Kinetics and Mechanism of the BrO + HO₂ Reaction

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Using the discharge flow-mass spectrometric technique, the kinetics and mechanism of the BrO + HO₂ reaction have been investigated in the temperature range 233-344 K. With an excess of HO₂ over BrO, the rate constant was found to be $k_1 = (4.77 \pm 0.32) \times 10^{-12} \exp[(580 \pm 100) / T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The reaction may proceed via two channels: BrO + HO₂ \rightarrow HOBr + O₂ (1a) and BrO + HO₂ \rightarrow HBr + O₃ (1b). Over the whole temperature range, HOBr was observed as the major product, whereas an upper limit was measured for channel 1b from the absence of detection of O₃: $k_{1b}/k_1 < 1.5\%$. The potential implications of these data are briefly discussed in relation to the stratospheric bromine/ozone interaction.

Introduction

Methyl bromide, from both natural and anthropic origins, is a major precursor of the active bromine which participates in the chemistry of stratospheric ozone. Several overviews of the stratospheric bromine/ozone interaction based on model calculations have been published so far (for example in refs 1 and 2). The potency of bromine, compared to chlorine, in destroying ozone on a per atom basis is well established. It is also generally accepted from the present knowledge of the chemistry and field observations that BrO radicals are the most abundant form of bromine in the stratosphere. Radical-radical reactions involving BrO may initiate ozone-destroying chain mechanisms, such as the BrO + ClO reaction, which is known for its synergistic effect in ozone depletion, especially in the antarctic stratosphere.³ The reaction of BrO with HO₂ radicals is another example of these reactions leading to the cycle

$$BrO + HO_{2} \rightarrow HOBr + O_{2}$$
(1)

$$HOBr + h\nu \rightarrow OH + Br$$

$$OH + O_{3} \rightarrow HO_{2} + O_{2}$$

$$Br + O_{3} \rightarrow BrO + O_{2}$$

$$2O_{3} \rightarrow 3O_{2}$$

Net:

If the HOBr-forming channel of reaction 1 is generally considered to be unique, at least at 298 K, the possibility of conversion of BrO to HBr via another channel cannot be ruled out, specially at lower temperature:

$$BrO + HO_2 \rightarrow HOBr + O_2$$
 $\Delta H = -45.1 \text{ kcal mol}^{-1}$
(1a)

 $BrO + HO_2 \rightarrow HBr + O_3$ $\Delta H = -7.7 \text{ kcal mol}^{-1}$ (1b)

The measurement of the branching ratio for channel 1b is of major importance for the stratospheric chemistry of bromine.⁴ The existence of this pathway would significantly reduce the potential of methyl bromide to deplete stratospheric ozone, thus

reducing the calculated ozone depletion potential of CH_3Br . For example, it has been calculated that a 10% branching ratio for the BrO + HO₂ channel forming HBr would decrease the ozone depletion potential of CH_3Br from 0.74 to 0.25.⁵

In this work, we report a direct kinetic and mechanistic study of reaction 1 using the discharge flow-mass spectrometry method. The temperature dependence of the rate constant has been measured in the temperature range 233-344 K. An upper limit for the branching ratio of channel 1b has also been measured down to 233 K.

Experimental Section

Double discharge flow reactors coupled to a modulated molecular beam mass spectrometer have been used. The apparatus has been described in detail before.⁶ The molecular beam, formed between the sampling cone ($\emptyset = 0.3 \text{ mm}$) and the skimmer ($\emptyset = 2 \text{ mm}$), was modulated by a chopper (between 10 and 50 Hz) and entered the electron impact ion source of the quadrupole mass spectrometer (BALZERS, QMG 420). The first chamber and the ion source chamber were pumped by an oil diffusion pump (2000 L/s) and a turbomolecular pump (560 L/s), respectively. The ion source of the mass spectrometer was surrounded by a liquid nitrogen trap in order to lower the detection limit of the species. The output signal from the electron multiplier was analyzed by a lock-in amplifier. The electron energy in the ion source was between 25 and 30 eV.

Different chemical sources have been used to produce the BrO and HO₂ radicals. A first source was used for HO₂ radicals, which were generated from the termolecular reaction $H + O_2 + M$. Since this reaction is not fast at low pressure, a discharge tube with two capillary restrictions was used in order to increase the pressure (up to around 40 Torr) and the HO₂ yield. However, under optimized conditions and using a large excess of O₂ over H atoms (produced from the microwave discharge in H₂ highly diluted in He), the maximum concentration obtained in the main reactor for HO₂ was about 5×10^{11} molecule cm⁻³ at 298 K, which was too low for the kinetic investigation of the BrO + HO₂ reaction where HO₂ had to be in excess over BrO.

Consequently, the chemical source used for HO_2 was the reaction of Cl atoms with a large excess of a mixture of CH_3OH and O_2 (in the ratio 1:2) following the sequence

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$$Cl + CH_{3}OH \rightarrow CH_{2}OH + HCl$$
$$CH_{2}OH + O_{2} \rightarrow HO_{2} + H_{2}CO$$

Chlorine atoms were generated by microwave discharge in Cl_2 at concentrations lower than 3×10^{13} molecule cm⁻³. The concentration of methanol was in the range $(1-4) \times 10^{14}$ molecule cm^{-3} . The HO₂ production was completed over the 15 cm length of zone 2 of the reactor (see Figure 1a). The absence of chlorine atoms entering the main reaction zone was confirmed from the absence of reaction of C₂H₃Br when this molecule was added upstream from zone 2 (the reaction Cl + $C_2H_3Br \rightarrow Br + C_2H_3Cl$ proceeds close to the collision frequency⁷). The mixture CH_3OH/O_2 was prepared using a dynamic method: oxygen was flowed through a bubbler containing liquid methanol and maintained at 273 K. The CH₃OH/O₂ ratio was adjusted by changing pressure in the bubbler. The absolute concentrations of CH_3OH and O_2 in the reactor were derived from the flow rate measurement of gaseous mixtures with known composition.

The range of concentration of HO₂ was $(4-48) \times 10^{11}$ molecule cm⁻³. The absolute concentration of HO₂ was measured by NO titration in the presence of an excess of C₂F₃Cl used as OH scavenger. This procedure was necessary to avoid the overestimation of HO₂ concentration which would have resulted from the reaction sequence

 $NO + HO_2 \rightarrow NO_2 + OH$ $OH + CH_3OH \rightarrow CH_2OH + H_2O$ $CH_2OH + O_2 \rightarrow HO_2 + H_2CO$

HO₂ concentration was obtained from the measurement of NO₂ formed in this titration experiment. The calibration at m/e = 46 was performed using a known flow of NO₂ and correction was made to account for the NO₂-N₂O₄ equilibrium. C₂F₃Cl and NO concentrations were varied and adjusted in the range $(0.5-2) \times 10^{15}$ molecule cm⁻³, with C₂F₃Cl in excess over NO in order to achieve a quasi-quantitative conversion of HO₂ into NO₂. The uncertainty associated with this determination of the absolute concentration of HO₂ was calculated from the simulation of the experimental conditions and was shown to be less than 2%.

HO₂ radicals were detected at the mass m/e = 33. At this mass, there was a significant contribution (between 20 and 40%) of ¹⁷O¹⁶O coming from the HO₂ source. However, this did not lead to any complication in the kinetic measurements of the BrO + HO₂ reaction, since the absolute concentration of HO₂ was deduced from the NO₂ calibration (see above). From the titration experiments, the detection limit of HO₂ radicals was around 2 × 10¹⁰ molecule cm⁻³. It appeared difficult to generate HO₂ radicals at concentrations higher than 8 × 10¹¹ molecule cm⁻³ at temperatures lower than 253 K. This will be discussed later.

The kinetic experiments were treated using a mean value for the HO₂ concentration over the reaction zone. This mean value was obtained during the titration experiments, by introducing NO successively at each end of the reaction zone. These measurements indicated that the homogeneous or/and heterogeneous loss rates of HO₂ radicals along the reaction zone were low, at least at T > 233 K. The HO₂ self-reaction in the gas phase is known to be slow:

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$



Figure 1. Diagrams of the reactors with the different configurations for the production of BrO and HO₂ radicals at T = 298 K (a, top) and at variable temperature (b, bottom).

$$k = 2.3 \times 10^{-13} \exp[(600 \pm 200)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1.8}$$

The experimental uncertainty resulting in HO₂ concentration measurements at 298 K was lower than 10% over the reaction zone. But at the lowest temperature (233 K), the HO₂ loss rate was higher, leading to a maximum estimated uncertainty on HO₂ concentration of 5 and 25% for reaction times around 10 and 20 ms, respectively.

Two sources have been used to generate BrO radicals. In the first source, excess Br_2 reacted with oxygen atoms produced by dissociation of O_2 in a microwave discharge:

O + Br₂ → BrO + Br

$$k = (2.0 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1.9}$$

This ozone-free source was used in the measurement of k_1 and in the tentative detection of O₃ as a product of the BrO + HO₂ reaction. In the second source, BrO was produced by the reaction of an excess of ozone with bromine atoms generated by dissociation of Br₂ in the same discharge:

Br + O₃ → BrO + O₂

$$k = (1.2 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1.8}$$

This source was used only for the tentative detection of HBr as a coproduct of O_3 in channel 1b of the BrO + HO₂ reaction at low temperature.

As for HO₂, the absolute concentration of BrO was measured by NO titration. Initial BrO concentrations lie between 4×10^{10} and 8×10^{11} molecule cm⁻³. The detection limit for BrO at m/e = 95 and 97 was 1×10^{10} molecule cm⁻³ for a signal to noise ratio equal to unity.

The homogeneous self-reaction of BrO was negligible at the BrO concentrations used:

BrO + BrO → 2Br + O₂

$$k = 4.0 \times 10^{-12} \exp[(190 \pm 150)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1.8}$$

BrO + BrO → Br₂ + O₂
 $k = 4.2 \times 10^{-14} \exp[(660 \pm 300)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1.8}$

The wall loss of BrO was also negligible, at 298 K, since the total loss rate measured for BrO radicals in the absence of HO₂ was in the range (0-8) s⁻¹ at this temperature. When the first BrO source was used $(O + Br_2)$, complications appeared at temperatures around 233 K since it was observed that the increase of the concentration of oxygen atoms relative to Br₂ led to the disappearance of BrO. This was easily explained by the occurrence of the secondary reaction O + BrO, for which $k = 1.7 \times 10^{-11} \exp[(260 \pm 150)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1.8}$ However, in this experiment when the concentration of O atoms was further decreased to recover the initial conditions $[O] \ll$ [Br₂], it was not possible to reobserve BrO radicals. Then, the BrO generation was stopped and mass spectrometric analysis of the gas phase was made while slowly heating the reactor. First, species appeared at around 243 K at m/e = 95 and 97 (BrO⁺). Then, between 248 and 253 K, increased signals were observed at the same masses together with signals at m/e =111 and 113 (BrO_2^+). A tentative explanation is the generation of higher bromine oxides at low temperature when the O concentration was increased. BrO2, which has already been observed in discharge flow experiments,10 or/and the dimer Br_2O_4 , which could also be produced under these conditions,¹¹ could have been formed on the cold surfaces of the reactor, thus preventing BrO detection.

The configuration of the two reactors used, with the various inlets for reactants, is given in Figure 1. Figure 1a shows the reactor used for the room temperature study, with a triple central injector. The production of BrO (from $O + Br_2$) and of HO₂ took place in regions 1 and 2 of the reactor, respectively. Both sources were moved simultaneously to vary the reaction time, which had the advantage of reducing any possible heterogeneous complication in the production of both radicals when the position of the injector was changed during the kinetic measurement. When this reactor was used at lower temperatures, a difficulty appeared in the production of HO₂, as already mentioned. While maintaining the same initial concentrations of precursors, the measured concentration of HO₂ decreased at $T \leq 250$ K and became negligible at 233 K. Simultaneously, the titration experiments with NO showed that no NO₂ was formed even though an important contribution at m/e = 46 was observed, which increased with decreasing temperature. This was interpreted by a possible change in the chemistry of the HO₂ source at low temperature. It is known from previous studies¹² that the temperature dependence of the $CH_2OH + O_2$ reaction is complex, with the possible formation of a stable intermediate, $HOCH_2O_2$. A competition between the decomposition of this adduct and its stabilization, with possible isomerization, could explain the experimental observations. The increase of the peak intensity at m/e = 46 could be due to the contribution of the $CH_2O_2^+$ cracking peak of the adduct at low temperature. Other peaks have been also observed at m/e = 61 and 63, which may correspond to the $HOCO_2^+$ and $HOCH_2O_2^+$ ions, respectively.

Consequently, a new arrangement for the production of HO_2 was used, with the $Cl + CH_3OH + O_2$ source located outside



Figure 2. Production of HO₂, detected at m/e = 33, in the Cl + CH₃OH + O₂ source as a function of temperature (symbols refer to different experiments; see text).

of the cold region of the reactor. In the new reactor, shown in Figure 1b, HO₂ radicals were produced at room temperature in a side-arm tube containing a capillary restriction to prevent any diffusion of the CH₃OH + O₂ mixture in the discharge zone. BrO radicals were produced in the central double injector from either the O + Br₂ or Br + O₃ source. A constant temperature in the main reaction zone of the reactor was maintained by the circulation of a liquid through a double jacket. The fluid used was water or ethanol for temperatures higher or lower than 300 K, respectively. The temperature was measured with a thermocouple located at the end of the central injector.

For the titration experiments, NO could be introduced into the reactor through inlets at each end of the reactor or through the central injector. As for the first reactor, C_2F_3Cl could be added along with NO during the HO₂ titration experiments.

Using this new configuration for the production of radicals, it was again observed that a significant decrease in HO₂ concentration occurred with decreasing temperature. A typical example is shown in Figure 2, where the intensity of the molecular peak m/e = 33 (HO₂⁺) is plotted as a function of temperature, for the same initial concentrations of HO₂ radicals $(6.5 \times 10^{12} \text{ molecule cm}^{-3})$. The concentrations of HO₂ radicals $(6.5 \times 10^{12} \text{ molecule cm}^{-3})$. The concentrations of the other reactants were $(1.1-1.3) \times 10^{13}$ for Cl₂, $(3.5-4.5) \times 10^{14}$ for CH₃OH, and 1×10^{15} for O₂ (in molecule cm⁻³). The inability to detect HO₂ at temperatures lower than 233 K could not be explained as it was in the first reactor but was attributed to the possible formation of a complex between HO₂ and methanol. Such an argument was already suggested in the interpretation of data obtained in the study of the self-reaction of HO₂ in the presence of methanol.¹³

Finally, due to experimental limitations in the production of either BrO or HO₂ radicals at low temperature, the lower limit of the temperature range of this study was 233 K.

In the two reactors, the total pressure (around 1 Torr of Helium) was measured in the middle of the reaction zone by a capacitance manometer (Baratron) with a precision of 0.15%. The specific dimensions of the reactors described in Figure 1 are as follows: i.d. of the main flow tube = 2.4 cm, i.d. of the multiple axial injectors = 0.4 (central injector of Figure 1a only), 0.7, and 1.1 cm. The typical length for the production zones of both HO₂ (Figure 1a) and BrO (Figure 1b) was 15 cm,



Figure 3. Pseudo-first-order plot of the rate constant at 298 K.

corresponding to a residence time in the central injector of ca. 10 ms, which allowed for a total consumption of the atomic precursors. The mean gas velocity in the main flow tube was in the range 600-2000 cm s⁻¹. The flow of the He carrier gas was typically 20 and 5 L h⁻¹ (STP) in the side-arm tube and in the axial injector, respectively. In the rate constant measurements, the corrections for the pressure gradient in the reactor and for the axial diffusion were lower than 2 and 3%, respectively. The walls of the reactors and injectors were coated with halocarbon wax in order to reduce heterogeneous loss of radicals. In the HO₂ source, the surface of the discharge tube was coated with orthophosphoric acid in order to increase the net yield of Cl atoms used as precursors.

Preparation and Purity of the Chemicals Used. Ozone was produced by electrical discharge through oxygen in an ozonizer (Trailigaz) and collected at around 30 Torr in a trap maintained at 193 K. Before use, ozone was purified of oxygen by pumping at 77 K. The oxygen (Alphagaz) had a purity \geq 99.995%. The NO used as a chemical titrant (Alphagaz, purity \geq 99.9%) was purified by trap to trap distillation in order to remove any trace of NO₂, which was verified by mass spectroscopic analysis in the flow system. Helium (Alphagaz, purity $\geq 99.9995\%$) was passed through a liquid nitrogen trap before use as the carrier gas. The other chemicals were NO_2 (Alphagaz, purity \geq 99.00%), Cl₂ (Ucar, purity \geq 99.0%), Br₂ (Aldrich, purity \geq 99.99%), CH₃OH (Prolabo, purity \geq 99.8%), and C_2F_3Cl (Fluorochem, purity $\geq 99.0\%$). In separate experiments, HOBr was prepared in order to characterize the mass spectrum of HOBr molecules produced in the BrO + HO₂ reaction. HOBr was generated by the reaction of OH with molecular bromine: $OH + Br_2 \rightarrow HOBr + Br^{14}$

Results

1. Kinetic Study. In the first reactor described above (Figure 1a), 34 independent measurements of the rate constant were performed at a total pressure between 1.02 and 1.19 Torr, with a mean flow velocity of 13.5 m s⁻¹, with the following initial concentrations of the radicals: $[BrO] = (0.8-4.8) \times 10^{11}$ molecule cm⁻³ and $[HO_2] = (1.0-4.8) \times 10^{12}$ molecule cm⁻³.

The temporal decays of BrO measured at m/e = 95 or 97 (BrO⁺) have led to the first-order plot given in Figure 3. The intercept $7.5 \pm 6.0 \text{ s}^{-1}$ is consistent with the BrO loss measured

TABLE 1: Kinetic Data Obtained for the BrO + HO₂ Reaction between 233 and 344 K

<i>T</i> (K)	$[HO_2] (10^{12} \text{ molecule cm}^{-3})$	$k^{I}(s^{-1})$
233	0.53	57.2
	0.54	80.2
	0.57	49.7
	0.61	79.7
	0.75	90.0
	0.93	88.6
243	0.50	29.0
	1.20	50.0
	1.20	53.3
	1.20	72.6
	1.30	92.4
253	1.00	30.0
	1.11	69.4
	1.13	50.4
	1.41	70.6
	1.46	78.6
266	1.10	33.3
	1.22	40.6
	1.23	40.4
	1.24	42.4
	1.30	52.0
	1.80	67.0
	2.10	101.8
303	0.91	29.1
	0.98	30.2
	1.12	35.7
	1.32	55.2
	1.38	35.7
	1.42	36.0
	1.44	67.3
	1.58	65.9
	2.10	70.3
	2.70	87.8
344	1.50	31.8
	2.30	60.4
	2.42	69.1

in the absence of HO₂ (between 0 and 8 s⁻¹) and confirms the low heterogeneous loss of BrO radicals at room temperature. The slope of the straight line obtained yielded the value for the rate constant of the BrO + HO₂ reaction at 298 K:

$$k_1 = (3.3 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The error is twice the standard deviation.

In the second reactor (Figure 1b), the rate constant has been measured as a function of temperature. Maintaining constant the temperature, total pressure, and gas flow velocity, the low concentration of BrO radicals could not always be kept constant on the time scale of the experiments. Consequently, the kinetic treatment had to take into account any variation in the initial BrO concentration, [BrO]₀. Thus, for each reaction time the BrO concentration was measured in the presence and in the absence of HO₂ radicals and the pseudo-first-order rate constant, k^{l} , could be calculated from the kinetic equation

$$-d \ln([BrO]_0/[BrO])/dt = k_1[HO_2] + k_w = k^1$$

Table 1 summarizes the conditions and results for the measurement of k^{I} in the temperature range 233-344 K. In all experiments, $[BrO]_{0}$ was at least 1 order of magnitude lower than the HO₂ concentration. k_{1} was either deduced from the plot $k^{I} = f([HO_{2}])$ or calculated from individual experiments in which the wall loss of BrO radicals was neglected. The difference between these two treatments was lower than 6% over the entire temperature range, which shows that the measurement of k_{1} was not significantly affected by heterogeneous complications in the temperature range of the study.



Figure 4. Temperature dependence of k_i .

TABLE 2: Summary of Data for k_1

•	-	
<i>T</i> (K)	$k_1 (10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$	
233	10.9 ± 2.1	
243	5.6 ± 1.4	
253	5.0 ± 1.1	
266	4.1 ± 0.6	
303	3.4 ± 0.6	
344	2.6 ± 0.3	

Similarly, it was shown from the pseudo-first-order plots that the zero intercepts, which should give the values of k_w at each temperature, ranged between -6 and 6 s^{-1} . These low values, without any clear trend as a function of temperature, confirm that the wall loss of BrO radicals could be neglected in the kinetic analysis. The mean values of the rate constants obtained at each temperature are summarized in Table 2. The quoted uncertainty is one standard deviation.

The Arrhenius representation of these data is shown in Figure 4. A negative temperature dependence is observed for the rate constant. In the temperature range of this study, it is possible to consider a linear dependence (which excludes the data measured at 233 K; see below) leading to the Arrhenius expression

$$k_1 = (4.77 \pm 0.32) \times 10^{-12} \exp[(580 \pm 100)/T] \text{ cm}^3 \text{ molecule s}^{-1} \text{ s}^{-1}$$

The uncertainties refer to two standard deviations. It is worth noting the important deviation from this linear dependence which was clearly and reproducibly observed at 233 K. A nonlinear dependence could have been considered, leading to a curvature at low temperature of the Arrhenius plot, similar to the behavior observed for instance for the $ClO + HO_2$ reaction.¹⁵ However, if a mechanistic interpretation may be given based on a possible change in the reaction mechanism (see discussion), other explanations exist. First, at the lowest temperature, HO₂ radicals may have been produced together with other reactive species coming from the HO₂ source, which would be consistent with the decreasing efficiency observed for the HO₂ production at low temperature (Figure 2). These species would not react with NO in the titration experiments but could react quickly with BrO, leading to an overestimation of the rate constant for the BrO + HO₂ reaction measured at 233 K. Such a species

TABLE 3: Reaction System Used in the Simulation Considering $k_{1b}/k_1 = 1\%^a$

reaction	$k (\mathrm{cm}^3 \mathrm{molecule}^{-1} \mathrm{s}^{-1})$
$BrO + HO_2 \rightarrow HOBr + O_2$	3.3×10^{-11}
$BrO + HO_2 \rightarrow HBr + O_3$	3.3×10^{-13}
$BrO + BrO \rightarrow Br + Br + O_2$	2.1×10^{-12}
$BrO + BrO \rightarrow Br_2 + O_2$	3.8×10^{-13}
$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	1.7×10^{-12}
$HO_2 + CH_2O \rightarrow products$	5.0×10^{-14}
$HO_2 + O_3 \rightarrow OH + 2O_2$	2.0×10^{-15}
$Br + O_3 \rightarrow BrO + O_2$	1.2×10^{-12}
$Br + HO_2 \rightarrow HBr + O_2$	2.0×10^{-12}
$OH + BrO \rightarrow products$	1.0×10^{-11}
$OH + Br_2 \rightarrow HOBr + Br$	4.2×10^{-11}
$OH + HBr \rightarrow H_2O + Br$	1.1×10^{-11}
$OH + HO_2 \rightarrow H_2O + O_2$	1.1×10^{-10}
$OH + H_2O_2 \rightarrow H_2O + HO_2$	1.7×10^{-12}
$BrO + wall \rightarrow products$	$k_{\rm w} = 3 {\rm s}^{-1}$

^{*a*} The rate constants (except k_{1a} , k_{1b} , and k_w), given at 298 K, are from ref.⁸

could be the adduct (HO₂-CH₃OH) already suggested to be formed at low temperature, even if this species was not detected mass spectrometrically at m/e = 65 with the ion source used. A second possible explanation is that the reactivity of BrO with the surface could be strongly modified in the lower temperature range. Evidence for such a change has also been shown in the independent experiments described in the Experimental Section, where heterogeneous loss of BrO could be significantly enhanced at 233 K. Finally, it is preferable not to consider the data obtained at 233 K in the kinetic analysis and to represent the dependence of the rate constant of the gas phase reaction between BrO and HO₂ as shown in Figure 4, which corresponds to the Arrhenius expression given above.

2. Mechanistic Study. The objective of this study was to measure, by a direct method, the branching ratio for the two anticipated channels (1a and 1b) from the yields of HOBr, HBr, and/or O_3 :

$$BrO + HO_2 \rightarrow HOBr + O_2$$
 (1a)

$$BrO + HO_2 \rightarrow HBr + O_3$$
 (1b)

HBr Measurements. Considering the necessarily low initial concentration used for BrO, the quantitative measurement of the product concentrations required very high detection sensitivity. Thus, it has been first attempted to enhance the possibility of detection of HBr in channel 1b by using similar initial concentrations of BrO and HO₂, i.e. higher BrO concentrations than in the kinetic study. The secondary chemistry which would become important has been simulated. The reaction system is given in Table 3. A sensitivity analysis allowed us to eliminate some secondary reactions (such as those involving OH radicals produced in the $HO_2 + O_3$ reaction). Due to the presence of HBr traces even in the purest Br_2 , the use of the $Br + O_3$ source instead of the $O + Br_2$ one was considered in this simulation. Under optimized conditions (with identical initial concentrations of BrO and HO₂ of 5×10^{12} molecule cm⁻³), it appeared that a 1% branching ratio for channel 1b would form a maximum of 4×10^{10} molecule cm⁻³ of HBr in a reaction time of 0.03 s. However, precise measurement of the branching ratio k_{1b}/k_1 under these conditions was not possible due to the lack of sensitivity in the HBr calibration due to interferences. Indeed, residual signals at m/e = 80 and $82 (HBr^+)$ were observed using either the $O + Br_2$ or the $Br + O_3$ source, which were not due to only the contribution of HBr present as impurity in Br₂. From simulations, it was also demonstrated that, when the $O + Br_2$ source of BrO was used, the $Br + HO_2$ reaction was negligible



Figure 5. Ratios of the BrO⁺ intensity with and without HO₂ (+) and of Δ (HOBr⁺)/ Δ (BrO⁺) (\blacklozenge) as a function of *t*[HO₂] at room temperature (see text).

and did not yield observable HBr:

Br + HO₂ → HBr + O₂
$$k = (1.5 \times 10^{-11}) \times \exp[-(600 \pm 600)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1.8}$$

If heterogeneous processes could be again the source of these residual signals, another complication would be due to the observed contribution of the HOBr molecule at m/e = 80 and 82. Consequently, it was not possible to determine the branching ratio k_{1b}/k_1 from the yield of HBr.

HOBr Measurements. HOBr, expected to be the major product through channel 1a, has been detected at m/e = 96 and 98 (HOBr⁺). Temporal increases in the intensity of the HOBr⁺ peak were observed in the kinetic study of the $BrO + HO_2$ reaction and were anticorrelated with the decreases in the BrO⁺ peak intensity. At 298 K, in the presence of an excess of HO₂ over BrO, it was also observed that the BrO⁺ peak intensity did not decrease to 0 at large reaction times. Figure 5 shows examples of relative intensities of the peak at the mass of BrO⁺ (I_{95}/I°_{95}) , with and without HO₂, as a function of reaction time. To summarize several measurements with different HO_2 initial concentrations, in the range $(1-2.5) \times 10^{12}$ molecule cm⁻³, the above ratio has been plotted as a function of $t[HO_2]$. For the experimental data corresponding to $t[HO_2] < 5 \times 10^{10}$ molecule cm⁻³ s, the best fit was obtained for $k_1 = 2.96 \times$ 10^{-11} cm³ molecule⁻¹ s⁻¹. This value perfectly agrees with the value measured in the kinetic experiments which were performed for short reaction times ($k_1 = 3.3 \times 10^{-11} \text{ cm}^3$ molecule⁻¹ s⁻¹). The solid line given in Figure 5 corresponds to this value. For larger reaction times (e.g. reaction times larger than 20×10^{-3} s for [HO₂] = 2.5×10^{12} molecule cm⁻³), a departure from the pure first-order decay is clearly observed (dashed line of Figure 5), indicating the contribution of another species at m/e = 95.

It was first considered that this contribution could be due to HOBr. Hence, in independent experiments, the mass spectrum of HOBr was recorded using the $OH + Br_2$ reaction as a source of HOBr (see the Experimental Section). The typical mass spectrum obtained, at an electron energy of 30 eV, is given in Table 4. The relative intensities are the mean values resulting from several experiments with different HOBr concentrations. The BrO⁺ ion fragment was shown to be present at a negligible

TABLE 4: Mass Spectrum of HOBr (at 30 eV) Using the $OH + Br_2$ Source

m/e	96	98	95	97	80	82
ion	HO ⁷⁹ Br ⁺	HO ⁸¹ Br ⁺	⁷⁹ BrO ⁺	⁸¹ BrO ⁺	H ⁷⁹ Br ⁺	H ⁸¹ Br ⁺
intensity	1000	960	7	7	80	40

level in the HOBr spectrum. Inversely, as discussed above, the contributions at m/e = 80 and 82 were significant. Since HOBr could not be precisely calibrated with the source used, the same sensitivity for HOBr at m/e = 96 and for BrO at m/e = 95 has been considered from the additivity rule of ionization cross sections for both species. Consequently, HOBr could not be responsible for the BrO⁺ ion observed at the large reaction times of the BrO decays.

Another candidate for the species contributing at m/e = 95 (BrO⁺) is the adduct BrOHO₂. Tentative detection of this adduct was performed at T = 303, 243, and 233 K. The following masses were searched for : 128/130 (BrOHO₂⁺), 127/129 (BrO₃⁺), 112/114 (HO₂Br⁺), and 111/113 (BrO₂⁺). Only very weak signals were detected, at the two lowest temperatures, at m/e = 112/114 and 111/113. It is speculative both to consider these ions as fragments of the adduct (which was not detected at its parent peak) and to attribute the residual signal at m/e = 95 to this adduct. Furthermore, this BrO⁺ signal was seen only at 298 K, where the lifetime of the adduct, if it exists, should be lower than at lower temperatures.

The ratio of the increase of the HOBr⁺ ion and of the decrease of the BrO⁺ ion (ΔI_{96} / ΔI_{95}) has also been measured, as shown in Figure 5. Similar plots were obtained for ΔI_{98} / ΔI_{97} . The data shown in Figure 5 have been obtained with the $O + Br_2$ source for BrO at T = 303 K in seven independent runs. Similar data have also been obtained with the $Br + O_3$ source and at lower temperatures down to 233 K, although the measurements could be made only on a narrow range of reaction times at these lower temperatures. It is observed that the ratio $\Delta I_{96}/\Delta I_{95}$ is nearly constant in the initial period, within the uncertainty limits, and then slightly increases at larger reaction times. This observation indicates that a species contributing at m/e = 96 is formed in the reaction, and it is not HOBr since the contribution of HOBr at m/e = 95 has been shown to be negligible. Again, another unidentified species contributing at m/e = 95 (BrO⁺) and possibly at m/e = 96 (HOBr⁺) is formed in the reaction system at large reaction times.

Finally, the formation of HOBr through channel 1a of the BrO + HO₂ reaction is definitely established. Considering an equal mass spectrometric detection sensitivity for HOBr and BrO at their parent peak m/e = 96 and 95, respectively, and the fact that the $\Delta I_{96}/\Delta I_{95}$ ratio is nearly unity within the uncertainty limits, the present data are not inconsistent with the possibility of channel 1a being unique. However, the existence of another channel with a low branching ratio cannot be excluded, considering the experimental uncertainty, partly due to the impossibility of an accurate calibration of HOBr.

 O_3 Measurements. To determine the branching ratio for the second channel (k_{1b}/k_1) , the ozone formation was tentatively observed at m/e = 48 (O_3^+) . These measurements were performed at 298 and 233 K, using the O + Br₂ source to generate BrO. The calibration of the mass spectrometer for ozone was achieved by flowing into the reactor O_3 + He mixtures of known composition. Then, in the presence of the BrO source only, it was verified that no change occurred in the ion intensity at m/e = 48. A small increase was observed when HO₂ radicals were generated in the absence of BrO, which could be explained by the contribution at this mass of the ion CHCl⁺, characteristic of a species present in the HO₂ source. Finally, when BrO radicals were added, no change at m/e = 48 was

observed for any reaction time. This measurement was repeated for several values of the initial BrO concentration up to 3×10^{11} molecule cm⁻³.

To establish an upper limit of the ratio k_{1b}/k_1 , the sensitivity of the mass spectrometer for ozone at m/e = 48 was precisely evaluated. A detection limit of 5×10^9 molecule cm⁻³, with a time constant of 10 s, was calculated. Since no O₃ was observed in the BrO + HO₂ reaction, even at the highest initial BrO concentrations ([BrO]₀ = 3×10^{11} molecule cm⁻³), the upper limit for the branching ratio of the HBr-forming channel, in the temperature range 233–298 K, was derived:

$$k_{1b}/k_1 < 1.5 \times 10^{-2}$$

Discussion

This paper gives the first published determination of the temperature dependence of the rate constant for the $BrO + HO_2$ reaction. The room temperature value, already reported without experimental details in a previous paper from our laboratory,⁴ $k_1 = (3.3 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule } ^{-1} \text{ s}^{-1} \text{ has been}$ confirmed in the two different discharge flow reactors used. This value also agrees with the data from the flash photolysis study performed at 298 K and 710 Torr total pressure.¹⁶ Using photolysis of Br₂/O₃/Cl₂/CH₃OH/O₂/He mixtures, the decays of BrO radicals observed by UV absorption were simulated, giving $k_1 = (3.4 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Data have also been reported on this reaction in a kinetic investigation using both molecular modulation and laser flash photolysis.¹⁷ Complications appeared in the molecular modulation experiments during the photolysis of O₃/Br₂/CH₃OH/O₂/Ar mixtures, since the rate constants derived from FACSIMILE modeling were found to be dependent on the CH₃OH concentration. This was attributed to the formation of an adduct, HO₂-CH₃OH, with a possible effect on the observed loss of BrO. A second analysis was made in laser flash photolysis of O₃/Br₂/H₂/O₂/Ar mixtures. Although the data were scattered, a value of $k_1 = (3 \pm 2) \times$ 10^{-11} cm³ molecule⁻¹ s⁻¹ was derived at 298 K. A general agreement seems to exist for the value of k_1 at 298 K, which is preferred over the previous value of a molecular modulation-UV absorption study, in which a much lower value (factor of 6) was reported.¹⁸

Considering now the temperature dependence of k_1 , the value used so far in modeling was derived from an estimate based on analogy with the ClO + HO₂ reaction, for which there exists only one temperature dependence study.¹⁵ The resulting recommended value based on the higher value of k_1 at 298 K was⁸

$$k_1 = 6.2 \times 10^{-12} \exp[(500 \pm 500)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

This value is very consistent with the present absolute determination of k_1 in the temperature range 233-344 K:

$$k_1 = (4.8 \pm 0.3) \times 10^{-12} \exp[(580 \pm 100)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The negative dependence, similar to that of the $ClO + HO_2$ reaction,¹⁵ is common for radical-radical reactions which occur via the formation of a long-lived complex. As discussed previously, a possible curvature in the Arrhenius plot, like that observed in the study of the $ClO + HO_2$ reaction, has not been considered in the final analysis of the present data. However, the formation of a complex with different possible structures may also be considered for the BrO + HO₂ reaction:

$BrO + HOO \rightarrow BrOHOO (I)$ or HOOBrO (II) or HOOOBr (III) (III)

HOBr may be produced either from adduct I via a simple H atom transfer mechanism or from adduct II after a fivemembered-ring formation. The cyclization of adduct III would have been necessary to produce HBr.

The product study required a careful control of experimental conditions. The HOBr and O₃ yield formed in channels 1a and 1b, respectively, could be measured in the reaction system used. HOBr was confirmed to be the major, and likely unique, brominated reaction product, and from the absence of ozone formation, an upper limit of 1.5×10^{-2} was determined for the branching ratio of channel 1b in the temperature range 233-298 K. This result is in good agreement with the recent study using an indirect approach, where the yield of HBr formed in channel 1b was determined by measuring an upper limit for the rate constant of the reverse reaction HBr + $O_3 \rightarrow HO_2$ + BrO in the temperature range 300-441 K.¹⁹ By extrapolation of their data at lower temperatures, the authors obtained a negligible value for k_{1b}/k_1 (<1 × 10⁻⁴ at stratospheric temperatures), which is consistent with the present determination. The present upper limit of this ratio is higher, but it has been measured by a direct method and in the temperature range of interest for the stratosphere. This method does not require one to know about the structure and the reactivity of the possible intermediate adduct. In contrast, the analysis in the study of the reverse reaction¹⁹ assumes that the forward and reverse processes occur as elementary reactions, which is not necessarily the case, since a complex mechanism with a long-lived adduct is a likely possibility, especially at low temperature.

The atmospheric implications of the results obtained in the present study have been discussed previously. Reaction 1 plays a major role in the bromine distribution in the stratosphere and is involved in a catalytical cycle which depletes ozone. From the present study, the HOBr formation rate is expected to increase at stratospheric temperatures: the rate constant k_1 increases by a factor 2 between 298 and 220 K. For example, at 220 K, this formation rate will be 12 times higher than that in models considering the previously recommended data for k_1^{18} and 2 times higher than that in recent models,⁴ where no temperature dependence was assumed for k_1 . Furthermore, there is stronger evidence for a negligible branching ratio for channel 1b forming HBr + O₃ at stratospheric temperatures. Previous modeling has shown that bromine partitioning is very sensitive to the ratio k_{1b}/k_1 , since a 0.1 value would have made HBr a major bromine species in the stratosphere.⁴ This is not supported by the field measurements of HBr in the stratosphere, which give an upper limit of only about 1 ppty.²⁰ Hence, the present measurement of the upper limit of 1.5×10^{-2} for the HBr branching ratio at temperatures relevant to the stratosphere is consistent with this finding. Consequently, HBr is very likely a minor reservoir for reactive bromine in the stratosphere. Additional evidence for a negligible HBr branching ratio has been given by a recent 2-D model²¹ involving detailed photochemistry. This model was used to set constraints on the effectiveness of bromine relative to chlorine for ozone loss, and the role of the $BrO + HO_2$ reaction was explored. The result was that a HBr yield greater than a few percent was not consistent with the in-situ observations of the abundances and latitudinal gradient of BrO at mid latitudes.

Concerning the ozone depletion potential (ODP) of CH₃Br, the existing uncertainties have been recently analyzed.²² The largest uncertainties were considered to result from uncertainties in the lifetime of CH₃Br and in the kinetics of the BrO + HO₂ reaction. Using a value for k_1 of 6.3 × 10⁻¹¹ cm³ molecule⁻¹ s^{-1} at stratospheric temperatures and a negligible branching ratio for the HBr channel, which are consistent with the data obtained in this study, the value of the steady-state ODP for CH₃Br was found between 0.38 and 0.64.²²

However, other laboratory findings could modify the present knowledge of stratospheric bromine chemistry. Firstly, the measurement of the UV/visible absorption cross sections of HOBr has been published recently.²³ Using these new data, the authors have calculated the photolysis rate of HOBr. For example, a value of 5×10^{-4} s⁻¹ was found for typical stratospheric conditions at 17 km altitude and 30° N latitude during summer. This is about 2–3 times lower than the values used in previous modeling calculations. Therefore, the HOBr molecule would possess a larger lifetime toward photolysis. The effect of both a higher value for k_1 and a lower photolysis rate of HOBr will increase the concentration of HOBr in the stratosphere. However, these two results will have opposite effects on the ozone-destroying cycle initiated by reaction 1.

In addition, other atmospheric processes involving HOBr have to be considered, such as heterogeneous chemistry. It has been found in the laboratory²⁴ that HOBr can be lost on sulfate aerosols with a high probability, which is to be taken into account in parallel with the daytime photolysis of HOBr. The resulting conversion of HOBr to active forms (Br₂ and/or BrCl) has also been measured on ice.²⁴ Very recently,²⁵ HOBr has been found as the product of a rapid heterogeneous hydrolysis of BrONO₂, a major stratospheric bromine reservoir, on sulfuric acid solutions. One consequence of this heterogeneous reaction would be the existence of an additional source of OH resulting from HOBr photolysis in the stratosphere. In the same study,²⁵ the interactions of BrONO₂ and HOBr with HCl, leading to BrCl formation, have also been investigated.

In conclusion, the new laboratory data obtained either in spectroscopic studies or in kinetic measurements of both gas phase and heterogeneous reactions will better define the chemistry of bromine in the stratosphere, the partitioning of brominated species, and the exact role of bromine in the stratospheric ozone depletion. However, these new laboratory data need to be confirmed, especially from complementary studies of the HOBr photolysis and of the BrO + HO₂ reaction.

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