The $Br + HO_2$ reaction revisited: absolute determination of the rate constant at 298 K

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The absolute determination of the rate constant for the reaction $Br + HO_2 \rightarrow HBr + O_2$ has been done at 298 K using the discharge-flow EPR method. The value $k_1 = (1.5 \pm 0.2) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ was obtained. Previous indirect measurements of k_1 from a discharge-flow, LIF/mass spectrometric study of the $Br/H_2CO/O_2$ system have been reinterpreted, leading to values for k_1 ranging from 1.0×10^{-12} to 2.2×10^{-12} cm³ molecule⁻¹ s⁻¹ at 298 K. These results are discussed and compared with other literature values.

1. Introduction

The influence of bromine species on global stratospheric ozone has been discussed by Yung et al. [1] who have suggested that a synergistic effect between bromine and chlorine could lead to a significant catalytical destruction of ozone in the lower stratosphere

$$ClO+BrO \rightarrow Br+Cl+O_2$$

$$Br+O_3 \rightarrow BrO+O_2$$

$$Cl+O_3 \rightarrow ClO+O_2$$

$$2O_3 \rightarrow 3O_2$$

McElroy et al. [2] have also considered that this cycle could contribute to the ozone-hole formation in the antarctic stratosphere during springtime. A recent analysis by Anderson et al. [3] of the field campaign of 1987 in Antarctica indicates that this cycle would contribute by approximately 20% to the ozone loss. Besides, the stratospheric observations made during a more recent campaign in the Arctic [4] seem also to indicate that bromine chemistry should play a similar role. In addition, the ozone variations observed at polar sunrise in spring in the lower arctic atmosphere (0-2 km) have been suggested to be linked to catalytic reactions of BrO_x radicals [5]. Therefore, the atmospheric bromine chemistry needs to be well known to assess clearly its significance under different atmospheric situations.

The title reaction,

$$Br + HO_2 \rightarrow HBr + O_2, \qquad (1)$$

is the main step forming a reservoir of Br atoms in the stratosphere since the only alternative process Br+H₂CO→HBr+HCO is less efficient. Three studies of reaction (1) have been published until now [6-8], all using the discharge-flow method with excess of Br over HO₂. The first measurement by Posey et al. [6] led to $k_1 = (2.2 \pm 1.1) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ at 298 K. These authors used mass spectrometry to monitor both Br and HO₂ species. In the subsequent study from our laboratory [7], a significantly higher value, $k_1 = (7.6 \pm 0.9) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ was found at 298 K. In this last work, reaction (1) was studied as a secondary step of the following sequence:

 $Br + H_2CO \rightarrow HBr + HCO$, (2)

$$HCO+O_2 \to HO_2 + CO. \tag{3}$$

Br atoms were directly analysed by mass spectrometry whereas HO₂ radicals were converted into OH via the reaction NO+HO₂ \rightarrow NO₂+OH. NO₂ and OH were analysed by mass spectrometry and laser-induced fluorescence (LIF), respectively. In a third study carried out between 260 and 390 K, Toohey et al. [8] found $k_1 = (1.98 \pm 0.05) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 298 K, which is significantly higher than our value. In this study, the Br atoms were monitored by resonance fluorescence and HO₂ by laser magnetic resonance.

Considering this discrepancy, we have reanalysed our previous data in the light of the most recent kinetic data available for the simulation of the chemical system $Br/Br_2/H_2CO/O_2$. We have also performed more direct experiments using the dischargeflow-electron-paramagnetic-resonance method.

2. Experimental

The experimental arrangement, first described in ref. [9] and schematically described in fig. 1, consisted of a quartz reactor (2.4 cm internal diameter) coated with halocarbon wax to reduce wall reactions. The reactor crossed the EPR large access cavity (Varian E 235) associated with a Varian E 112 EPR spectrometer. Br atoms and HO₂ radicals were generated separately in the reactor by means of two microwave discharges. Br atoms were flowed into the reactor through a side-arm tube located 55 cm upstream of the EPR cavity. HO₂ radicals were produced in the central tube (9 mm outer diameter) which was movable along the reactor axis. The HO₂ production resulted from the following sequence

$$Cl+CH_3OH\rightarrow CH_2OH+HCl$$
, (4)

$$CH_2OH + O_2 \rightarrow HCHO + HO_2, \qquad (5)$$

where Cl atoms were produced by microwave dissociation of Cl_2 .

Br atoms were directly analysed by EPR, whereas HO_2 were indirectly monitored by complete conversion of HO_2 via the fast reaction with NO, excess NO being added 10 cm upstream of the EPR cavity

NO+HO₂
$$\rightarrow$$
NO₂+OH,
 $k_5 = 8.3 \times 10^{-12}$ at 298 K [10]. (6)

In a first series of experiments, Br atoms were produced by microwave dissociation of Br_2 highly diluted in helium. The dissociation yield of Br_2 was typically 50%, and undissociated Br_2 reacted with OH in the HO₂/OH conversion zone:

OH+Br₂→HOBr+Br,

$$k_7 = 1.6 \times 10^{-10}$$
 at 298 K [11]. (7)

The resulting OH consumption was significant at the highest Br_2 concentrations used, but computer simulations have shown that this had no effect on the validity of the k_1 measurements by indirect mon-



Fig. 1. Experimental arrangement used for the kinetic investigation of the Br+HO₂ reaction.

itoring of HO_2 at the OH signal. Nevertheless, in a second series of experiments, a Br source free of Br_2 was used in order to increase the sensitivity of the OH signal. Br atoms were produced by the reaction

Cl+C₂H₃Br→C₂H₃Cl+Br,

$$k_8 = 4 \times 10^{-11}$$
 at 298 K [12], (8)

with Cl generated by microwave dissociation in Cl₂. C_2H_3Br was used in excess over Cl atoms in order to prevent the fast reaction between Cl and HO₂ (k= 4.1×10^{-11} cm³ molecule⁻¹ s⁻¹ at 298 K [10]). Excess C_2H_3Br also reacted with OH in the HO₂/OH conversion zone, but the resulting OH consumption was much lower than in the presence of Br₂ for two reasons: (i) the excess C_2H_3Br could be adjusted to a minimum value whereas the Br₂ excess was governed by the dissociation yield of Br₂; (ii) the rate constant for OH + C_2H_3Br is approximately 10 times lower than that of the OH + Br₂ reaction, as shown from independent kinetic measurements: k (OH + C_2H_3Br) was found to be $(4.0\pm0.2)\times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 298 K [13].

This value is to be compared to the only previous determination: $(6.8 \pm 0.7) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ obtained by the laser photolysis resonance fluorescence technique [14].

The mean linear velocity of gases in the reactor was around 21 m/s and total pressure around 1 Torr.

All gases, excepting helium, were stored in 10 ℓ bulbs. Helium (99.9995%) was passed through a liquid-nitrogen trap to remove impurities. The reactants used (Br₂, Cl₂, CH₃OH, O₂, NO, NOCl, C₂H₃Br, He) had the best commercial purity available.

3. Results and discussion

The reaction of Br atoms with HO₂ was studied under the pseudo-first-order conditions using an excess of Br atoms over HO₂. The rate constant k_1 was derived from the expression

$$-d\ln[HO_2]/dt = k_1[Br]$$
.

The absolute concentration of Br atoms was measured by EPR, by reference to a known concentration of O_2 , as described previously [15]. Br atoms

were also titrated against NO produced by the reaction

$$Br + NOCl \rightarrow NO + BrCl$$
,

$$k_9 = 1 \times 10^{-11}$$
 at 298 K [16]. (9)

Good agreement was observed between the two calibration methods.

The pseudo-first-order plots obtained from the above kinetic expression are reported in fig. 2. Twenty experiments were performed using both sources of Br. The range of initial Br atom concentration used was $(0.8-4.5) \times 10^{13}$ cm⁻³ and the initial HO₂ concentration was around 2×10^{11} cm⁻³.

The rate constant derived at 298 K is

 $k_1 = (1.5 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The error represents two standard deviation. The intercept is $-3.6 \pm 2.7 \text{ s}^{-1}$, which is near zero and compatible with the negligible wall loss of HO₂ radicals experimentally observed (from -5 to $+5 \text{ s}^{-1}$).

The value of k_1 is approximately two times higher than our previous determination [7] and slightly lower, although the uncertainty ranges overlap, than the more recent value of Toohey et al. [8]: $k_1 =$ $(2.0\pm0.3)\times10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 298 K.

In our previous work, k_1 was obtained by computer simulation of the kinetics of the Br/H₂CO/O₂ system. These kinetics have been remodeled using



Fig. 2. Plot of the pseudo-first-order rate of HO₂ decay as a function of Br concentration at 298 K: $k_1 = (1.5 \pm 0.2) \times 10^{-12} \text{ cm}^3$ molecule⁻¹ s⁻¹. Source of Br atoms: (\oplus) discharge in Br₂; (∇) reaction Cl+C₂H₃Br.

the up-dated kinetic data for the elementary steps involved in the mechanism. In these previous experiments, Br atoms were generated in the flow tube by microwave dissociation of Br₂. H₂CO was flowed through a movable sliding injector and O₂ was added at a fixed position upstream from the H₂CO injector. Typical concentrations were: $[Br]_0 = (2-6) \times 10^{14}$ cm⁻³, $[H_2CO]_0 < \frac{1}{10} [Br]_0$ and $[O_2] = 1.6 \times 10^{16}$ cm⁻³.

The following main steps were considered in the simulation:

 $Br + H_2CO \rightarrow HBr + HCO$,

$$k_2 = 1.1 \times 10^{-12} [10], \qquad (2)$$

$$Br+HCO \rightarrow HBr+CO$$
, (10)

$$O_2 + HCO \rightarrow HO_2 + CO$$
,

$$k_3 = 5.5 \times 10^{-12} \, [10] \,, \tag{3}$$

$$Br + HO_2 \rightarrow HBr + O_2 , \qquad (1)$$

 $NO + HO_2 \rightarrow NO_2 + OH$,

$$k_6 = 8.3 \times 10^{-12} [10] . \tag{6}$$

The HO₂ kinetics were also indirectly monitored by converting HO_2 into OH following reaction (6) and analysing OH or NO₂ by LIF and mass spectrometry, respectively. NO was introduced a few centimeter upstream from the analysis LIF cell which was located 6 cm upstream from the sampling cone of the mass spectrometer. The above mechanism was used in the computer simulation of the HO₂ kinetics. since the HO₂ production by reaction (3) could not be completed in the reaction zone corresponding to the kinetic treatment of the HO₂ decay. In the simulation, the value used for k_{10} was determined in separate experiments where NO was added together with O_2 . In such a system, reaction (1) became negligible compared to reaction (6). The value of k_{10} could be derived from measurements of OH produced as a function of the initial concentrations of Br, H₂CO and O₂, and from computer simulation of reactions (2), (3), (6) and (10). The resulting value for k_{10} was $(2.8 \pm 1.2) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹.

In this simulation, the following reaction was not considered:

$$Br_2 + HCO \rightarrow HCOBr + Br$$
. (11)

The rate constant for this reaction has been recently measured [17]: $k_{11} = 7.1 \times 10^{-11}$ at 298 K. This value is consistent with that obtained very recently for the similar reaction CH₃CO+Br₂ \rightarrow CH₃CBrO+Br: $k = (1.08 \pm 0.38) \times 10^{-10}$ at 298 K [18]. Considering both this high value of k_{11} and the significant Br₂ concentrations in our previous experiments due to the dissociation yield of Br₂ (around 50%), one must not neglect reaction (11). Therefore, this reaction has been included in the computer simulation of the experiments for the measurement of k_{10} and the resulting value derived for k_{10} was significantly lower than that previously calculated: $k_{10} = 1.9 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ (instead of 2.8×10^{-10}).

Considering reaction (10) with this new value of its rate constant together with the new reaction (11), we carried out a computer modeling of the previous experiments where NO was added upstream of the LIF cell in order to derive k_1 . This retreatment of all the data given in fig. 3 of ref. [7] leads to new values in the following range:

$$k_1 = (1.0-2.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
.

The mean value in this range appears to be about twice higher than our previous determination: $k_1 =$ 7.6×10^{-13} . This difference particularly shows that the HO₂ production rate from reaction (3) is greatly influenced by reaction (11) since their rates had similar magnitude in our experiments (the rate ratios of reactions of HCO with O₂ and Br₂ ranged between 0.75 and 2.3). The present recalculated values of k_1 can only be given in the above uncertainty range which is apparently large, but it can be considered to be reasonable for such an indirect determination. Nevertheless, this range overlaps our present direct determination of k_1 as well as the value of Toohey et al. [8]. The k_1 values now available are reported in table 1.

For atmospheric application, the present determination of k_1 confirms that reaction (1) and the reaction of Br with H₂CO in the lower stratosphere are the major processes forming HBr which acts as a temporary reservoir of Br atoms in the stratosphere. The rates of these reactions are therefore key factors to determine the importance of HBr in the partitioning of bromine in the stratosphere, and hence to assess the role of bromine in ozone deple-

Table 1 Rate constant for reaction $Br + HO_2 \rightarrow HBr + O_2$

| k, 298 K (cm ³ molecule ⁻¹ s ⁻¹) | Technique *) | Ref. |
|---|--|---|
| $\frac{(2.2 \pm 1.1) \times 10^{-13}}{(7.6 \pm 0.9) \times 10^{-13}}$ $(1.98 \pm 0.05) \times 10^{-12}$ $(1.5 \pm 0.2) \times 10^{-12}$ $(1.0-2.2) \times 10^{-12}$ | DF-MS DF-MS/LIF DF-LMR/RF DF-EPR DF-MS/LIF | [6] [7] [8] ^{b)} this work this work ^{c)} |

^{a)} DF=discharge flow; MS=mass spectrometry; LIF=laser-induced fluorescence; LMR=laser magnetic resonance; RF=resonance fluorescence; EPR=electron paramagnetic resonance.

- ^{b)} $k = (1.4 \pm 0.2) \times 10^{-11} \exp(590 \pm 140) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ in}$ the range 260–390 K.
- ^{c)} Range of values obtained from re-interpretation of previous experiments of ref. [7].

tion. Models using the current chemistry indicate that the major bromine species would not be HBr but BrO. This is in contrast with a recent interpretation of infrared field measurements which led to the conclusion that HBr could be the major stratospheric bromine species [19]. However, the k_1 value obtained in our present work, which agrees with the recent determination of Toohey et al. [8], shows that reaction Br+HO₂ will be too slow to explain this field observation of HBr.

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