

Temperature Dependence of the Rate Constant for the HO₂ + BrO Reaction

Matthew J. Elrod, Roger F. Meads, Jennifer B. Lipson, John V. Seeley, and Mario J. Molina*

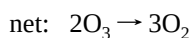
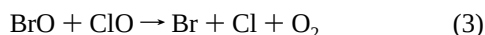
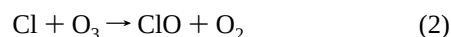
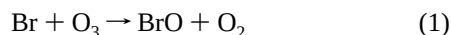
Departments of Earth, Atmospheric and Planetary Sciences and of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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The rate constant for the HO₂ + BrO reaction has been measured using the turbulent flow technique with high-pressure chemical ionization mass spectrometry for the detection of reactants and products. At room temperature and 100 Torr pressure, the rate constant (and the two standard deviation error limit) was determined to be $(1.4 \pm 0.3) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. The temperature dependence of the rate constant was investigated between 298 and 210 K, and the data was fit to the following Arrhenius expression: $(2.5 \pm 0.8) \times 10^{-12} \exp[(520 \pm 80)/T]$ cm³ molecule⁻¹ s⁻¹. Although the negative activation energy value agrees well with the current recommendation for stratospheric modeling, our absolute values for the rate constant are about a factor of 2 lower than this same recommendation.

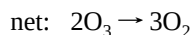
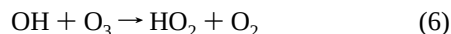
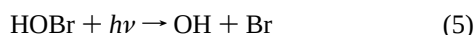
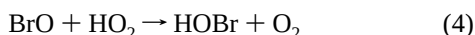
Introduction

Of the halogens which exist in significant quantities in the stratosphere, bromine participates in particularly efficient catalytic cycles which result in a net destruction of ozone. While fluorine and chlorine atoms are capable of abstracting hydrogen atoms from a number of atmospherically abundant species (thus terminating their catalytic chains), bromine atoms abstract hydrogen from only a few minor stratospheric components.¹ In addition, the power of bromine compounds to destroy ozone is greatly enhanced by the following synergistic cycle with chlorine:²



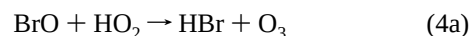
Despite the fact that bromine compounds are more than 2 orders of magnitude less abundant than chlorine compounds in the stratosphere, it has been recently estimated that such chemistry involving bromine species is responsible for ~25% of the ozone loss observed during the Antarctic ozone hole event,³ and up to 40% of the loss over the Arctic in winter.⁴ Important anthropogenic sources of bromine include methyl bromide and the halons, which are used for fumigation and fire retardation, respectively.⁵

There has been recent interest in another catalytic cycle involving bromine that was also originally suggested in 1980, but was dismissed as unimportant because the rate constant for reaction 4 (based on the first kinetic study of that reaction) was too slow in the atmosphere to contribute significantly to ozone depletion:²



New experimental results^{6–10} have suggested that reaction 4 proceeds at a substantially faster rate than had been indicated by previous measurements,¹¹ and may indeed play a major role in ozone-related bromine chemistry. For example, model calculations based on the new rate constant obtained by Poulet *et al.* indicated an increase from 1.14 to 1.45% column ozone loss at midlatitudes from bromine compounds alone.⁶ However, a consensus has not yet been achieved for the room temperature rate constant for HO₂ + BrO.

Reaction 4 might also proceed via a second channel which is thermodynamically feasible ($\Delta H = -7.7$ kcal mol⁻¹):



Since this reaction is a chain-terminating step, even a relatively small branching ratio would lead to substantially less ozone depletion by bromine-containing compounds. Thus far, however, laboratory experiments,^{9,12} field studies,¹³ and modeling results¹⁴ have consistently placed low upper limits (<2%) on this channel.

As Wennberg *et al.* pointed out in their analysis of field data for several important atmospheric species obtained during the Stratospheric Photochemistry, Aerosols, and Dynamics Expedition (SPADE),¹⁵ the interpretation of the results is hindered by uncertainties in the laboratory-measured rate constants. This is due to the fact that most such rate constant determinations have not been carried out at pressures and temperatures characteristic of the lower stratosphere. In this article we describe our investigation of the kinetics of reaction 4 conducted at pressures near 100 Torr and at a range of temperatures extending to those found in the lower stratosphere using a turbulent flow tube coupled to a high-pressure chemical ionization mass spectrometer. We have previously shown that the turbulent flow tube technique can be used to accurately determine the rate constants of reactions at pressures ranging from 50 to 760 Torr and at temperatures as low as 180 K.^{16–18} As in our recent study of HO₂ + NO (ref 19), we use a new detection system—high-pressure chemical ionization mass spectrometry—to detect many species relevant to the HO₂ + BrO reaction with high sensitivity.

Experimental Section

A schematic of the experimental apparatus is presented in Figure 1 and is similar to that used in our previous study of HO₂ + NO.¹⁹ The flow tube was constructed with 2.2 cm i.d.

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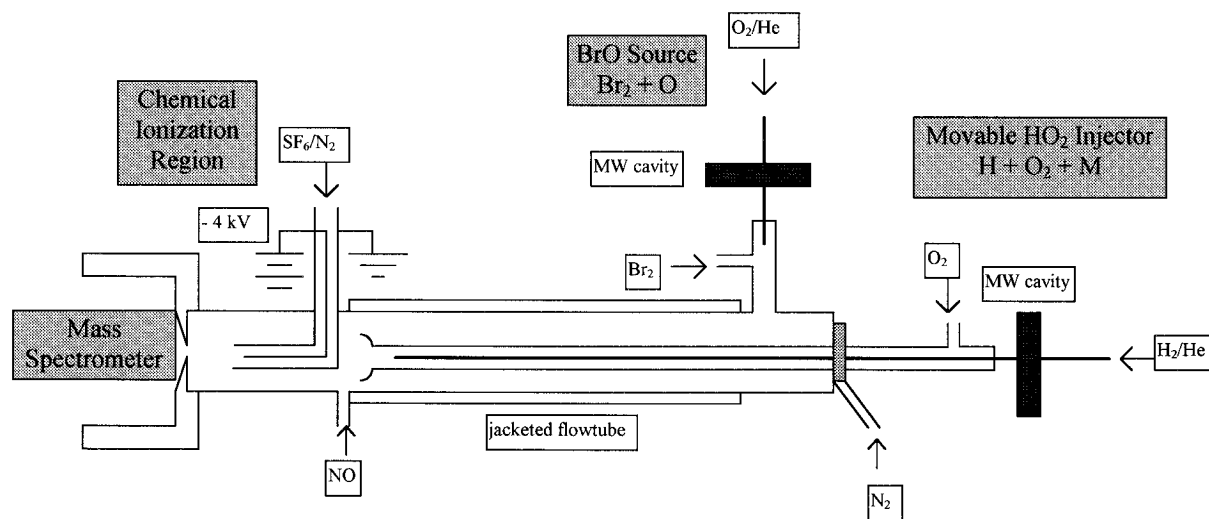


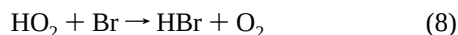
Figure 1. Schematic of experimental apparatus.

Pyrex tubing and was 120 cm in total length. A large flow of nitrogen carrier gas (~ 50 STP L min⁻¹) was injected at the rear of the flow tube. The gases necessary to generate BrO were introduced through a 10 cm long 12.5 mm diameter sidearm located at the rear of the flow tube. HO₂ was generated in a triple-nested movable injector. The outer encasement (made from corrugated Teflon tubing) was used so that the injector could be moved to various injector positions without breaking any vacuum seals, as well as to prevent ambient gases from condensing on cold portions of the injector. A fan-shaped Teflon device was placed at the end of the injector in order to enhance turbulent mixing. The corona ion source was placed between the temperature regulated flow tube and the inlet to the quadrupole mass spectrometer. All gas flows were monitored with calibrated mass flow meters. The flow tube pressure was measured upstream of the corona ion source using a 0–1000 Torr capacitance manometer. The temperature was determined at both the entrance and exit points of the temperature regulated region of the flow tube using Cu-constantan thermocouples.

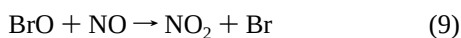
BrO was generated using the following reaction:



($k_7 = 2.0 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹).²⁰ Oxygen atoms were produced by combining a 0.5 STP L min⁻¹ flow of helium (99.999%), which had passed through a silica gel trap immersed in liquid nitrogen, with a 0.1–0.5 STP mL min⁻¹ flow of a 1% O₂ (99.995%)/He mixture which then passed through a microwave discharge produced by a Beenakker cavity operating at 50 W. To generate BrO, the oxygen atoms were then injected into a sidearm and mixed with an excess of Br₂ ($\sim 10^{12}$ molecule cm⁻³) in order to ensure that no oxygen atoms were introduced into the main flow. The simultaneous generation of bromine atoms results in insignificant loss of HO₂ through reaction 8:



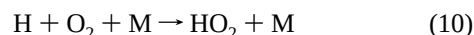
($k_8 = 2.0 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹)²¹ and does not affect the values of the measured BrO pseudo-first-order decays. However, this secondary reaction does lead to higher background levels of HBr. Absolute BrO concentrations were periodically determined by the titration reaction:



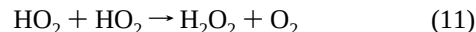
($k_9 = 2.1 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹)²¹ and subsequent calibration of the NO₂ mass spectrometer signal. Purified NO/

N₂ mixtures were passed through a silica gel trap immersed in a dry ice/ethanol bath to further reduce the background NO₂ contribution. For this study, BrO concentrations ranged from 0.25 to 1.0×10^{11} molecule cm⁻³.

HO₂ was generated by the following reaction:



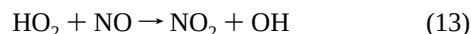
The rate constant for reaction 10 at 100 Torr is 2.0×10^{-13} cm³ molecule⁻¹ s⁻¹ (ref 21). Because HO₂ was introduced through a movable injector where the corresponding concentrations are ~ 30 times higher than in the main flow tube, the disproportionation reaction



($k_{11} = 1.8 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 100 Torr)²¹ is a concern in the production of large quantities of HO₂. By taking advantage of the long lifetime of H atoms, this difficulty was surmounted by using a nested injector which kept the hydrogen atoms (entrained in the inner 3 mm Pyrex tube) and oxygen molecules (entrained in the outer 6 mm Pyrex tube) separate throughout all but the last 1 cm of the injector. The hydrogen atoms were allowed to mix with a very large excess of O₂ (5×10^{17} molecule cm⁻³ inside the injector) for only about 1 ms, allowing reaction 10 to virtually go to completion, but preventing significant recombination of HO₂. Hydrogen atoms were generated by combining a 2.5 STP L min⁻¹ flow of helium (99.999%) with a 0.2–5.0 STP mL min⁻¹ flow of a 2% H₂ (99.999%)/He mixture which then passed through a molecular sieve trap immersed in liquid nitrogen and finally through a microwave discharge produced by a Beenakker cavity operating at 70 W. Some OH was generated by this source, but it was adequately removed by the excess of Br₂ present in the flow tube. For reasons of convenience, absolute HO₂ concentrations were routinely determined by the titration of H atoms:



($k_{12} = 1.6 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹)²⁰ and the modeling of reaction 10 and competing side reactions to determine actual HO₂ concentrations. For all conditions used in this study, HO₂ concentrations were found to be at least 90% of the titrated H atom concentrations. Direct titrations of HO₂



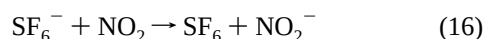
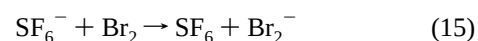
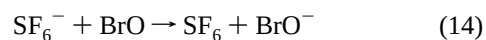
($k_{13} = 8.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)¹⁹ were periodically performed (in a manner similar to that described for BrO) to verify the accuracy of the H + Br₂ method. Although the HO₂ concentrations used in this study were low enough to avoid significant homogeneous recombination of HO₂ (usually <10% loss over the entire reaction zone [~ 25 ms]), HO₂ losses as high as 40% (at 210 K) were observed at the lowest temperatures achieved in this study. Using the extrapolated value²¹ for k_{10} at 210 K and the highest HO₂ concentration ($10^{12} \text{ molecule cm}^{-3}$) used at that temperature, the loss of HO₂ from homogeneous recombination is predicted to be only 17%. Some of this unexpectedly high loss might be due to wall reactions. However, considering that the HO₂ recombination is a complex-mode reaction, extrapolation to low temperatures could well underestimate the actual rate constant value. We are planning to conduct additional experiments to investigate these possibilities. In any case, we used the *mean* HO₂ concentration present in the reaction zone to determine the bimolecular rate coefficient; for conditions typical of our experiments, modeling results indicate that this approximation results in values accurate to within 5% of the true rate constant. The mean HO₂ concentrations were determined as follows: Since the HO₂ concentrations, which were routinely titrated, were determined at the time = initial position of the reaction zone, the actual average HO₂ concentrations were lower. To correct for this, the time = final and time = initial mass spectrometer signals for HO₂ were used to scale the titrated HO₂ concentrations. In the low-pressure studies of Larichev *et al.*⁹ much higher HO₂ concentrations ($5 \times 10^{12} \text{ molecule cm}^{-3}$) were used and similar scaling methods were applied. Li *et al.*¹⁰ used even higher HO₂ concentrations ($8 \times 10^{12} \text{ molecule cm}^{-3}$) and also presumably used some sort of scaling method. HO₂ concentrations used in this study ranged from 0.5 to $2.0 \times 10^{12} \text{ molecule cm}^{-3}$. In order to insure pseudo-first-order kinetic conditions, [BrO] was kept at most $1/_{10}$ as large as [HO₂].

Most of the chemical species relevant to this study (HO₂, BrO, HOBr, NO₂, Br₂, and HBr) were chemically ionized with the SF₆[−] reagent ion and then detected with the quadrupole mass spectrometer. SF₆[−] was produced in the ion source by passing $\sim 5 \times 10^{12} \text{ molecule cm}^{-3}$ of SF₆ mixed with a large N₂ flow ($10 \text{ STP L min}^{-1}$) over the corona discharge. The corona ion source consisted of a steel needle held at an electric potential of -4 kV and a grounded 6 mm stainless steel tube counter-electrode, which (with a ballast resistor of $100 \text{ M}\Omega$) resulted in a discharge current of about $30 \mu\text{A}$. The needle body was electrically isolated from the counterelectrode with a piece of Pyrex tubing. In order to confine the corona ionization process to SF₆ alone and to control the ion-molecule reaction time, another piece of Pyrex tubing (of variable length) was used to direct the SF₆[−] downstream into the main flow tube effluent.

Ions were detected with a quadrupole mass spectrometer housed in a two-stage differentially pumped vacuum chamber. Flow tube gases (neutrals and ions) were drawn into the front chamber through a 0.1 mm aperture, which was held at a potential of -130 V . The ions were focused by three lenses constructed from 3.8 cm i.d. , 4.8 cm o.d. copper gaskets. The front chamber was pumped by a $6 \text{ in. } 2400 \text{ L s}^{-1}$ diffusion pump. The gases entered the rear chamber through a skimmer cone with a 1.2 mm orifice (held at -20 V) which was placed $\sim 5 \text{ cm}$ from the front aperture. The rear chamber was pumped by a 500 L s^{-1} turbomolecular pump. Once the ions passed through the skimmer cone, they were mass filtered and detected with a quadrupole mass spectrometer.

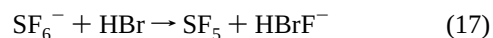
In the chemical ionization scheme employed here, BrO, Br₂, and NO₂ are detected as their parent negative ions by

charge-transfer reactions with SF₆[−]:



The rate constant for reaction 14 has not been measured, while the rate coefficients for reactions 15 and 16 are 5.1×10^{-10} and $1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively.²²

HBr is detected as HBrF[−] through a fluoride transfer reaction with SF₆[−]:



The rate constant for reaction 17 is $5.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (ref 22). HOBr is detected as SF₅O[−] (ref 23) and HO₂ is detected as SF₄O₂[−], presumably through multistep pathways. In our previous study of HO₂ + NO, we detected HO₂ as O₂[−] via a F[−] reagent ion chemical ionization scheme.¹⁹

For the low-temperature studies, HCFC-123 was used as a coolant for the jacketed flowtube, and the nitrogen carrier gas was also precooled by passing it through a copper coil immersed in either a HCFC-123 or a liquid N₂ reservoir followed by resistive heating. The temperature was controlled in the reaction region to within 1 K .

Results and Discussion

In our earlier work, we reported that our chemical ionization detection scheme resulted in sensitivities of 100, 200, and 1000 ppt (at 100 Torr) for NO₂, HO₂, and OH, respectively.¹⁹ Although we did not carry out formal calibrations of the mass spectrometer for the bromine species detected with this method (Br₂, BrO, HBr, HOBr), it was apparent that these species could be detected with a similar sensitivity to that obtained for NO₂. The mass spectrometer signals for these compounds were found to be linear over the range of concentrations used in this work. The stated sensitivity was more than adequate for the present work; actually, it was necessary to degrade the sensitivity of the spectrometer (by decreasing the ion-molecule reaction time) to allow the introduction of greater amounts of reactants—which were necessary to study the relatively slow HO₂ + BrO reaction—without inducing complications from secondary ion-molecule processes.

Bimolecular rate constants were obtained via the usual pseudo-first-order approximation method, using HO₂ as the excess reagent. Typical BrO decay curves as a function of injector distance are shown in Figure 2. The first-order rate constants obtained from fitting the BrO decay curves were plotted against [HO₂] in order to determine the bimolecular rate constant, as shown in Figure 3. This approach for determining bimolecular rate constants assumes that deviations from the plug flow approximation are negligible. Under the conditions present in our turbulent flow tube, Seeley *et al.*¹⁹ estimated that these deviations result in apparent rate constants which are at most 8% below the actual values. Hence, the flow corrections were neglected as they are smaller than the sum of the other likely systematic errors in the measurements of gas flows, temperature, detector signal, pressure, and absolute HO₂ concentrations. Indeed, we consider the major source of error in our experiments to arise from the determination of [HO₂] from the titration and scaling procedures outlined above. Considering such sources of error, we estimate that rate constants can be determined with an accuracy of $\pm 30\%$ (2σ).

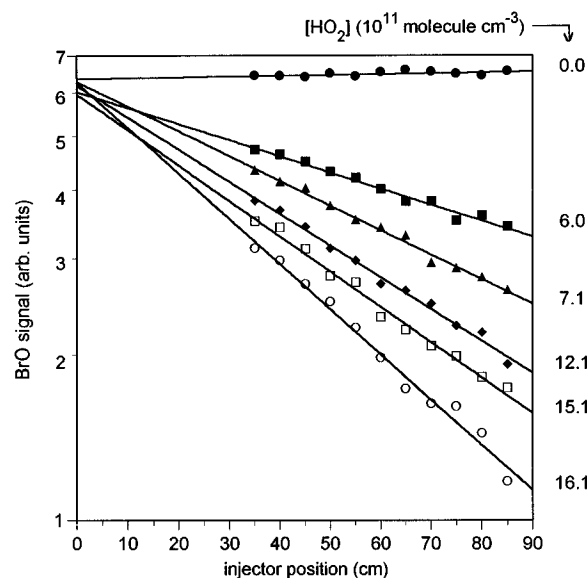


Figure 2. Typical set of BrO signals as a function of injector distance. This data set was obtained under the following conditions: $P = 100$ Torr; $T = 298$ K, average velocity = 1375 cm s^{-1} ; Reynolds number = 2600.

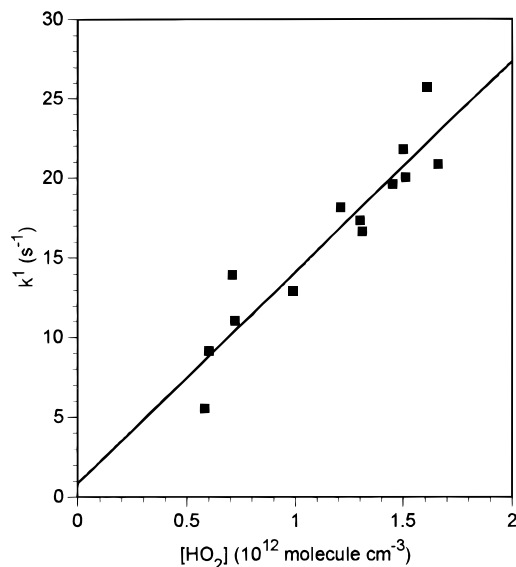


Figure 3. Typical plot of k^1 as a function of $[\text{HO}_2]$. This plot was obtained under the same conditions as listed in Figure 2.

We performed four separate determinations of the rate constant at 298 K (see Table 1 for a complete list of experimental conditions and measured rate constants) and arrived at the mean value of $k = (1.4 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; the uncertainty represents the two standard deviation statistical error in the data and is not an estimate of systematic errors. Table 2 contains a comparison of all reported rate constants for the HO₂ + BrO reaction near room temperature. Although our value indicates a significantly faster rate constant than was determined in the original study of Cox and Shepard,¹¹ our result is about a factor of 2 lower than some of the other recent studies and the current JPL recommended value.²¹ However, the very recent low-pressure measurements of Li *et al.*¹⁰ are in excellent agreement with our findings.

We performed several measurements at temperatures between 298 and 210 K in order to establish the temperature dependence of the rate constant for conditions relevant to the lower stratosphere. The rate constant approximately doubled as the temperature was lowered over this range. From the data listed

TABLE 1: Summary of Experimental Conditions and Measured Rate Constants

T (K)	P (Torr)	velocity (cm s^{-1})	Reynolds number	$k \pm 2\sigma$ (10^{-11} cm^3 $\text{molecule}^{-1} \text{ s}^{-1}$)
298	100	1375	2600	1.32 ± 0.30
298	97	1800	3300	1.38 ± 0.24
298	99	1500	2750	1.44 ± 0.30
298	95	1675	2700	1.50 ± 0.28
283	92	1450	2850	1.68 ± 0.34
273	95	1425	2970	1.64 ± 0.32
270	90	1570	3120	1.69 ± 0.32
263	98	1570	3400	1.66 ± 0.22
260	92	1900	4250	2.09 ± 0.36
253	92	1575	3600	2.01 ± 0.32
253	107	1420	3820	2.10 ± 0.40
249	93	1850	4350	2.33 ± 0.56
243	94	1740	4420	1.99 ± 0.40
230	91	1550	4100	2.63 ± 0.81
220	92	1260	3600	2.67 ± 0.46
216	90	1680	4970	2.55 ± 0.94
210	94	1500	4900	2.95 ± 0.92

TABLE 2: Comparison of Measured Rate Constants Near Room Temperature

technique ^a	P (Torr)	k (10^{-11} cm^3 $\text{molecule}^{-1} \text{ s}^{-1}$)	ref(s)
MM/UV	760	0.5	11
DF-LF/EIMS	1	3.3	6,9
FP/UV	760	3.4	7
MM/UV	760	3.2	8
LP/UV	760	3.0	8
DF-LF/EIMS	1–3	1.7 ^b	10
		1.3 ^c	
DF-TF/CIMS	100	1.4	this work

^a MM, molecular modulation; FP, flash photolysis; LP, laser photolysis; DF, discharge flow; LF, laminar flow; TF, turbulent flow; UV, ultraviolet spectroscopy detection; EIMS, electron impact mass spectrometry detection; CIMS, chemical ionization mass spectrometry detection. ^b With HO₂ as excess reagent. ^c With BrO as excess reagent.

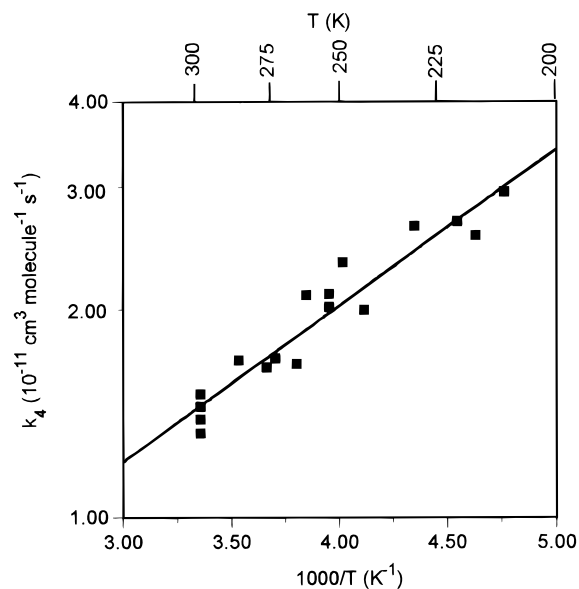


Figure 4. Arrhenius plot for the reaction HO₂ + BrO; the least-squares fit to the data yields the expression $k(T) = (2.5 \pm 0.8) \times 10^{-12} \exp[(520 \pm 80)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

in Table 1 and plotted in Figure 4, we obtain the Arrhenius expression $k(T) = (2.5 \pm 0.8) \times 10^{-12} \exp[(520 \pm 80)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. In the only other temperature dependence study to date, Larichev *et al.*⁹ fit data ranging from 343 to 243 K to an Arrhenius expression and obtained a similar temperature

dependence, but a preexponential factor that was about 2 times larger than our result. The current JPL recommendation²¹ for the temperature dependence of this reaction was chosen by analogy to the $\text{HO}_2 + \text{ClO}$ reaction, and we find the recommended temperature dependence to be in good agreement with our data. Larichev *et al.*⁹ also reported the existence of a reproducible, non-Arrhenius data point at 233 K—the lowest temperature attained in their study. The anomalously fast rate constant determined at that temperature was tentatively ascribed to the formation of an intermediate complex. However, we find no such anomalous behavior in the rate constant for temperatures as low as 210 K as shown in Figure 4. This is an important point since the significant departure from Arrhenius behavior observed by Larichev *et al.* beginning at 233 K is suggestive of a nearly collision-limited rate constant at stratospherically relevant temperatures. Recent attempts to constrain the rate constant for this reaction from measurements of the OH/HO_2 ratio²⁴ and BrO and total inorganic bromine²⁵ in the lower stratosphere suggest a range of rate constants which are slower than the rate constant obtained by extrapolation of the Larichev *et al.* data, while our direct measurement of the rate constant for $\text{HO}_2 + \text{BrO}$ at 210 K is easily within the range of possible rate constants proposed to be consistent with the present interpretation of the field data.

We were unable to address the importance (or existence) of the secondary product channel (reaction 4a) for the $\text{HO}_2 + \text{BrO}$ reaction using our current radical generation and detection scheme, because of problems with the sensitive detection of O_3 and HBr in the presence of the other reactants. With the large quantities of O_2 required for the production of HO_2 , the SF_6^- chemical ionization scheme yields small amounts of O_3^- , thus preventing the sensitive detection of ozone in the presence of oxygen. In addition, the BrO source produces high levels of bromine atoms which react with HO_2 and the flow tube walls to create relatively high background HBr signals. However, these problems can potentially be circumvented by employing different synthetic schemes. Nonetheless, mass spectral scans were taken at each temperature to search for possible changes in the product distribution, but we were unable to establish limits on the generation of reaction four products other than HOBr .

Conclusions

The results presented here extend the measurements of the rate constant for $\text{HO}_2 + \text{BrO}$ to conditions representative of the lower stratosphere. We find that the absolute value of the rate constant is more than a factor of 2 lower than the current JPL recommendation, although our relative temperature dependence agrees well with the same recommendation. While our room temperature results do not agree with several other previous measurements, they are in excellent agreement with the most recent low-pressure study by Li *et al.*¹⁰ Also, we do not find evidence for non-Arrhenius behavior below 243 K, as suggested in the previous temperature dependence study.⁹ In addition, our direct measurement of the rate constant at 210 K is in agreement with the range of rate constants that would be consistent with field observations at the same temperature.^{24–25} Our direct results should place more stringent constraints on

the partitioning of bromine species in the stratosphere and on the ozone depletion potentials of compounds such as methyl bromide.

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