THE CHEMISTRY OF BROMINE IN THE STRATOSPHERE:
INFLUENCE OF A NEW RATE CONSTANT FOR THE REACTION BRO+HO

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ABSTRACT

The impact of new laboratory data for the reaction
BrO + HO₂ ---> HOBr + O₂ in the depletion of global
stratospheric ozone has been estimated using a one-
dimensional photochemical model taking into account the
heterogeneous reaction on sulphate aerosols which converts
N₂O₅ into HNO₃. Assuming an aerosol loading 2 times as
large as the “background” and a reaction probability of 0.1
for the above heterogeneous reaction, the 6 fold increase in
the measured rate constant for the reaction of BrO with HO₂
increases the computed depletion of global ozone produced by
20 ppt of total bromine from 2.01% to 2.36%. The use of the
higher rate constant increases the HOBr mixing ratio and
makes the bromine partitioning and the ozone depletion very
sensitive to the branching ratio of the potential channel
forming HBr in the BrO + HO₂ reaction.

1. INTRODUCTION

Bromine compounds play a significant role in both the
depletion of global stratospheric ozone (Wofsy et al., 1975),
(Yung et al., 1980) and in the perturbed chemistry which
leads to the ozone hole formation in polar stratospheric
regions (Mac Elroy et al., 1986).

Assuming kinetic data available in 1980, Yung et al.
(1980) concluded that the catalytic cycle involving the
reaction BrO + ClO was the main cycle involving bromine
compounds to destroy odd oxygen in the lower stratosphere.
More specifically, the rate constant they assume for the
reaction:

BrO + HO₂ ---> HOBr + O₂ (1)

was too low to make the following cycle significant:

Br + O₃ ---> BrO + O₂
BrO + HO₂ ---> HOBr + O₂ (1)
HOBr + hv ---> OH + Br (3)
OH + O₃ ---> HO₂ + O₂ (4)

net: 2O₃ ---> 3O₂

Recently, Poulet et al. (1992) have reported a rate
constant for reaction (1) which has been measured at
LCSR/CNRS to be 6 times higher than the preferred value
given in the kinetic data bases (De More et al., 1990). The
new value is k₁ = 3.3 × 10⁻¹³ cm³ molecule⁻¹ s⁻¹ instead of k₁ =
5.0 × 10⁻¹² cm³ molecule⁻¹ s⁻¹. In their modelling of the influence
of this new kinetic data on the stratospheric chemistry, they
show that the reduction of global ozone column density
produced by 20 ppt of bromine is increased from 1.14% to
1.45%. They conclude that the above cycle is no longer
insignificant to deplete ozone. Besides, they point out that a
possible channel for reaction (1) yielding HBr and O₃ as
products could decrease significantly the ozone depletion
assuming the new kinetic data. They found that with a 10%
branching ratio for the HBr forming channel of reaction (1),
20 ppt of bromine would deplete the ozone column by only
0.6%. This channel may occur at low temperatures, but this
has to be established by laboratory studies.

The present paper describes the impact of the new
kinetic data on the bromine chemistry of the lower
stratosphere in the presence of aerosols.

2. IMPACT OF THE BrO + HO₂ REACTION IN
PRESENCE OF AEROSOLS

A 1D steady state photochemical model has been used
to estimate the effect of the new kinetic data on both the
bromine partitioning in the stratosphere and the global ozone
depletion due to bromine compounds in the presence of an
aerosol layer. This layer is assumed to reduce the
concentration of the NOₓ compounds. The effect of the
possible occurrence of the HBr forming channel in reaction (1)
is also investigated.

The 1D model has been recently described
(Ramaroson et al., 1992). This model includes the species of
the Oₓ, HOₓ, NOₓ, ClOₓ and BrOₓ families and the source
species: N₂O₅, H₂O₂, CH₄, CO, CFCₓ, CHₓCl and CHₓBr. The
vertical temperature and total concentration profiles are taken
from the U.S. Standard Atmosphere (1976). The kinetic and
photochemical data used are essentially those recommended
in the last NASA-JPL report (De More et al., 1990). Those
concerning the bromine species are reported in Table I.
following heterogeneous reaction on sulfate aerosols has been taken into account:

\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \text{ (sulfuric acid solution)} \rightarrow 2\text{HNO}_3 \]  

The reaction probability has been assumed to be \( \gamma = 0.1 \) which is consistent with measurements of Hanson and Ravishankara (1991). A sulfate aerosol area profile twice as high as the “background” 1979 values over Laramie, Wyoming (Hofmann and Solomon, 1989) has been adopted in the calculations (Rodriguez et al., 1991). The stratospheric aerosol layer is assumed to be saturated and all the \( \text{HNO}_3 \) produced in reaction (5) is immediately released in the gas-phase.

The steady-state vertical distribution of the source species and families are computed by iterations from 0 to 60 km, by step of 1 km. The diurnal averaged production and loss terms needed are calculated before each iteration, which

<table>
<thead>
<tr>
<th>Table I: Reactions involving bromine compounds and rate coefficients</th>
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<tbody>
<tr>
<td>CH(_2)Br + h(\nu) → CH(_3) + Br</td>
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<tr>
<td>BrCl + h(\nu) → Br + Cl</td>
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<tr>
<td>BrONO(_2) + h(\nu) → BrO + NO(_2)</td>
</tr>
<tr>
<td>HOBr + h(\nu) → OH + Br</td>
</tr>
<tr>
<td>BrCl + h(\nu) → Br + Cl</td>
</tr>
<tr>
<td>Br + OH → BrO + H (\text{exp (4300)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})</td>
</tr>
<tr>
<td>Br + O(_3) → BrO + O (\text{exp (2350)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})</td>
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<tr>
<td>Br + ClO → BrCl + O (\text{exp (5300)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})</td>
</tr>
<tr>
<td>Br + ClO → BrCl + O (\text{exp (2350)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})</td>
</tr>
<tr>
<td>Br + NO → Br + NO(_2) (\text{exp (3600)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})</td>
</tr>
<tr>
<td>Br + BrO → Br + BrO (\text{exp (1500)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})</td>
</tr>
<tr>
<td>Br + HO(_2) → Br + HO (\text{exp (4600)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})</td>
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<tr>
<td>Br + ClO → Br + ClO (\text{exp (4600)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})</td>
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</table>

Figure 1 compares the computed vertical distributions of \( \text{NO}_2 \), HO\(_2\), and CIO at noon if reaction (5) is included in the photochemical scheme (case b) with the same vertical distributions if (5) is not included (case a). Reaction (5) leads to an important sink of \( \text{NO}_x \) (NO + \( \text{NO}_2 \) + \( \text{NO}_3 \) + \( 2 \times \text{N}_2\text{O}_5 \)), as well as to an additional source of HO\(_2\) due to the subsequent photolysis of \( \text{HNO}_3 \). Chlorine compounds are also affected by this reaction. High levels of HO\(_2\) through the reaction of OH with HCl, increase the concentration of the reactive chlorine species \( \text{Cl} + \text{CIO} + \text{ClONO}_2 \). Low values of \( \text{NO}_2 \) shift the partitioning between CIO and ClONO\(_2\) in favour of CIO. Figure 1 shows that reaction (5) decreases the NO\(_2\) concentration by 45% and increases the concentration of HO\(_2\) and CIO by respectively 36% and 100%, at 20 km.

These results are globally consistent with the 2D model calculations of Rodriguez et al. (1991). We may assume in consequence that the results of our 1D calculations concerning the influence of the new kinetic data for reaction (1) on both the partitioning of bromine and the ozone depletion are realistic at least globally.

Figure 2 shows the combined effect of the high rate constant \( k_1 \) and of the occurrence of reaction (5), on the diurnal averaged concentration of bromine species. Concentrations of Br\(_2\) and BrONO\(_2\) are mainly affected by reaction (5) in the same manner than chlorine compounds. HOBr is affected by both the reaction (5) and the high constant \( k_1 \). At 20 km its averaged concentration is increased.
by a factor 20.

The effect of the new rate constant on the efficiency of the catalytic cycles involving bromine compounds to deplete global ozone has been also computed. Four cycles have been assumed: the two cycles already mentioned which involve \( \text{BrO} + \text{ClO} \) (cycle I) and \( \text{BrO} + \text{HO}_2 \) (cycle II) together with those which involve \( \text{BrO} + \text{BrO} \) (cycle III) and \( \text{BrO} + \text{O} \) (cycle IV). Figure 3 shows the odd oxygen destruction rates by cycles I to IV using the new kinetic data for reaction (1). The odd oxygen destruction rate by all the other cycles is also shown for comparison. The calculations show that the new rate constant has no effect on cycles I, III and IV. Figure 3 shows that the rate of cycle II increases by a factor 6 similarly to the increase of the new rate constant. This was expected because reaction (1) is the limiting step of cycle II.

The destruction rate by cycle II is lower than the destruction rate by cycle I by about a factor 4.5 at 20 km. As it can be seen from Figure 4 in Poulet et al. (1992), this factor was only 3 when reaction (5) was not taken into account. The importance of cycle II to deplete ozone is therefore reduced by the presence of aerosols, relatively to cycle I. It remains nevertheless significant.

To quantify the impact of the new rate constant to deplete ozone, the percentage of ozone decrease versus altitude produced by 20 ppt of bromine has been calculated (Figure 4) using successively the low and the high value for the rate constant \( k_t \). From these calculations, it is found that the new rate constant leads to an increased reduction of the ozone column density from 2.01% to 2.36%. This is significantly higher than the reduction of 1.14% and 1.45% reported by Poulet et al. (1992).

The channel of reaction (1) yielding HBr and O3 is not unlikely, mainly at low temperature. Laboratory studies have to establish the branching ratio of this channel. As already pointed out (Poulet et al., 1992), even a small value of this ratio will lead to a large increase of the concentration of HBr in the lower stratosphere making HBr one of the most abundant species of the bromine family (Figure 5). Figure 4 shows also, the percentage of ozone decrease versus altitude produced by 20 ppt of bromine for a 10% branching ratio of the HBr forming channel and the higher value of \( k_t \). We observe a strong decrease of the ozone reduction. The calculations lead to a decrease of the ozone column density...
of only 0.75%. These results were expected because HBr is a more efficient reservoir of active bromine than HOBr. We can observe that the inclusion of reaction (5) in the photochemical scheme increases the difference in the reduction of the computed ozone column assuming 10% and 0% for the branching ratio of the HBr forming channel. Using reaction (5) and the higher value of $k_{1}$, the decrease of the reduction of the ozone column is from 2.36% to 0.75%. Neglecting reaction (5), the decrease was only from 1.45% to 0.6%.

3. CONCLUSION

The modelling results presented in this paper, compared with those of Poulet et al. (1992) which did not take into account the heterogeneous reaction:

$$N_{2}O_{5} + H_{2}O \rightarrow 2 HNO_{3}$$

in the aerosol layer, show that the importance of the catalytic cycle involving the reaction BrO + HO$_{2}$ is reduced compared to the cycle involving the reaction BrO + ClO, but remains significant. In the present calculations, the ozone column density reduction produced by 20 ppt of total bromine increases from 2.01% (with the lower rate constant $k_{1}$) to 2.36% (with the higher rate constant $k_{2}$) assuming an aerosol loading twice as high as the “background”.

An increase in the aerosol loading would not change significantly these conclusions. Others calculations have been repeated assuming the surface area profile available at Laramie at the maximum of the El Chichon eruption (Hofmann and Solomon, 1989) which was about 25 times as large as the “background”. As already pointed out by Rodriguez et al. (1991) the reduction of the ozone column density is not too much affected by this large aerosol loading because the concentration of the NOx compounds relatively to the concentration of HNO$_{3}$ becomes independent of the above heterogeneous reaction when aerosol loading increases. In the presence of this large surface area profile, we calculate a reduction of the ozone column density of 2.6% produced by 20 ppt of bromine with the lower rate, constant for the reaction of BrO with HO$_{2}$ and a reduction of 3% with the higher rate constant. The cycle involving the reaction BrO + HO$_{2}$ would be therefore significant to deplete ozone even in presence of a large aerosol loading if the new rate constant is taken into account.

The calculations made assuming a 10% branching ratio for the HBr forming channel of reaction BrO + HO$_{2}$ shows an increasing importance of this channel if the above heterogeneous reaction in the aerosol layer is included and when the aerosol loading is increased. This channel would decrease the reduction of the density ozone column produced by bromine species. When the heterogeneous reaction was not included in the photochemical scheme a 10% branching ratio decreases the reduction of the ozone column from 1.45% to 0.6% using the new rate constant, assuming 20 ppt of total bromine. When the heterogeneous reaction is used, the decrease is from 2.36% to 0.75% with a aerosol loading 2 times as large as the “background” and 3% to 0.85% with a loading 25 times as large as the ”background”.

Ozone depletion by bromine species is therefore very dependent on the branching ratio for the HBr forming channel of reaction (1). Laboratory investigations are therefore needed, at low temperature, to measure this branching ratio as well as in-situ measurements of HBr. Park et al. (1989) report a far-infrared measurement of 20 ppt at 28 km while Traub et al. (1992) report three measurements and conclude to an upper limit of 4 ppt at 32 km. After Traub et al. (1992), Park and his co-workers now agree that 20 ppt is in fact a tentative upper limit. Our calculations (Figure 5) give 6 ppt at 32 km, assuming a 10% branching ratio. A few percent for this branching ratio would not be therefore inconsistent with the measurements of Traub et al. (1992). Other measurements are obviously needed.

REFERENCES


Hanson, D.R. and A.R. Ravishankara, The reaction probabilities of ClONO$_{2}$ and N$_{2}$O$_{5}$ on 40 to 75% sulfuric acid solutions, J. Geophys. Res., 96, 17307-17314, 1991.


