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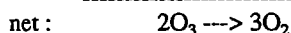
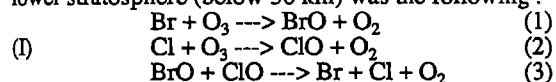
ROLE OF THE $\text{BrO} + \text{HO}_2$ REACTION IN THE STRATOSPHERIC CHEMISTRY OF BROMINEGilles Poulet¹, Michel Pirre², Françoise Maguin¹, Radiela Ramaroson³ and Georges Le Bras¹

Abstract. The impact of new laboratory data for the reaction $\text{BrO} + \text{HO}_2 \rightarrow \text{HOBr} + \text{O}_2$ has been estimated in a one-dimensional photochemical modelling of bromine/ozone stratospheric chemistry. The reported 6 fold increase in the measured value for the rate constant of this reaction significantly increases both the HOBr mixing ratio and the global ozone depletion due to bromine compounds (the calculated ozone loss increases from 1.14% to 1.45% for a 20 ppt total bromine content). The higher rate constant makes the bromine partitioning and the ozone depletion very sensitive to the branching ratio of the potential channel forming HBr in the $\text{BrO} + \text{HO}_2$ reaction. The influence of the existing uncertainty in the photolysis rate of HOBr is also analysed.

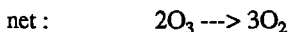
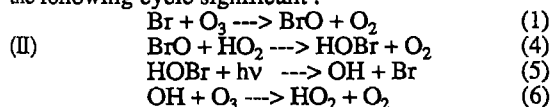
Introduction

Bromine compounds interact with ozone in the stratosphere through chemical cycles as is observed with chlorine species (Wofsy et al., 1975 ; Yung et al., 1980). Recently, bromine has been considered to play a significant role in the perturbed chemistry invoked to explain springtime ozone hole formation in polar stratospheric regions (Mac Elroy et al., 1986). Besides, the photochemistry of bromine has been suggested recently to explain the bromine/ozone anti-correlation observed in the lower Arctic troposphere (Barrie et al., 1988).

In their modelling of the influence of bromine compounds on the chemistry of the lower stratosphere, Yung et al. (1980) concluded that the catalytic cycle which had the major impact on the destruction of odd oxygen in the lower stratosphere (below 30 km) was the following :



The conclusions of Yung et al. were based on the use of the kinetic data available at that time. More specifically, the rate constant taken for reaction (4) : was too low to make the following cycle significant :



The rate constant used for reaction (4) by Yung et al. ($k_4 = 4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) was based on the value measured for the similar reaction of ClO with HO_2 . This value appeared to be confirmed in the first experimental

determination ($5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) by Cox and Sheppard (1982) and is still the preferred value given in the kinetic data bases (e.g. De More et al., 1990). However, with the much higher value of k_4 (6 fold increase) recently obtained at the CNRS-LCSR, cycle (II) may no longer be insignificant, particularly in the lower stratosphere.

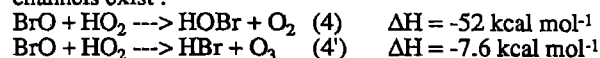
The present paper briefly reports the new kinetic data obtained for the $\text{BrO} + \text{HO}_2$ reaction, and describes the impact of this result on the modelling of stratospheric photochemistry. Within the modelling, the uncertainties still existing on the mechanism of this reaction have also been considered.

Kinetic study of the $\text{BrO} + \text{HO}_2$ reaction

The results of a recent kinetic study carried out at the CNRS-LCSR are reported only briefly here, since a more detailed version will be published elsewhere (Maguin et al.). The apparatus, previously described (Poulet et al., 1990), consists of a double discharge flow reactor coupled to a quadrupole mass spectrometer. BrO was produced by the reaction $\text{O} + \text{Br}_2 \rightarrow \text{BrO} + \text{Br}$ (excess of Br_2) and HO_2 was generated from $\text{Cl}/\text{CH}_3\text{OH}/\text{O}_2$ mixtures (excess of CH_3OH and O_2). The rate constant for reaction (4) was determined under pseudo-first order conditions monitoring BrO by mass spectrometry as a function of reaction time in the presence of excess HO_2 . The concentration of HO_2 , as determined from titration with NO, ranged from 1 to $5 \times 10^{12} \text{ cm}^{-3}$. From the pseudo-first order kinetic treatment, the rate constant obtained at 298K was : $k_4 = (3.3 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The error represents two standard deviations. This direct measurement of k_4 is around 6 times higher than the only other previously published determination (Cox and Sheppard, 1982) obtained using the molecular modulation-UV absorption technique, where O_3 was photolysed in the presence of Br_2 , H_2 and O_2 . Due to the indirect way of determining k_4 in the experiments of Cox and Sheppard, k_4 was measured with rather poor precision : $k_4 = (5^{+5}_{-3}) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In contrast, our value of k_4 is in good agreement with a recent measurement (Bridier et al., 1991) derived from flash photolysis-UV absorption experiments, where mixtures of Br_2 , O_3 , Cl_2 , CH_3OH and O_2 were photolysed and the rate constant $k_4 = (3 \pm 2) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ indirectly obtained from the computer modelling of the experimental kinetics.

This new and higher value for k_4 fits correctly with the reactivity trend for the reactions of HO_2 with halogen oxide radicals. The rate constant at 298K increases from 5×10^{-12} for ClO (De More et al., 1990) to 3×10^{-10} for IO (Maguin et al., 1992), with an intermediate value for BrO.

In the present work, detection of reaction products was also attempted by mass spectrometry. Two exothermic channels exist :



The only product observed at 298K was HOBr suggesting that channel (4') yielding HBr would be negligible at 298K, which indeed does not preclude its occurrence at the lower temperatures of the stratosphere.

Modelling study of the impact of the $\text{BrO} + \text{HO}_2$ reaction

The 6 fold higher value obtained for k_4 has been used as input data in a 1D steady state photochemical model. The

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aim of this calculation was mainly to estimate the effect of this new kinetic data on the bromine partitioning in the stratosphere and on the ozone depletion due to bromine compounds. The effect of the possible occurrence of the HBr forming channel in the BrO + HO₂ reaction at low temperatures, which remains to be established by laboratory studies, was also investigated.

The 1D model of the CNRS-LPCE which was used has been recently described (Ramaroson et al., 1991). This model includes the species of the O_x, HO_x, NO_x, ClO_x and BrO_x families and the source species : N₂O, H₂O, CH₄, CO, CFC_s, CH₃Cl and CH₃Br. The kinetic and photochemical data used are essentially those recommended in the NASA-JPL report (De More et al., 1990). Those concerning the bromine species are reported in Table I. To calculate the photodissociation rates, solar fluxes are computed taking into account their attenuation by O₂ and O₃, using the vertical profiles of O₃ given by Krueger and Minzner (1976), and by Rayleigh scattering in a spherical geometry.

The steady-state vertical distributions of the source species and families are computed by iterations from 0 to 60 km, in steps of 1 km. The diurnal averaged production and loss terms needed are calculated before each iteration. The short-lived species are computed, at each level, by using a box model constrained by the vertical distribution of the source species and families obtained in the previous iteration. The results presented in this paper are the 24 hourly averaged vertical distributions of the various species.

The model has been used first to calculate the partitioning of the BrO_x species as a function of altitude, for a mixing ratio of total bromine at the ground of 20 pptv, which is consistent with the present atmospheric content, as recently discussed by Salawitch et al. (1988). The BrO_x species are Br, BrO, HBr, HOBr, BrONO₂ and BrCl. They represent the total bromine content at altitudes higher than 25 km since, at this altitude, the bromine precursor considered in our model (CH₃Br) is totally consumed. A total atmospheric chlorine content of 3.2 ppb was used, in agreement with the current estimations.

Several calculations have been performed, corresponding to different cases which are summarized in Table II. In the first calculation (case 1), all the kinetic data used for bromine reactions were those from the NASA-JPL data base (De More et al., 1990). Therefore, the rate constant for the BrO + HO₂ reaction was taken as $k_4 = 5 \times 10^{-12}$ cm³molecule⁻¹s⁻¹ and only the channel yielding HOBr was considered. For the photodissociation rate of HOBr, a mean estimated value of 1.5×10^{-3} s⁻¹, independent of altitude, was considered. This value was based on the value of the cross

Table II: Cases considered in the model calculations

Case	J(HOBr)	k ₄ (cm ³ molecule ⁻¹ s ⁻¹)	k ₄ ' (cm ³ molecule ⁻¹ s ⁻¹)
1	1.5 10 ⁻³ s ⁻¹	5.0 10 ⁻¹²	0
2	1.5 10 ⁻³ s ⁻¹	3.3 10 ⁻¹¹	0
3	(a)	3.3 10 ⁻¹¹	0
4	(a)	4.5 10 ⁻¹²	5.0 10 ⁻¹¹
5	(a)	2.97 10 ⁻¹¹	3.3 10 ⁻¹¹
6	(a)	5.0 10 ⁻¹²	0

(a): computed from Schindler (1991)

section of HOCl red shifted by 300 nm (Yung et al., 1980). In a second calculation (case 2), all the input data of case 1 were used, except the rate constant for the BrO + HO₂ reaction, for which our determination was taken: $k_4 = 3.3 \times 10^{-11}$ cm³molecule⁻¹s⁻¹. In the absence of measurements of k_4 as a function of temperature, k_4 was assumed to be temperature independent in the atmospheric temperature range (220-300K). This assumption is reasonable when regarding the high value measured here for k_4 at 298K. The comparison of the results of "case 1" and "case 2", given in Figures 1 and 2 respectively, shows that the increase in k_4 has only a minor effect on the BrO_x partitioning at any altitude except for HOBr. The HOBr mixing ratio increases drastically, e.g. by a factor 6 between 20 and 30 km. BrONO₂ remains the major bromine reservoir, but HOBr becomes more abundant than HBr above 20 km.

In the calculations of cases 1 and 2, the photolysis rate of HOBr, J(HOBr), may be a major source of uncertainty, since this rate was only an estimate (see above). There is no experimental data published so far for the cross section of HOBr, only preliminary measurements by Schindler (1991). These new data qualitatively confirm the red shift assumed by Yung et al. (1980), but yield higher photodissociation rates. The value of J(HOBr), calculated from these experimental cross sections, was used in the model calculations of case 3 (using the high k_4 , as in case 2). The only resulting change is a decrease of HOBr concentration (Figure 2). Nevertheless, the HOBr concentrations are still significantly higher (around 2.5 times at 20 and 30 km) than those of case 1 with low k_4 and low J(HOBr).

Other calculations were made with low k_4 (case 4) and high k_4 (case 5), assuming a branching ratio of 10 % for the HBr forming channel of the BrO + HO₂ reaction:



In these calculations and the ones following, the high value for the photodissociation rate of HOBr was used. The results show (Figure 3) that the bromine partitioning is very sensitive to the branching ratio of channel (4'), since HBr

Table I: Reactions involving bromine compounds and rate coefficients in case 1

CH ₃ Br + hv → CH ₃ + Br	(a)
BrO + hv → Br + O	(a)
BrONO ₂ + hv → Br + NO ₂	(a)
HOBr + hv → OH + Br	(a)
BrCl + hv → Br + Cl	(a)
CH ₃ Br + OH → products ^(b)	$6.8 \cdot 10^{12} \exp(-850/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
Br + O ₃ → BrO + O ₂	$1.7 \cdot 10^{11} \exp(-800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
Br + O → Br + O ₂	$3.0 \cdot 10^{11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
BrO + ClO → Br + ClOO	$2.9 \cdot 10^{12} \exp(220/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
BrO + ClO → Br + OClO	$1.6 \cdot 10^{12} \exp(430/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
BrO + ClO → BrCl + O ₂	$5.8 \cdot 10^{13} \exp(170/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
BrO + NO → Br + NO ₂	$8.8 \cdot 10^{13} \exp(260/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
BrO + BrO → Br + Br + O ₂	$1.4 \cdot 10^{12} \exp(150/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
Br + HO ₂ → HBr + O ₂	$1.5 \cdot 10^{11} \exp(-600/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
HBr + OH → Br + H ₂ O	$1.1 \cdot 10^{11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
BrO + HO ₂ → HOBr + O ₂	$5.0 \cdot 10^{12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
BrO + OH → Br + HO ₂	$1.0 \cdot 10^{11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
HBr + O → Br + OH	$5.8 \cdot 10^{11} \exp(-1500/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
Br + CH ₂ O → HBr + CHO	$1.7 \cdot 10^{11} \exp(-800/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
BrO + NO ₂ + M → BrONO ₂ + M ^(c)	$k_4 = 5.2 \cdot 10^{-11} (T/300)^{-2.2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ $k_4 = 9.0 \cdot 10^{-12} (T/300)^{-2.2} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

(a): see text for the photodissociation rate calculations

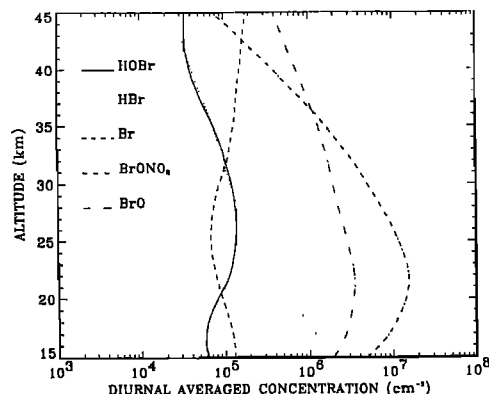
(b): considered in the model as the limiting step for the Br production from CH₃Br(c): $k = \left(\frac{k_0[M]}{1 + k_0[M]/k_c} \right) \cdot 0.6 \left(1 + [\log_{10}(k_0[M]/k_c)]^2 \right)^{-1}$ 

Fig. 1. Diurnal averaged concentrations of the BrO_x species as a function of altitude: $k_4 = 5 \times 10^{-12}$ cm³molecule⁻¹s⁻¹, $k_4' = 0$, J(HOBr) = 1.5×10^{-3} s⁻¹ (case 1).

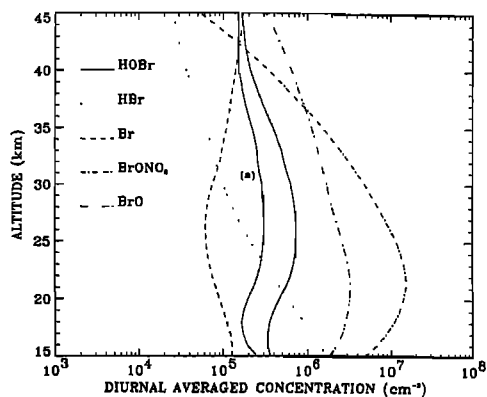
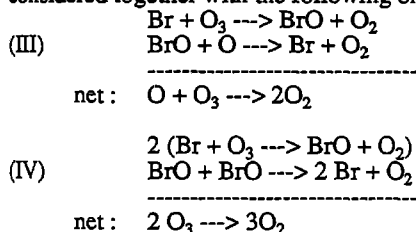


Fig. 2. Diurnal averaged concentrations of the BrO_y species as a function of altitude: $k_4 = 3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_4 = 0$, $J(\text{HOBr}) = 1.5 \times 10^{-3} \text{ s}^{-1}$ (case 2). (a) : HOBr profile under conditions of case 2, except $J(\text{HOBr})$ calculated from experimental UV spectrum of Schindler, 1991 (case 3).

concentration is significantly increased, e.g. by a factor 3.5 between 20 and 30 km, in case 5 (high k_4) compared to case 4 (low k_4). It is also important to notice that, in this case, HBr would become the major bromine species together with BrONO₂ in the lower stratosphere. This would qualitatively support a recent interpretation of a field observation of HBr by far infrared emission, concluding that HBr could be the major stratospheric bromine species (Park et al., 1989).

Beside the effect on the BrO_y partitioning discussed above, the new k_4 value may have an impact on the ozone depletion by the bromine compounds, through the catalytical cycles involving bromine radicals which deplete odd oxygen. The efficiencies of these cycles have been compared, using in the model calculations the low k_4 (case 6) and high k_4 (case 3). Cycles (I) and (II), already mentioned, have been considered together with the following ones :



The odd oxygen destruction rates by cycles (I) to (IV) have been calculated (Figure 4), under conditions of both low

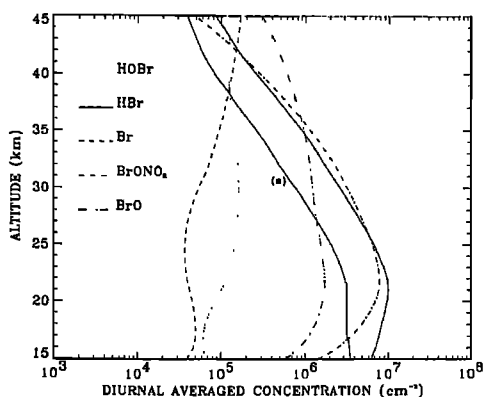


Fig. 3. Diurnal averaged concentrations of the BrO_y species as a function of altitude: $k_4 = 3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_4 = 3.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (case 5). (a) : HBr profile under conditions of case 4 (case 5, except $k_4 = 4.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_4 = 5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).

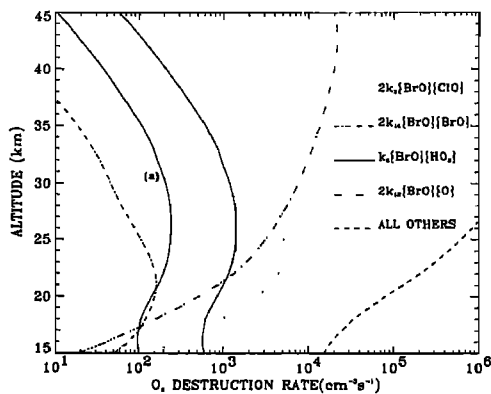


Fig. 4. Rates of odd oxygen destruction by bromine cycles (I) to (IV). "All others" is the total odd oxygen destruction rate by the other cycles. $k_4 = 3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k_4 = 0$ (case 3). (a): rate of odd oxygen destruction by cycle (II) under conditions of case 6 (case 3, except $k_4 = 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).

and high k_4 . The odd oxygen destruction rate by all the other cycles (excluding the bromine ones) is also given for comparison. Unlike cycles (I), (III) and (IV), the rate of cycle (II) increases by a factor around 6, similar to the increase in k_4 (Figure 4). This was expected since reaction (4) is the limiting step of cycle (II) either with low or high k_4 value. This also demonstrates the negligible role of HOBr as a BrO reservoir with the photodissociation coefficients presently considered for HOBr. With the new k_4 value, cycle (II) becomes significant in the lower stratosphere, although cycle (I) remains dominant around 20 km, as previously calculated by Yung et al.(1980).

The effect of the new k_4 value on the ozone depletion by bromine compounds has been quantified by calculating the percentage of ozone decrease versus altitude produced by 20 ppt of bromine, using successively the low and high k_4 values (Figure 5). From these calculations, it was found that the increase of k_4 led to an increased reduction of the ozone column density from 1.14% to 1.45%. The calculated column densities of ozone were the following : $8.488 \times 10^{18} \text{ molecule cm}^{-2}$ (no bromine), $8.391 \times 10^{18} \text{ molecule cm}^{-2}$ (20 ppt of bromine, low k_4), and $8.365 \times 10^{18} \text{ molecule cm}^{-2}$ (20 ppt of bromine, high k_4). Therefore, the new k_4 value has a significant impact on the predicted ozone depletion by the bromine compounds at their present levels in the atmosphere. The ozone depletion of 1.14%, calculated with the low k_4 , is

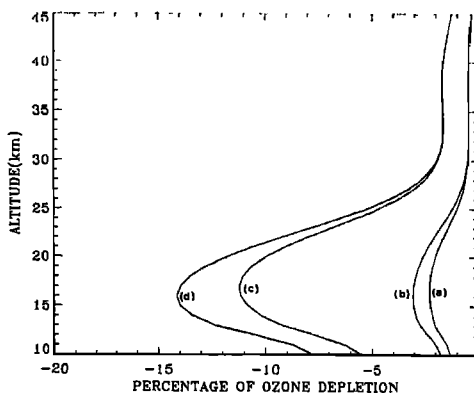


Fig. 5. Percentage of ozone depletion by 20 ppt of bromine as a function of altitude. (a): $k_4 = 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (case 6); (b): $k_4 = 3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (case 3). Increase from 20 to 100 ppt of bromine: (c): $k_4 = 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (case 4); (d): $k_4 = 3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (case 3).

much lower than the 2.4% obtained by Yung et al.(1980) under similar conditions. This is likely due to the use by these authors of an estimated value for the rate constant of the reaction $\text{BrO} + \text{NO}_2 \rightarrow \text{BrONO}_2$, which is lower than the currently recommended value based on experimental measurements (De More et al., 1990).

The impact of the new k_4 value on ozone depletion has also been calculated considering a scenario where the bromine content of the atmosphere would increase from 20 to 100 ppt. The resulting percentage of ozone decrease versus altitude is given in Figure 5, using successively the low k_4 and high k_4 values (case 6 and case 3). Upon integration of these curves, it was found that such an increase in bromine would decrease the ozone column density by 5.42% (low k_4) or 6.40% (high k_4).

In contrast, the calculations made with a 10% branching ratio for the HBr forming channel of reaction (4) show a significant decrease of the ozone depletion when k_4 is increased : the ozone column density is decreased by 1.0% and 0.6% for 20 ppt of bromine, using respectively the low and high k_4 values (cases 4 and 6). Besides, the calculated depletion due to an increase of bromine from 20 to 100 ppt decreases from 4.43% (low k_4) to 2.62% (high k_4). Such effects were expected considering that HBr is a more efficient reservoir for BrO than HOBr.

Conclusion

From the present modelling calculations, the new rate constant reported in this paper for the reaction of BrO with HO₂ and the potential existence of an HBr forming channel have a significant effect both on the bromine partitioning and on the ozone depletion by the bromine compounds in the global lower stratosphere. However, the importance of this reaction, involved in cycle (II), could be reduced in the future if the BrO + ClO reaction, involved in cycle (I), becomes more important as a result of the predicted increase of the ClO concentrations in the lower stratosphere. Furthermore, this increase of ClO could be enhanced by heterogeneous production on ice crystals which could become more important in the lower stratosphere, even outside of the polar regions, as a result of an increasing stratospheric content of H₂O associated with a possible temperature decrease induced by the greenhouse effect. An increase of ClO may also occur in the lower stratosphere within the next few years as a consequence of the expected NO_x depletion due to the recent eruption of the Pinatubo volcano, as has already been suggested by Arnold et al.(1990) for the previous eruption of El Chichon. In such a case, however, the real impact of the BrO + HO₂ reaction will also depend on the possible increase of both HO_x (OH, HO₂) and BrO resulting from the decreased importance of the HNO₃, HO₂NO₂ and BrONO₂ reservoir species. In conclusion, whatever the evolution of the chemical composition of the stratosphere, the potential stratospheric importance of the BrO + HO₂ reaction flagged in this paper requires further laboratory kinetic and photochemical investigation particularly concerning the rate constant of this reaction at low temperature, the branching ratio of the HBr forming channel and the UV absorption cross sections of HOBr.

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