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THE CHEMISTRY OF BROMINE IN THE STRATOSPHERE: INFLUENCE OF A NEW RATE CONSTANT FOR THE REACTION BRO+HO_2

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ABSTRACT

The impact of new laboratory data for the reaction $BrO + HO_2 \rightarrow HOBr + O_2$ 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 N_2O_5 into HNO_3. 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 HO_2 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 + HO_2 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:

$$BrO + HO_2 \dashrightarrow HOBr + O_2 \qquad (1)$$

was too low to make the following cycle significant:

$$\begin{array}{lr} Br + O_3 \dashrightarrow BrO + O_2 & (2) \\ BrO + HO_2 \dashrightarrow HOBr + O_2 & (1) \\ HOBr + h\nu \dashrightarrow OH + Br & (3) \\ OH + O_3 \dashrightarrow HO_2 + O_2 & (4) \\ \hline \text{net:} \quad 2O_3 \dashrightarrow 3O_2 & \end{array}$$

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 $k_1 = 3.3\ 10^{-11}\ cm^3.molecule^{-1}.s^{-1}$ instead of $k_1 = 5.0\ 10^{-12}\ cm^3.molecule^{-1}.s^{-1}$. 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 O_3 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 + HO_2 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 NO_X compounds. The effect of the possible occurence 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 O_X, HO_X, NO_Y, ClO_Y and BrO_Y families and the source species: N_2O, H_2O, CH_4, CO, CFC$_s$, CH_3Cl and CH_3Br. 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.The following heterogeneous reaction on sulfate aerosols has been taken into account:

$$N_2O_5 + H_2O \text{ (sulfuric acid solution) } \text{--->} \ 2HNO_3 \qquad (5)$$

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 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 requires the diurnal evolution of the short-lived species. Starting with realistic vertical distributions, convergence is obtained after 12 iterations. In the calculations, a total chlorine content of 3.2 ppb and a total bromine content of 20 ppt have been used.

Table I: Reactions involving bromine compounds and rate coefficients

$CH_3Br + h\nu \rightarrow CH_3 + Br$	(a)
$BrO + h\nu \rightarrow Br + O$	(a)
$BrONO_2 + h\nu \rightarrow Br + NO_2$	(a)
$HOBr + h\nu \rightarrow OH + Br$	(a)
$BrCl + h\nu \rightarrow Br + Cl$	(a)
$CH_3Br + OH \rightarrow \text{products}^{(b)}$	$6.8\ 10^{-13} \exp(-850/T)$ cm^3 molecule^{-1} s^{-1}
$Br + O_3 \rightarrow BrO + O_2$	$1.7\ 10^{-11} \exp(-800/T)$ cm^3 molecule^{-1} s^{-1}
$BrO + O \rightarrow Br + O_2$	$3.0\ 10^{-11}$ cm^3 molecule^{-1} s^{-1}
$BrO + ClO \rightarrow Br + ClOO$	$2.9\ 10^{-12} \exp(220/T)$ cm^3 molecule^{-1} s^{-1}
$BrO + ClO \rightarrow Br + OClO$	$1.6\ 10^{-12} \exp(430/T)$ cm^3 molecule^{-1} s^{-1}
$BrO + ClO \rightarrow BrCl + O_2$	$5.8\ 10^{-13} \exp(170/T)$ cm^3 molecule^{-1} s^{-1}
$BrO + NO \rightarrow Br + NO_2$	$8.8\ 10^{-12} \exp(260/T)$ cm^3 molecule^{-1} s^{-1}
$BrO + BrO \rightarrow Br + Br + O_2$	$1.4\ 10^{-12} \exp(150/T)$ cm^3 molecule^{-1} s^{-1}
$Br + HO_2 \rightarrow HBr + O_2$	$1.5\ 10^{-11} \exp(-600/T)$ cm^3 molecule^{-1} s^{-1}
$HBr + OH \rightarrow Br + H_2O$	$1.1\ 10^{-11}$ cm^3 molecule^{-1} s^{-1}
$BrO + HO_2 \rightarrow HOBr + O_2$	$5.0\ 10^{-12}$ cm^3 molecule^{-1} s^{-1}
$BrO + OH \rightarrow Br + HO_2$	$1.0\ 10^{-11}$ cm^3 molecule^{-1} s^{-1}
$HBr + O \rightarrow Br + OH$	$5.8\ 10^{-11} \exp(-1500/T)$ cm^3 molecule^{-1} s^{-1}
$Br + CH_2O \rightarrow HBr + CHO$	$1.7\ 10^{-11} \exp(-800/T)$ cm^3 molecule^{-1} s^{-1}
$BrO + NO_2 + M \rightarrow BrONO_2 + M^{(c)}$	$k_0 = 5.2\ 10^{-31}\ (T/300)^{-3.2}$ cm^6 molecule^{-2} s^{-1} $k_\infty = 9.0\ 10^{-12}\ (T/300)^{-2.0}$ cm^3 molecule^{-1} s^{-1}

(a): see text for the photodissociation rate calculations

(b): considered in the model as the limiting step for the Br production from CH_3Br

(c): $k = \left(\frac{k_0[M]}{1 + k_0[M]/k_\infty}\right) 0.6^{\left(1 + [\log_{10}(k_0[M]/k_\infty)]^2\right)^{-1}}$

Figure 1 compares the computed vertical distributions of NO_2, HO_2 and ClO 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 NO_X ($NO + NO_2 + NO_3 + 2 \times N_2O_5$), as well as to an additional source of HO_X due to the subsequent photolysis of HNO_3. Chlorine compounds are also affected by this reaction. High levels of HO_X, through the reaction of OH with HCl, increase the concentration of the reactive chlorine species ($Cl + ClO + ClONO_2$). Low values of NO_2 shift the partitioning between ClO and $ClONO_2$ in favour of ClO. Figure 1 shows that reaction (5) decreases the NO_2 concentration by 45% and increases the concentration of HO_2 and ClO by respectively 36% and 100%, at 20 km.

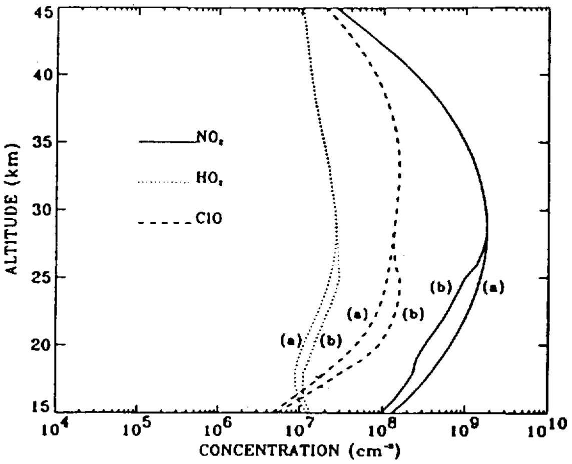

Figure 1: Vertical distribution, at noon, of the concentrations of NO_2, HO_2 and ClO. Case (a): reaction (5) is not included. Case (b): reaction (5) is included.

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 occurence of reaction (5), on the diurnal averaged concentration of bromine species. Concentrations of BrO 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

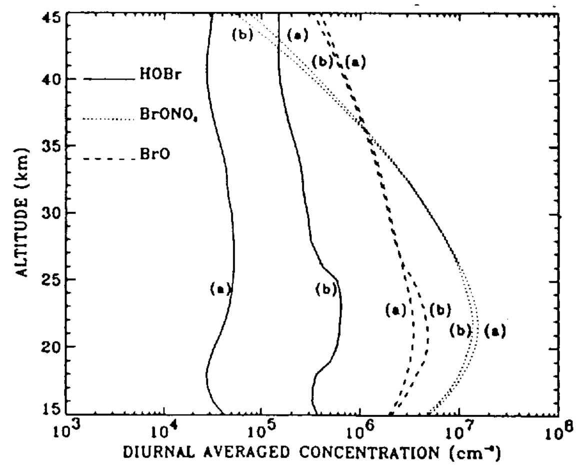

Figure 2: Vertical distribution of the diurnal averaged concentration of HOBr, $BrONO_2$ and BrO. Case (a): reaction (5) is not included and $k_1 = 5.0\ 10^{-12}$ cm^3.molecule^{-1}.s^{-1}. Case (b): reaction (5) is included and $k_1 = 3.3\ 10^{-11}$ cm^3.molecule^{-1}.s^{-1}.

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 mentionned which involve BrO + ClO (cycle I) and BrO +HO_2 (cycle II)together with those which involve BrO + BrO (cycle III) and BrO + 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.

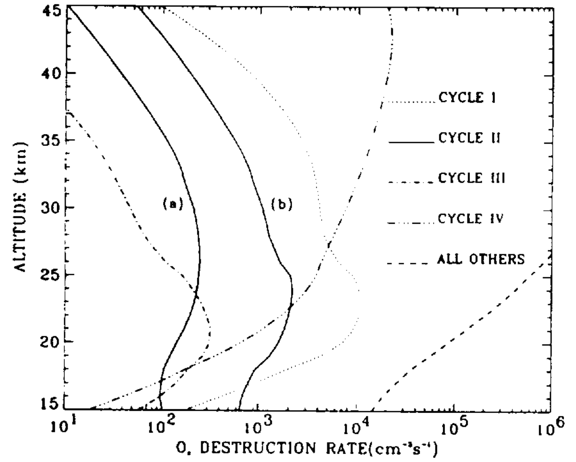

Figure 3: Odd oxygen destruction rate by catalytic cycles I, II, III and IV defined in the text, as a function of altitude, ALL OTHERS refers to the sum of the destruction rates due to the cycles which do not involved bromine species. Reaction (5) is included in the phochemical scheme. The destruction rates for cycles I, III, IV and ALL OTHERS are computed with k_1 = 3.3 10^{-11} cm^3.molecule^{-1}.s^{-1}. For cycle II, case (a): k_1 = 5.0 10^{-12} cm^3.molecule^{-1}.s^{-1}, case (b): k_1 = 3.3 10^{-11} cm^3.molecule^{-1}.s^{-1}

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_1. 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_1. We observe a strong decrease of the ozone reduction. The calculations lead to a decrease of the ozone column density

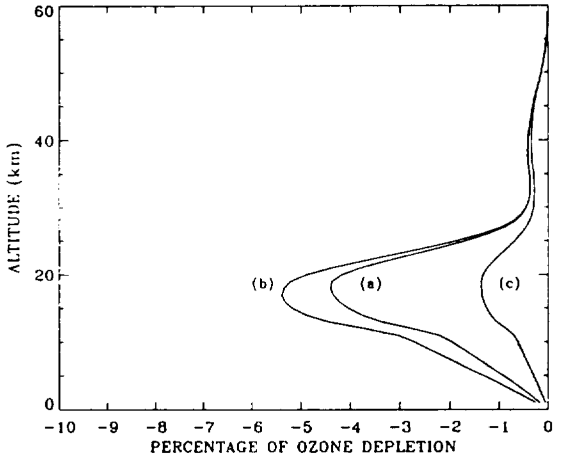

Figure 4: Percentage of ozone depletion produced by 20 ppt of bromine, as a function of altitude. Heterogeneous reaction (5) is included. Case (a): k_1 = 5.0 10^{-12} $cm^3.s^{-1}$, branching ratio for the Hbr forming ratio is zero. Case (b): k_1 = 3.3 10^{-11} $cm^3.s^{-1}$, branching ratio is zero. Case (c): k_1 = 3.3 10^{-11} $cm^3.s^{-1}$, branching ratio is 10%.

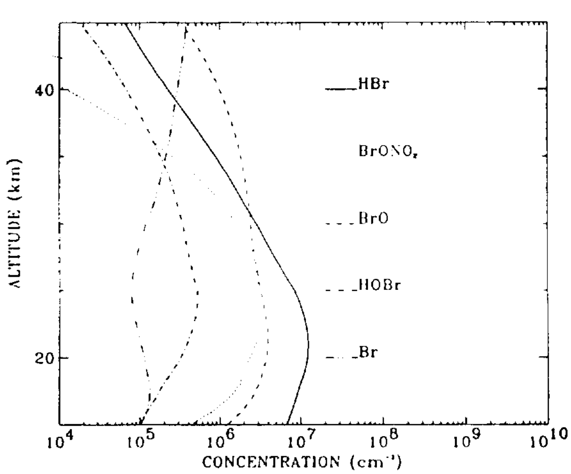

Figure 5: Vertical distribution of the concentration of bromine species, at noon. Reaction (5) is included, k_1= 3.3 10^{-11} cm^3.molecule^{-1}s^{-1}, the branching ratio for the HBr forming channel is 10%.

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:

$$N_2O_5 + H_2O \dashrightarrow 2\ HNO_3$$

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_1) assuming an aerosol loading twice as high as the "background".

An increase in the aerosol loading would not changed 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 NO_X 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.

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