

A model study of the potential role of the reaction BrO + OH in the production of stratospheric HBr

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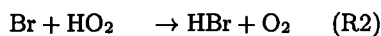
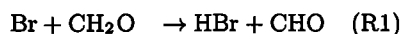
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Abstract. We have used a constrained one-dimensional photochemical model to investigate the effect of a potential minor channel of the fast reaction between BrO + OH to produce HBr. There is no direct evidence for this reaction but the analogous yield of HCl from ClO + OH is thought to be about 5%. With only a 1-2% yield of HBr the modelled HBr mixing ratio between 20-30 km increases from around 0.5 parts per 10¹² by volume (pptv) to 1-2 pptv. This brings the model into agreement with recent balloon-borne observations of stratospheric HBr. Should BrO + OH produce HBr with around 1-2% yield then this reaction will dominate HBr production between 20-35 km. As the main loss of HBr is reaction with OH this will lead to steady state HBr:BrO partitioning which is independent of other species, and temperature.

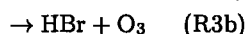
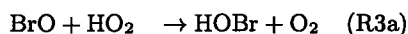
Introduction

Two groups have recently reported observations of stratospheric HBr using far infrared emission. Following the initial observation of an upper limit of 4 parts per 10¹² by volume (pptv) by [Traub *et al.*, 1992], the same group derived an average HBr mixing ratio of 2.0±0.8 parts per 10¹² by volume (pptv) in the altitude range 22-34 km based on 7 balloon flights between 1988 and 1994 around 34°N [Johnson *et al.*, 1995]. [Johnson *et al.*, 1995] also presented the first daytime and nighttime profiles in this altitude range. From the second group, [Carlotti *et al.*, 1995] reported HBr observations of 1.15±0.46 pptv (using the updated values given by [Nolt *et al.*, 1997]) between 20-36.5 km at 34°N in May 1993. [Nolt *et al.*, 1997] reported measurements from May 1994 showing an average HBr mixing ratio of 1.31±0.39 pptv between 20-36.5 km. [Nolt *et al.*, 1997] were also able to derive a vertical profile of HBr.

These observations of around 1-2 pptv of HBr are larger than model predictions which consider production due to (R1) and (R2) only:

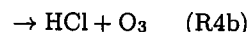


This prompted suggestions that the reaction between BrO and HO₂ may have a minor channel producing HBr.



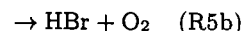
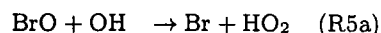
[Johnson *et al.*, 1995] showed that their results could be con-

sistent with a 0-2% yield for reaction (R3b). Following this, [Nolt *et al.*, 1997] argued that a yield for reaction (R3b) of around 1-2% is required to reproduce their observations. [Larichev *et al.*, 1995] reported an upper limit for the channel (R3b) of 1.5% from the non-observation of O₃ as a product of this reaction, while [Mellouki *et al.*, 1994] studied the reverse reaction of (R3b) and predicted that the upper limit for the yield of (R3b) is in fact less than 0.01%. Hence, it seems that even the modest 1-2% requirement of [Nolt *et al.*, 1997] is unlikely. The small branching ratio for (R3b) mirrors that found for the analogous chlorine reaction:

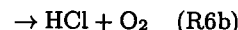
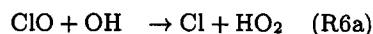


where (R4b) has been shown to be very small at room temperature, i.e. less than 2% [Leck *et al.*, 1980; Leu, 1980; Burrows and Cox., 1981; Finkbeiner *et al.*, 1995]. At the lowest temperature studied (220 K), [Finkbeiner *et al.*, 1995] observe that (R4b) is 5±2%, at 700 Torr but less than 1% at 2 Torr. Hence [Finkbeiner *et al.*, 1995] suggest that the rate of reaction (R4b) may be pressure dependent, in which case, over stratospheric pressures, the yield of (R4b) will be less than 5%.

Here we consider whether the reaction between BrO + OH



may have a channel which produces HBr and can therefore resolve the HBr discrepancy. For the analogous chlorine reaction



both [Hills and Howard, 1984] and [Burrows *et al.*, 1984] report that the yield of (R6b) could be as high as 15%. Although [Poulet *et al.*, 1986] have observed a much smaller value for the yield of (R6b), within the uncertainties of their measurements, it could still be 10%. Very recently, direct laboratory measurements of the yield of DCl from ClO + OD have indicated a branching ratio of 6±2% at 210 K, with a similar yield of HCl from ClO + OH [Lipson *et al.*, 1997]. Therefore, since (R3) and (R4) display similar behaviour with respect to products, it is not unreasonable to expect (R5) and (R6) to do the same. The only reported study of (R5) is by [Bogan *et al.*, 1996]. These workers report a rate constant at 300 K ($k_5 = 7.5 \pm 4.2 \times 10^{11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) which is 7.5 times faster than the 1994 NASA Panel recommendation [DeMore *et al.*, 1994], although the quoted error is large. [Bogan *et al.*, 1996] suggest that the reaction

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proceeds via the [HOBr] intermediate, and that the large rate constant is due to the promotion of efficient spin-orbit mixing of singlet and triplet surfaces in this [HOBr] complex by the heavy Br atom. They also present theoretical calculations which imply that both channels (5a) and (5b) can arise from the decomposition of the [HOBr] intermediate, although, as in the chlorine case, that the dominant product channel is likely to be (R5a), and not (R5b). Such an assertion is not unreasonable since (R5a) involves simple HOO-Br bond fission, whereas (R5b) will involve the formation of a four-centred rearrangement of the [HOBr] complex. Nevertheless, using some realistic estimates for the activation energies for the decomposition of the [HOBr] complex into the two product channels, [Bogan *et al.*, 1996] calculate that the yield of (R5b) could conceivably be in the region of 1%. Since the reported variation of k_6 with temperature is either nil [Burrows *et al.*, 1984], or increasing slightly with decreasing temperature [Hills and Howard, 1984], it is reasonable to assume that k_5 is invariant with temperature. Therefore, given that it is reasonable to assume that both (R5) and (R6) proceed along similar potential energy surfaces [Bogan *et al.*, 1996] and that the yield of (R6b) is around 5-15%, we are justified in expecting some HBr formation from (R5).

In this paper we use a constrained one-dimensional (1D) photochemical model to investigate the effect of reaction (R5b) on the abundance of stratospheric HBr. We have necessarily assumed that reaction (R5) occurs with the rate determined by [Bogan *et al.*, 1996] and does not vary with temperature.

One-Dimensional Model Experiments

We have used a 1D column model based on the photochemical scheme from the TOMCAT model [Chipperfield *et al.*, 1995]. The model contains a comprehensive description of stratospheric O_x , NO_y , Cl_y , Br_y (Br, BrO, HBr, HOBr, BrONO₂ and BrCl), HO_x and CH_4 oxidation chemistry and photochemical data is generally taken from [DeMore *et al.*, 1997]. The model has 22 levels from the ground to 0.3 hPa (around 60 km). Photolysis rates are calculated using full spherical geometry up to 95° SZA. For this study all of the species in the model were integrated separately, with no assumptions of photochemical equilibrium, using a 5 minute timestep. The model was integrated for 4 days to obtain a repeating diurnal cycle.

For this study we have performed a series of 1D model experiments for the conditions of the [Nolt *et al.*, 1997] balloon flight. The model was run at 34°N for May 15. The model profiles of temperature, H_2O , and O_3 were constrained by simultaneous balloon measurements [M. Carlotti, personal communication, 1996]. The model CH_4 profile was taken from Halogen Occultation Experiment (HALOE) observations for 34°N, 246°E, 4 days later on May 19, 1994. The other 1D model fields were initialised using output from a two-dimensional (latitude-height) model. The model total inorganic bromine (Br_y) in the middle/upper stratosphere was 20 pptv. The yield of HBr from reaction (R5b) was varied from 0 (run A), 1% (run B), 2% (run C), 3% (run D) to 5% (run E).

Results and Discussion

It is first useful to consider what the basic 1D model calculates for the partitioning of the principal Br_y species using the currently recommended kinetics. Figure 1 shows the vertical distribution of these bromine species calculated in run A (0% yield). BrO is the major daytime Br_y species between 20-40 km with a mixing ratio of 10-15 pptv. Between 20-30 km the mixing ratios of BrONO₂ and HOBr are much less: 3-4 pptv and 2-3 pptv respectively. The mixing ratio of HBr is only around 0.4 pptv in this region. Note the relatively large mixing ratios of atomic Br between 20-30 km; this is due to the fast photolysis of BrO which forms an odd-oxygen null cycle with $Br + O_3$.

Figure 2 shows the modelled HBr profiles for experiments A-E compared with the retrieved profile of [Nolt *et al.*, 1997]. The model results can also be compared with the average observations of [Johnson *et al.*, 1995] and [Carlotti *et al.*, 1995] which were obtained under similar conditions (e.g. latitude and season). With a 0% yield for reaction (R5b) the model HBr profile is around 0.4 pptv between 20-35km, which is much less than the average observation of [Nolt *et al.*, 1997]. With only a 1% channel for reaction (R5b) the HBr mixing ratio increases to around 1 pptv. The best agreement with the average results of [Nolt *et al.*, 1997] would be obtained for a yield of around 1.5%. Similarly, a yield of around 1-2% for reaction (R5b) would be sufficient to reproduce the observations of [Johnson *et al.*, 1995] and [Carlotti *et al.*, 1995].

Figure 3 shows the calculated abundance of HBr at 28 km for experiments A-E. All experiments show little variation. Again a yield of 1-2% for (R5b) give best agreement with the observations.

Figure 4a shows the contributions of the 3 HBr production reactions considered in the 1D model for run B. With a 1% yield for reaction (R5b) this contributes around 60% of the total production in the range 20-40 km. At lower

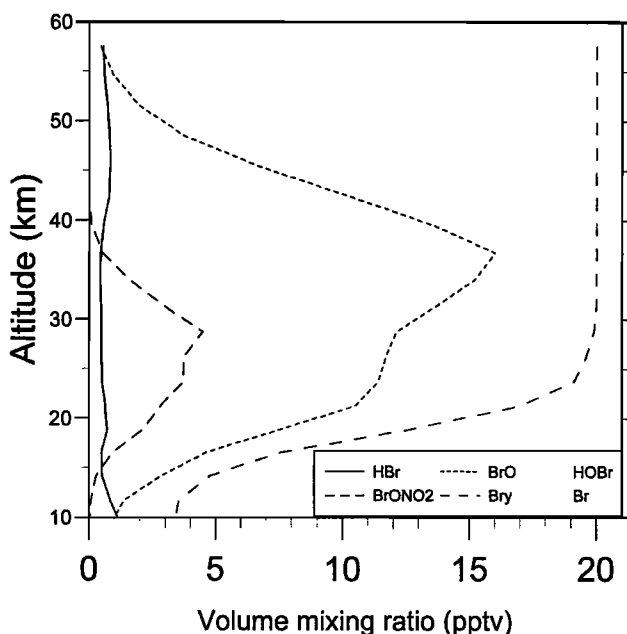


Figure 1. Vertical profiles of principal model Br_y species at 34°N at 1200 from model run A.

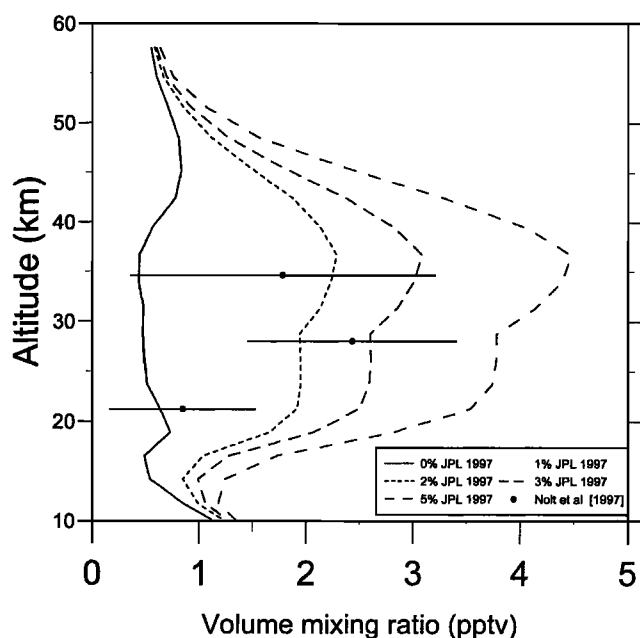
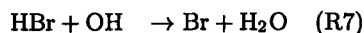


Figure 2. Vertical profiles of HBr at 34°N at 1200 from model runs A, B, C, D and E. Also shown are the altitude-resolved observations of *Nolt et al.* [1997].

altitudes production from $\text{Br} + \text{CH}_2\text{O}$ dominates while at higher altitudes $\text{Br} + \text{HO}_2$ is most important. The main sink of HBr in the lower-mid stratosphere is:



The other HBr sinks treated in the model are reaction with $\text{O}(^1\text{D})$ and $\text{O}(^3\text{P})$. The lifetime of HBr, and the loss rate due to only reaction (R7), is shown in Figure 4b. The lifetime of HBr is therefore around a few hours between 20–30 km, and this explains the small diurnal cycle exhibited in Figure 3. Therefore, if $\text{BrO} + \text{OH}$ is indeed the major source of stratospheric HBr, the steady state concentration of HBr

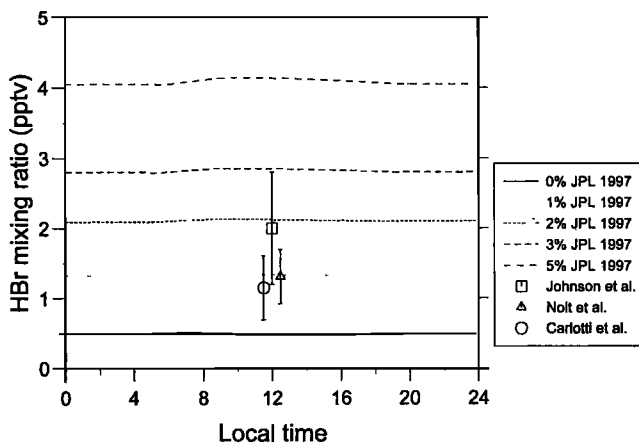


Figure 3. Mixing ratio of HBr at 28 km, 34°N from model runs A, B, C, D and E. Also shown are the average observations of *Johnson et al.*, [1995], *Carlotti et al.*, [1995] and *Nolt et al.* [1997]. These time-averaged observations are plotted near 12 local time for convenience only.

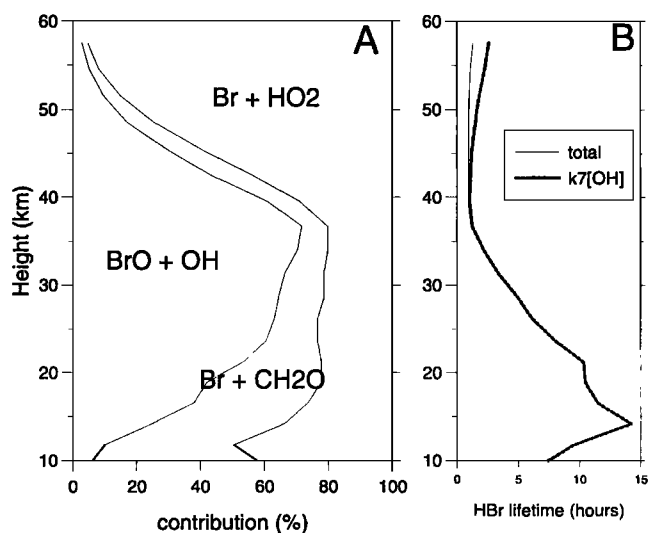


Figure 4. a) Percentage contribution of model reactions (R1), (R2) and ((R5b) to total HBr production rate at noon from model run B with a 1% yield for reaction (R5b). Contribution is proportional to area of each region. b) Photochemical lifetime of HBr (hours) due to reaction only with OH ($1/(k_7[\text{OH}])$), and the overall lifetime due to reaction with OH, $\text{O}(^3\text{P})$ and $\text{O}(^1\text{D})$ from run B.

will be, to a first approximation, independent of OH:

$$\frac{[\text{HBr}]}{[\text{BrO}]} = \frac{k_{5b}}{k_7}$$

Both k_{5b} and k_7 are currently believed to be independent of temperature [*DeMore et al.*, 1997] and so this ratio can be calculated to be $6.8 \times Y$, where Y is the fractional yield of HBr from reaction (R5). Obviously, simultaneous observations of BrO and HBr would be useful for verifying this partitioning. This simple ratio for the partitioning of HBr to BrO justifies the extension of our constrained 1D model runs for May 1994 to HBr observations made at other times.

Although this study shows that production of HBr from $\text{BrO} + \text{OH}$ may resolve the discrepancy between the observation and models there may be another, unknown, source of HBr. However, this is unlikely to be production of HBr from the photolysis of HOBr (which would be energetically possible at wavelengths less than about 440 nm). [*Benter et al.*, 1995] observed a quantum yield of Br of > 0.95 , and observed no evidence of HBr formation despite a high sensitivity.

Conclusions

Our model results clearly indicate that only a very small yield of HBr from (R5) is required to resolve the discrepancy between modelled and measured HBr, if k_5 is indeed as fast as recently measured. The large error on the recommended value of k_5 , and our assumption of temperature invariance should be noted, however. Although there is no direct experimental evidence for such a yield, the fact that the channel forming HCl is evident (around 5%) for the analogous chlorine system (R6) strongly suggests that HBr should be formed from (R5). In addition, the theoretical calculations of [*Bogan et al.*, 1996] are not inconsistent with a yield of

(R5b) of around 1%. Direct laboratory measurements of the yield of HBr from (R5), and an accurate determination of k_5 at stratospheric temperatures, are evidently necessary to resolve this issue.

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