Kinetics of the $\text{BrO} + \text{HO}_2 \rightarrow \text{products}$ Reaction Over the Temperature Range 233-348 K

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Abstract
The reaction $\text{BrO} + \text{HO}_2 \rightarrow \text{products}$ is the rate-limiting step in a key catalytic ozone destruction cycle in the lower stratosphere. In this study a discharge flow reactor coupled with molecular beam mass spectrometry has been used to study the $\text{BrO} + \text{HO}_2$ reaction over the temperature range 233-348 K. Rate constants were measured under pseudo-first order conditions in separate experiments with first $\text{HO}_2$ and then $\text{BrO}$ in excess in an effort to identify possible complications in the reaction conditions. At 298 K, the rate constant was determined to be $(1.73 \pm 0.61) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ with $\text{HO}_2$ in excess and $(2.05 \pm 0.64) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ with $\text{BrO}$ in excess. The combined results of the temperature-dependent experiments gave the following fit to the Arrhenius expression: $k = (3.13 \pm 0.33) \times 10^{10} \exp(536 \pm 206/\text{K})$ where the quoted uncertainties represent two standard deviations. The reaction mechanism is discussed in light of recent ab initio results on the thermochemistry of isomers of possible reaction intermediates.

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Introduction

Bromine chemistry plays a key role in the catalytic obstruction of stratospheric ozone. The most important bromine-containing source gas, methyl bromide, has an ozone depletion potential which exceeds the limits set by international treaties, and will be phased out in developed countries by the year 2010. However, because methyl bromide has both biogenic and anthropogenic source fluxes which are highly uncertain, the budgets and atmospheric lifetime of methyl bromide have not been accurately determined. Most other bromine source gases of importance, including the halons, are entirely anthropogenic in origin and their production has ceased in developed countries. Despite the regulatory controls in place however, there are many issues relating to both the gas-phase and heterogeneous chemistry of bromine compounds that require further investigation.

The catalytic cycles that contribute to the destruction of ozone by bromine were first described by Wofsy et al. and Yung et al. By analogy to the well-known O + ClO cycle, Wofsy et al. proposed the cycle

\[
\begin{align*}
\text{Br} + \text{O}_3 & \rightarrow \text{BrO} + \text{O}_2 \\
\text{BrO} + \text{O} & \rightarrow \text{Br} + \text{O}_2 \\
\text{Net} & \rightarrow \text{O} + \text{O}_2 \rightarrow 2\text{O}_2
\end{align*}
\]

This cycle has its greatest effect on ozone destruction in the middle and upper stratosphere. Yung et al. pointed out several additional cycles that are particularly important in the lower stratosphere that couple bromine radicals with the odd hydrogen and odd chlorine radical families:

\[
\begin{align*}
\text{Br} + \text{O}_3 & \rightarrow \text{BrO} + \text{O}_2 \\
\text{BrO} + \text{H}_2\text{O}_2 & \rightarrow \text{HOBr} + \text{O}_2 \\
\text{HOBr} + \text{hv} & \rightarrow \text{OH} + \text{Br}
\end{align*}
\]
In these cycles, reactions 3 and 4 are the rate-limiting steps. Reaction 4 has been studied extensively over the temperature and pressure range relevant to the stratosphere and is reasonably well understood. In contrast, significant kinetic and mechanistic uncertainties remain in the understanding of reaction 3.

The first study of reaction 3 was carried out by Cox and Sheppard who reported a rate coefficient of $0.5^{+0.5}_{-0.3} \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 303 K and 7150 Torr total pressure using molecular-nodulation coupled with ultraviolet absorption. Three recent studies, however, have reported values of $k_{298}$ which were more than 6 times larger than the work of Cox and Sheppard including two discharge flow/mass spectrometry studies from the CNRS group and a flash photolysis/ultraviolet absorption study from the group at Bordeaux. These measurements have a major effect on atmospheric model predictions of bromine partitioning in the lower stratosphere, the relative magnitudes of the odd oxygen destruction cycles involving bromine and the ozone depletion potential of methyl bromide. More recently however, a discharge flow/mass spectrometry study by Iliod et al. reported a significantly smaller value of $k_{298}$, $(1.4 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The large discrepancies between the previously reported results and the importance of this reaction in stratospheric bromine chemistry motivated the study reported here. In this work, the BrO + HO$_2$ reaction was investigated over the temperature range 233-348 K using the

$$011-103 \rightarrow \text{HO}_2 + 02$$

Net $2O_2 \rightarrow O_2$

and

$$\text{Br} + O_3 \rightarrow \text{BrO} + O_2$$
$$\text{Cl} + O_3 \rightarrow \text{ClO} + O_2$$
$$\text{ClO} + \text{BrO} \rightarrow \text{Br} + \text{Cl} + O_2$$

Net $2O_3 \rightarrow 3O_2$ (4)
discharge flow/massspectrometry technique. In an effort to identify possible complications in the reaction conditions, rate coefficients were measured using several different BrO and IIO₂ sources and separately with BrO and IIO₂ as the excess reagent.

**Experimental**

"The experimental apparatus used in these studies has been described previously. Details of the flow reactor and sliding injector are shown in Figure 1. The reactor consisted of a 80 cm-long, 4.86 cm-id. Pyrex tube which was covered on the inside with a layer of 0.05 cm thick TFE Teflon sheet to reduce BrO and IIO₂ wall loss. The reactor temperature was varied between 233 and 348 K by circulating cooled methanol or heated ethylene glycol through an outer Pyrex jacket. The temperatures of the circulating fluids were measured with a thermocouple located in the outer jacket of the reactor and controlled to within ±2 K using a thermostatted heat exchanger. A steady state gas flow (total pressure of 1-3 Torr) was maintained in the flow tube with a 00 cfm mechanical pump (Welch 1396). Helium was used as the main buffer gas and was admitted through sidearm located upstream of the reactor. The mean gas velocity in the flow tube ranged between 800 and 2000 cm s⁻¹; resulting in residence times between 30-75 ms in the 60 cm reaction zone. In order to carry out kinetics measurements at low temperatures, a heated double sliding injector was employed. It consisted of two concentric tubes having i.d.'s of 8 and 10.2 mm, respectively. The movable injector was heated by passing current through heating wire wrapped around the outer injector tube. This tube was thermally isolated from the flow tube with a vacuum jacket. The injector temperature was controlled by varying the voltage applied to the heating wire and measured with a thermocouple contacting the outer surface of the injector. Measurements showed that for a reactor wall
temperature of 233 K, a constant temperature of 298 K could be maintained inside the injector. Under these conditions the temperature of the outer surface of the injector vacuum jacket was 280 K. As discussed below, we found that heating the injector was very important in minimizing complications associated with the production of BrO and H2O2 at low temperatures.

Mass spectrometric detection of reactants and products was carried out by continuous sampling at the downstream end of the flow tube through a three-stage differentially-pumped beam inlet system. The mass spectrometer (Extrel Model C50) consisted of an electron-impact ionizer, a quadruple mass filter, and a channeltron detector. Beam modulation was accomplished with a 2001 Hz tuning fork type chopper placed inside the second stage of the mass spectrometer. Ion signals from the channeltron were sent to a lock-in amplifier that was referenced to the chopper frequency. The amplified analog signals were digitized (Analog Devices RTI/8 15) and recorded by a microcomputer.

Radical Production

In order to minimize systematic errors caused by unknown secondary reactions in the radical sources, the main flow tube and the reactor walls, we used several different reactions to produce BrO and H2O2 and the kinetic runs were carried out with both BrO and H2O2 as the excess reagent. The radical source conditions are summarized in Table 1 and described in detail below.

Two methods were used to produce BrO: (a) reaction of Br2 with atomic oxygen generated by microwave discharge of O2/He,

\[ \text{O} + \text{Br}_2 \rightarrow \text{BrO} + \text{Br} \]  \hspace{1cm} (5)

\[ k_5(298 \text{ K}) = 1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \]  \hspace{1cm} (4)
and (b) reaction of ozone with bromine atoms generated in a microwave discharge of Br$_2$/He,

$$Br + O_3 \rightarrow BrO + O_2$$  \hspace{1cm} (1)

$$k_1 (298 \text{ K}) = 1.2 \times 10^{-12} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}(4)$$

For either of these source reactions, BrO radicals undergo rapid self-reaction, producing Br with about 850/0 efficiency at room temperature:

$$BrO + BrO \rightarrow 2Br + O_2$$  \hspace{1cm} (6)

$$k_6 (298 \text{ K}) = 2.1 \times 10^{-12} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}(4)$$

The highest concentrations of BrO were obtained using the Br+O$_3$ source in the presence of excess O$_3$. In this case, Br formed in reaction 6 was rapidly recycled back to BrO. For the Br+O$_3$ source, $-4 \times 10^{13}$ molecule cm$^{-3}$ of Br$_3$ was flowed through a 1.27-cm-o.d. quartz discharge tube with 350 sccm helium carrier gas. After passing through the 30 cm-long central injector tube, $(1 - 10) \times 10^{14}$ molecule cm$^{-3}$ of O$_3$ was introduced through the sidearm of the injector with 50 sccm of carrier helium gas, producing $(1 - 5) \times 10^{12}$ molecule cm$^{-3}$ BrO radicals in the reactor. The O+Br$_2$ source was unable to produce BrO at these concentrations due to the lower microwave discharge efficiency of oxygen and BrO recombination, but this source was satisfactory for use in experiments where 1 IO$_2$ was the excess reagent.

For the generation of HO$_2$, two separate methods were used: (a) reaction of hydrogen peroxide with atomic fluorine generated from microwave discharge of F$_2$,

$$F + H_2O_2 \rightarrow HO_2 + HF$$  \hspace{1cm} (7)

$$k, (298 \text{ K}) = 4.98 \times 10^{-1} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}(13)$$

and (b) reaction of atomic chlorine from microwave discharge of Cl$_2$ with methanol followed by further reaction with oxygen,
\[ \text{Cl} + \text{CH}_2\text{OH} \rightarrow \text{CH}_2\text{O}\text{H} + \text{HCl} \]  

\[ k_8(298 \text{ K}) = 5.4 \times 10^{-11} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \]

\[ \text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CH}_2\text{O} \]  

\[ k_9(298 \text{ K}) = 9.1 \times 10^{-12} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \]

As in our previous studies of \( \text{H}_2\text{O}_2 \) kinetics using this apparatus \(^4\), we found that method (a) was suitable for producing large concentrations of \( \text{H}_2\text{O}_2 \) at room temperature. Using the same sidearm arrangement as used for \( \text{Br} + \text{O}_2 \) with the quartz discharge tube replaced by an alumina tube, a small flow (5-20 seem) from a premixed \( \text{So}/\text{O}_2/\text{He} \) cylinder was mixed with a larger (400 seem) helium flow which passed through the discharge. Dissociation of \( \text{I}_2 \) was typically greater than 90\% \( \text{H}_2\text{O}_2 \) was added through the sidearm of the movable injector with 650 seem of carrier helium gas bubbling through the 90\% \( \text{H}_2\text{O}_2 \) solution. The reaction of \( \text{F} \) with \( \text{H}_2\text{O}_2 \) was completed within 1 ms and the initial \( \text{F} \) atom concentration, and thus the \( \text{H}_2\text{O}_2 \) concentration, was adjusted by varying the \( \text{F}_2 \) flow. About 1014 molecule \( \text{cm}^{-3} \) of \( \text{H}_2\text{O}_2 \) was brought into the injector, and the production of \( \text{HO}_2 \) in the reactor was initially in the range \( (1-8) \times 10^{12} \text{ molecule cm}^{-3} \). This method was restricted to temperatures above 253 K due to condensation of \( \text{H}_2\text{O}_2 \) and \( \text{H}_2\text{O} \) on the flow tube walls which resulted in very high wall loss rates for \( \text{H}_2\text{O}_2 \).

Using method (b), chlorine atoms were formed by discharging a flow of 5-10 seem of 1\% \( \text{Cl}_2 \) in helium to which was added an additional helium flow of 250-500 seem. Chlorine atoms reacted in the sidearm with \( \text{CH}_3\text{OI} \) obtained from a 5-10 sccm helium flow through a methanol saturator held at a pressure of 400 Torr and a temperature of 25 C. An oxygen flow of 20-40 seem was added along with the methanol. Using this method the highest \( \text{H}_2\text{O}_2 \) concentration that could be produced was \( \sim 1.5 \times 10^{12} \text{ molecule cm}^{-3} \). The major difficulty with this method was that flowing a large quantity of methanol into the reactor created a large \( \text{m/e} = 33 \) background signal.
which interfered with the \( \text{HO}_2 \) radical detection. This interference decreased substantially with decreasing methanol concentration. Thus for kinetics studies of reaction 3 with \( \text{BrO} \) in excess, method (b) was used to produce \( \text{HO}_2 \) as the minor reagent.

Both \( \text{BrO} \) and \( \text{HO}_2 \) radicals were detected using electron impact ionization mass spectroscopy at the parent peaks, \( m/e = 95(\text{BrO}^+) \) and \( m/e = 33(\text{HO}_2^+) \). When \( \text{H}_2\text{O} \) was used as the \( \text{HO}_2 \) precursor, there was an \( m/e = 33 \) contribution arising from the fragmentation of \( \text{H}_2\text{O}_2 \) and from the wing of the much larger \( m/e = 34 \) peak. This interference was minimized by optimizing the quadrupole resolution and the ionizer electron energy. Table 2 shows the \( m/e = 33 \) signal intensity as function of electron energy for the \( \text{F} + \text{H}_2\text{O}_2 \) system. It can be seen that the ratio of \( \text{HO}_2 \) signal to background \( m/e = 33 \) contribution was maximized at an electron energy of 19 eV, which was subsequently used in all kinetics studies.

Absolute concentrations of both \( \text{BrO} \) and \( \text{HO}_2 \) were calibrated by chemical conversion to \( \text{NO} \) with excess \( \text{NO} \), i.e.

\[
\text{BrO} \rightarrow \text{Br} + \text{NO}_2 \tag{10}
\]

\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \tag{11}
\]

This was accomplished by introducing the \( \text{BrO} \) or \( \text{HO}_2 \) radicals from the movable injector and \( \text{NO} \) from the sidearm of the reactor, with the injector placed in a downstream position such that the reaction time between \( \text{NO} \) and the calibrated radical was \( \leq 3 \) ms. The concentration of added \( \text{NO} \) was in the range \( (1-5) \times 10^{14} \text{ molecule cm}^{-3} \). The conversion factors were determined from the ratio of the change in \( \text{NO}_2 \) ion signal at \( m/e = 46 \), \( S_{46} \), to the change in the radical signal, \( S_{33} \) or \( S_{44} \). \( \Delta S_{46}/\Delta S_{33} = 0.40 \pm 0.08 \) and \( \Delta S_{46}/\Delta S_{44} = 1.8 \pm 0.4 \). The radical calibrations were then
obtained from absolute calibrations of the mass spectrometer at m/e 46 using known concentrations of NO₂.

Special care was taken for the IO₂ calibration since IO₂ could be regenerated by the reactions,

\[
\text{OH} + \text{IO}_2 \rightarrow \text{IO} + \text{HO}_2
\]

\[
k_{11} (298 \text{ K}) = 1.7 \times 10^{-2} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}(4)
\]

or

\[
\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{IO} + \text{CH}_3\text{OOH}
\]

\[
\text{IO} + \text{O}_2 \rightarrow \text{IO}_2 + \text{IO}
\]

One way to prevent this IO₂ regeneration in the titration was adding a large excess (~10¹⁵ molecule cm⁻³) of C₂F₅Cl which reacts rapidly with OH to form a stable adduct. However, it was found that this concentration of C₂F₅Cl reduced the responsivity of the mass spectrometer by ~6% due to a reduction in the efficiency of the ionizer. An alternative OH scavenger which had a negligible effect on the mass spectrometer was molecular bromine, Br₂. The reaction of Br₂ with OH is very fast,

\[
\text{Br}_2 + \text{OH} \rightarrow \text{HOBr} + \text{Br}
\]

\[
k_{12} (298 \text{ K}) = 4.2 \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}(4)
\]

thus when 5x 10¹⁵ molecule cm⁻³ of Br₂ was introduced into the reactor, the OH I radical was scavenged in less than 0.5 ms. The product of the OH + Br₂ reaction, HOBr, had no effect on the calibration. The detection limits for the radicals were 2 x 10⁹ molecule cm⁻³ for BrO and 8 x 10⁹ molecule cm⁻³ for HO₂ (S/N = 2 for a 10 s integration time.)
First-order wall loss coefficients were measured for both H2O2 and BrO and found to be less than 5 s⁻¹ at low radical concentrations (<5 × 10¹¹ molecule cm⁻³). For the runs with excess H2O2, the effective wall loss increased at the highest H2O2 concentrations, presumably due to the 11O2 self-reaction. As a first order approximation, the H2O2 concentration for the kinetic run was derived by averaging the concentrations at the upstream and downstream ends of the reaction zone. Simulations showed that the error arising from this approximation was ≤ 5%. In the case of excess BrO, the same procedure was employed although the wall loss was always less than 4 s⁻¹.

The gases used in this work had the following stated purities: He, 99.999%; NO, 99%; NO₂, 99.5% and Cl₂ (10% in H₂). F₂ (5% in He) and O₂ (99.999%). Br₂ (99.8%) was obtained was purified by vacuum distillation at 195 K. 11O2 was obtained commercially at a concentration of 70 wt % and purified to ≥ 94 wt % prior to use by vacuum distillation at room temperature. Ozone was produced by passing O₂ through an ozonizer and storing the product on silica gel at 195 K. During the experiments, O₃ was maintained at 195 K and evaporated into the reactor with a known flow of He. In order to avoid the potential explosion hazard associated with the condensation of ozone in the liquid nitrogen trap of the mechanical pump, efforts were made to decompose the ozone downstream of the 11O2 tube. This was accomplished efficiently by heating the effluent from the flow tube to approximately 300 °C in a 50-cm-long quartz tube containing copper scouring pads.

Results
Measurements of $k_3$ were carried out by monitoring the decay of either BrO or H\textsubscript{2}O\textsubscript{2} as a function of reaction time. Bimolecular rate constants were obtained using the well-known steady state flow tube method,\textsuperscript{12} in which the first-order decay rate constant, $k_1'$, was determined from the slope of a plot of the logarithm of either BrO or H\textsubscript{2}O\textsubscript{2} signal vs. reaction time. In all experiments the minor reactant was introduced into the flow tube through a fixed sidearm and the excess reagent was added through the sliding injector. In experiments in which H\textsubscript{2}O\textsubscript{2} was the minor species, the signal was corrected by subtracting the m/e = 33 signal contribution from the H\textsubscript{2}O\textsubscript{2} precursors as discussed above. In these experiments, the H\textsubscript{2}O\textsubscript{2} concentration did not change appreciably with injector position as determined from measurements of the m/e 34 peak. The observed decays were then corrected for axial diffusion and for loss of BrO or H\textsubscript{2}O\textsubscript{2} on the injector according to eq (1), \textsuperscript{2}

$$k_{i,\text{corr}}' = k_3' \left(1 + \frac{1}{4\pi D v^2} \right) + k_p$$

where $D$ is the diffusion coefficient, $v$ is the mean bulk flow velocity, and $k_p$ is the first order loss of BrO or H\textsubscript{2}O\textsubscript{2} on the outside surface of the sliding injector (injector loss). Diffusion coefficient estimates were based on the data of Marrero and Mason.\textsuperscript{17} The estimated $D$ values for BrO varied from 0.43 atm cm\textsuperscript{2} s\textsuperscript{-1} at 233 K to 0.84 atm cm\textsuperscript{2} s\textsuperscript{-1} at 348 K and for H\textsubscript{2}O\textsubscript{2} varied from 0.49 to 0.97 atm cm\textsuperscript{2} s\textsuperscript{-1} over the same temperature range. The corrections for axial diffusion were always less than 1\textsuperscript{o,oo}.

**Kinetics of BrO and H\textsubscript{2}O\textsubscript{2} decay at 298 K.** A typical BrO decay as function of the injector position at 298 K is shown in Figure 2. The BrO decay appeared to be linear within the time domain studied, and the BrO was completely titrated to our detection limit at high H\textsubscript{2}O\textsubscript{2} concentrations ([H\textsubscript{2}O\textsubscript{2}] $> 5 \times 10^{12}$ molecule cm\textsuperscript{-3}). With initial BrO concentrations of $(2-5) \times 10^{11}$
molecule cm$^{-3}$ and 110$_2$ concentrations of $(1-8) \times 10^{12}$ molecule cm$^{-3}$, the dependence of $k_3^\prime$ on [HO$_2$] is shown in Figure 3. $k_3^\prime$ varied from 20 to 160 s$^{-1}$ in the 110$_2$ concentration range of interest. Figure 3 also shows the results of measurements of $k_3^\prime$ taken over a range of flow velocities and total pressures to check for the presence of systematic errors such as bimolecular wall reactions. For flow velocities of 750-1800 cm s$^{-1}$ and total reactor pressures of 1-3 Torr the first-order decay of BrO due to reaction with HO$_2$ was independent of these parameters. From the slope of linear least squares fit through all the data at 298 K, $k_3$ was determined to be $(1.73 \pm 0.61) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, where (and hereafter) the quoted uncertainty is at the 95% confidence level and includes both random and systematic errors.

The behavior of HO$_2$ in the presence of excess BrO was also investigated. Figure 4 shows a typical HO$_2$ decay as function of injector position over the BrO concentration range $(1.3-4.5) \times 10^{12}$ molecule cm$^{-3}$ at 298 K. Twenty four runs were performed at 298 K and the bimolecular rate coefficient for reaction 3 in excess BrO was derived as $(2.05 \pm 0.64) \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ from a linear least-squares fit to the data in Figure 5.

**Temperature dependence of the rate coefficient for reaction 3.** Rate constants for reaction 3 were measured over the temperature range 233-348 K using both excess BrO and excess HO$_2$ with the source reactions and inlet conditions shown in Table 1. Both secondary reactions and wall reactions limited the temperature range of the study. These complications will be discussed in detail below.

At temperatures between 298 K and 348 K, both the BrO (excess reagent, Br+O$_3$ source) and HO$_2$ (minor reagent, Cl+Cl I,011 source) ion signals were well-behaved with no significant complications. Above 348 K, there was significant regeneration of 110$_2$ as indicated by the m/e =
33ion signal reaching a steady-state at long reaction times (t>65ms). A possible explanation for this behavior is secondary production of HIO₂ arising initiated by the thermal decomposition of HOBr:

\[
\begin{align*}
\text{HIO}_2 + \text{BrO} & \rightarrow \text{HOBr} + \text{O}_2 \\
\text{HOBr} + \text{M} & \rightarrow \text{OI} + \text{Br} - \text{t M} \\
\text{O} + \text{BrO} & \rightarrow \text{HIO}_2 + \text{Br}
\end{align*}
\]

This effect limited to 348 K the maximum temperature for which reliable kinetics results could be obtained.

At temperatures below 298 K, a number of processes interfered with the production of both BrO and HIO₂. For HIO₂ produced using the F⁺H₂O₂ source, the maximum concentration that could be achieved decreased significantly below about 270 K. The dependence of the observed m/e = 33 signal on temperature is shown in Figure 6. For these experiments, HIO₂ was produced in an unheated injector and the temperature was measured in the flow tube jacket which was not in thermal equilibrium with the injector due to the time lag in cooling and heating. The observed signal decrease in the cooling cycle and increase in the heating cycle are attributed to adsorption and resorption of I₂O and I₁₂O₂ on the flow tube and injector walls. The decrease in the I₁O₂ concentration is due to both an increase in the I₁O₂ wall loss rate on the coated surfaces and the removal of I₂O₂ from the gas phase. The use of the heated injector eliminated these problems in the injector itself, but deposition of I₁₂O and I₂O₂ on the flow tube walls remained a problem at temperatures below 253 K. As in the experiments of Larichev et al., we observed that the Cl⁺CH₃O⁻I + O₃ source efficiency decreased rapidly at temperatures below about 250 K in the unheated injector. Larichev et al. dealt with this problem by moving their HIO₂ source reactor to a sidearm in the uncooled region of the flow tube, but since HIO₂ was the excess reagent in
their experiments, this introduced the first-order BrO wall loss into their observed decay rates. In our experiments at low temperatures, 1102 was the minor reagent and the Cl+CH3OH+O2 source could be used in the sidearm at room temperature without requiring a separate measurement of the wall loss.

The temperature dependence of the BrO' ion signal using the O+Br2 source in the sidearm is shown in Figure 7. As in the case of 1102, the BrO concentration in the flow tube displays a hysteresis in the cooling/warming cycle indicating the presence of complex wall reactions. Observation of the flow tube surface at low temperature revealed a solid layer on the injector surface with a white-yellow color. This layer was observed using both the O+Br2 and Br+O1 sources. We further studied this solid layer using the heated injector. This was carried out by cooling the injector for one hour with the BrO source on, then switching off the source and warming the injector while scanning the mass spectrometer for desorption products. Three major species were simultaneously detected at m/e = 95/97 (BrO'), m/e = 111/113 (OBrO' or BrOO'), and m/e = 174 (Br2O'), which peaked at injector temperatures of -260 K, 270 K, and 280 K, respectively. Parent mass peaks corresponding to other higher oxides such as Br2O3, Br3O5 or Br2O7 could not be detected but if these species were formed, they would likely have fragmented and contributed to the daughter fragments indicated above.

Higher bromine oxides have been observed several times previously in discharge-flow/mass spectroscopy studies of oxygen-bromine systems. The detailed formation mechanisms are not known but wall reactions play a key role in the formation and interconversion of the bromine oxides, and the primary products may be both OBrO and Br2O. The surface reactions appear to require the presence of O(1P) and/or metastable oxygen
O\textsubscript{2}(\Lambda^1\Sigma) from the microwave discharge. In order to characterize the products of the wall reactions occurring in the flow reactor, separate experiments were carried out using similar discharge-flow systems coupled to UV-visible and submillimeter absorption spectrometers\textsuperscript{20}. In both systems, the product of an O\textsubscript{2} discharge reacted with a flow of Br\textsubscript{2} at low temperature (-20 °C) to form the same yellow-white solid observed in the D\textsubscript{2}/MS apparatus. The vapor from the solid was recorded by the spectrometers after the deposition of the solid was discontinued. In the UV/visible apparatus, an intense progression of vibrational bands was observed in the 380-620 nm spectral region which was nearly identical to the spectrum observed by Rattigan et al. in the steady-state photolysis of Br\textsubscript{2}-O\textsubscript{3} mixtures and assigned to OBrO\textsuperscript{+1}. In the submillimeter spectrometer, a large number of rotational lines were observed \textsuperscript{22}. Analysis of the spectra identified the source of the lines as isotopomers of both OBrO and Br\textsubscript{2}O.

Adding NO to the desorbing species resulted in the formation of NO, most likely from the NO+OBrO reaction:

$$\text{OBrO} + \text{NO} \rightarrow \text{BrO} + \text{NO}_2$$

Under conditions where the bromine oxides were formed (low temperature, O + Br\textsubscript{2} source, unheated injector) this reaction interfered with the mass spectrometric calibration of BrO.

When the resistively heated injector was used, most of the problems associated with the low-temperature production of BrO and 1102 were eliminated, and this system was used for all of the low temperature studies. The wall loss of radicals at low temperatures was examined with the heated injector. The first-order BrO wall loss was negligible down to 210 K but the 11O\textsubscript{2} wall loss increased significantly with decreasing temperature. As shown in Figure 8, the 11O\textsubscript{2} wall loss was ~7 s\textsuperscript{-1} at 298 K, increasing to 64 s\textsuperscript{-1} at 213 K. The large wall loss rate of 11O\textsubscript{2} at low
temperature restricted the range of reliable kinetics measurement for reaction 3 to 233 K and above.

Kinetics data were obtained over the temperature ranges 233-348 K with BrO in excess and 253-298 K with HO2 in excess. The rate constant data are summarized in Table 3 and an Arrhenius plot is shown in Figure 9. From these data it is apparent that the rate coefficient has a negative temperature dependence. For the three temperatures at which both excess BrO and excess HO2 data are available, the rate constants using excess BrO are systematically 20-25% larger, but the data overlap within the ±2σ error limits. Although the data show a small non-linear Arrhenius temperature dependence, the curvature lies well within the uncertainty of the measurements. A linear least-squares fit gives the following Arrhenius expression:

\[ k_3 = (3.13±0.33) \times 10^{-2} \exp\left(536±206/f^c\right). \]

The reaction products for BrO + HO2 were briefly studied with HO2 in excess. HOBBr was found to be the predominant reaction product based on approximate absolute mass spectrometric calibrations of HOBBr. Small IBr mass peaks were also detected at 298 K, but it was not possible to ascribe them to the IBr formation channel of reaction 3 since other processes such as Br + HO2 and Br + H2O2 and wall reactions could also contribute to HBr formation.

Discussion

Effects of Secondary Reactions. The agreement (within 20%) between rate coefficients obtained under excess HO2 and excess BrO conditions shows that, in general, there are no significant complications from secondary reactions. ‘There are a few processes that need to be considered explicitly, however. The reaction
\[
\text{OII} + \text{BrO} \rightarrow \text{II}_2 + \text{Br} \quad k_{298} = 7.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

has been studied recently by Bogan et al.\textsuperscript{23} and found to be significantly faster than previously estimated.\textsuperscript{4} In the kinetic runs which used excess \text{II}_2, simulations show that an OII impurity equal to about \textit{0.2[HIO]}, could effectively double the observed first-order disappearance rate of BrO under conditions where there are no other removal paths for OII. In our system, OH is formed in the HIO\textsubscript{2} source as a result of the reaction of fluorine atoms with water vapor which is present as an unavoidable impurity in \text{H}_2\text{O}\textsubscript{2}. Conditions in the source are adjusted in the \text{H}_2\text{O}\textsubscript{2} source to allow the fast reaction

\[
\text{OII} + \text{HIO}_2 \rightarrow \text{H}_2\text{O} + 0_2 \quad k_{298} = 1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]

to scavenge most of the OII on the time scale of the source chemistry. The HIO\textsubscript{2} source should therefore be a negligible source of OI (less than \textit{1x1010 cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} in the flow tube). In addition, Br\textsubscript{2} is present at concentration around \textit{10^{13} molecule cm}^{-2} from the BrO source. This concentration of Br\textsubscript{2} is sufficient to scavenge OII rapidly from the reaction

\[
\text{OII} + \text{Br}_2 \rightarrow \text{HOBr} + \text{Br}
\]
as discussed above. The absence of significant impurity concentrations of OII from the \text{IIO}_2 source was verified in separate experiments which set a conservative upper limit of \textit{10^9 molecule cm}^{-3} for HOBr when the H0\textsubscript{2} source was on and the BrO discharge was off.

The reaction

\[
\text{Br} + \text{II}_2 \rightarrow \text{HBr} + \text{O}_2 \quad k_{298} = 2.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}
\]
is a potential secondary removal pathway for \text{IIO}_2 in the excess BrO experiments because the BrO+BrO reaction is a source of Br in the flow tube. Simulations show that most of the Br...
reacts with O$_3$, which regenerates BrO and suppresses the concentration of Br to the point where removal of HO$_2$ by Br can be neglected.

**Comparison of Results with Previous Studies:** The results of previous kinetics studies of the HO$_2$ + BrO reaction are summarized in Table 4 and in Figure 9. The measured values of $k_{298}$ fall into three groups: the early measurement of Cox and Sheppard at 5x10-12 cm$^3$ molecule$^{-1}$ s$^{-1}$, the considerably higher values around 3.3x10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ from Poulet et al. 7, Arichev et al. 8 and Bridier et al. 9, and the intermediate values in the range (1.4-2.0)x10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ from Elrod et al. 10 and this work. The significant difference between the results from this work and the two studies of the Orleans group is puzzling because both groups used discharge-flow/mass spectroscopy systems at low pressure with similar radical sources. There are, however, some differences in methodology which may account for the disagreement. Both studies used the Cl + CH$_3$OH reaction to produce HO$_2$. This source is strongly affected by wall reactions below about 250 K as observed in both studies. Arichev et al. dealt with this problem by producing HO$_2$ in a sidearm at room temperature in the flow tube. This approach eliminates problems associated with the reduced efficiency of the source at low temperature, but since the excess reagent (HO$_2$) is not injected from the moveable inlet, the first-order wall loss of HO$_2$ contributes to the measured first-order rate constant. Complications associated with the Cl + Cl$_2$O source at low temperatures were circumvented in the present study by always keeping the sliding injector source at room temperature using the integral heating coil. This approach maintains the advantage of introducing the excess reagent through the sliding injector.

The values of $k_{298}$ obtained in the three temperature dependence studies range over a factor of about 2.4 but the measured values of I/Br are remarkably similar as seen in Table 4. All three studies report a moderately negative temperature dependence with the values ranging from...
-520 to -580 K\textsuperscript{1}. In the study of Larichev et al., the measurement of \( k_3 \) at 233 K was not considered in the determination of I/R because it fell considerably off the Arrhenius line described by their 243-344 K data. In the present work the Arrhenius plot was linear over the 233-348 K temperature range, and in the study of Ebrod et al. the plot was linear over the range 210-298 K.

Reaction Mechanism: The mechanism for the formation of I\textsubscript{IOX} from H\textsubscript{2}O\textsuperscript{+} XO, where X=Cl or Br, has not been established with certainty but \textit{ab initio} calculations are available which provide estimates of the stabilities of the possible reaction intermediates. In the system involving Cl, Francisco and Sander calculated enthalpies of formation for several 1 I\textsubscript{ClO\textsubscript{3}} isomers using both isodesmic reactions at the Q-RII(1)16-311 G(2df,2p) level and G1/G2 theory 24. Values of \( \Delta H_{f,0} \) (in kcal mole\textsuperscript{-1}) were determined to be 110C1O\textsubscript{2} (4.2), 1100OC1 (9.1), 1100C1O (25), and 110ClO\textsubscript{3} (46. 1). For 110OC1O and 1100OC1 these results are significantly different from the values obtained from the bond additivity calculations of Stimpfle et al. 25. The most stable isomer, 110C1O\textsubscript{2} is unlikely to form from H\textsubscript{2}O\textsuperscript{+} C1O because of the extensive rearrangement required. The next most stable intermediate, 1100OC1, is the likely intermediate in the reaction pathway leading to HCl through formation of a five-membered transition state followed by HCl elimination, however, the small branching ratio measured for this pathway implies the existence of a significant exit channel barrier \textsuperscript{26-28}. The likely intermediate in the formation of 110Cl is 110OC1O as suggested by Stimpfle et al. 25 because the observed negative temperature dependence is more consistent with a mechanism involving a strongly bound intermediate (1100C1O) than the weakly bound intermediate involved in hydrogen abstraction (ClOHOO).
The thermochemistry of the IIO₂ + BrO system is qualitatively similar to its chlorine counterpart. The BrO + IIO₂ reaction has several exothermic reaction pathways:

\[
\begin{align*}
\text{BrO} + \text{IIO}_2 & \rightarrow \text{IHOBr} + \text{O}_2, \quad \Delta H_{f}^{\circ} = -46.5 \pm 4 \text{ kcal mole}^{-1} \quad (3a) \\
& \rightarrow \text{IIBr} + \text{O}_3, \quad \Delta H_{f}^{\circ} = -7.1 \pm 2 \text{ kcal mole}^{-1} \quad (3b) \\
[\text{IIO}_2\cdot\text{BrO}] & \rightarrow \text{IIO}_2\cdot\text{IIBrO}_0 \quad (3C)
\end{align*}
\]

where \(\text{IIO}_2\cdot\text{BrO}\) denotes a collisionally stabilized adduct. Several previous studies including the present work found that reaction 3a was an important, if not the predominant, reaction channel but were not able to establish that the branching ratio for reaction 3a was unity. On the other hand, there is positive evidence that the branching ratio for reaction 3b is quite small. Larichev et al. were unable to detect \(\text{O}_3\) in their study of reaction 3 and set an upper limit of \(0.015\) for \(\frac{k_{3b}}{k_3}\) over the temperature range 233-298 K. Mellouki et al. inferred an upper limit of \(\sim 1 \times 10^{-4}\) for \(\frac{k_{3b}}{k_3}\) at 300 K based on studies of the reverse reaction,

\[
\text{IIBr} + \text{O}_3 \rightarrow \text{IIO}_2 \cdot 1 \text{ BrO} \quad (-3b)
\]

using laser magnetic resonance detection of \(\text{IIO}_2\). There have been no indications from any previous study that reaction 3 results in the formation of a stable adduct as indicated in reaction 3c. *Ab initio* calculations by Guha and Francisco at the 1131. YP/6-311++G(3df,3pd) level show that the enthalpies of formation of \(\text{IIBrO}_3\) isomers increase in the order \(\text{IIOBrO}_2: \text{IIOOBr}: \text{IIOBrO}_0: \text{IIBrOOO}\). This is the same ordering as the analogous system involving chlorine. While absolute energies for \(\text{IIBrO}_3\) isomers are not yet available, it is clear from the observed negative temperature dependence of the f IIOBr channel that potential energy surfaces are qualitatively similar to the chlorine system. The 298 K rate constants for the 1102 +
XO reactions increase significantly as X is substituted in the order Cl:Br:I. Began et al. have attributed this to the increasing tendency of the larger XO species to access the available triplet surfaces through spin-orbit coupling. Other factors that may contribute to the observed rate constant enhancement are stronger long-range interactions between IO₂ and XO, and progressive loosening of the HOO XO transition state.

Atmospheric Implications:

The combined results of this study and the work of Elrod et al. strengthen the case for a smaller rate coefficient for reaction 3 than the value that appears in the 1994 NASA Data Evaluation. This will have the effect of slightly lowering the overall catalytic destruction rate of ozone by bromine, and consequently the ozone depletion potential of ClIBr. The reduction in k₃ will have the effect of repartitioning bromine from IOBr into BrO, which will increase the rate of the BrO+CIO cycle, partially offsetting the effect on the HO₂+BrO cycle.

Summary

We have studied the kinetics of the reaction of BrO with HO₂ over the temperature range 233-348 K using the technique of discharge flow/mass spectrometry. Variations in experimental conditions such as flow velocity, reactor total pressure, and the excess reactant (1102 or M-O) had no effect on the measured rate coefficients within the 2σ error limits. At 298 K, the rate coefficient was determined to be $(1.73 \pm 0.61) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ with HO₂ in excess and $(2.05 \pm 0.64) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ with BrO in excess, respectively. The combined data from the excess BrO and excess HO₂ experiments were fit to an Arrhenius expression which gave $k₃=$
(3.13±0.33) \times 10^{-12} \exp(536\pm206/)$. These results obtained here, along with the measurements of 1 \text{Hrod et al. contrast with three recent studies giving 298 K rate constants} that are about a factor of two larger. The reasons for the discrepancy are not well understood.

**Acknowledgement**

This research was performed by the Jet Propulsion Laboratory, California Institute Technology, under contract with National Aeronautics and Space Administration. We are grateful to J. S. Francisco and S. Guha for providing details of their ab\textit{initio} calculations on HBrO$_3$, and to David Natzic and Juergen Linke for their expert technical assistance in this work.
References

Table 1. Summary of Radical Source Reactions and Reactor Conditions for the BrO + HO₂ Reaction.

<table>
<thead>
<tr>
<th>Radical</th>
<th>Source Stoichiometry</th>
<th>Source Reaction(s)</th>
<th>Source Location</th>
<th>Flow Tube Temperature</th>
<th>Concentration (10⁻³ molecule cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HO₂</td>
<td>excess</td>
<td>F + H₂O₂</td>
<td>injector</td>
<td>253-298</td>
<td>1.8</td>
</tr>
<tr>
<td>HO₂</td>
<td>minor</td>
<td>Cl + CH₃OH</td>
<td>sidearm</td>
<td>233-348</td>
<td>0.1-1.5</td>
</tr>
<tr>
<td>BrO</td>
<td>excess</td>
<td>Br + O₃</td>
<td>injector</td>
<td>233-348</td>
<td>1.5</td>
</tr>
<tr>
<td>BrO</td>
<td>minor</td>
<td>O + Br₂</td>
<td>sidearm</td>
<td>253-298</td>
<td>0.1-0.5</td>
</tr>
</tbody>
</table>

Table 2. Signal (rev) at m/e = 33 as a Function of Ionizer Electron Energy for the F + H₂O₂ system.

<table>
<thead>
<tr>
<th>Ionizer Electron Energy (eV)</th>
<th>18</th>
<th>17</th>
<th>20</th>
<th>21</th>
<th>22</th>
<th>23</th>
<th>24</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Signal I-rem 1 + H₂O₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) Signal from H₂O₂ alone</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) - (b)</td>
<td>1.8</td>
<td>2.0</td>
<td>3.1</td>
<td>3.6</td>
<td>5.3</td>
<td>6.6</td>
<td>9.3</td>
<td>8.9</td>
</tr>
</tbody>
</table>

¹Emission current was 1.0 ma.
Table 3. Summary of Experimental Conditions and Measured Rate Constants for the Reaction H\textsubscript{2}O\textsubscript{2} + BrO → Products.

<table>
<thead>
<tr>
<th>Pressure (Torr)</th>
<th>Temperature (K)</th>
<th>(k_3 \times 10^{11}) (cm(^3) molecule(^{-1}) s(^{-1}))</th>
<th>(\text{Excess Reagent})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>348</td>
<td>1.35±0.44</td>
<td>BrO</td>
</tr>
<tr>
<td>1</td>
<td>323</td>
<td>1.76±0.52</td>
<td>BrO</td>
</tr>
<tr>
<td>1</td>
<td>298</td>
<td>2.05±0.64</td>
<td>BrO</td>
</tr>
<tr>
<td>1-3</td>
<td>298</td>
<td>1.73±0.61</td>
<td>HO\textsubscript{2}</td>
</tr>
<tr>
<td>1</td>
<td>273</td>
<td>2.62±0.87</td>
<td>BrO</td>
</tr>
<tr>
<td>1</td>
<td>273</td>
<td>2.06±0.62</td>
<td>HO\textsubscript{2}</td>
</tr>
<tr>
<td>1</td>
<td>253</td>
<td>2.80±1.11</td>
<td>BrO</td>
</tr>
<tr>
<td>1</td>
<td>253</td>
<td>2.32±0.65</td>
<td>HO\textsubscript{2}</td>
</tr>
<tr>
<td>1</td>
<td>233</td>
<td>3.06±1.15</td>
<td>BrO</td>
</tr>
</tbody>
</table>

Table 4. Comparison of Rate Constant Measurements for the Reaction H\textsubscript{2}O\textsubscript{2} + BrO → Products

<table>
<thead>
<tr>
<th>Reference</th>
<th>Technique</th>
<th>Pressure (1'torr)</th>
<th>Temperature (K)</th>
<th>(k_3 \times 10^{11}) (cm(^3) molecule(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cox and Sheppard(^6)</td>
<td>MP/UV</td>
<td>760</td>
<td>303</td>
<td>0.50±0.5(^{0.3}_{0.3})</td>
</tr>
<tr>
<td>Poulet et al.(^7)</td>
<td>DF/MS</td>
<td>1</td>
<td>298</td>
<td>3.3±0.5</td>
</tr>
<tr>
<td>Bridier et al.(^9)</td>
<td>FP/UV</td>
<td>760</td>
<td>298</td>
<td>3.4±1.0</td>
</tr>
<tr>
<td>Larichev et al.(^8)</td>
<td>DF/MS</td>
<td>1</td>
<td>233-344</td>
<td>(0.48±0.03)exp[(580±100)/T]</td>
</tr>
<tr>
<td>Elrod et al.(^10)</td>
<td>DF/MS</td>
<td>100</td>
<td>210-298</td>
<td>(0.25±0.08)exp[(520±80)/T]</td>
</tr>
<tr>
<td>This Work</td>
<td>DF/MS</td>
<td>1</td>
<td>233-348</td>
<td>(0.31±0.03)exp[(540±210)/T]</td>
</tr>
</tbody>
</table>
Figure Captions:

**Figure 1.** Experimental apparatus arrangement for kinetics study of BrO + HO₂.

**Figure 2.** BrO decay in the presence of excess HO₂ at 298 K. HO₂ was produced using the F + H₂O₂ source. HO₂ concentrations are in units of 10⁻¹² molecule cm⁻³.

**Figure 3.** First-order decay rate of BrO, $k'_3$, as a function of [H₂O₂] at 298 K. (0) $P_{\text{total}} = 1$ Torr and $v = 750$ cm s⁻¹, (0) $P_{\text{total}} = 1$ Torr and $v = 1600$ cm s⁻¹, (Δ) $P_{\text{total}} = 3$ Torr and $v = 1800$ cm s⁻¹, (-) best fit.

**Figure 4.** HO₂ decay in the presence of excess BrO at 298 K. BrO was produced using the Br + O₃ source. BrO concentrations are in units of 10⁻² molecule cm⁻³.

**Figure 5.** First-order decay rates, $k'_3$, of 1102 as a function of [BrO] at 298 K (A), 253 K (0), and 348 K (0).

**Figure 6.** HO₂ signal intensity as a function of flow tube temperature using the F + 11202 source, (0) cool-down, (□) warm-up.

**Figure 7.** BrO signal intensity as a function of flow tube temperature using the O + Br₂ source, (0) cool-down, (□) warm up.

**Figure 8.** Effective wall loss rate constant for 1102 as a function of reactor temperature (0) 298 K, (□) 2.73 K, (A) 253 K, (V) 233 K, (0) 213 K.

**Figure 9.** Temperature dependence of the rate constant for the BrO + HO₂ reaction: (0) this work, excess H₂O₂; (Cl) this work, excess BrO; ( ) Poulet et al. 7; (V) Lariachev et al. 8; (0) Bridier et al. 9; (Cl) Elrod et al. 8; (O) best fit to data from this work.
EXPERIMENTAL APPARATUS FOR KINETICS STUDY OF BrO + HO

TO PUMPS

QUADRUPOLE RODS

IONIZER

ELECTRON MULTIPLIER

LOCK-IN AMPLIFIER

TO PUMPS

TO PUMPS

TO PUMPS

BEAM CHOPPER

REACTOR

F + H₂O₂ REGION

MICROWAVE DISCHARGE

HEATED SLIDING INJECTOR *

HEATING WIRE

VACUUM JACKET

THERMOCOUPLE

MICROWAVE DISCHARGE CAVITY
[BrO] (10^{11} \text{ molecule cm}^{-3})

[\text{INJECTOR POSITION} (\text{cm})]

[110_z](10^" \text{ cm}^{-3})= 0.0

1.01

2.54

3.68

5.13

6.64
Figure 8

[HO2] (10^{11} molecule cm^{-3}) vs INJECTOR POSITION (cm)
BrO + HO₂ → HOBr + O₂

- This work, excess H₂O₂
- This work, excess BrO
- Poulet et al.
- Bridier et al.
- Larichev et al.
- Elrod et al.

k₃ (10⁻¹¹ cm³ molecule⁻¹ s⁻¹)

1000/T