_2$ + CH$_3$O$_2$ reaction may need to be considered as a significant degradation pathway (Tyndall et al., 2001). Moreover, these cross reactions between peroxy radicals potentially lead to several different products. The reactions between alkyl RO$_2$ and HO$_2$ proceed via the formation of a short-lived tetroxide intermediate ROOOOH, which decomposes to form different products (Wallington et al., 1997). In most cases, the major product is the hydroperoxide RO$_2$H. However, for halogenated peroxy radicals, other final products arise, with yields depending on the nature and the number of the halogen atoms in the RO$_2$ species (Lesclaux et al., 1997). Another question to properly close the degradation scheme is the fate of the species produced by the RO$_2$ radical reactions, which can undergo washout (depending on their solubility), photolysis, or react with OH (or Cl) to form inorganic bromine species (Br$_y$) as end-products.
The second goal of this paper is to study the influence of these different parameters, i.e. the oxidant concentration, the level of NOx pollution and the relative importance of the different peroxy radical cross reactions, on the final chemical product distribution. Especially, the different mechanisms discussed above, the partitioning between the different PGs (organics and inorganics) produced in the lower atmosphere and the ability of these PGs to reach the TTL in the case of convection are studied. For that, the solubility of each species is determined by attributing an individual Henry’s law constant and only the least soluble species are considered to potentially reach the TTL. As a conclusion, the importance of each reaction is discussed and simplified chemical schemes of VSLS degradation are established, to be more conveniently used in future simulations.

This paper is organized as follows: Section 2 gives a detailed chemical degradation scheme for bromoform and dibromomethane. Section 3 describes the atmospheric model used for this study and Section 4 presents the results and the discussion of the atmospheric simulations.

2. Chemical mechanisms for the atmospheric degradations of CHBr3 and CH2Br2

This section presents the different degradation pathways of the main bromine VSL source gases, bromoform (CHBr₃) and dibromomethane (CH₂Br₂) in the atmosphere, and tools to establish, on the one hand, the chemical scheme and, on the other hand, the solubility of the brominated products. The mechanism is based on the general scheme of the halomethane degradation proposed by Ko and Poulet et al. (2003). The removal of bromine SGs occurs via OH and Cl reactions and photolysis. The peroxy radicals (RO₂) produced in the first oxidation steps can react with species such as NO, NO₂, HO₂ and CH₃O₂ to form aldehydes, hydroperoxides and alcohols as intermediate organic products.

The reaction scheme of peroxy radicals are complex and depend on the atmospheric conditions, in particular on the NOx concentration (Tyndall et al., 2001). When the abundance of NOx is high (more than a few parts per billion volume mixing ratios (ppbv)), the fate of peroxy radicals is dominated by their reaction with NO. Under conditions of low NOx levels (less than few tens of pptv), the cross-reactions of RO₂ with CH₃O₂ or HO₂ dominate with respect to the reaction with NO. When the abundance of NOx is moderated (from few tens of pptv to some ppbv), all these reactions are in competition. Finally, the oxidation scheme of
VSLS terminates by reactions of the intermediate products with OH and photodissociations, leading to inorganic bromine production.

The atmospheric reaction mechanisms of analogous chlorinated peroxy radicals, especially the reactions between RO$_2$ and HO$_2$, are well known from laboratory studies (Catoire et al., 1994; Catoire et al., 1996; Wallington et al., 1997) or from computational calculations (Hou et al., 2005), whereas this is not the case for brominated peroxy radical reactions. Consequently, computational calculations have been performed to help establishing the most likely chemical mechanisms by determining the standard reaction enthalpies of RO$_2$ + HO$_2$ reactions. The computational methods and the estimations of Henry’s law constants are explained below, before presenting the detailed mechanisms of the atmospheric degradation of the VSLS.

2.1. Computational methods for the estimation of the standard reaction enthalpies at 298 K of the RO$_2$ + HO$_2$ reaction

In order to determine the energetically most favorable reaction pathways for the cross reactions RO$_2$ + HO$_2$, *ab initio* calculations of the standard reaction enthalpies have been performed. All calculations used the GAUSSIAN03 (Frisch et al., 2004) and GAUSSIAN09 (Frisch et al., 2009) software packages. Geometric parameters were fully optimized with the second Möller-Plesset perturbation method (Møller and Plesset, 1934) combined with the Dunning’s correlation consistent basis set cc-pVTZ (Dunning et al., 1989; Kendall et al., 1992; Woon et al., 1993; Peterson et al., 1994; Wilson et al., 1996). Scaled vibrational frequencies and scaled Zero-Point Energies (ZPE) were determined within the harmonic approximation at the same level of theory as that for geometries. The *ab initio* vibrational frequencies were multiplied by an appropriate scaling factor (0.95) (Johnson, 2011). Electronic energies were obtained employing the single and double coupled cluster theory with inclusion of a perturbative estimation for triple excitation (CCSD(T)) (Cizek et al., 1969; Pople et al., 1987; Purvis et al., 1982; Scuseria et al., 1988; Scuseria et al., 1989) with the aug-cc-pVTZ basis set. The frozen-core approximation has been applied to the CCSD(T) calculations. This means that the inner shells are excluded when estimating the correlation energy. Though the CCSD(T) approach is considered as a “golden standard”, providing a good balance between cost and accuracy, it is still possible to improve the coupled cluster energies estimating the effects of higher excitations, i.e. the full configuration-interaction energies as proposed by Goodson (2002). This is referred to as continued fraction approximation (cf). We applied the cf-correction in the energetics of the studied reactions.
Reaction enthalpies at 298 K were computed using the KISTHEP program (Henon et al., 2003). The BSSE was not considered here because the common counterpoise correction is estimated to be relatively small for a large basis set involving diffuse functions such as the aug-cc-pVTZ basis set and for reaction enthalpies involving species which are neither adducts nor Van der Waals molecular complexes. Table 1 lists the reaction enthalpies $\Delta H^\circ$ at 298 K calculated at the CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ level of theory with and without the cf-correction. As shown in Table 1, there is little influence of the cf-correction on the calculated reaction enthalpies at 298 K ($< 0.9$ kcal mol$^{-1}$) demonstrating the convergence of the reported values.

The results obtained indicate that the reactions between CH$_2$BrO$_2$, CHBr$_2$O$_2$, CBr$_3$O$_2$ radicals and HO$_2$ are strongly exothermic with the exception of the reaction pathways (6b’), (20b’) and (35b’). The exothermicity is observed to increase with increasing bromine substitution of the reactant. Our calculated values of $\Delta H^\circ_{298K}$ for reaction pathways (6a), (6b’), (20a), (20b’), (35a), (35b’)) are in good agreement with the values obtained by McGivern et al. (2004) at a different level of theory (CCSD(T)/cc-pVTZ//MP2(Full)/6-311+G(d)). Interestingly, our results are also in very good agreement with the calculations of Hou et al. (2005) for the channels (a), (b), (b’) and (c) of the analogous chlorine compounds.

The chemical model, established in the next sections, takes into account all these results.

2.2. Estimation methods for the Henry’s law constants

The halogenated organic intermediate products are more or less soluble. The Henry’s law constants are not known for complex halogenated species. Consequently, we used the Bond Contribution Method (BCM) (Meylan and Howard, 1991) or the Molecular Connectivity Index (MCI) method (Nirmalakhandan and Speece, 1988) to estimate them. These methods attribute a “contribution value” for each different atom and/or each bond present in the molecule, depending on their chemical nature, and estimate the Henry’s law constant from these values.

Meylan and Howard (1991; BCM) attributed a contribution value for each bond in the molecule (C-C, C-H, C-O, C-Br…) and applied some correction factors to certain chemical classes (alcohols, cyclic alkane …). By summing all the contribution values, the log water to air partition coefficient (LWAPC) is found, which corresponds to the decimal logarithm of the unitless Henry’ law constant $k_{H}^o$ in the chemical equilibrium for a given species A defined by the dimensionless ratio of the species concentrations in the two phases:
A (gas) $\leftrightarrow$ A (liquid) with $k^o_H = \frac{C_{A(\text{liq})}}{C_{A(\text{gas})}}$

Usually, the Henry’ law constant is defined as $k^o_H = \frac{C_{A(\text{liq})}}{P_{A(\text{gas})}}$, where $C_{A(\text{liq})}$ and $P_{A(\text{gas})}$ are the concentration of the species in the liquid phase and the partial pressure in the gas phase in units of mol L$^{-1}$ and atm, respectively. The unitless Henry’ law constant is converted into mol L$^{-1}$ atm$^{-1}$ by dividing by the temperature (298 K) and the gas constant ($8.205746 \times 10^{-5}$ L mol$^{-1}$ atm K$^{-1}$).

Nirmalakhandan and Speece (1988; MCI) developed an equation to estimate the unitless Henry’s law constants taking into consideration three different parameters: the polarizability parameter, the molecular connectivity index and the hydrogen bonding index. The polarizability parameter is calculated from the different atoms (C, H, Br…) and functions (aldehyde, ketone…) present in the molecule, the molecular connectivity index characterizes the bond in the molecule and the hydrogen bonding index is equal to 1 if the molecule contains an electronegative element attached directly to a carbon atom holding a hydrogen atom.

Before estimating the Henry’s law constant of our bromine products, we have tested the two methods by comparisons with well-known Henry’s law constants (referenced by Sander et al., 1999). Table 2 shows these comparisons. For small peroxides and alcohols, BCM is better than MCI method, which overestimates the values for peroxides and underestimates them for alcohols. So we used this method for brominated peroxides and alcohols (CH$_n$Br$_{3-n}$OOH and CH$_n$Br$_{3-n}$OH, with $n = 0, 1, or 2$). Both methods are in excellent agreement for the estimation of aldehydes and ketones Henry’s law constants. However, BCM estimates the constant from the bond between each atom and treats carbonyl groups (C=O) as single atoms. Their authors (Meylan and Howard, 1991) established the values of each bond but with no value for the bond CO-Br. MCI method uses the contribution of each atom of the molecule, i.e. C, O and Br as single atoms, and moreover considers aldehydes and ketones as subgroups of the molecule for which an additional contribution to the Henry’s law constant is attributed. Consequently MCI enables the estimate of Henry’s law constants for brominated aldehydes or ketones, and we used this method in this case. These two estimation methods allowed us to derive an order of magnitude value for the Henry’s law constants. The results of the estimated Henry’s law constants for the bromine compounds present in our model are reported in Table 3. The most soluble organic species are CBr$_3$O$_2$H, CHBr$_2$O$_2$H, CBr$_3$OH and CHBr$_2$OH with Henry law’s constants higher than $10^4$ mol L$^{-1}$ atm$^{-1}$, whereas the least soluble organics are CBr$_2$O, CHBrO and the brominated methyl peroxyxinitrates (RO$_2$NO$_2$) with constants lower than $10^3$ mol L$^{-1}$ atm$^{-1}$. Note that HBr is very soluble, even
with a very low Henry’s law constant, but with a high acidity constant \( (K_a = 10^9) \) leading to a high effective constant (Yang et al., 2005). Seinfeld and Pandis (2006) proposed that species with Henry’s law constants lower than \( 10^3 \) mol L\(^{-1}\) atm\(^{-1}\) are considered less soluble, whereas species with constants between \( 10^3 \) and \( 10^4 \) mol L\(^{-1}\) atm\(^{-1}\) are moderately soluble and species with constants higher than \( 10^4 \) mol L\(^{-1}\) atm\(^{-1}\) are very soluble. For our study, we considered only two classes: species with constants higher than \( 10^4 \) mol L\(^{-1}\) atm\(^{-1}\) as very soluble, and species with constants lower than \( 10^4 \) mol L\(^{-1}\) atm\(^{-1}\) as less soluble, so HOBr, CH\(_2\)BrO\(_2\)H and CH\(_2\)BrOH join the latter group. Indeed, for a cloud with a typical liquid water content of 1 g m\(^{-3}\) of air (Seinfeld and Pandis, 2006), a constant of \( 10^4 \) mol L\(^{-1}\) atm\(^{-1}\) corresponds to a mass aqueous fraction of 20%.

2.3. Bromoform degradation mechanism

In the atmospheric degradation of CHBr\(_3\), the first step is either the reaction with OH, Cl or photolysis. The different pathways, oxidation or photolysis, do not form the same intermediate products (CBr\(_3\)O\(_2\) and CHBr\(_2\)O\(_2\)). According to Ko and Poulet et al. (2003), CHBr\(_3\) is the only brominated VSLS (with CHBr\(_2\)Cl) for which photolysis is as important as the reaction with OH, by comparison with other VSLS for which OH oxidation dominates.

2.3.1. OH- or Cl-initiated oxidation of CHBr\(_3\)

The oxidation of CHBr\(_3\) by OH or Cl (Ko and Poulet, 2003 and reference therein; Kamboures et al., 2002) leads to H-abstraction to form CBr\(_3\) radical, which is rapidly converted into CBr\(_3\)O\(_2\) radical in the presence of ambient oxygen:

\[
\text{CHBr}_3 + \text{OH} + \text{O}_2 \rightarrow \text{CBr}_3\text{O}_2 + \text{H}_2\text{O} \quad (1)
\]

\[
\text{CHBr}_3 + \text{Cl} + \text{O}_2 \rightarrow \text{CBr}_3\text{O}_2 + \text{HCl} \quad (2)
\]

Then, depending on the atmospheric conditions the brominated peroxy radical may react with NO, NO\(_2\), HO\(_2\) and CH\(_3\)O\(_2\). The reaction of CBr\(_3\)O\(_2\) with NO leads exclusively to CBr\(_3\)O radical (Mc Givern et al., 2002 and 2004; Wallington et al., 1997), which dissociates rapidly by Br-elimination, by analogy with CH\(_2\)BrO (Chen et al., 1995; Orlando et al., 1996):

\[
\text{CBr}_3\text{O}_2 + \text{NO} \rightarrow \text{CBr}_3\text{O} + \text{NO}_2 \quad (3)
\]

\[
\text{CBr}_3\text{O} \rightarrow \text{CBr}_2\text{O} + \text{Br} \quad (4)
\]

The reaction of peroxy radicals with NO\(_2\) proceeds exclusively via a termolecular recombination reaction (Wallington et al., 1997):

\[
\text{CBr}_3\text{O}_2 + \text{NO}_2 + \text{M} \leftrightarrow \text{CBr}_3\text{O}_2\text{NO}_2 + \text{M} \quad (5)
\]
The reaction between CBr$_3$O$_2$ and HO$_2$ leads to formation of the hydroperoxide CBr$_3$O$_2$H and/or the ketone CBr$_2$O:

\[ \text{CBr}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CBr}_3\text{O}_2\text{H} + \text{O}_2 \]  

(6a)

\[ \text{CBr}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CBr}_2\text{O} + \text{HOBr} + \text{O}_2 \]  

(6b)

Mc Givern et al. (2004) considered another pathway (6b’) corresponding to a different geometry of the tetroxide intermediate (ROOOOH), but with one same final product (CBr$_2$O) as (6b) after rapid Br-elimination from CBr$_3$O:

\[ \text{CBr}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CBr}_3\text{O} + \text{OH} + \text{O}_2 \]  

(6b’)

The similar reactions for chlorinated peroxy radicals have been well studied by experimental means under laboratory conditions by Catoire et al. (1994) and Catoire et al. (1996) and by theoretical calculations by Hou et al. (2005), leading to kinetic data (rate parameters and branching ratios for the pathways). The brominated organic peroxy radical reactions have only been studied by Mc Givern et al. (2004) using theoretical Rice-Ramsperger-Kassel-Marcus (RRKM) calculations, but these authors did not consider all the possible pathways as Hou et al. (2005) did for chlorinated compounds. Our calculations of the reaction enthalpies, presented in Section 2.1, for the reactions (6a), (6b) and (6b’) are in good agreement with the work of these authors for the brominated and chlorinated peroxy radicals, as detailed in Section 2.1 and shown in Table 1. The experimental results of Catoire et al. (1996) for the equivalent reaction of chlorine compounds showed that CCl$_3$O is the single product under laboratory conditions. They observed the production of HOCl, suggesting that pathway (b) is the main pathway. However, our theoretical results, consistent with the previous ones reported above, suggest that CBr$_3$O$_2$H (from pathway (a)) and CBr$_2$O + HOBr (from pathway (b)) are the main products of the reaction between CBr$_3$O$_2$ and HO$_2$, being the more exothermic reactions. In addition, according to Hou et al. (2005), for the study of chlorinated compounds, the main product is CCl$_3$O$_2$H due to the lower potential energy barrier of reaction (a) than (b), in addition to its significant exothermicity. They explain the experimental results of Catoire et al. (1996) by the fact that pathway (a) for chlorine (forming CCl$_3$O$_2$H) is exothermic enough (-44.2 kcal mol$^{-1}$) to allow for the dissociation of CCl$_3$O$_2$H into CCl$_2$O and HOCl (needing 38 kcal mol$^{-1}$). Therefore, by analogy with chlorine, we consider the branching ratio for reaction (6a) to be $k_{6a}/k_6 = 1$.

Finally, the cross reaction between CBr$_3$O$_2$ and CH$_3$O$_2$ may occur via two different pathways (Wallington et al., 1992; Shallcross et al., 2005):

\[ \text{CBr}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{CBr}_3\text{O} + \text{Br} + \text{CH}_2\text{O} + \text{HO}_2 \]  

(7a)

\[ \text{CBr}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{CBr}_3\text{OH} + \text{CH}_2\text{O} + \text{O}_2 \]  

(7b)
In fact, in a first step channel (7a) produces two alkoxy radicals, CBr$_3$O and CH$_3$O, which rapidly form carbonyl dibromide CBr$_2$O (by Br-atom elimination) and formaldehyde CH$_2$O (by reaction with O$_2$), respectively. Channel (7b) leads to perbrominated methanol (CBr$_3$OH) and formaldehyde. For the analogous chlorine cross reaction (CCl$_3$O$_2$ + CH$_3$O$_2$) the experimental branching ratio $k_{7a}/k_7$ was indirectly found to be 0.5 ± 0.2 (Catoire et al., 1996). These reactions are not documented for brominated compounds, so we chose to follow the indication of Madronich et al. (1990) who proposed a method to estimate the branching ratios for the cross reaction (CH$_3$O$_2$ + CBr$_3$O$_2$) from the self reactions of the two reactants of the cross reaction, here CH$_3$O$_2$ and CBr$_3$O$_2$. The self reaction of CH$_3$O$_2$ occurs via two pathways with branching ratios different from zero, $k_{8a}/k_8 = 0.4$ and $k_{8b}/k_8 = 0.6$ (Tyndall et al., 1998):

\[
\begin{align*}
\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 & \rightarrow 2 \text{CH}_3\text{O} + \text{O}_2 \quad (8a) \\
\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 & \rightarrow \text{CH}_3\text{OH} + \text{CH}_2\text{O} + \text{O}_2 \quad (8b)
\end{align*}
\]

Most of the self reactions of the halogenated peroxy radicals, such as CF$_2$ClCH$_2$O$_2$, CFCl$_2$CH$_2$O$_2$ (Tuazon et al., 1994), CH$_3$CHClO$_2$ (Maricq et al., 1993), CH$_2$ClO$_2$ and CHCl$_2$O$_2$ (Niki et al., 1980; Catoire et al., 1996) and CCl$_3$O$_2$ (Catoire et al., 1996), occur exclusively via one pathway:

\[
\text{RO}_2 + \text{RO}_2 \rightarrow 2 \text{RO} + \text{O}_2 \quad (9)
\]

with R being this time the substitute organic radical. So we use $k_{9a}/k_9 = 1.0$. If we apply the method of simple averaging from Madronich et al. (1990) in our cases, we find $k_{7a}/k_7 = 0.7$ and $k_{7b}/k_7 = 0.3$, which we used for our simulations.

Overall the above reactions implying CBr$_3$O$_2$ produce four brominated organics products: CBr$_2$O, CBr$_3$O$_2$NO$_2$, CBr$_3$O$_2$H and CBr$_3$OH. These compounds are more or less hydrosoluble and their Henry’s law constants have been evaluated in Section 2.2.

Other possible sinks in the atmosphere are gas phase reactions:

- for CBr$_3$O (Libuda et al., 1991):

\[
\begin{align*}
\text{CBr}_3\text{O} + h\nu & \rightarrow \text{CO} + 2 \text{Br} \quad (10)
\end{align*}
\]

- for CBr$_3$O$_2$NO$_2$, based on analogous chlorinated compounds (Köppenkastrop and Zabel, 1991):

\[
\begin{align*}
\text{CBr}_3\text{O}_2\text{NO}_2 + \text{M} & \rightarrow \text{CBr}_3\text{O}_2 + \text{NO}_2 + \text{M} \quad (11)
\end{align*}
\]

and by analogy with CH$_3$O$_2$NO$_2$ (Atkinson et al., 2006):

\[
\begin{align*}
\text{CBr}_3\text{O}_2\text{NO}_2 + h\nu & \rightarrow \text{CBr}_3\text{O}_2 + \text{NO}_2 \quad (12a) \\
\text{CBr}_3\text{O}_2\text{NO}_2 + h\nu & \rightarrow \text{CBr}_2\text{O} + \text{Br} + \text{NO}_3 \quad (12b)
\end{align*}
\]

- for CBr$_3$O$_2$H, based on the reaction of CH$_3$O$_2$H (Atkinson et al., 2006):
The overall reaction scheme discussed in this section is summarized in Fig. 1 and all kinetic data used are given in Table 4. The references for the chosen kinetic data are detailed in Section 3.

2.3.2. Photolysis of CHBr3

The photolysis of CHBr3 leads to the direct elimination of a Br atom and the formation of the peroxide radical CHBr2O2:

CHBr3 + hν → CHBr2O2 + Br  

(16)

Similarly to CBr3O2, CHBr2O2 reacts with NO to form CHBr2O (Mc Givern et al., 2004; Wallington et al., 1997) and then CHBrO:

CHBr2O2 + NO → CHBr2O + NO2  

(17)

CHBr2O → CHBrO + Br  

(18)

The termolecular reaction of CHBr2O2 with NO2 also occurs:

CHBr2O2 + NO2 + M ↔ CHBr2O2NO2 + M  

(19)

For the reaction between CHBr2O2 and HO2 three pathways may take place:

CHBr2O2 + HO2 → CHBr2O2H + O2  

(20a)

CHBr2O2 + HO2 → CHBrO + HOBr + O2  

(20b)

CHBr2O2 + HO2 → CBr2O + H2O + O2  

(20c)

As previously, Mc Givern et al. (2004) considered another pathway corresponding to a different geometry in the intermediate:

CHBr2O2 + HO2 → CHBr2O + OH + O2  

(20b’)

Mc Givern et al. (2004) studied only pathways (a) and (b’), giving branching ratios of 0.59 and 0.41, respectively. But they did not consider pathway (c), as suggested by Wallington et al. (1996) for chlorinated compounds, which forms carbonyl dibromide CBr2O. Our calculations of reaction enthalpies (Section 2.1) give results similar to those for chlorinated compounds found by Hou et al. (2005), as shown in Table 1. As explained previously, the cross reaction proceeds via a tetroxide intermediate ROOOOH, and depending on the geometry of this tetroxide, the final products are different (pathways a, b or b’, c). As previously stated (Section 2.3.1), Hou et al. (2005) found CHCl2O2H as the main product in their study of the analogous chlorinated compound reaction, due to the exothermicity and the
lower potential energy barrier of channel (a) with respect to channels (b) and (c), and explained the non observation of CHCl\textsubscript{2}O\textsubscript{2}H in the experimental results of Catoire et al. (1996) by the decomposition of CHCl\textsubscript{2}O\textsubscript{2}H into CHClO. The branching ratios found for chlorinated compounds by Catoire et al. (1996) were k\textsubscript{20b}/k\textsubscript{20} = 0.7 and k\textsubscript{20c}/k\textsubscript{20} = 0.3. By analogy, assuming CHCl\textsubscript{2}O\textsubscript{2}H is totally converted into CHClO, due to the exothermicity of reaction (a) for chlorinated compounds, i.e. the reaction proceeds mainly through channel (20a) and the realistic branching ratio would be k\textsubscript{20a}/k\textsubscript{20} = 0.7 and k\textsubscript{20c}/k\textsubscript{20} = 0.3. Consequently, for the brominated compounds, we set k\textsubscript{20a}/k\textsubscript{20} = 0.7 and k\textsubscript{20c}/k\textsubscript{20} = 0.3.

The reaction between CHBr\textsubscript{2}O\textsubscript{2} and CH\textsubscript{3}O\textsubscript{2} can proceed via three pathways. According to the estimation method of Madronich et al. (1990) again, we can approximate the branching ratio of the cross reaction, k\textsubscript{21a}/k\textsubscript{21} = 0.7 and k\textsubscript{21b}/k\textsubscript{21} = 0.3 and k\textsubscript{21c}/k\textsubscript{21} = 0:

\begin{align*}
\text{CHBr}_2\text{O}_2 + \text{CH}_3\text{O}_2 & \rightarrow \text{CHBrO} + \text{Br} + \text{CH}_2\text{O} + \text{HO}_2 \quad (21a) \\
\text{CHBr}_2\text{O}_2 + \text{CH}_3\text{O}_2 & \rightarrow \text{CHBr}_2\text{OH} + \text{CH}_2\text{O} + \text{O}_2 \quad (21b) \\
\text{CHBr}_2\text{O}_2 + \text{CH}_3\text{O}_2 & \rightarrow \text{CBr}_2\text{O} + \text{CH}_3\text{OH} + \text{O}_2 \quad (21c)
\end{align*}

Finally, the gas phase removal of CBr\textsubscript{2}O, CHBrO, CHBr\textsubscript{2}O\textsubscript{2}NO\textsubscript{2}, CHBr\textsubscript{2}O\textsubscript{2}H and CHBr\textsubscript{2}OH are achieved via OH reaction, thermal decomposition and photolysis:

- for CBr\textsubscript{2}O (Libuda et al. 1991):
  \begin{align*}
  \text{CBr}_2\text{O} + \text{h}\nu & \rightarrow \text{CO} + 2\text{Br} \quad (22)
  \end{align*}

- for CHBrO (Libuda et al. 1991):
  \begin{align*}
  \text{CHBrO} + \text{h}\nu + \text{O}_2 & \rightarrow \text{CO} + \text{Br} + \text{HO}_2 \quad (23)
  \end{align*}

- for CHBr\textsubscript{2}O\textsubscript{2}NO\textsubscript{2}, by analogy with chlorinated compounds (Köppenkastrop and Zabel, 1991):
  \begin{align*}
  \text{CHBr}_2\text{O}_2\text{NO}_2 + \text{M} & \rightarrow \text{CHBr}_2\text{O}_2 + \text{NO}_2 + \text{M} \quad (24)
  \end{align*}

and by analogy with CH\textsubscript{3}O\textsubscript{2}NO\textsubscript{2} (Atkinson et al., 2006):

\begin{align*}
\text{CHBr}_2\text{O}_2\text{NO}_2 + \text{h}\nu & \rightarrow \text{CHBr}_2\text{O}_2 + \text{NO}_2 \quad (25a) \\
\text{CHBr}_2\text{O}_2\text{NO}_2 + \text{h}\nu & \rightarrow \text{CHBrO} + \text{Br} + \text{NO}_3 \quad (25b)
\end{align*}

- for CHBr\textsubscript{2}O\textsubscript{2}H, based on the reaction of CH\textsubscript{3}O\textsubscript{2}H (Atkinson et al., 2006):
  \begin{align*}
  \text{CHBr}_2\text{O}_2\text{H} + \text{h}\nu & \rightarrow \text{CHBrO} + \text{Br} + \text{OH} \quad (26) \\
  \text{CHBr}_2\text{O}_2\text{H} + \text{OH} & \rightarrow \text{CHBr}_2\text{O}_2 + \text{H}_2\text{O} \quad (27)
  \end{align*}

- for CHBr\textsubscript{2}OH:
  \begin{align*}
  \text{CHBr}_2\text{OH} + \text{OH} + \text{O}_2 & \rightarrow \text{CBr}_2\text{O} + \text{HO}_2 + \text{H}_2\text{O} \quad (28)
  \end{align*}

The later reaction is assumed to proceed by the same mechanism as methanol (Atkinson et al., 2006).
All reactions and kinetic parameters are gathered in Table 4 and Fig. 1.

2.4. Dibromomethane degradation mechanism

For CH₂Br₂, reaction with OH is generally the major loss process (Ko and Poulet et al., 2003). The degradation of CH₂Br₂ is described in a similar way as for CHBr₃.

2.4.1. OH- or Cl-initiated oxidation of CH₂Br₂

The oxidation of CH₂Br₂ by OH or Cl leads to the H-abstraction to form CHBr₂ and after reaction with O₂, forms CHBr₂O₂:

\[
\begin{align*}
\text{CH}_2\text{Br}_2 + \text{OH} + \text{O}_2 & \rightarrow \text{CHBr}_2\text{O}_2 + \text{H}_2\text{O} \quad (29) \\
\text{CH}_2\text{Br}_2 + \text{Cl} + \text{O}_2 & \rightarrow \text{CHBr}_2\text{O}_2 + \text{HCl} \quad (30)
\end{align*}
\]

The peroxy radical formed in this way is the same as from the CHBr₃ photolysis and its degradation kinetics and mechanism have thus been already described in the previous section. This degradation way of CH₂Br₂ is summarized in Table 5 and Fig. 1.

2.4.2. Photolysis of CH₂Br₂

The photolysis of CH₂Br₂ leads to the direct elimination of a Br atom and the formation of the peroxy radical CH₂BrO₂:

\[
\text{CH}_2\text{Br}_2 + \text{hv} \rightarrow \text{CH}_2\text{BrO}_2 + \text{Br} \quad (31)
\]

CH₂BrO₂ can react with NO to form CH₂BrO (McGivern et al., 2004; Wallington et al., 1997) and then CH₂O (Chen et al. 1995):

\[
\begin{align*}
\text{CH}_2\text{BrO}_2 + \text{NO} & \rightarrow \text{CH}_2\text{BrO} + \text{NO}_2 \quad (32) \\
\text{CH}_2\text{BrO} & \rightarrow \text{CH}_2\text{O} + \text{Br} \quad (33)
\end{align*}
\]

The reaction of CH₂BrO₂ with NO₂ proceeds via:

\[
\text{CH}_2\text{BrO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{CH}_2\text{BrO}_2\text{NO}_2 + \text{M} \quad (34)
\]

Also, the reaction between CHBr₂O₂ and HO₂ may have three pathways:

\[
\begin{align*}
\text{CH}_2\text{BrO}_2 + \text{HO}_2 & \rightarrow \text{CH}_2\text{BrO}_2\text{H} + \text{O}_2 \quad (35a) \\
\text{CH}_2\text{BrO}_2 + \text{HO}_2 & \rightarrow \text{CH}_2\text{O} + \text{HOBr} + \text{O}_2 \quad (35b) \\
\text{CH}_2\text{BrO}_2 + \text{HO}_2 & \rightarrow \text{CHBrO} + \text{H}_2\text{O} + \text{O}_2 \quad (35c)
\end{align*}
\]

McGivern et al. (2004) considered pathways (a) and (b’) only. Channel (b’) gives as product CH₂BrO, OH and O₂ and then CH₂O and Br after CH₂BrO rapid decomposition.

As previously stated, the reaction enthalpies we calculated are in agreement with the theoretical data of McGivern et al. (2004) for brominated compounds, and of Hou et al.
for chlorinated compounds. We used the branching ratio of the analogous chlorine
compounds, \( k_{35a}/k_{35} = 0.2 \) and \( k_{35c}/k_{35} = 0.8 \) (Catoire et al. 1996). However, experimental
results of Chen et al. (1995) indirectly suggested the quasi exclusive CH2BrO2H formation,
and another theoretical study for CH2ClO2 reaction (Wei and Zheng, 2007) reported that
CH2ClO2H is the predominant product. Consequently, we also tested in another simulation the
branching ratios, \( k_{35a}/k_{35} = 0.9 \) and \( k_{35c}/k_{35} = 0.1 \).

The reaction between CH2BrO2 and CH3O2 may occur via three channels. As
previously stated, we have used the method proposed by Madronich et al. (1990) to estimate
the branching ratio and found \( k_{36a}/k_{36} = 0.7 \), \( k_{36b}/k_{36} = 0.3 \) and \( k_{36c}/k_{36} = 0: \)

\[
\begin{align*}
\text{CH2BrO2 + CH3O2} & \rightarrow \text{CH2O + Br + CH3O + O2} \quad (36a) \\
\text{CH2BrO2 + CH3O2} & \rightarrow \text{CH2BrOH + CH2O + O2} \quad (36b) \\
\text{CH2BrO2 + CH3O2} & \rightarrow \text{CHBrO + CH2OH + O2} \quad (36c)
\end{align*}
\]

Then, CH2BrO2NO2, CH2BrO2H, CHBrO and CH2BrOH are transformed via OH reaction,
thermal decomposition or photolysis:

- for CHBrO (Libuda et al. 1991):

\[
\text{CHBrO + h\nu +O2 \rightarrow CO + Br + HO2} \quad (37)
\]

- for CH2BrO2NO2, by analogy with chlorinated compounds (Köppenkastrop and Zabel,
1991):

\[
\begin{align*}
\text{CH2BrO2NO2 + M} & \rightarrow \text{CH2BrO2 + NO2 + M} \quad (38) \\
\text{CH2BrO2NO2 + h\nu} & \rightarrow \text{CH2BrO2 + NO2} \quad (39a) \\
\text{CH2BrO2NO2 + h\nu} & \rightarrow \text{CH2O + Br + NO3} \quad (39b)
\end{align*}
\]

- for CH2BrO2H, based on the mechanism of CH3O2H (Atkinson et al., 2006):

\[
\begin{align*}
\text{CH2BrO2H + h\nu} & \rightarrow \text{CH2O + Br + OH} \quad (40) \\
\text{CH2BrO2H + OH} & \rightarrow \text{CH2BrO2 + H2O} \quad (41)
\end{align*}
\]

- for CH2BrOH, based on the mechanism of CH3OH + OH (Atkinson et al., 2006):

\[
\begin{align*}
\text{CH2BrOH + OH + O2} & \rightarrow \text{CHBrO + H2O + HO2} \quad (42)
\end{align*}
\]

Table 5 and Fig. 1 summarize the overall degradation mechanism for CH2Br2 and the
corresponding kinetic data. The choice of the kinetic data is detailed in Section 3.

3. Description of the model used for the atmospheric simulations
The model used to study the degradation of bromoform and dibromomethane under atmospheric conditions is the meteorological/tracer transport model CATT-BRAMS (Coupled Aerosol Tracer Transport-Brazilian Regional Atmospheric Modeling system; Freitas et al. 2009) coupled on-line with the chemistry model described below. CATT-BRAMS is a 3D limited-area model, which is used here as a “pseudo” one dimensional model. For this, we run the model on a very small geographical domain and we set the initial conditions for the meteorological parameters horizontally uniform and vertically from a radiosounding corresponding to a stable atmosphere. These initial conditions are such that the atmosphere remains stable for the whole simulation duration. Stable atmospheric conditions are chosen to allow us studying the chemical degradation of bromoform and dibromomethane regardless of atmospheric perturbations such as convective transport and subsequent scavenging. A complementary study was conducted by Marécal et al. (2011) focusing on the impact on the local scale of tropical deep convection on the bromoform transport and chemical processing, including aqueous chemistry. Marécal et al. (2011) also used the CATT-BRAMS model with a fine horizontal resolution (1 km) allowing the cloud scale processes to be explicitly resolved (i.e. without convection parameterization).

In the present study, we use cyclic boundary conditions for the meteorological and chemical variables and a small geographical domain leading to 3D-chemical simulation fields quasi-uniform horizontally in the simulation, as checked \textit{a posteriori}. With this setup, the model is not computationally costly. This allows us to run a large set of chemical reaction mechanism simulations to study in detail CHBr$_3$ and CH$_2$Br$_2$ degradations under realistic atmospheric conditions from surface to the upper troposphere.

The general setup common to all simulations is given hereafter. The specific characteristics of the different sensitivity simulations are given in Section 4.1. The model is set with 33 vertical levels spanning from the surface to 24 km altitude with layer depths increasing with altitude from 48 m near the surface to 1 km above 5.36 km height. The model is initialized vertically using the pressure, temperature and relative humidity data from the radiosounding launched from Darwin (Australia, 12°S–131°E) on 16 November 2005 at 2300UT in the frame of the SCOUT-O3 European Project (http://www.ozone-sec.ch.cam.ac.uk/scout-o3/). We chose Darwin because it is located close to a warm ocean and coastal region where natural bromoform and dibromomethane emissions are expected to be strong (e.g. Quack and Wallace, 2003). The model starts on the radiosounding date and time. All simulations are performed for a time period of 10 days for CHBr$_3$ and 50 days for CH$_2$Br$_2$, corresponding to their estimated lifetime found in this region and season by our model.
Apart from CHBr$_3$ and CH$_2$Br$_2$ chemical degradation, a simple scheme including the chemical reaction mechanisms for CO, CH$_4$, total inorganic reactive nitrogen (NO$_y$) and hydrogen oxide radicals (HO$_x$) taken from Barth et al. (2007) has been used to simulate tropospheric chemistry. Chlorine chemistry has not been taken into account. Even if the reaction with Cl atom can be considered as loss mechanism for CHBr$_3$ and CH$_2$Br$_2$, reaction with OH remains the major loss mechanism. To avoid high increase of OH radicals in the lowest levels, dry deposition is applied to HNO$_3$ and O$_3$. The detailed bromine chemistry scheme implemented has been described in Section 2. We take into account 19 bromine-containing products deriving from the 2 SGs (CHBr$_3$, CH$_2$Br$_2$), including 14 organics PGs (CBr$_3$O$_2$, CHBr$_2$O$_2$, CH$_2$BrO$_2$, CBr$_3$O$_2$H, CHBr$_2$O$_2$H, CH$_2$BrO$_2$H, CBr$_3$O$_2$NO$_2$, CHBr$_2$O$_2$NO$_2$, CH$_2$BrO$_2$NO$_2$, CBr$_2$O, CHBrO, CBr$_3$OH, CHBr$_2$OH and CH$_2$BrOH) and 5 inorganic PGs (Br, BrO, BrONO$_2$, HOBr and HBr).

For the initialization of the chemical species concentrations we have used outputs from the global Chemistry-Transport model (CTM) MOCAGE (Josse et al., 2004; Bousserez et al., 2007). They provide the background chemical conditions in which the degradation of bromoform and dibromomethane are simulated. MOCAGE is based on the photochemical scheme RACM (Stockwell et al. 1997) for tropospheric chemistry and on REPROBUS (Lefèvre et al. 1994) for stratospheric chemistry. It includes a parameterization of convection representing subgrid scale transport and scavenging by deep convection. It also includes parameterizations for turbulent diffusion and dry deposition. We initialized CH$_4$, HNO$_3$, NO and NO$_2$, O$_3$ and CO mixing ratio by MOCAGE outputs from a specific simulation. The chosen horizontal resolution is a global 2°×2°, with 47 vertical levels extending from the ground up to 5 hPa. Emissions correspond to those given by the former Intergovernmental Panel on Climate Change (IPCC) exercise, except for biogenic emissions which follow the inventory Global Emissions Inventory Activity (GEIA, http://www.geiacenter.org/). MOCAGE being a CTM, external meteorological forcings are necessary. In this simulation, 6-hourly analyses from ARPEGE Meteo-France’s operational meteorological forecast model have been used. After a one-month spin-up, MOCAGE has been run for November 2005, and averaged over that month to provide initial conditions for the CATT-BRAMS model.

The present work reports modeling results for 2 scenarios (CLEAN and MODERATE), with tropospheric conditions ranging from clean to moderately polluted air masses. All simulations take place at the same latitude and longitude (12°S, 131°E). However, to initialize the simulation under realistic conditions of moderate pollution and clean atmosphere, we have used the MOCAGE model outputs for Darwin (12°S, 131°E) and for the
Pacific Ocean (5°N, 149°E), respectively. Initialization values at 1 km altitude for the 2 scenarios are given in Table 6. In addition, bromoform volume mixing ratio, as shown in Fig. 2, is initialized in two different ways: firstly by using the mean tropical data from ground to 19 km altitude (Fig. 2A) referenced by Montzka and Reimann et al. (2011) and secondly, by using the maximum values of the experimental data from Yokouchi et al. (2005) at ground along coasts of tropical islands in Pacific ocean (23.8 pptv for Kiribati, 1.9°N, 157°W) and the mean value of the observations from 10 km to 17 km altitude referenced by Montzka and Reimann et al. (2011) (Fig. 2B). Dibromomethane concentrations are initialized by the maximum values of the observations referenced by Montzka and Reimann et al. (2011) shown in Fig. 3. The missing data are interpolated from concentration profile observations (reported by Hossaini et al., 2010). The CHBr₃ and CH₂Br₂ degradations have been studied without other bromine sources during the simulations. Consequently, the total bromine during the simulations represents the bromine introduced at the beginning.

Most of the reaction rate constants used are from JPL (Sander et al., 2011), IUPAC (Aktinson et al., 2006), and MCM (Master Chemical Mechanism; Jenkin et al., 1997). Photolysis rates are computed on-line using Fast-TUV (Tie et al., 2003) consistently with the radiative calculations of the meteorological model (Toon et al., 1989). The kinetics parameters for the brominated VSLS degradation reactions are not well known. Consequently, we applied the rate constants of the reactions of analogous chlorine-containing species to the bromine reactions, when available. However, for the reactions CHBr₃O₂ + NO, CH₂BrO₂ + NO, CBr₃O₂ + OH, CHBr₂O₂H + OH and CH₂BrO₂H + OH, the analogous chlorine rate constants are not known, and thus the generalized reactions RO₂ + NO and RO₂ + OH proposed by Jenkin et al. (1997) are used. All the rate constants associated with the reaction mechanisms described in Section 2 are gathered in Table 4 for CHBr₃ and in Table 5 for CH₂Br₂. The photolysis data of the reactions are from JPL 2011 (Sander et al., 2011), except for the brominated RO₂H and RO₂NO₂ for which the absorption cross sections of CH₃O₂H and CH₃O₂NO₂ have been used, respectively.

4. Modeling of the atmospheric degradation of CHBr₃ and CH₂Br₂: results and discussion

4.1. Chemical mechanism setup of the simulations
First, the 2 scenarios of clean and moderately polluted atmospheres (Table 6) have been tested in the reference simulation, including all the reactions for the 2 different initializations of bromoform (Fig. 2A and 2B). Then, the influences of the reaction \( \text{RO}_2 + \text{NO}_2 \) in simulation #1 and of the reaction \( \text{RO}_2 + \text{CH}_3\text{O}_2 \) in simulation #2 with respect to the reference simulation have been tested. In simulation #3, the influence of the branching ratio values in the cross reactions \( \text{RO}_2 + \text{HO}_2 \) has been analyzed by comparing the best current estimates with the values \( k_{6a}/k_6 = k_{6b}/k_6 = 0.5 \) for \( \text{CBr}_3\text{O}_2 + \text{HO}_2 \) and \( k_{20a}/k_{20} = k_{20b}/k_{20} = 0.5 \) for \( \text{CHBr}_2\text{O}_2 + \text{HO}_2 \) (Hossaini et al., 2010). All these sensitivity tests have been performed in clean atmosphere and for the bromoform initialization from Fig. 2B (maximum values). All the chemical mechanism setups are summarized in Table 7 for CHBr3.

For dibromomethane degradation, both clean and moderately polluted atmosphere scenarios have been tested in the reference simulation (Table 8). A sensitivity test on the effect of the branching ratio for the \( \text{CH}_2\text{BrO}_2 + \text{HO}_2 \) reaction has been performed under clean atmospheric conditions (for reasons described in Section 4.3). Indeed, there is some uncertainty associated to them. The experimental results of Chen et al. (1995) and theoretical results of Wei and Zheng (2007) suggested the predominant formation of \( \text{CH}_2\text{BrO}_2\text{H} \) for the reaction between \( \text{CH}_2\text{BrO}_2 \) and \( \text{HO}_2 \), i.e. \( k_{35a}/k_{35} = 1 \). However, the branching ratios used in the reference simulation, by analogy to the chlorinated compound, were \( k_{35a}/k_{35} = 0.2 \) (formation of \( \text{CH}_2\text{BrO}_2\text{H} \)) and \( k_{35c}/k_{35} = 0.8 \) (formation of HCHO and \( \text{H}_2\text{O} \)).

In addition, the Henry’s law constants for each intermediate degradation product derived in Section 2.2 have been explicitly taken into account for the interpretation of the results in each simulation. To assess the effect of the changes in the chemical scheme setup, the temporal evolution of each species is described and their solubility is discussed. The vertical profiles of each species are also discussed for altitudes below 6 km. The 6 km altitude corresponds to the maximum altitude for clouds containing liquid water in general. Indeed, the solubility regarding the Henry’s law constant does not make sense at higher altitude where clouds are principally composed of ice. The results above 6 km are used only for the discussion of the lifetime of the species. Finally, for each case, the quantities of bromine potentially able to reach the TTL are discussed only in relation to the solubility of each species, which corresponds to the sum of the least soluble products, that is species with Henry’s law constants lower than \( 10^4 \) mol L\(^{-1}\) atm\(^{-1}\) (the inorganics Br, BrO, HOBr, and the organics \( \text{CBr}_2\text{O}, \text{CHBrO}, \) and for dibromomethane degradation, \( \text{CH}_2\text{BrOH} \) and \( \text{CH}_2\text{BrO}_2\text{H} \)), as detailed in Section 2.2. However even if highly soluble, BrONO\(_2\) is included in the
calculation of Br able to reach the TTL since this species undergoes hydrolysis in clouds and rain droplets, leading to the release of HOBr (Yang et al., 2005):

\[ \text{BrONO}_2 + \text{H}_2\text{O}_{(aq)} \rightarrow \text{HOBr} + \text{HNO}_3 \]  

(43)

HOBr has low solubility and may also reach the TTL.

HBr is not taken into account as potentially able to reach the TTL because it has a high acidity constant \( K_a = 10^9 \) leading to a high effective Henry’s law constant as detailed in Section 2.2 (Yang et al., 2005).

4.2. **CHBr\(_3\) degradation**

4.2.1. **Influence of air pollution on the reference simulation**

The influence of a moderate increase in the NO\(_y\) concentration (NO\(_x\) and HNO\(_3\)) on CHBr\(_3\) degradation has been considered as indicated in Table 6. The overall lifetime of CHBr\(_3\) depends on its reaction with OH and its photolysis. Fig. 4A and Fig. 4B show the lifetimes due to the reaction with OH (\( \tau_{\text{OH}} \)) and the photolysis (\( \tau_{\text{photolysis}} \)) and the total lifetime \( \tau_{\text{total}} \) of CHBr\(_3\) deduced (\( 1/\tau_{\text{total}} = 1/\tau_{\text{photolysis}} + 1/\tau_{\text{OH}} \)) for the two atmospheric conditions, clean and polluted atmospheres. We observe the reduction of \( \tau_{\text{photolysis}} \) and on the contrary, the increase of \( \tau_{\text{OH}} \) with altitude because of the decrease of OH concentration (Fig. 5) and the increase of actinic flux with altitude. That means the contribution of the reaction with OH to the global lifetime decreases with the altitude and becomes quasi insignificant at 10 km altitude. So, the photolysis lifetime becomes quasi similar to the global lifetime \( \tau_{\text{total}} \) at 10 km height (Fig. 4). The same trend is observed for both atmospheric conditions. However, the values of the lifetimes diverge, depending on the pollution conditions. The simulation shows that a moderate pollution leads to higher OH radical concentrations (due to the increase in O\(_3\) production) at the lower altitude levels (< 10 km), as seen in Fig. 5 (for 10-days of OH average concentration). Therefore the CHBr\(_3\) lifetime due to OH reaction is reduced in polluted atmosphere, as shown in Fig. 4. For instance the CHBr\(_3\) lifetime due to OH at 5 km height decreases from 45.2 days in clean atmosphere to 31.8 days in a moderately polluted atmosphere, and consequently decreases the total lifetime at this altitude from 10.1 to 9.4 days. These lifetimes are lower than the local tropospheric lifetime of CHBr\(_3\) of 26 days given by Ko and Poulet et al. (WMO, 2003) at 5 km. This is due to the higher OH concentration we used (\( 4 \times 10^6 \) molecule cm\(^{-3} \) compared to \( 1 \times 10^6 \) molecule cm\(^{-3} \) in Ko and Poulet, 2003), and
to the stronger solar actinic flux used in our study, which takes place in November at low
latitude (12.4°S).

Fig. 6 shows the vertical profiles of Br derived for the different species: CHBr₃, total
organics, HBr and total inorganics except HBr, at 4 different dates (17 November 2005, i.e. 1
day after the beginning of the simulation, and 20, 23, 26 November 2005) and for the
initializations used, as given in Fig. 2A. Fig. 6 (top panel) shows the decrease of Br contained
in CHBr₃ from one day to another, more efficient in polluted atmosphere due to OH increase,
as discussed above. Due to the CHBr₃ degradation, the concentration of Br from the organics
(CBr₃O₂, CHBr₂O₂, CBr₂O, CHBrO, CBr₃O₂H, CHBr₂O₂H, CBr₃O₂NO₂, CHBr₂O₂NO₂,
CBr₃OH or CHBr₂OH) increases and starts to decrease at the end of the simulation, i.e.
between the 23 and 26 November (upper middle panel). In polluted atmosphere, the organics
production and degradation are more efficient than in clean atmosphere, but follow
approximately the same evolution as a function of time. Finally, due to the degradation of
bromoform and organics, the production of inorganics as HBr, BrO, BrONO₂, HOBr and Br is
observed (Fig. 6, lower middle and bottom panels). The production of HBr is more efficient in
clean atmosphere, particularly at the end of the simulation. On the contrary, the other
inorganics (BrO, BrONO₂, HOBr and Br) are produced most often in a polluted atmosphere
with a maximum occurring at 1.5 km height. HBr is the final product of the PG degradation. It
is formed by the reaction of bromine atom with HO₂ and HCHO. The time to reach this final
state closely depends on the formation of the inorganic bromine atom reservoir HOBr and
BrONO₂. In a clean atmosphere, HOBr production is more important compared to the
production of BrONO₂. In the case of a more polluted atmosphere, inorganic bromine
reservoir is principally composed of BrONO₂ because the reaction between BrO and NO₂,
leading to the formation of BrONO₂, is more efficient than the reaction between BrO and
HO₂. BrONO₂ lifetime (1.5 h) is larger than HOBr lifetime (15 min). Consequently, HBr is
less rapidly produced in a polluted atmosphere than in a clean atmosphere. The rapid decrease
at low altitude (below 1 km) and the rapid increase observed for all inorganic PGs (except
HBr), which is more evident after the 20 November, is the consequence of the OH profile
(Fig. 5). The OH profile is linked to the O₃ and HNO₃ profiles. In particular, the lower part of
the OH profile is decreasing because of the dry deposition of O₃ and HNO₃. All these
conclusions for initialization with the CHBr₃ profile shown in Fig 2A are identical when
assuming the Fig. 2B initialization, i.e. the values of all the PGs increase in the same
proportions. For all species, the profile trends are similar as a function of the degradation time
at all altitudes. In the following, the discussion focuses on the results at 1 km altitude, at which the maximum values of organics and inorganics are observed.

Fig. 7 shows the sum of the least soluble species (CBr_2O, CHBrO, HOBr, Br, BrO and BrONO_2) and the sum of the most soluble species (CBr_3O_2H, CHBr_2O_2H, CBr_3OH, CHBr_2OH and HBr) for both scenarios (clean and polluted atmospheres) at 1 km height. Fig. 7A corresponds to the initial CHBr_3 mixing ratio of Fig. 2A, and Fig. 7B refers to the initial CHBr_3 mixing ratio of Fig. 2B. At the beginning of the simulation, the most soluble species and least soluble species are in comparable mixing ratios in the clean atmosphere. After three days of simulation, the most soluble species mixing ratios become more important and keep increasing in the clean atmosphere. On the contrary, during all the simulations in the polluted atmosphere, the least soluble species dominate. The concentration of the least soluble species increases and then becomes quasi stable after a few days of simulation for both scenarios.

Table 9 shows the relative partitioning of Br atom contained in each species after 10 days of simulation (the approximate lifetime of CHBr_3). Since mixing ratios of the least soluble species are quasi stable after a few days of simulation, the following results are available for this period. Around 48% (45.3 – 49.9%) of the total number of bromine atoms is in the form of inorganic species for both scenarios (clean and moderately polluted atmospheres) in the reference simulation. As shown previously, in the clean atmosphere the inorganic species dominate, mainly in the form of HBr (36% among 45.3%), which is essentially washed out. In the polluted atmosphere, the contribution of inorganic species (HOBr, Br, BrONO_2, BrO representing 26.4% among the 49.9% of total inorganic products) is similar to that of HBr (23.5%) and is mainly due to BrONO_2. BrONO_2 formed via the reaction between BrO and NO_2 is more abundant due to higher NO_2 concentrations in the moderately polluted atmosphere. After 10 days of simulation, for both scenarios around 18% (17.1-19.2%) of bromine is contained in the organics species. However, a detailed observation of these organic species shows that the temporal evolution of the least soluble species (CHBrO, CBr_2O, CBr_3O_2NO_2 and CHBr_2O_2NO_2) is different, compared to the most soluble species (CBr_3O_2H, CHBr_2O_2H, CBr_3OH and CHBr_2OH), depending on the scenario (clean or moderately polluted atmosphere). The production of the most soluble organic species given above decreases from 3.9% to 2.6% of the total bromine from clean to polluted atmosphere, because the cross reactions between peroxy radicals are more important in a clean atmosphere, as explained in Section 2. In contrast, the production of the least soluble species (mainly CBr_2O and CHBrO) increases from 13.2% to 16.6% of the total bromine from clean
to polluted atmospheres. Among these species, the production of CBr$_3$O$_2$NO$_2$ and CHBr$_2$O$_2$NO$_2$ is more important in a polluted atmosphere but remains negligible.

In summary, the production of the least soluble species such as CBr$_3$O and CHBrO for organics and BrO, HOBr, BrONO$_2$ and Br for inorganics increases from 22.5% of the total bromine in clean atmosphere to 43% in moderately polluted atmosphere, as seen in Table 9.

4.2.2. Influence of the peroxy radicals reactions

Table 7 summarizes all the reactions of the peroxy radicals which have been taken into account in the simulations. The impact of the RO$_2$ + NO$_2$ reactions has been studied in simulation #1, where these reactions were removed compared to the reference simulation where they were included. The importance of these reactions depends on the NO$_x$ level. For high NO$_x$ level, the reactions between RO$_2$ and NO$_2$ may enter in competition with the reactions between RO$_2$ and NO. Under our conditions of NO$_x$ level (0.036 ppbv and 0.061 ppbv), there is no effect on CHBr$_3$ degradation because the production of RO$_2$NO$_2$ species are negligible (Table 9).

The RO$_2$ + CH$_3$O$_2$ reactions have also been considered in our reference simulation and compared when removed in simulation #2. The production of the organic and inorganic products differs between simulations. The implementation of the RO$_2$ + CH$_3$O$_2$ reactions (reference simulation) decreases the production yields of CBr$_3$O$_2$H and CHBr$_2$O$_2$H formed in RO$_2$ + HO$_2$ reactions, as shown in Table 9. The different peroxy radical reactions are indeed in competition, depending on their relative rates. The rate constant values of the reactions between CBr$_3$O$_2$ and CH$_3$O$_2$ (reaction (7)) and between CBr$_3$O$_2$ and HO$_2$ (reaction (6)) are $6.6 \times 10^{-12}$ and $5.1 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298K, respectively. The rate constant values of the reactions between CHBr$_2$O$_2$ and CH$_3$O$_2$ (reaction (20)) and between CHBr$_2$O$_2$ and HO$_2$ (reaction (21)) are $1.2 \times 10^{-12}$ and $5.9 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K, respectively. Considering the average during 10 days simulation volume mixing ratios of HO$_2$ (10.9 ppt) and CH$_3$O$_2$ (1.8 ppt) derived from the simulations, the RO$_2$ + CH$_3$O$_2$ reaction is thus around 5 times (for RO$_2$ = CBr$_3$O$_2$) to 30 times (for RO$_2$ = CHBr$_2$O$_2$) slower than the RO$_2$ + HO$_2$ reaction. Nevertheless, its occurrence leads to a decrease of the (RO$_2$ + HO$_2$) product yields, CBr$_3$O$_2$H and CHBr$_2$O$_2$H. To conclude on the effect of the RO$_2$ + CH$_3$O$_2$ reaction on CHBr$_3$ degradation mechanism, bromine mixing ratio potentially able to reach the TTL decreases from 23.7% of the total bromine (10.3 pptv) (simulation #2) to 22.5% of the total bromine (9.3 pptv) (reference simulation) for clean atmosphere, as seen in Table 9. Indeed, the soluble
species CBr$_3$OH (formed in reaction (7b)) and HBr are produced in more abundant quantities in the reference simulation, whereas the least soluble species CBr$_2$O and BrONO$_2$ are produced more often in simulation #2.

We have also investigated the difference between the present chemical scheme and that proposed by Hossaini et al. (2010) in simulation #3 for the clean atmosphere, in which the cross reactions (RO$_2$ + HO$_2$ and RO$_2$ + CH$_3$O$_2$) are more important since the NO$_x$ level is lower (Table 6). The difference between simulation #3 and simulation #2 is only in the branching ratios for the reaction between RO$_2$ and HO$_2$ (reactions (6) and (20)). In simulation #2 and the reference simulation, reaction between CBr$_3$O$_2$ and HO$_2$ produces exclusively CBr$_3$O$_2$H (6a), and reaction between CHBr$_2$O$_2$ and HO$_2$ produces 70% CHBr$_2$O$_2$H (20a) and 30% CBr$_2$O (20c). In simulation #3, reaction (6) produces 50% CBr$_3$O$_2$H (6a) and 50% CBr$_2$O (6b), and reaction (20) produces 50% CHBr$_2$O$_2$H (20a) and 50% CHBrO (20b). Table 9 shows that these branching ratio modifications for simulation #3 reduce the productions of CBr$_2$O (from 12.8% to 9.6%), CBr$_3$O$_2$H (from 1.0% to 0.6%) and CHBr$_2$O$_2$H (from 1% to 0.8%) but raise the production of CHBrO (from 1.5% to 1.9%), as organics products. By inspecting the chemical scheme more precisely (Fig. 1), we can notice that for simulation #2 or the reference simulation, the 100% CBr$_3$O$_2$H produced by pathway (6a) subsequently decomposes in CBr$_2$O and Br, whereas for simulation #3, the 50% CBr$_3$O$_2$H produced by pathway (6a) gives CBr$_2$O in the same amount, and 50% CBr$_2$O are produced by pathway (6b). Consequently, the production of CBr$_3$O$_2$H decreases in simulation #3 to 0.6%. Similarly, in simulation #2, the reaction between CHBr$_2$O$_2$ and HO$_2$ produces CBr$_2$O and principally CHBr$_2$O$_2$H and then CHBrO, whereas in simulation #3, the same reaction produces as much CHBr$_2$O$_2$H (and then CHBrO) as CHBrO instead of CBr$_2$O in the simulation #2. Consequently, the production of CHBr$_2$O$_2$H decreases in simulation #3 compared to simulation #2. Globally, the production of CBr$_2$O decreases and the production of CHBrO increases in simulation #3. About the inorganic products, some changes are observable between the two simulations: simulation #3 results in an increase of these products to 46.1% with respect to 42.9% (#2), as shown in Table 9. Consequently, the change in the branching ratios in the reaction between RO$_2$ and HO$_2$ decreases the bromine concentration that could reach the TTL from 23.7% of the total bromine (10.3 pptv) (simulation #2) to 21.5% (8.8 pptv) (#3) mainly because the soluble species HBr is more produced in the simulation #3 and the less soluble species CBr$_2$O is more produced in simulation #2.

The differences between the reference simulation and simulation #3 are the addition of the RO$_2$ + CH$_3$O$_2$ (and the negligible RO$_2$ + NO$_2$) reaction in the reference simulation and the
changes in the branching ratio of the reactions between RO₂ and HO₂. The changes in simulation #3 reduce mainly the production of organic products (from 17.1% the reference to 12.9% for simulation #3), mainly in the form of the highly insoluble species CBr₂O and consequently reduce the total bromine that could reach the TTL from 22.5% (9.3 ppt) for the reference simulation to 21.5% (8.8 ppt) for simulation #3.

To conclude, as seen in Table 9, changes in the cross reactions have weak influences on the distribution of the organic and inorganic products. The bromine volume mixing ratio that could reach the TTL is around 22.5% of the total initial bromine.

These sensitivity tests permit the establishment of a simplified chemistry scheme for bromoform degradation. The reaction between RO₂ and NO₂ is not taken into account because it produces negligible mixing ratios of RO₂NO₂. Only pathways (a) and (c) are considered for the reaction between RO₂ and HO₂ and the reaction between CHBr₂O₂ and CH₃O₂ can be neglected because the product ratios from this reaction are 0 to 0.2% of the total bromine. The simplified chemical scheme is shown in Fig. 8. However, even if the previous tests on the degradation scheme have shown weak influence, the production of organic products remains important. The simplification of the CHBr₃ degradation scheme by the direct production of 3 Br atoms leads to underestimate the bromine potentially able to reach the TTL by 20% to 50%, depending on the NOₓ atmospheric pollution.

4.3. CH₂Br₂ degradation

The influence of a moderate increase in the NOₓ concentration (NOₓ and HNO₃) on CH₂Br₂ degradation in the reference simulation has been tested. Then, some changes in the branching ratios in the reaction between CH₂BrO₂ and HO₂ have been tested in simulation #1.

According to Montzka and Reimann et al. (2011), CH₂Br₂ has a total lifetime longer than CHBr₃. The change in the atmospheric conditions from a clean to a polluted atmosphere increases the OH concentration and significantly influences the global lifetime of CH₂Br₂, decreasing from 72 days in a clean atmosphere to 53 days in a polluted atmosphere at 5 km height. Again, the higher CH₂Br₂ tropospheric lifetime of 120 days given by Ko and Poulet et al. (WMO, 2003) at 5 km height is due to the lower OH concentration used for their calculations (1 × 10⁶ molecules cm⁻³) and to the stronger solar actinic flux used in our study, which takes place in November at low latitude (12.4°S).

Fig. 9 shows the time evolution (during 50 days from 17 November to 5 January) of the vertical profiles of Br contained in several species. Br mixing ratio from CH₂Br₂ decreases
with time (top panel), less rapidly at the end of the simulation due to the decrease in the OH concentration. Br mixing ratio from organics increases during the first four days of the simulation and then decreases to form inorganics species. HBr is formed as a major product and keeps increasing during the simulation until the 20 December and then start decreasing. The other inorganic species increase and then become stable. CH$_2$Br$_2$ mixing ratio decreases more rapidly in the moderately polluted atmosphere (Fig. 9B). The production of organics species is more efficient in the moderately polluted atmosphere at the beginning of the simulation. The production of HBr is also more efficient in moderately polluted atmosphere. HBr is the final product of the PG degradation and the CH$_2$Br$_2$ degradation is more rapid in the moderately polluted atmosphere. The difference in lifetime between the polluted atmosphere and the clean atmosphere is more pronounced for CH$_2$Br$_2$ degradation (by 20 days) than for CHBr$_3$ degradation (by 1 day). Consequently, the more rapid degradation of CH$_2$Br$_2$ in the polluted atmosphere produces more rapidly the other inorganic species and then HBr, compared to the CHBr$_3$ degradation. Finally, the inorganic species mixing ratios are more important in the polluted atmosphere. As for CHBr$_3$, the results are only discussed at 1 km altitude.

Fig. 10 shows the sum of the least soluble species (CBr$_2$O, CHBrO, CH$_2$BrO$_2$H, CH$_2$BrOH, HOB, Br, BrO and BrONO$_2$) and the sum of the most soluble species (CHBr$_2$O$_2$H, CHBr$_2$OH and HBr) for both scenarios (clean and polluted atmosphere) at 1 km height. At the beginning of the simulation, the most soluble and least soluble species have comparable mixing ratios in the clean atmosphere. After 3 days of simulation, the soluble species become more important and keep increasing, and the least soluble species become quasi stable in clean atmosphere. On the contrary, during 21 days of simulation in the polluted atmosphere, the least soluble species dominate and then the soluble species become more important and keep increasing.

As for CHBr$_3$, the total bromine produced from CH$_2$Br$_2$ degradation that could reach the TTL has been calculated from the least soluble species (CBr$_2$O, CHBrO, Br, BrO, BrONO$_2$ and HOB), resulting in an important increase of the total bromine, from 8.8% (0.19 pptv) in the clean atmosphere to 20.2% (0.42 pptv) in a moderately polluted atmosphere. The latter value is mainly due to the more efficient degradation of CH$_3$Br$_2$ giving principally inorganic products, including species other than HBr, with low solubility, as seen in Fig. 10 and Table 10.

Modification in the branching ratios for the reaction between CH$_2$BrO$_2$ and HO$_2$ has also been tested in simulation #1. The experimental results of Chen et al. (1995) are tested,
with \( k_{35a}/k_{35} = 0.9 \) (formation of \( \text{CH}_2\text{BrO}_2\text{H} \)) and \( k_{35c}/k_{35} = 0.1 \) (formation of \( \text{HCHO} \) and \( \text{H}_2\text{O} \)). Significant changes in the degradation products are not observable when the branching ratios are changed since all the species produced by the photolysis of \( \text{CH}_2\text{Br}_2 \) (leading to \( \text{CH}_2\text{BrO}_2 \)) are totally negligible.

The atmospheric degradation scheme of \( \text{CH}_2\text{Br}_2 \) can be simplified. The photolysis pathway can be neglected and the \( \text{OH} \) or \( \text{Cl} \) pathway to form \( \text{CHBr}_2\text{O}_2 \) is similar to the \( \text{CHBr}_3 \) photolysis pathway, leading to the degradation mechanism from Fig. 8.

5. Conclusions

Detailed atmospheric degradation schemes for bromoform (\( \text{CHBr}_3 \)) and dibromomethane (\( \text{CH}_2\text{Br}_2 \)) have been established and implemented into a pseudo 1D model including the atmospheric chemistry of \( \text{CH}_4 \), \( \text{CO} \), \( \text{HO}_x \), \( \text{NO}_x \), \( \text{NO}_y \) and \( \text{O}_x \).

To help to set up the degradation schemes, standard reaction enthalpies at 298 K for the different pathways of the peroxy radical (\( \text{RO}_2 \) with \( \text{R} = \text{CH}_2\text{Br}, \text{CHBr}_2 \) or \( \text{CBr}_3 \)) reactions with \( \text{HO}_2 \) have been calculated using quantum chemistry tools. These calculations, combined with previous results, have helped to estimate the relative importance of the different pathways. Brominated methyl hydroperoxides (\( \text{RO}_2\text{H} \)) are suggested to be the main products of these reactions.

Two empirical methods have been used to estimate the brominated organics Henry’s law constants. The results show that the least soluble organic species resulting from the VSLS degradations are \( \text{CBr}_2\text{O} \), \( \text{CHBrO} \) (and negligible \( \text{CBr}_3\text{O}_2\text{NO}_2 \) and \( \text{CHBr}_3\text{O}_2\text{NO}_2 \), and negligible \( \text{CH}_2\text{BrO}_2\text{H} \), \( \text{CH}_2\text{BrOH} \) and \( \text{CH}_2\text{BrO}_2\text{NO}_2 \) for \( \text{CH}_2\text{Br}_2 \) degradation). The potential ability of the product gases (PGs) to be transported in the TTL in regard to their solubility in case of deep convection has been computed in the 1D model under high sunlight conditions. The least soluble PGs can contribute to bromine in the stratosphere additionally to the original substances.

\( \text{CHBr}_3 \) and \( \text{CH}_2\text{Br}_2 \) concentrations have been initialized at the beginning of the simulations and then the degradation of these species has been studied without other bromine sources during the simulations. Consequently, the total bromine during the simulations represents the bromine introduced at the beginning. The full degradation scheme of \( \text{CHBr}_3 \) and \( \text{CH}_2\text{Br}_2 \) has been performed for two well defined scenarios of a clean and moderately
polluted atmosphere, as representative of a tropical coastal region where natural bromoform and dibromomethane emissions are expected to be important. For CHBr$_3$ degradation in a clean atmosphere, it is shown that approximately 22% of the total initial bromine is transformed into low solubility inorganic (Br, BrO, HBrO, BrONO$_2$: 9%) and organic (CBr$_2$O, CHBrO: 13%) species, and thus able to reach the TTL. A moderate rise in pollution (increase of NO$_x$ by a factor of 2 and HNO$_3$ by a factor of 3) has been tested. When this type of pollution is considered, the total bromine potentially able to reach the TTL increases to 43% (26% of inorganics and 17% of organics).

According to the simulations the reactions between RO$_2$ and NO$_2$ have no effect on the bromoform degradation in clean and moderately polluted atmospheres. The importance of RO$_2$ + CH$_3$O$_2$ reactions has been tested in one sensitivity study in a clean atmosphere. It has a negligible effect on bromoform degradation, with the production of more soluble species and consequently a decrease in the amount of bromine potentially able to reach the TTL from 23.7% (without the CH$_3$O$_2$ reaction) to 22.5% (with the CH$_3$O$_2$ reaction).

Modifications in the branching ratios for the reaction between RO$_2$ and HO$_2$ have also been tested in a clean atmosphere. 100% for the CBr$_3$O$_2$H formation (k$_{6a}$/k$_6$ = 1) in the case of CBr$_3$O$_2$ + HO$_2$ reaction, and 70% for the CHBr$_2$O$_2$H formation (k$_{20a}$/k$_{20}$ = 0.7) and 30% for the CBr$_2$O formation (k$_{20c}$/k$_{20}$ = 0.3) in the case of the CHBr$_2$O$_2$ + HO$_2$ reaction have been used as they are the best current estimates. These branching ratios are used instead of the values used until now, k$_{6a}$/k$_6$ = 0.27 or 0.5, k$_{6b}$/k$_6$ = 0.73 or 0.5, and k$_{20a}$/k$_{20}$ = 0.59 or 0.5, k$_{20b}$/k$_{20}$ = 0.41 or 0.5 (Mc Givern et al., 2004; Hossaini et al., 2010). This results in a small impact for the total bromine originating from CHBr$_3$ potentially able to reach the TTL: 23.7% in our simulation, instead of 21.5% for the previous used branching ratio values, as shown in Table 9.

The full CH$_2$Br$_2$ degradation scheme has been tested in a clean atmosphere and shows that approximately 8.8% (1.3% of organics and 7.5% of inorganics) of the total bromine potentially is able to reach the TTL. As observed for CHBr$_3$ degradation, a pollution rise induces the production of less soluble species and consequently increases significantly the Br quantity that could reach the TTL to 20.2% (1.3% of organics and 18.9% of inorganics).

From this study, degradation schemes for bromoform and dibromomethane have been derived for modeling clean and moderately polluted atmospheres, as shown in Fig. 8. According to the simulations, dibromomethane degradation by photolysis is considered insignificant. The reactions between peroxy radicals and NO$_2$ produce species with negligible mixing ratios and have been removed in the final chemical scheme. Thus, only the pathways
of the reactions for RO$_2$ with HO$_2$, NO and CH$_3$O$_2$ are considered. Moreover, the formation of
CHBr$_2$OH and CHBrO from the reaction between CHBr$_2$O$_2$ and CH$_3$O$_2$ appeared to be
negligible (< 0.2% production) and has been removed in the final scheme. Finally, in contrast
to CHBr$_3$, the production of organics species from CH$_2$Br$_2$ degradation could be neglected
and the degradation scheme could also be reduced to the simple reaction CH$_2$Br$_2$ + OH or Cl
→ 2 Br.

In this paper we do not study the effect of more polluted urban atmosphere on
bromoform and dibromomethane degradations and in particular, the importance of the
reaction between RO$_2$ and NO$_2$ when the level of NO$_x$ is very high. More complex chemistry
(including volatile organic compounds) should be integrated to the modeling system in order
to simulate an urban atmosphere in the vicinity of the tropical western Pacific, like the
Singapore atmosphere.

Acknowledgments

This work has been supported by the EU project SHIVA (226224-FP7-ENV-2008-1). The numerical simulations were performed on the cluster of the Centre de Calcul Scientifique en Région Centre. CATT-BRAMS is free software provided by CPTEC/INPE and distributed under the CC-GNU-GPL license. The ab initio calculations were supported by the Centre de Calcul de l’Université Reims Champagne-Ardenne (ROMEO2) and the Centre de Ressources Informatiques de Haute Normandie (CRIHAN) for providing computing time for part of the theoretical calculations.

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Table 1: Standard reaction enthalpies at 298 K calculated at the CCSD(T)/aug-cc-pVTZ//MP2/cc-pVTZ level of theory with and without the cf-correction involved in the reaction between the brominated methyl peroxy radicals and HO2.

<table>
<thead>
<tr>
<th>Reactiona</th>
<th>$\Delta H^{\circ}_{298K}$ (kcal mol$^{-1}$)</th>
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<tr>
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<tr>
<td>CBr$_3$O$_2$ + HO$_2$ $\rightarrow$ CBr$_3$O$_2$H + O$_2$</td>
<td>6a</td>
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<tr>
<td>CBr$_3$O$_2$ + HO$_2$ $\rightarrow$ CBr$_3$O + HOBr + O$_2$</td>
<td>6b</td>
</tr>
<tr>
<td>CBr$_3$O$_2$ + HO$_2$ $\rightarrow$ CBr$_3$O + OH + O$_2$</td>
<td>6b'</td>
</tr>
<tr>
<td>CHBr$_2$O$_2$ + HO$_2$ $\rightarrow$ CHBr$_2$O$_2$H + O$_2$</td>
<td>20a</td>
</tr>
<tr>
<td>CHBr$_2$O$_2$ + HO$_2$ $\rightarrow$ CHBrO + HOBr + O$_2$</td>
<td>20b</td>
</tr>
<tr>
<td>CHBr$_2$O$_2$ + HO$_2$ $\rightarrow$ CHBr$_2$O + OH + O$_2$</td>
<td>20b'</td>
</tr>
<tr>
<td>CHBr$_2$O$_2$ + HO$_2$ $\rightarrow$ CBr$_2$O + H$_2$O + O$_2$</td>
<td>20c</td>
</tr>
<tr>
<td>CH$_2$BrO$_2$ + HO$_2$ $\rightarrow$ CH$_2$BrO$_2$H + O$_2$</td>
<td>35a</td>
</tr>
<tr>
<td>CH$_2$BrO$_2$ + HO$_2$ $\rightarrow$ CH$_2$O + HOBr + O$_2$</td>
<td>35b</td>
</tr>
<tr>
<td>CH$_2$BrO$_2$ + HO$_2$ $\rightarrow$ CH$_2$BrO + OH + O$_2$</td>
<td>35b'</td>
</tr>
<tr>
<td>CH$_2$BrO$_2$ + HO$_2$ $\rightarrow$ CHBrO + H$_2$O + O$_2$</td>
<td>35c</td>
</tr>
</tbody>
</table>

*a* The molecular oxygen is in its electronic ground state.

*b* the values in parentheses correspond to the CCSD(T)/aug-cc-pVTZ energies without the cf-correction.
Table 2: Comparisons of well-known Henry’s law constants (mol L\(^{-1}\) atm\(^{-1}\)) (referenced by Sander et al. 1999) with estimated Henry’s law constants using the two methods, Bond Contribution Method (BCM) and Molecular Connectivity Index method (MCI).

<table>
<thead>
<tr>
<th></th>
<th>BCM</th>
<th>MCI</th>
<th>Experimental (Sander et al., 1999)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aldehydes</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)CHO</td>
<td>15</td>
<td>15</td>
<td>17</td>
</tr>
<tr>
<td>C(_2)H(_3)CHO</td>
<td>11</td>
<td>12</td>
<td>13</td>
</tr>
<tr>
<td>C(_4)H(_6)CHO</td>
<td>4.8</td>
<td>7.5</td>
<td>6.4</td>
</tr>
<tr>
<td><strong>Ketones</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)COCH(_3)</td>
<td>20</td>
<td>18</td>
<td>27</td>
</tr>
<tr>
<td>C(_2)H(_3)COCH(_3)</td>
<td>15</td>
<td>15</td>
<td>20</td>
</tr>
<tr>
<td><strong>Peroxides</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)O(_2)H</td>
<td>147</td>
<td>1501</td>
<td>310</td>
</tr>
<tr>
<td>C(_2)H(_4)O(_2)H</td>
<td>110</td>
<td>132</td>
<td>340</td>
</tr>
<tr>
<td>OHCH(_2)O(_2)H</td>
<td>4.0(\times 10^6)</td>
<td>7.5(\times 10^6)</td>
<td>1.7(\times 10^6)</td>
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<tr>
<td><strong>Alcohols</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>CH(_3)OH</td>
<td>235</td>
<td>195</td>
<td>230</td>
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<tr>
<td>C(_2)H(_3)OH</td>
<td>176</td>
<td>167</td>
<td>160</td>
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<td>C(_3)H(_7)OH</td>
<td>132</td>
<td>131</td>
<td>130</td>
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<tr>
<td><strong>Compounds with bromine</strong></td>
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<tr>
<td>CHB(_r)_3</td>
<td>8.9</td>
<td>2.4</td>
<td>2.1</td>
</tr>
<tr>
<td>CH(_2)_Br(_2)</td>
<td>1.0</td>
<td>1</td>
<td>1.1</td>
</tr>
<tr>
<td>C(_2)_H(_4)_Br(_2)</td>
<td>0.8</td>
<td>0.8</td>
<td>1.5</td>
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Table 3: Henry’s law constants ($k^o_H$) of the intermediate products gases (PGs).

<table>
<thead>
<tr>
<th>Species</th>
<th>$k^o_H$ (298 K) (mol L$^{-1}$ atm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HBr</td>
<td>0.71$^a$</td>
</tr>
<tr>
<td>HOBr</td>
<td>$6.1 \times 10^3$$^a$</td>
</tr>
<tr>
<td>CBr$_3$O$_2$H</td>
<td>$1.9 \times 10^3$$^b$</td>
</tr>
<tr>
<td>CHBr$_2$O$_2$H</td>
<td>$2.24 \times 10^4$$^b$</td>
</tr>
<tr>
<td>CH$_2$BrO$_2$H</td>
<td>$2.58 \times 10^3$$^b$</td>
</tr>
<tr>
<td>CHBrO</td>
<td>74$^c$</td>
</tr>
<tr>
<td>CBr$_2$O</td>
<td>21.5$^c$</td>
</tr>
<tr>
<td>CBr$_3$O$_2$NO$_2$</td>
<td>401$^b$</td>
</tr>
<tr>
<td>CHBr$_2$O$_2$NO$_2$</td>
<td>304$^b$</td>
</tr>
<tr>
<td>CH$_2$BrO$_2$NO$_2$</td>
<td>35$^b$</td>
</tr>
<tr>
<td>CBr$_3$OH</td>
<td>$1.5 \times 10^5$$^b$</td>
</tr>
<tr>
<td>CHBr$_2$OH</td>
<td>$1.73 \times 10^4$$^b$</td>
</tr>
<tr>
<td>CH$_2$BrOH</td>
<td>$2.0 \times 10^3$$^b$</td>
</tr>
</tbody>
</table>

$^a$ Sander et al., 1999.  
$^c$ Molecular Connectivity Index (MCI: Nirmalakhandan and Speece, 1988).
Table 4: Summary of the kinetic data used for the degradation of bromoform.

<table>
<thead>
<tr>
<th>No</th>
<th>Reactions</th>
<th>Rate constants (cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>Comments</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CHBr$_3$ + OH</td>
<td>1.35×10$^{-12}$ exp(-600/T)</td>
<td></td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>3</td>
<td>CHBr$_3$ + Cl</td>
<td>4.85×10$^{-12}$ exp(-850/T)</td>
<td></td>
<td>Kambanis et al. (1997)</td>
</tr>
<tr>
<td>16</td>
<td>CHBr$_3$ + hv</td>
<td></td>
<td>Absorption Cross Section</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>4</td>
<td>CBr$_3$O$_2$ + NO</td>
<td>7.3×10$^{-12}$ exp(270/T)</td>
<td>From k(CCl$_3$O$_2$ + NO)</td>
<td>Dognon et al. (1985)</td>
</tr>
<tr>
<td>5</td>
<td>CBr$_3$O$_2$ + NO$_2$</td>
<td>$k_0=2.9×10^{-29}$ (T/300)$^{-0.8}$, $k_{\infty}=1.3×10^{-11}$ (T/300)$^{-1}$</td>
<td>From k(CCl$_3$O$_2$ + NO$_2$)</td>
<td>Caralp et al. (1988)</td>
</tr>
<tr>
<td>6</td>
<td>CBr$_3$O$_2$ + HO$_2$</td>
<td>4.8×10$^{-13}$ exp(706/T)</td>
<td>From k(CCl$_3$O$_2$ + HO$_2$)</td>
<td>Branching ratio section 2.3.1</td>
</tr>
<tr>
<td>7</td>
<td>CBr$_3$O$_2$ + CH$_3$O$_2$</td>
<td>6.6×10$^{-12}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>CHBr$_2$O$_2$ + NO</td>
<td>3.81×10$^{-12}$ exp(360/T)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>CHBr$_2$O$_2$ + NO$_2$</td>
<td>2.9×10$^{-29}$ (T/300)$^{-0.8}$, 1.3×10$^{-11}$ (T/300)$^{-1}$</td>
<td>From k(CCl$_3$O$_2$ + NO$_2$)</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>CHBr$_2$O$_2$ + HO$_2$</td>
<td>5.6×10$^{-13}$ exp(700/T)</td>
<td>From k(CHCl$_2$O$_2$ + NO)</td>
<td>Branching ratio section 2.3.2</td>
</tr>
<tr>
<td>21</td>
<td>CHBr$_2$O$_2$ + CH$_3$O$_2$</td>
<td>1.2×10$^{-12}$</td>
<td>K, assumed constant with temperature</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>CBr$_3$O + hv</td>
<td></td>
<td>Absorption Cross Section</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>CBr$_3$O$_2$NO$_2$ + M</td>
<td>$k_0=6.3×10^{-3}$ exp(-10235/T)[N$<em>2$], $k</em>{\infty}=1.42×10^{-16}$ exp(-1500/T)</td>
<td>From k(CCl$_3$O$_2$NO$_2$+M)</td>
<td>Köppenkastrop and Zabel (1991)</td>
</tr>
<tr>
<td>12</td>
<td>CBr$_3$O$_2$NO$_2$ + hv</td>
<td></td>
<td>Absorption Cross Section of CH$_3$O$_2$NO$_2$</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>CBr$_3$O$_2$H + hv</td>
<td></td>
<td>Absorption Cross Section of CH$_3$O$_2$H</td>
<td>Vaghjiani and Ravishankara (1989)</td>
</tr>
<tr>
<td>14</td>
<td>CBr$_3$O$_2$H +OH</td>
<td>1.9×10$^{-12}$ exp(190/T)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>CHBrO + hv</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>CHBr$_2$O$_2$NO$_2$ + M</td>
<td>$k_0=6.3×10^{-3}$ exp(-10235/T)[N$<em>2$], $k</em>{\infty}=1.42×10^{-16}$ exp(-1500/T)</td>
<td>From k(CCl$_3$O$_2$NO$_2$+M)</td>
<td>Köppenkastrop and Zabel (1991)</td>
</tr>
<tr>
<td>25</td>
<td>CHBr$_2$O$_2$NO$_2$ + hv</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>CHBr$_2$O$_2$H + hv</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>CHBr$_2$O$_2$H + OH</td>
<td>1.9×10$^{-12}$ exp(190/T)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>CBr$_3$OH+OH</td>
<td>3.6×10$^{-14}$</td>
<td>k(CCl$_3$O$_2$ + OH) at 298 K, assumed constant with temperature</td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>CBr$_2$OH+OH</td>
<td>9.34×10$^{-13}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5: Summary of the kinetic data used for the degradation of dibromomethane.

<table>
<thead>
<tr>
<th>No</th>
<th>Reactions</th>
<th>Rate constants (cm$^3$.molecule$^{-1}$.s$^{-1}$)</th>
<th>Comments</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>29</td>
<td>CH$_2$Br$_2$ + OH</td>
<td>$2 \times 10^{-12} \exp(-840/T)$</td>
<td></td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>30</td>
<td>CH$_2$Br$_2$ + Cl</td>
<td>$6.3 \times 10^{-12} \exp(-800/T)$</td>
<td></td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>31</td>
<td>CH$_2$Br$_2$ + hv</td>
<td></td>
<td>Absorption Cross Section</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>17</td>
<td>CHBr$_2$O$_2$ + NO</td>
<td>$3.81 \times 10^{-12} \exp(360/T)$</td>
<td>From k(CHCl$_2$O$_2$ + NO) at 298 K, assumed constant with</td>
<td>Jenkin et al. (1997)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>temperature</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>CHBr$_2$O$_2$ + NO$_2$</td>
<td>$9.2 \times 10^{-29} (T/300)^6$ $1.5 \times 10^{-11} (T/300)^{-0.7}$</td>
<td>From k(CCl$_3$O$_2$ + NO$_2$)</td>
<td>Caralp et al. (1998)</td>
</tr>
<tr>
<td>20</td>
<td>CHBr$_2$O$_2$ + HO$_2$</td>
<td>$5.6 \times 10^{-11} \exp(700/T)$</td>
<td>Branching ratio section 2.4.2</td>
<td>Catoire et al. (1996)</td>
</tr>
<tr>
<td>21</td>
<td>CHBr$_2$O$_2$ + CH$_3$O$_2$</td>
<td>$1.2 \times 10^{-12}$</td>
<td>From k(CHCl$_2$O$_2$ + CH$_3$O$_2$) at 298 K, assumed constant</td>
<td>Shallcross et al. (2005)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>with temperature</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>CH$_2$BrO$_2$ + NO</td>
<td>$4 \times 10^{-12} \exp(300/T)$</td>
<td>Temperature dependence from k(RO$_2$ + NO)</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>34</td>
<td>CH$_2$BrO$_2$ + NO$_2$</td>
<td>$9.2 \times 10^{-29} (T/300)^6$ $1.5 \times 10^{-11} (T/300)^{-0.7}$</td>
<td>From k(CCl$_3$O$_2$ + NO$_2$)</td>
<td>Caralp et al. (1998)</td>
</tr>
<tr>
<td>35</td>
<td>CH$_2$BrO$_2$ + HO$_2$</td>
<td>$3.3 \times 10^{-13} \exp(822/T)$</td>
<td>From k(CHCl$_2$O$_2$ + HO$_2$)</td>
<td>Catoire et al. (1994)</td>
</tr>
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<td>Branching ratio section 2.3.2</td>
<td>Villenave et al. (1996)</td>
</tr>
<tr>
<td>36</td>
<td>CH$_2$BrO$_2$ + CH$_3$O$_2$</td>
<td>$2.51 \times 10^{-12}$</td>
<td>From k(CHCl$_2$O$_2$ + CH$_3$O$_2$) at 298 K, assumed constant</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>with temperature</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>CBr$_2$O + hv</td>
<td></td>
<td>Absorption Cross Section</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>38</td>
<td>CH$_2$BrO$_2$NO$_2$ + M</td>
<td>$k_0=6.3 \times 10^{-5} \exp(-10235/T)[N_2]$</td>
<td>From k(CCl$_3$O$_2$NO$_2$+M)</td>
<td>Köppenkastrop and Zabel</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_{\infty}=1.42 \times 10^{16} \exp(-1500/T)$</td>
<td></td>
<td>(1991)</td>
</tr>
<tr>
<td>39</td>
<td>CH$_2$BrO$_2$NO$_2$ + hv</td>
<td></td>
<td>Absorption Cross Section of CH$_3$O$_2$NO$_2$</td>
<td>Atkinson et al. (2006)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Vaghjian and Ravishankara</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1989)</td>
</tr>
<tr>
<td>40</td>
<td>CH$_2$BrO$_2$H + hv</td>
<td></td>
<td>Absorption Cross Section of CH$_3$O$_2$H</td>
<td></td>
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<tr>
<td>41</td>
<td>CH$_2$BrO$_2$H + OH</td>
<td>$1.9 \times 10^{-12} \exp(190/T)$</td>
<td>From RO$_2$H + OH</td>
<td>Jenkin et al. (1997)</td>
</tr>
<tr>
<td>23</td>
<td>CHBr$_2$O + hv</td>
<td></td>
<td>Absorption Cross Section</td>
<td>Sander et al. (2011)</td>
</tr>
<tr>
<td>24</td>
<td>CHBr$_2$O$_2$NO$_2$ + M</td>
<td>$k_0=6.3 \times 10^{-5} \exp(-10235/T)[N_2]$</td>
<td>From k(CCl$_3$O$_2$NO$_2$+M)</td>
<td>Köppenkastrop and Zabel</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_{\infty}=1.42 \times 10^{16} \exp(-1500/T)$</td>
<td></td>
<td>(1991)</td>
</tr>
<tr>
<td>25</td>
<td>CHBr$_2$O$_2$NO$_2$ + hv</td>
<td></td>
<td>Absorption Cross Section of CH$_3$O$_2$NO$_2$</td>
<td>Atkinson et al. (2006)</td>
</tr>
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<td></td>
<td></td>
<td>Vaghjian and Ravishankara</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1989)</td>
</tr>
<tr>
<td>26</td>
<td>CHBr$_2$O$_2$H + hv</td>
<td></td>
<td>Absorption Cross Section of CH$_3$O$_2$H</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>CHBr$_2$O$_2$H + OH</td>
<td>$1.9 \times 10^{-12} \exp(190/T)$</td>
<td>From RO$_2$H + OH</td>
<td>Jenkin et al. (1997)</td>
</tr>
<tr>
<td>42</td>
<td>CH$_2$BrOH + OH</td>
<td>$1.8 \times 10^{-12}$</td>
<td>From k(CH$_2$ClO$_2$ + OH)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>at 298 K, assumed constant with temperature</td>
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</table>
Table 6: Initial volume mixing ratios in parts per billion (ppbv) used in the model for the two simulation scenarios, from MOCAGE CTM outputs (see text for details).

<table>
<thead>
<tr>
<th>Model Parameter</th>
<th>Scenario at 1000 m</th>
<th>CLEAN</th>
<th>MODERATE</th>
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<tr>
<td>O₃</td>
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<td>29</td>
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</tr>
<tr>
<td>NOₓ</td>
<td>0.036</td>
<td>0.061</td>
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</tr>
<tr>
<td>HNO₃</td>
<td>0.78</td>
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<td>CO</td>
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<td>64</td>
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<tr>
<td>CH₄</td>
<td>1590</td>
<td>1557</td>
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</tr>
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</table>
### Table 7: Reactions tested in the different simulations for CHBr$_3$.

<table>
<thead>
<tr>
<th>Simulation</th>
<th>Scenario</th>
<th>CHBr$_3$ initialization</th>
<th>RO$_2^+$</th>
<th>RO$_2^+$</th>
<th>RO$_2$ + HO$_2$</th>
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<tr>
<td>Reference</td>
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<td>included</td>
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<td>1$^a$</td>
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<tr>
<td></td>
<td>Fig. 2A and 2B</td>
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<td></td>
<td></td>
<td>0.7$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.3$^b$</td>
</tr>
<tr>
<td>#1</td>
<td>CLEAN and MODERATE</td>
<td>not</td>
<td>included</td>
<td>included</td>
<td>1$^a$</td>
</tr>
<tr>
<td></td>
<td>Fig. 2B</td>
<td></td>
<td></td>
<td></td>
<td>0.7$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.3$^b$</td>
</tr>
<tr>
<td>#2</td>
<td>CLEAN</td>
<td>not</td>
<td>not</td>
<td>not</td>
<td>0.5$^a$</td>
</tr>
<tr>
<td></td>
<td>Fig. 2B</td>
<td></td>
<td></td>
<td></td>
<td>0.5$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0$^b$</td>
</tr>
<tr>
<td>#3</td>
<td>CLEAN</td>
<td>not</td>
<td>not</td>
<td>not</td>
<td>0.5$^a$</td>
</tr>
<tr>
<td></td>
<td>Fig. 2B</td>
<td></td>
<td></td>
<td></td>
<td>0.5$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0$^b$</td>
</tr>
</tbody>
</table>

(a), (b), (c): branching ratios for the channels of RO$_2$ + HO$_2$ reaction as defined in Table 1 or Fig. 1.

/: Channel not possible

$^a$: RO$_2$ = CBr$_3$O$_2$

$^b$: RO$_2$ = CHBr$_3$O$_2$
Table 8: Reactions tested in the different simulations for CH₂Br₂.

<table>
<thead>
<tr>
<th>n°</th>
<th>Scenario</th>
<th>RO₂⁺NO₂</th>
<th>RO₂⁺CH₃O₂</th>
<th>RO₂ + HO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ref</td>
<td>CLEAN and</td>
<td>included</td>
<td>included</td>
<td>(a)</td>
</tr>
<tr>
<td></td>
<td>MODERATE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>included</td>
<td></td>
<td></td>
<td>(b)</td>
</tr>
<tr>
<td></td>
<td>included</td>
<td></td>
<td></td>
<td>(c)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CLEAN</td>
<td>included</td>
<td>included</td>
<td>0.7^a</td>
</tr>
<tr>
<td>#1</td>
<td>included</td>
<td></td>
<td></td>
<td>0.3^a</td>
</tr>
</tbody>
</table>

(a), (b), (c): branching ratios for the channels of RO₂ + HO₂ reaction as defined in Table 1 and Fig. 1.

Channel not possible

^a: RO₂ = CHBr₂O₂

^b: RO₂ = CH₂BrO₂
Table 9: Relative partitioning of Br atom at the end of the simulation (i.e. after 10 days), at 1 km altitude, in CHBr₃ degradation for the source gas, organic and inorganic species: for the reference simulation, simulation #2 and simulation #3 in the clean atmosphere and for the reference simulation in the moderately polluted atmosphere (for the simulation conditions, see Tables 6 and 7).

<table>
<thead>
<tr>
<th>Source gas</th>
<th>Clean atmosphere</th>
<th>Moderate pollution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reference simulation</td>
<td>Simulation # 2</td>
</tr>
<tr>
<td>CHBr₃</td>
<td>37.5 %</td>
<td>40.9 %</td>
</tr>
<tr>
<td>Organic products</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHBrO</td>
<td>11.8 %</td>
<td>12.8 %</td>
</tr>
<tr>
<td>CBr₂O</td>
<td>1.4 %</td>
<td>1.5 %</td>
</tr>
<tr>
<td>CBr₃O₂H</td>
<td>0.6 %</td>
<td>1.0 %</td>
</tr>
<tr>
<td>CHBr₂O₂H</td>
<td>0.8 %</td>
<td>1.0 %</td>
</tr>
<tr>
<td>CBr₃OH</td>
<td>2.3 %</td>
<td>/</td>
</tr>
<tr>
<td>CHBr₂OH</td>
<td>0.2 %</td>
<td>/</td>
</tr>
<tr>
<td>CBr₃O₂</td>
<td>&lt; 0.01 %</td>
<td>&lt; 0.01 %</td>
</tr>
<tr>
<td>CHBr₂O₂</td>
<td>&lt; 0.01 %</td>
<td>&lt; 0.01 %</td>
</tr>
<tr>
<td>CBr₃O₂NO₂</td>
<td>&lt; 0.01 %</td>
<td>/</td>
</tr>
<tr>
<td>CHBr₂O₂NO₂</td>
<td>&lt; 0.01 %</td>
<td>/</td>
</tr>
<tr>
<td>Inorganic products</td>
<td>45.3 %</td>
<td>42.9 %</td>
</tr>
<tr>
<td>HBr</td>
<td>36 %</td>
<td>33.5 %</td>
</tr>
<tr>
<td>BrO</td>
<td>1.1 %</td>
<td>1.0 %</td>
</tr>
<tr>
<td>HOB₃R</td>
<td>3.0 %</td>
<td>2.9 %</td>
</tr>
<tr>
<td>BrOONO₂</td>
<td>5.1 %</td>
<td>5.4 %</td>
</tr>
<tr>
<td>Br</td>
<td>0.1 %</td>
<td>0.1 %</td>
</tr>
<tr>
<td>Br₃max a (pptv)</td>
<td>(0.9 – 9.3)</td>
<td>(10.3)</td>
</tr>
<tr>
<td></td>
<td>(Fig. 2A – 2B)</td>
<td>(Fig. 2B)</td>
</tr>
</tbody>
</table>

a: Maximum Br (in %) potentially able to reach the tropical tropopause layer (TTL).
Table 10: Relative partitioning of Br atom at the end of the simulation (i.e. after 50 days), at 1 km altitude, in CH$_2$Br$_2$ degradation for the source gas, organic and inorganic species: for the reference simulation in clean atmosphere and for the reference simulation in polluted atmosphere (for the simulation conditions, see Table 8).

<table>
<thead>
<tr>
<th></th>
<th>Clean atmosphere</th>
<th>Moderate pollution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reference simulation</td>
<td>Reference simulation</td>
</tr>
<tr>
<td><strong>Source gas</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_2$Br$_2$</td>
<td>54.4 %</td>
<td>39.5 %</td>
</tr>
<tr>
<td><strong>Organic products</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CBr$_2$O</td>
<td>1.0 %</td>
<td>1.0 %</td>
</tr>
<tr>
<td>CHBrO</td>
<td>0.3 %</td>
<td>0.3 %</td>
</tr>
<tr>
<td>CHBr$_2$O$_2$H</td>
<td>0.3 %</td>
<td>0.2 %</td>
</tr>
<tr>
<td>CHBr$_2$OH</td>
<td>0.1 %</td>
<td>0.1 %</td>
</tr>
<tr>
<td><strong>Inorganic products</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HBr</td>
<td>36.3 %</td>
<td>40.1 %</td>
</tr>
<tr>
<td>BrO</td>
<td>1.5 %</td>
<td>2.8 %</td>
</tr>
<tr>
<td>HOB</td>
<td>3.3 %</td>
<td>8.6 %</td>
</tr>
<tr>
<td>BrONO$_2$</td>
<td>2.6 %</td>
<td>7.4 %</td>
</tr>
<tr>
<td>Br</td>
<td>0.1 %</td>
<td>0.1 %</td>
</tr>
<tr>
<td><strong>Br$_{\text{max}}$</strong>$^a$</td>
<td>8.8 %</td>
<td>20.2 %</td>
</tr>
<tr>
<td>(pptv)</td>
<td>(0.19)</td>
<td>(0.42)</td>
</tr>
</tbody>
</table>

$^a$: Maximum Br (in %) potentially able to reach the TTL.
Fig. 1: Chemical mechanisms of bromoform (CHBr₃) and dibromomethane (CH₂Br₂) degradations. A: Initial steps reaction (OH, Cl and photolysis). B: Brominated peroxy radical reaction degradation mechanism, B.1: CBr₃O₂, B.2: CHBr₂O₂ (common to both molecules) and B.3: CH₂BrO₂. Stable intermediate products are enclosed in dotted line boxes and final inorganic bromine inside full line boxes. The decomposition reactions are indicated by dashed arrows.

Fig. 2: Bromoform vertical profiles used for the initialization of the simulations (see Section 3). A: mean tropical data, and B: maximum tropical data, given by Montzka and Reimann et al. (2011; open diamonds), Yokouchi et al. (2005; full triangles) and Hossaini et al. (2010; dashed lines).

Fig. 3: Dibromomethane vertical profile used for the initialization of the simulations (see Section 3) from Montzka and Reimann et al. (2011; open diamonds) and dashed line is an interpolation from observed mixing ratio profiles (Hossaini et al., 2010).

Fig. 4: CHBr₃ total lifetime \( \tau_{\text{total}} \) (bold line) in the overall simulated domain due to the reaction with OH (dot-dashed line) and due to the photolysis (dotted line) in the clean atmosphere (left panel) and in the moderately polluted atmosphere (right panel).

Fig. 5: 10-days simulation average for OH vertical profiles (molecules cm⁻³) in the clean atmosphere (full line) and in the moderately polluted atmosphere (dashed line).

Fig. 6: Vertical profiles of Br contained in CHBr₃ (top), in the total organics (upper middle), in HBr (lower middle), and in the total inorganics (bottom) except HBr, on 17 November (open circle), on 20 November (open square), on 23 November (cross) and on 26 November (open triangle), for the clean atmosphere (left panels) and the polluted atmosphere (right panels) for the bromoform initialization from Fig. 2A.

Fig. 7: Time dependence of Br partitioning between the most soluble species (CBr₃O₂H, CHBr₂O₂H, CBr₃OH, CHBr₂OH, HBr) and the least soluble species (BrO, BrONO₂, Br, HOBr, CBr₂O, CHBrO, CBr₃O₂NO₂ and CHBr₂O₂NO₂) for the reference simulation (see Table 7) in the clean atmosphere (top panels) and in the polluted atmosphere (bottom panels). A: CHBr₃ initialization from Fig. 2A (Montzka and Reimann et al., 2011), and B: CHBr₃ initialization from Fig. 2B (Yokouchi et al., 2005 and Montzka and Reimann et al., 2011).

Fig. 8: Simplified chemical mechanism of bromoform (CHBr₃) and dibromomethane (CH₂Br₂) degradations. Stable intermediate products are enclosed in dashed line boxes for the
least soluble species, in dotted line boxes for the most soluble species, and the final inorganic bromine in full line boxes.

Fig. 9: Vertical profiles of Br contained in CH$_2$Br$_2$ (top), in the total organics (upper middle), in HBr (lower middle) and in the total inorganics (bottom) except HBr on 17 November (open circle), on 03 December (open square), on 20 December (cross) and on 05 January (open triangle), for the clean atmosphere (left panels) and the polluted atmosphere (right panels).

Fig. 10: Time dependence of Br partitioning between the most soluble species (CHBr$_2$O$_2$H, CH$_2$BrO$_2$H, CHBr$_2$OH, CH$_2$BrOH, HBr) and the least soluble species (BrO, BrONO$_2$, Br, HOBr, CBr$_2$O, CHBrO, CHBr$_2$O$_2$NO$_2$ and CH$_2$BrO$_2$NO$_2$) for the reference simulation in the clean atmosphere (left panel) and in the polluted atmosphere (right panel).
Fig. 1: Chemical mechanisms of bromoform (CHBr₃) and dibromomethane (CH₂Br₂) degradations. A: Initial steps reaction (OH, Cl and photolysis). B: Brominated peroxo radical reaction degradation mechanism, B.1: CBr₃O₂, B.2: CHBr₂O (common to both molecules) and B.3: CH₂BrO₂. Stable intermediate products are enclosed in dotted line boxes and final inorganic bromine inside full line boxes. The decomposition reactions are indicated by dashed arrows.
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Fig. 5: 10-days simulation average for OH vertical profiles (molecules cm$^{-3}$) in the clean atmosphere (full line) and in the moderately polluted atmosphere (dashed line).
Fig. 6: Vertical profiles of Br contained in CHBr₃ (top), in the total organics (upper middle), in HBr (lower middle), and in the total inorganics (bottom) except HBr, on 17 November (open circle), on 20 November (open square), on 23 November (cross) and on 26 November (open triangle), for the clean atmosphere (left panels) and the polluted atmosphere (right panels) for the bromoform initialization from Fig. 2A.
Fig. 7: Time dependence of Br partitioning between the most soluble species (CBr$_3$O$_2$H, CHBr$_2$O$_2$H, CBr$_3$OH, CHBr$_2$OH, HBr) and the least soluble species (BrO, BrONO$_2$, Br, HOBr, CBr$_2$O, CHBrO, CBr$_3$O$_2$NO$_2$ and CHBr$_2$O$_2$NO$_2$) for the reference simulation (see Table 7) in the clean atmosphere (top panels) and in the polluted atmosphere (bottom panels). A: CHBr$_3$ initialization from Fig. 2A (Montzka and Reimann et al., 2011), and B: CHBr$_3$ initialization from Fig. 2B (Yokouchi et al., 2005 and Montzka and Reimann et al., 2011).
Fig. 8: Simplified chemical mechanism of bromoform (CHBr$_3$) and dibromomethane (CH$_2$Br$_2$) degradations. Stable intermediate products are enclosed in dashed line boxes for the least soluble species, in dotted line boxes for the most soluble species, and the final inorganic bromine in full line boxes.
Fig. 9: Vertical profiles of Br contained in CH₂Br₂ (top), in the total organics (upper middle), in HBr (lower middle) and in the total inorganics (bottom) except HBr on 17 November (open circle), on 03 December (open square), on 20 December (cross) and on 05 January (open triangle), for the clean atmosphere (left panels) and the polluted atmosphere (right panels).
Fig. 10: Time dependence of Br partitioning between the most soluble species (CHBr₂O₂H, CH₂BrO₂H, CHBr₂OH, CH₂BrOH, HBr) and the least soluble species (BrO, BrONO₂, Br, HOBr, CBr₂O, CHBrO, CHBr₂O₂NO₂ and CH₂BrO₂NO₂) for the reference simulation in the clean atmosphere (left panel) and in the polluted atmosphere (right panel).