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Rate Constant of the BrO + BrO Reaction over the Temperature Range 220 – 950 K

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Abstract

The kinetics of the self-reaction of BrO radicals has been studied over a wide temperature range (T = 220 – 950 K) at 2 Torr total pressure of He using a low pressure flow reactor combined with a quadrupole mass spectrometer: BrO + BrO $\rightarrow$ 2Br + O_2 (1a) and BrO + BrO $\rightarrow$ Br_2 + O_2 (1b). The overall rate constant for this reaction (defined by d[BrO]/dt = -2k_1[BrO]^2) was found to be $k_1 = k_{1a} + k_{1b}$ = (1.32±0.09)×10^{-12} exp(182±22/T) cm^{3}molecule^{-1}s^{-1} at T = 220-950 K (where the uncertainties represent precision at the 2σ level). The channel-specific rate constant for the Br_2 + O_2 forming channel (1b) was determined at T = 220-450 K: k_{1b} = (2.83±0.35)×10^{-13} exp(34±36/T) cm^{3}molecule^{-1}s^{-1} (with 2σ uncertainties). As a result of the comparative analysis of the present data and those from the previous studies, the following Arrhenius expressions are recommended from the present work: k_1 = 1.4×10^{-12} exp(200/T) at T = 220-950 K (independent of pressure at least for T≥ 250K) and k_{1b} = 3.2×10^{-13} exp(34/T) cm^{3}molecule^{-1}s^{-1} at T = 220-450 K and total pressure of 2 Torr, with a conservative estimate of uncertainty of 25%, independent of temperature.

Keywords: BrO, self-reaction, rate coefficient, temperature dependence.

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Supporting Information is available in the online issue at www.wileyonlinelibrary.com.

1 INTRODUCTION

The BrO radical is the major form of active bromine-containing species in the atmosphere and is involved in several catalytic cycles of ozone destruction.[1] The BrO + BrO reaction is slow compared to the reactions of these radicals with other atmospheric species (e.g. ClO, HO_2, NO) due to relatively low concentrations of BrO in the atmosphere, and, as a result, is of limited importance in the atmospheric chemistry. Although this reaction is not of direct atmospheric significance, the information on its kinetics and products is important in laboratory studies of BrO chemistry and, for example, in studies of the reactions of oxygen atoms, which may employ detection of small concentrations of O-atoms via their conversion to BrO in reaction with Br_2.[2-4]

The kinetics of the self-reaction of BrO

$$BrO + BrO \rightarrow Br + Br + O_2 \quad (1a)$$

$$BrO + BrO \rightarrow Br_2 + O_2 \quad (1b)$$

$$BrO + BrO\ (+M) \rightarrow Br_2O_2\ (+M) \quad (1c)$$

has been studied very extensively in the past.[5-18] All the available temperature dependent measurements indicate a negative temperature dependence of the total rate constant ($k_1 = k_{1a} + k_{1b} + k_{1c}$); however, the absolute values of k_1 differ by a factor of 1.6.[7,9,13,15,18] Current evaluations of the kinetics[19,20] recommend rate constants based on the largest of the measured values of k_1.[15] The temperature dependence of the reaction pathway (1b) is even more uncertain. The existing temperature-dependent kinetic data[8,13,18] are sparse and scattered and are further complicated by an apparent pressure dependence of the rate constant observed at low temperatures and high pressures.[13,18] As a result, it is not currently possible to make a reliable recommendation of the rate constant k_{1b} and, in general, for the partitioning of the products of the BrO + BrO reaction as a function of temperature.

The objective of the present work was to determine the total rate constant of the BrO + BrO reaction, k_1, and the partial rate constant of the channel (1b), k_{1b}, over an extended temperature range (220 – 950 K for the total rate constant) in order to better specify these quantities in comparison with previous experimental data.

2 EXPERIMENTAL

The rate constants of the title reaction were measured at a total pressure of nearly 2 Torr of He in a discharge flow reactor combined with a modulated molecular beam mass spectrometer.[17,21] Two flow reactors were used. The first one (Figure S1, Supporting Information), used at low temperatures (220 – 318 K), consisted of a Pyrex tube (45 cm length and 2.4 cm i.d.) with a jacket for the thermostated liquid circulation (ethanol). The inner surface of the reactor as well as of the movable injector of O and Br atoms was coated with halocarbon wax (HW) in order to minimize their heterogeneous loss. The second flow reactor, operating at high temperatures (T = 296 – 950 K), consisted of an electrically heated Quartz tube (45 cm length and 2.5 cm i.d.) with water-cooled attachments (Figure S2, Supporting Information).[22]

Two methods were used to produce BrO radicals. In the first one, BrO was formed in reaction of oxygen atoms with excess Br_2:

$$O + Br_2 \rightarrow \quad BrO + Br \qquad (2)$$

$k_2 = 9.85\times10^{-16}\ T^{1.41}\ \exp(543/T)\ cm^3 molecule^{-1} s^{-1}$ over T = 220-950 K.[23]

Second method employed reaction of Br atoms with ozone,

$$Br + O_3 \rightarrow \quad BrO + O_2 \qquad (3)$$

$k_3 = 1.6\times10^{-11}\ \exp(-780/T)\ cm^3 molecule^{-1} s^{-1}$ over T = 195-422 K.[19]

Oxygen and bromine atoms were generated from the microwave discharge in O_2/He (Figure S1) and Br_2/He mixtures (Figure S2), respectively. Absolute concentrations of BrO radicals were determined using their chemical conversion to NO_2 through reaction (4) in an excess of NO with subsequent detection of the NO_2 formed ($[BrO]_0 = [NO_2]_{formed}$):

$$BrO + NO \rightarrow Br + NO_2 \qquad (4)$$

$k_4 = 8.8\times10^{-12}\ \exp(260/T)\ cm^3 molecule^{-1} s^{-1}$ (T = 224-425K) [19]

Another method of the absolute calibration of BrO signals used reaction (3) in an excess of ozone. In this case, the concentration of BrO was related to the fraction of Br_2 dissociated in the microwave discharge: $[BrO] = [Br]_0 = 2\Delta[Br_2]$. The results of the measurements of the absolute concentrations of BrO by the two methods were consistent within 10%. Ozone was produced by an ozonizer (Trailigaz) and was collected in a liquid nitrogen trap before dilution with helium and storage at room temperature in a calibrated volume flask. The absolute concentrations of all stable species (NO_2, Br_2, O_3) in the reactor were calculated from their

flow rates obtained by monitoring the pressure drop of a known volume of a manometrically prepared mixture of each substance in He. All species were detected by mass spectrometry at their parent peaks: m/z= 46 (NO_2^+), 160 (Br_2^+), 48 (O_3^+), 95/97 (BrO^+).

3 RESULTS AND DISCUSSION

3.1 Measurements of k_1

The total rate constant of the title reaction was determined from the kinetics of BrO consumption in the temperature range 220-950 K and 2.0-2.2 Torr total pressure of He. Temporal profiles of BrO, generated through reaction (2) in excess of Br_2 ([Br_2] = (0.6-1.8)×10^{14} molecule cm^{-3}), were monitored for different initial concentrations of the radicals. Typical examples of the temporal profiles of BrO observed at two extreme temperatures of the study (T = 220 and 950 K) are shown in Figure 1. All other experimental data observed at different temperatures of the study are shown in Figure S3 (Supporting Information). The BrO decays were processed using a simple kinetic mechanism:

$$\text{BrO} + \text{BrO} \rightarrow \text{products} \qquad (1)$$

$$\text{BrO} + \text{wall} \rightarrow \text{loss} \qquad (5)$$

Reaction 5 corresponds to the heterogeneous loss of BrO radicals on the wall of the flow reactor (k_w). In the frame of the two step mechanism (reactions 1 and 5), the rate of BrO consumption is:

$$d[\text{BrO}]/dt = -2k_1[\text{BrO}]^2 - k_w[\text{BrO}]$$

An analytical solution of this differential equation leads to the following expression for the temporal profiles of BrO radicals:

$$[\text{BrO}] = \frac{k_w[\text{BrO}]_0}{(2k_1[\text{BrO}]_0+k_w)\times\exp(k_w t)-2k_1[\text{BrO}]_0} \qquad (\text{I})$$

At each temperature, the rate constant of reaction (1) was derived from the global fit to all experimental kinetic runs using equation (I) with two variable parameters, k_1 and k_w. The ranges of the initial concentrations of BrO radicals used and the results obtained for k_1 and k_w at different temperatures are shown in Table 1. The measurements of k_1 at T = 296K and T ≥ 334 K have been carried out in an uncoated quartz reactor; the measurements at other temperatures were performed in the reactor coated with halocarbon wax.

As shown in Table 1, initial concentration of BrO radicals was varied by a large amount. This strong variation of $[BrO]_0$ allows one to determine two variables in equation (I), k_1 and k_w, practically independently of each other. At the lowest concentrations of BrO, the BrO loss kinetics is not sensitive to k_1, while at the highest $[BrO]_0$, the kinetics of BrO is driven mainly by consumption of the radicals in reaction (1). This is demonstrated in Figure S4 (Supporting Information): one can see that variation of k_1 by 10% leads to a significant deviation of the calculated BrO profiles (dashed lines) from the experimental data points at highest $[BrO]_0$, but has a negligible impact at lowest initial concentration of BrO. We estimate a statistical uncertainty of ≈ 10% on the determination of k_1 through the fit to the experimental data with equation (I). The total combined uncertainty on the measurements of k_1 was estimated to be of nearly 15%, by adding in quadrature (square root of the sum of squares) the statistical (1σ) error (10%) and those on the measurements of the flows (5%), pressure (2%), temperature (1%), and absolute concentrations (10%) of BrO radicals.

3.2 Measurements of k_{1b}

A similar approach was employed for the measurements of the rate constant k_{1b} of the Br_2 $+O_2$ forming pathway of the BrO self-reaction:

$$BrO + BrO \rightarrow Br + Br + O_2 \quad (1a)$$

$$BrO + BrO \rightarrow Br_2 + O_2 \quad (1b)$$

In this case, BrO radicals were generated through reaction of Br atoms with ozone,

$$Br + O_3 \rightarrow BrO + O_2 \quad (3)$$

with the Br-atoms being formed by the microwave discharge of Br_2/He mixtures. All experiments were carried out in the presence of relatively high concentrations of ozone in the reactor: $[O_3] = (0.6\text{-}2.0)\times10^{15}$ molecule cm^{-3}. In the presence of ozone, Br atoms formed in channel (1a) are rapidly converted back to BrO in reaction (3) and, as a result, channel (1a) does not contribute to BrO consumption. Experiments were conducted in the temperature range 220-450 K: the highest temperature of the study was limited by the observed thermal decomposition of ozone. Typical examples of the temporal profiles of BrO observed at T = 300K are shown in Figure 2. Profiles from studies at other temperatures are presented in Figure S5 (Supporting Information). A procedure similar to that used for the determination of k_1 was applied to the treatment of the observed BrO decays. At each temperature, the

rate constant of reaction (1b) was derived from the global fit to all the experimental kinetic runs using equation (II) with two variable parameters, k_{1b} and k_w:

$$[\mathrm{BrO}] = \frac{k_w[\mathrm{BrO}]_0}{(2k_{1b}[\mathrm{BrO}]_0+k_w)\times\exp(k_w t)-2k_{1b}[\mathrm{BrO}]_0} \qquad \text{(II)}$$

Experimental conditions and the results obtained for k_{1b} and k_w at different temperatures are shown in Table 2. The measurements of k_{1b} at T = 318K and T ≤ 286 K have been carried out in the reactor coated with halocarbon wax; the uncoated quartz reactor was used at other temperatures.

In another series of experiments carried out at T = 260K and in the presence of O_3 in the reactor, the yield of Br_2, product of reaction (1b), was measured. The concentration of Br_2 formed was monitored as a function of the consumed concentration of BrO at a fixed reaction time of 0.06 s. Results are shown in Figure 3. The slope of the straight line in Figure 3 provides $[Br_2]_{formed}/[BrO]_{consumed}$ = 0.517 ± 0.005 (1σ), indicating that one molecule of Br_2 is formed per two consumed molecules of BrO, in agreement with the stoichiometry of reaction (1b). The slightly negative intercept in Figure 3 seems to indicate that the wall loss of BrO (whose relative contribution to BrO consumption increases with decrease of $[BrO]_0$) most probably leads to Br_2 formation. The results of the measurements of the Br_2 yield seem to confirm the correctness of the measurements of the absolute concentrations of the species involved and suggest that under the experimental conditions of the measurements of k_{1b} the consumption of BrO is actually due to channel (1b). The formation of Br_2 in reaction (1b) was also directly observed in three other previous mass spectrometric studies of reaction (1).[9,11,17]

3.3 Comparison with previous measurements

Reaction (1) was quite intensively studied in the past. All previous work can be divided into three categories: measurements of the overall rate constant (k_1), measurements of the channel-specific rate constant, k_{1b}, and measurements of k_{1a}/k_1, the branching to the main (1a) channel.

3.3.1 *Total rate constant k_1*

Results of previous direct room-temperature measurements of k_1 are summarized in Table 3. Not included in Table 3 is the value of k_1 = (3.1±0.4)×10^{-12} $cm^3 molecule^{-1} s^{-1}$, which is an

indirect measurement reported by Bridier et al.[12] from a FP/UV study, wherein the rate constant was extracted from the simulation of BrO profiles upon Br_2 photolysis in Br_2/O_3 mixtures (with $[Br]/[O_3]$ = 0.013-1.5) and using k_{1b}/k_1 = 0.16. Although the results from different studies vary by up to a factor of 1.6, they overlap within reported experimental uncertainties. It can be noted that uncertainties given for some values of k_1 in Table 3 refer only to the statistical precision. This is the case, for example, for the highest value of k_1 = (3.51±0.35)×10^{-12} $cm^3molecule^{-1}s^{-1}$, reported by Gilles et al.,[15] for which the authors estimated an additional systematic uncertainty of 20% and an additional 10% uncertainty on absorption cross section of BrO. The value of k_1 from the present study is in better agreement with the lower of the previous values of k_1, in the range (2.2-2.8)×10^{-12} $cm^3molecule^{-1}s^{-1}$. All previous work can be divided into two groups: those realized with mass spectrometric detection of BrO in discharge flow reactors and with monitoring UV absorption of BrO in flash photolysis systems. In previous DF/MS studies of Clyne and Watson[5] (k_w not reported), Turnipseed et al.[9] (k_w not reported), Lançar et al.[11] (k_w reported to be negligible) and Barnes et al.[10] (k_w = 4.8±3.8 s^{-1}) the contribution of the wall loss of BrO to consumption of the radicals was not taken into account, i.e. the reported values of k_1 can potentially be somewhat overestimated. The results of the UV absorption studies depend directly on the values of the absorption cross section of BrO (σ^{BrO}) at the monitoring wavelength, generally 338.5 nm. In this context, it should be noted that fairly close values of σ^{BrO} were used in the measurements of k_1 shown in Table 3: 1.48,[14] 1.55,[18] 1.41[16] and 1.63×$10^{-17}cm^2molecule^{-1}$.[15] Sander and Watson[7] have measured and used σ^{BrO}(339nm) = 1.14×$10^{-17}cm^2molecule^{-1}$. Current evaluations of kinetic data tend to scale k_1 data (≈10% increase) from earlier FP/UV studies to the highest UV absorption cross section reported by Gilles et al.,[15] although Gilles et al.[15] estimated 10% uncertainty on the absorption cross section measured in their study. In addition, this scaling is not always justified considering that the cross section depends on spectral transition and instrumental resolution. Consequently, the use of σ^{BrO} determined with apparatus employed in the measurements of k_1[7,16] seems to be preferable. Finally, considering the present results and the above analysis of the previous data, we would recommend k_1 = (2.7±0.6)×10^{-12} $cm^3molecule^{-1}s^{-1}$ at T = 298K from the present study.

The results of direct measurements of the temperature dependence of the overall rate constant of reaction (1) are shown in Figure 4. One data point of Turnipseed et al.[9] (k_1 =

$(4.57\pm1.7)\times10^{-12}$ $cm^3molecule^{-1}s^{-1}$ at T = 253K) was excluded. Harwood et al.[18] observed pressure dependence of k_1 at T ≤ 250 K (increase with increasing pressure) which was attributed to the formation of a stabilized BrOOBr dimer in the termolecular channel 1c,

$$BrO + BrO\ (+M) \rightarrow Br_2O_2\ (+M) \qquad (1c)$$

competing with the bimolecular channels of reaction (1). The values of k_1 obtained at lowest (100 Torr) and highest (788 Torr) pressure of their study at T = 238 and 222 K are shown in Figure 4. The pressure dependence of k_1 is in contradiction, at least, with the present work and that of Sander and Watson[7] who found k_1 to be independent of pressure in the range 50-475 Torr. An excellent agreement of the present k_1 data, measured at nearly 2 Torr total pressure of He, with the work of Sander and Watson[7] seems to support the pressure independence of k_1. In addition, the absolute value of $k_1 = (1.80\pm0.26)\times10^{-12}$ $cm^3molecule^{-1}s^{-1}$ measured by Harwood et al. at T = 222K and P = 103 Torr is significantly lower than $k_1 = (3.10\pm0.46)\times10^{-12}$ $cm^3molecule^{-1}s^{-1}$ measured in this work at T = 220K and a total pressure as low as 2 Torr.

Looking at Figure 4, one can note that all the available temperature dependent k_1 data exhibit a small negative temperature dependence and the absolute values of k_1 from different studies (except those of Gilles et al.[15] and of Harwood et al.[18] at T < 250K) are in excellent agreement. In the most extended temperature dependent study of Gilles et al.[15] the following Arrhenius expression was reported: $k_1 = (1.70\pm0.45)\times10^{-12}\ \exp(215\pm50/T)$ $cm^3molecule^{-1}s^{-1}$ (T = 204-388K). Current recommendations of k_1 for use in atmospheric modelling are based primarily on this expression.[19,20] The k_1 data from the present work can be represented as $k_1 = (1.32\pm0.09)\times10^{-12}\ \exp(182\pm22/T)$ $cm^3molecule^{-1}s^{-1}$ (T = 220-950K, with quoted 2σ uncertainties). Taking the average activation energy factor from two studies, E/R = -200 K, in combination with $k_1 = (2.7\pm0.6)\times10^{-12}$ $cm^3molecule^{-1}s^{-1}$ at T = 298K (as discussed above), we would recommend the following Arrhenius expression,

$$k_1 = 1.4\times10^{-12}\ \exp(200/T)\ cm^3molecule^{-1}s^{-1}$$

(solid blue line in Fig. 4) in the temperature range (200 – 950) K and with conservative uncertainty of 25% at all temperatures (dashed blue lines in Figure 4).

3.3.2 *Rate constant k_{1b}*

Previous direct near room-temperature measurements of k_{1b} are summarized in Table 4. The value of k_{1b} from the present study is in good agreement (within 10%) with those reported by Sander and Watson,[7] Turnipseed et al.[9] and Harwood et al.[18] The value obtained by Cox et al.[8] using a molecular modulation technique, k_{1b} = (6.6 ± 2.0) × 10^{-13} cm^3 $molecule^{-1}$ s^{-1}, is much greater compared with all other measurements, which all lie within a factor of 1.6 and overlap within reported experimental uncertainties. The average of the studies listed in Table 4 (with the exception of k_{1b} data from Cox et al.[8] and also from Lançar et al.[11] and Rowley et al.,[14] re-measured in later studies by the same groups),[17,18] k_{1b} = (3.6 ± 0.7) × 10^{-13} cm^3 $molecule^{-1}$ s^{-1}, seems to be an appropriate value to recommend based on currently available data.

All data from direct temperature dependent measurements of k_{1b} are shown in Figure 5. A virtually temperature independent value of k_{1b} = (2.83±0.35)×10^{-13} exp(34±36/T) $cm^3molecule^{-1}s^{-1}$ (T = 220-450K, with 2σ uncertainties) was measured in the present study. A similar very small temperature dependence of k_{1b} was observed by Cox et al.,[8] although the absolute values of the rate constant are a factor of 2 higher than in the present work. Mauldin et al.[13] and Harwood et al.[18] observed a pressure dependence of k_{1b} (an increase with increasing pressure) at T = 220K and T = 238, 220K, respectively. The data of Mauldin et al.[13] and Harwood et al.[18] at low temperatures, k_{1b} + k_{1c}[M], are shown in Figure 5 only at the extremes of the pressure range used (74-552 Torr and 103-778 Torr, respectively), connected by vertical lines. In our opinion, the existing data on the impact of pressure on kinetics of reaction (1) at low temperatures should be viewed with some caution. Harwood et al.[18] attributed the observed pressure dependence of the BrO+BrO reaction to the formation of a stabilized BrOOBr dimer in the termolecular channel (1c), while in the study of Mauldin et al.[13] it was attributed to the Br_2+O_2 forming channel (1b). Harwood et al.[18] noted that an excessively large negative temperature coefficient for the recombination reaction (1c), estimated in their study at low temperatures, indicates a problem with either the data or its analysis. Another point is that the results from two pressure dependence studies differ significantly (see Figure 5). Clearly, additional kinetic and direct product studies of the BrO+ BrO reaction at low temperatures and as a function of pressure are needed in order to better understand the reaction mechanism. Considering the temperature dependence of k_{1b} observed in the present work and the average value of k_{1b} = (3.6±0.7)×10^{-13} $cm^3molecule^{-1}s^{-1}$ at T = 298K, the following Arrhenius expression,

$k_{1b} = 3.2\times10^{-13}$ exp(34/T) $cm^3molecule^{-1}s^{-1}$

(solid blue line in Figure 5), can be recommended (at least, at low pressures) from the present study in the temperature range (220 – 450) K and with conservative uncertainty of 25% (dashed blue lines in Figure 5). One can note that this expression differs significantly from current recommendations: k_{1b} = 0.28×10^{-13} exp(860/T)[19] and k_{1b} = 0.29×10^{-13} exp(840/T) $cm^3molecule^{-1}s^{-1}$ (dotted line in Figure 5).[20]

3.3.3 *Branching ratio k_{1a}/k_1*

The branching ratio between the two bimolecular channels of reaction (1) at room temperature has been determined in multiple studies through the measurements of quantum yields for Br_2-photosensitized decomposition of ozone[7,13,14] or direct measurements, generally, of k_{1b} and k_1.[7,9,11,14,17] In a previous study from this group,[17] the production of Br atoms in reaction channel (1a) was observed and quantified. The concentration of Br atoms was monitored as a function of the consumed concentration of BrO, which allowed the determination of the branching ratio for the Br atom forming channel (1a): $k_{1a}/k_1 = \Delta[Br]/\Delta[BrO] = 0.84 \pm 0.03$.[17] All previous measurements (reporting k_{1a}/k_1 in the range 0.84-0.88) are in agreement that $k_{1a}/k_1 = 0.85 \pm 0.03$ at T = 298K. The corresponding value from the present work calculated as $(k_1 - k_{1b})/k_1 = 0.87 \pm 0.04$ agrees well with the previous data. All the results of temperature dependent measurements of k_{1a}/k_1 are shown in Fig. 6. The data shown in Figure 6 are those measured through Br_2-photosensitized decomposition of ozone[6,8,13] and calculated using reported values of k_{1a} and k_1[18] or k_{1b} and k_1 (this work). One can note very good agreement between the results from different studies around room temperature. The branching ratio data from the present low pressure study (between 0.89 and 0.85 in the temperature range 220-450K) exhibit a very small negative temperature dependence, $k_{1a}/k_1 = 0.8\times\exp(25/T)$, although it could be considered as temperature independent within the experimental uncertainty. This contrasts with the results from studies at high pressures, which report a significant decrease in k_{1a}/k_1 at lower temperatures. Mauldin et al.[13] determined the branching ratio to be 0.84 at 298 K and 0.68 at 220 K, independent of pressure, and observed an additional absorption feature with a peak absorption at 312 nm which was tentatively attributed to Br_2O_2. In contrast, the values of k_{1a}/k_1 (calculated with the rate constant data reported for k_{1a} and k_1 by Harwood et al.[18]) display a very pronounced pressure dependence: decreasing from 0.65 to 0.47 (shown

in Figure 5 for two extreme pressures connected by vertical line) and from 0.33 to 0.09 (not shown in Figure 5) upon increasing the total pressure from 105 to 778 Torr at T = 235 and 220K, respectively. It should be noted that the values of k_{1a} reported by Harwood et al.[18] could be highly uncertain since k_{1a}, as reported in their paper, was effectively determined from the difference in the BrO decay rates in the presence and absence of ozone, and results in the presence of ozone (k_{1b} + k_{1c}[M]) were obtained in terms of a mechanism including a competition, at low temperatures, between collisional stabilization and unimolecular dissociation of an excited BrOOBr* intermediate. In any case, it is clear that both high pressure studies[13,18] demonstrate a decrease of k_{1a}/k_1 at low temperatures (pressure dependent or not), which contrasts with the present work realized at low pressure. In addition, Mauldin et al.,[13] using the values of the branching ratio k_{1a}/k_1 = 0.68 and k_{1b} obtained at 220 K in their study, calculated k_1 increasing from $(2.0 \pm 0.4)\times10^{-12}$ at 100 Torr to $(3.1 \pm 0.3)\times10^{-12}$ $cm^3molecule^{-1}s^{-1}$ at 400 Torr. The value of k_1 at 100 Torr is significantly lower than $k_1 = (3.1 \pm 0.5)\times10^{-12}$ $cm^3molecule^{-1}s^{-1}$ measured in the present work at T = 220 K and 2 Torr total pressure, which is in conflict with predicted positive pressure dependence of the total rate constant.

The probable mechanism of the BrO + BrO reaction was repeatedly discussed in previous studies:

$$BrO + BrO \leftrightarrow BrOOBr^* \quad (6,-6)$$

$$BrOOBr^* \rightarrow BrOO + Br \quad (7a)$$

$$BrOOBr^* \rightarrow Br_2 + O_2 \quad (7b)$$

$$BrOOBr^* + M \leftrightarrow BrOOBr + M \quad (8,-8)$$

$$BrOOBr \rightarrow BrOO + Br \quad (9a)$$

$$BrOOBr \rightarrow Br_2 + O_2 \quad (9b)$$

$$BrOO \rightarrow Br + O_2 \quad (10)$$

In the framework of this mechanism, the effect of pressure on the kinetics and products of reaction (1) is determined by the possible stabilization of the excited intermediate BrOOBr* in reaction (8) and the fate of the formed BrOOBr, specifically, its stability and the partitioning of the products of its decomposition in reactions (9a) and (9b), which can be different from that of BrOOBr* (reactions (7a) and (7b)). The experimental data available on reaction (1) at low temperatures, where the impact of total pressure is expected to be more

pronounced, are rather limited. It is clear that further detailed experimental studies of the BrO+BrO reaction at low temperatures and as a function of pressure are required to confirm the pressure dependence of the overall kinetics and distribution of the reaction products and to better elucidate the reaction mechanism.

4 CONCLUSION

In this work, using a discharge-flow reactor combined with mass spectrometry, we have measured the rate constant of the self-reaction of the BrO radical (an important intermediate in atmospheric chemistry) as a function of temperature over an extended temperature range, 220–950 K, and total pressure of about 2 Torr. The temperature dependence of the overall rate constant of this reaction was found to be consistent with most previous measurements at T = 220-400 K and was extended to higher temperatures (T = 950 K). Direct detection of the reaction product, Br_2, in the presence of high concentrations of ozone showed that the consumption of BrO radicals under such conditions was exclusively due to the $BrO + BrO \rightarrow Br_2 + O_2$ reaction and the rate constant for this specific channel was determined at T = 220-450 K. Comparison of the present low pressure data with previous measurements at higher pressures reveals some disagreements at low temperatures and highlights the need for further detailed experimental studies of the reaction at low temperatures and as a function of pressure.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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TABLES LEGENDS

TABLE 1 Summary of the measurements of the total rate constant (k_1) of the reaction BrO + BrO $\rightarrow$ products

TABLE 2 Summary of the measurements of the rate constant k_{1b} of the reaction BrO + BrO $\rightarrow$ Br_2 + O_2

TABLE 3 Summary of the direct measurements of the total rate constant of the reaction BrO+BrO at T = 298.

TABLE 4 Summary of the direct measurements of k_{1b} at T = 298

TABLES

TABLE 1 Summary of the measurements of the total rate constant (k_1) of the reaction BrO + BrO → products

T (K)	No./exp.[a]	$[BrO]_0$ [b]	k_w [c]	k_1 [d]
220	8	1.12-11.4	8.44	3.10
238	9	1.18-15.5	5.13	2.97
260	10	0.98-13.7	4.78	2.62
286	9	1.19-19.2	4.13	2.4
296	10	1.72-16.0	5.06	2.25
297	10	1.11-13.3	3.21	2.56
318	11	0.81-17.1	6.13	2.38
334	10	1.72-19.2	5.94	2.20
385	9	1.74-14.6	7.13	2.08
450	8	1.54-13.4	7.34	1.92
550	9	0.81-13.3	3.13	1.87
695	11	0.78-12.9	1.77	1.74
950	9	0.89-13.6	0.51	1.63

[a] Number of kinetic runs.
[b] Units of 10^{12} molecule cm^{-3}.
[c] Units of s^{-1}.
[d] Units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, estimated uncertainty on k_1 is nearly 15%.

TABLE 2 Summary of the measurements of the rate constant k_{1b} of the reaction BrO + BrO → Br_2 + O_2

T (K)	No./exp.[a]	$[BrO]_0$ [b]	k_w [c]	k_{1b} [d]
220	7	3.09-24.2	3.67	0.335
238	8	2.68-39.6	3.51	0.31
260	10	1.50-30.8	1.42	0.319
286	13	1.84-30.9	0.59	0.317
300	13	1.29-40.2	1.15	0.317
318	12	2.07-30.2	0.0001	0.335
335	14	0.77-36.2	1.01	0.326
385	15	0.46-33.2	1.16	0.305
450	14	0.48-27.8	0.22	0.292

[a] Number of kinetic runs.
[b] Units of 10^{12} molecule cm^{-3}.
[c] Units of s^{-1}.
[d] Units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}, estimated uncertainty on k_{1b} is nearly 15%.

TABLE 3 Summary of the direct measurements of the total rate constant of the reaction BrO+BrO at T = 298.

k_1[a] (10^{-12} cm^3 $molecule^{-1}$ s^{-1})	Method[a]	Reference
2.17±0.68	FP/UV	Sander and Watson[7]
2.98±0.42	FP/UV	Rowley et al.[14]
3.51±0.35	FP/UV	Gilles et al.[15]
2.8±0.5	FP/UV	Laszlo et al.[16]
2.90±0.28	FP/UV	Harwood et al.[18]
3.20±0.65	DF/MS	Clyne and Watson[5]
2.45±0.26[b]	DF/MS	Turnipseed et al.[9]
3.2±0.5	DF/MS	Lançar et al.[11]
2.7±0.5	DF/MS	Barnes et al.[10]
2.75±0.35	DF/MS	Bedjanian et al.[17]
2.43±0.36	DF/MS	This work

[a] DF/MS: discharge flow reactor/mass spectrometry; FP/UV: flash photolysis/UV absorption.
[b] T = 304 K.

TABLE 4 Summary of the direct measurements of k_{1b} at T = 298

k_{1b} (10^{-13} cm^3 $molecule^{-1}$ s^{-1})	Method[a]	Reference
6.9±1.4[b]	MM/UV	Cox et al.[8]
3.46±0.68	FP/UV	Sander and Watson[7]
2.94±0.98[c]	DF/MS	Turnipseed et al.[9]
4.7±1.5	DF/MS	Lançar et al.[11]
4.45±0.82	FP/UV	Mauldin et al.[13]
4.68±0.68	FP/UV	Rowley et al.[14]
4.0±0.5	DF/MS	Bedjanian et al.[17]
3.12±0.12	FP/UV	Harwood et al.[18]
3.17±0.48	DF/MS	This work

[a] DF/MS: discharge flow reactor/mass spectrometry; FP/UV: flash photolysis/UV absorption; MM/UV: molecular modulation/UV absorbtion.
[b] T = 303 K.
[c] T = 304 K.

FIGURE LEGENDS

FIGURE 1 Temporal profiles of BrO radicals observed at T = 220 (a) and 950 K (b) with different initial concentrations of the radicals. Solid lines correspond to the fit to the experimental data using Equation (I). Partially shown error bars represent maximum uncertainty of 5% on the measurements of relative concentrations of BrO.

FIGURE 2 Temporal profiles of BrO radicals observed at T = 300K with different initial concentrations of the radicals and in the presence of ozone in the reactor. Solid lines correspond to the fit to the experimental data using Equation (II). Partially shown error bars represent maximum uncertainty of 5% on the measurements of relative concentrations of BrO

FIGURE 3 Concentration of Br_2 formed in reaction (1) in presence of ozone as a function of consumed concentration of BrO (T = 260K). Solid line corresponds to a linear fit to the experimental data. Partially shown error bars represent typical 10% uncertainties on the measurements of the absolute concentrations of the respective species.

FIGURE 4 Summary of the direct temperature dependent measurements of k_1. The error bars correspond to estimated 15% uncertainty on the measurements of k_1 in the present work; uncertainties on previous measurements are given as reported in respective studies.

FIGURE 5 Summary of the direct temperature dependent measurements of k_{1b}. The error bars correspond to estimated 15% uncertainty on the measurements of k_{1b} in the present work; uncertainties on previous measurements are given as reported in respective studies.

FIGURE 6 Summary of the temperature dependent measurements of the branching ratio k_{1a}/k_1.