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ROLE OF THE BRO + HO2 REACTION IN THE STRATOSPHERIC CHEMISTRY OF BROMINE

Gilles Poulet, Michel Pirre, Françoise Maguin, Radiela Ramaroson and Georges Le Bras

Abstract. The impact of new laboratory data for the reaction BrO + HO2 → HOBr + O2 has been estimated in a one-dimensional photochemical modelling of bromine/ozone stratospheric chemistry. The reported 6 fold increase in the rate constant makes the higher rate constant of this reaction the dominant bromine/ozone reaction in the lower stratosphere. The measured value for the rate constant of this reaction is consistent with the much higher value of k4 (6 fold increase) recently obtained at the CNRS-LCSR, cycle (II) may no longer be significant, particularly in the lower stratosphere.

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:

1. Br + O3 → BrO + O2
2. Cl + O3 → ClO + O2
3. BrO + HO2 → Br + HO2 + O2
4. HOBr + hv → OH + Br

The rate constant for reaction (4) was determined by applying a pseudo-first order kinetic treatment, the rate constant k4 = (3 4- 2) x 10^-11 cm^3 molecule^-1 s^-1 indirectly obtained from a computer modelling of the experimental kinetics.

This new and higher value for k4 fits correctly with the reactivity trend for the reactions of HO2 with halogen oxide radicals. The rate constant at 298K increases from 5 x 10^-12 for ClO (De More et al., 1990) to 3 x 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:

BrO + HO2 → HOBr + O2 (4) ΔH = -52 kcal mol^-1
BrO + HO2 → HBr + O3 (4) ΔH = -7.6 kcal mol^-1

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 BrO + HO2 reaction

The 6 fold higher value obtained for k4 has been used as input data in a 1D steady state photochemical model. The
Table I: Reactions involving bromine compounds and rate coefficients in case 1

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3Br + hv → CH2Br + Br</td>
<td>( k = 6.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} )</td>
</tr>
<tr>
<td>Br + O3 + NO → BrO + H + NO2</td>
<td>( k = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} )</td>
</tr>
<tr>
<td>CH3Br + OH → CH2Br + H + O</td>
<td>( k = 3.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} )</td>
</tr>
<tr>
<td>BrO + Br + O3 → BrO2 + O2</td>
<td>( k = 2.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} )</td>
</tr>
<tr>
<td>BrO + ClO → Br + ClO</td>
<td>( k = 1.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} )</td>
</tr>
<tr>
<td>BrO + NO → Br + NO2</td>
<td>( k = 5.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} )</td>
</tr>
<tr>
<td>BrO + BrO → Br2 + O2</td>
<td>( k = 8.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} )</td>
</tr>
<tr>
<td>BrO + Br → Br2 + O</td>
<td>( k = 1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} )</td>
</tr>
<tr>
<td>BrO + H2O → Br + O3</td>
<td>( k = 3.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} )</td>
</tr>
<tr>
<td>HBr + OH → Br + H2O</td>
<td>( k = 1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} )</td>
</tr>
<tr>
<td>BrO + NO → BrO2 + NO</td>
<td>( k = 0.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} )</td>
</tr>
<tr>
<td>BrO + H2O → BrOOH + O2</td>
<td>( k = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} )</td>
</tr>
</tbody>
</table>

(a): see text for the photodissociation rate calculations
(b): considered in the model as the limiting step for the Br production from CH3Br
(c): \( k = \frac{k_{\text{obs}}[M]}{1 + k_{\text{obs}}[M]/k_{\text{ref}}} \)

The 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 BrO 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 O3, HO2, NO, ClO, and BrO, families and the source species: NO2, H2O, HCl, CO, CFCl3, 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 O3 and O4, 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 BrOy species as a function of altitude, for a mixing ratio of total bromine at the ground of 20 ppv, which is consistent with the present atmospheric content, as recently discussed by Salawitch et al. (1988). The BrOy species are BrO, BrO2, HBr, BrONO2, BrONOO 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 \( k_4 = 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) independent of altitude, which our determination was taken: \( k_4 = 3.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). 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 BrO2 partitioning at any altitude except for HBr. The BrO2 mixing ratio increases drastically, e.g. by a factor 6 between 20 and 30 km. BrONOO2 remains the major bromine reservoir, but HBr becomes more abundant than HBr above 20 km.

In the calculations of cases 1 and 2, the photolysis rate of HBr, \( J(\text{HBr}) \), 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 HBr, 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 \( J(\text{HBr}) \), 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 HBr concentration (Figure 2). Nevertheless, the HBr 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 \( J(\text{HBr}) \).

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:

\[ \text{BrO} + \text{HO2} \rightarrow \text{HBr} + \text{O3} \]  

(4')

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

![Fig. 1. Diurnal averaged concentrations of the BrOy species as a function of altitude: \( k_4 = 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \), \( k_4 = 0 \), \( J(\text{HBr}) = 1.5 \times 10^{-3} \text{ s}^{-1} \) (case 1).](image-url)
Fig. 2. Diurnal averaged concentrations of the BrO, species as a function of altitude: $k_4 = 3.3 \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$, $k_f = 0$, J(HOBr) = $1.5 \times 10^3 \text{s}^{-1}$ (case 2). (a): HOBr profile under conditions of case 2, except J(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 BrONO$_2$ 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$_2$ partitioning discussed above, the new $k_4$ value may have an impact on the ozone depletion by the bromine compounds, through the catalytic 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:

- $\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2$
- $\text{BrO} + \text{O} \rightarrow \text{Br} + \text{O}_2$

 net: $\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$

- $2(\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2)$
- $\text{BrO} + \text{BrO} \rightarrow 2\text{Br} + \text{O}_2$

 net: $2\text{O}_3 \rightarrow 3\text{O}_2$

The odd oxygen destruction rates by cycles (I) to (IV) have been calculated (Figure 4), under conditions of both low 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. (1989).

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
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 BrO + NO2 → BrONO2, 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 3.42% (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 NOx depletion due to the recent eruption of 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 HOx (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 HOBrr.

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