



Rate constant for the reaction SO+BrO \rightarrow SO2+Br

J. Brunning and L. Stief

Citation: The Journal of Chemical Physics **85**, 2591 (1986); doi: 10.1063/1.451066 View online: http://dx.doi.org/10.1063/1.451066 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/85/5?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

Temperature dependence of the rate constants for the H+Br2 and D+Br2 reactions J. Chem. Phys. **94**, 4896 (1991); 10.1063/1.460574

Rate constant of the gas phase reaction of SO3 with H2O J. Chem. Phys. **89**, 4853 (1988); 10.1063/1.455680

Boron atom reactions. II. Rate constants with O2, SO2, CO2, and N2O J. Chem. Phys. **74**, 3287 (1981); 10.1063/1.441534

Rate constants for the reactions of atomic boron with O2, SO2, CO2, and N2O J. Chem. Phys. **70**, 5422 (1979); 10.1063/1.437453

Rate of the reaction O+SO2+M→SO3+M J. Chem. Phys. **63**, 5411 (1975); 10.1063/1.431347



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 128.114.34.22 On: Fri, 28 Nov 2014 17:15:08

Rate constant for the reaction $SO + BrO \rightarrow SO_2 + Br$

J. Brunning^{a),b)} and L. Stief

Astrochemistry Branch, Laboratory for Extraterrestrial Physics, NASA/Goddard Space Flight Center, Greenbelt, Maryland 20771

(Received 14 April 1986; accepted 29 May 1986)

The rate of the radical-radical reaction SO + BrO \rightarrow SO₂ + Br has been determined at 298 K in a discharge flow system near 1 Torr pressure with detection of SO and BrO via collision-free sampling mass spectrometry. The rate constant was determined using two different methods: measuring the decay of SO radicals in the presence of an excess of BrO and measuring the decay of BrO radicals in excess SO. The results from the two methods are in reasonable agreement and the simple mean of the two values gives the recommended rate constant at 298 K, $k = (5.7 \pm 2.0) \times 10^{-11}$ cm³ s⁻¹. This represents the first determination of this rate constant and it is consistent with a previously derived lower limit based on SO₂ formation. Comparison is made with other radical-radical reactions involving SO or BrO. The reaction SO + BrO \rightarrow SO₂ + Br is of interest for models of the upper atmosphere of the Earth and provides a potential coupling between atmospheric sulfur and bromine chemistry.

INTRODUCTION

The kinetics and mechanism of the elementary reactions of the SO radical are important not only for an understanding of the reactions of free radicals but also for an understanding of the role of SO radicals in the atmospheric chemistry of the Earth and Venus and in the combustion chemistry of sulfur compounds. In the upper atmosphere of the Earth, SO may be oxidized to SO₂ via reaction with O₂, O₃, OH, NO₂, ClO, BrO, etc. For the atmosphere of Venus, reactions of SO with O, HO₂, ClO, and SO are of interest. Many of these reactions are also of importance in high temperature combustion processes.

We have previously reported results¹ for the reactions of SO with NO_2 and ClO and have now extended these studies to the reaction

$$SO + BrO \rightarrow SO_2 + Br$$
 (1)

Employing the technique of discharge flow-mass spectrometry, absolute rate constants for reactions, Eqs. (2) and (3), were determined by monitoring the decay of SO in an excess of NO₂ and ClO, respectively:

$$SO + NO_2 \rightarrow SO_2 + NO,$$
 (2)

$$SO + ClO \rightarrow SO_2 + Cl.$$
 (3)

The rate constant for the SO + NO₂ reaction was determined to be $k_2 = (1.37 \pm 0.10) \times 10^{-11}$ cm³ s⁻¹ and independent of temperature from 210 to 363 K. This result is in good agreement with recent previous direct, absolute measurements^{2,3} as well as an earlier relative measurement⁴ all at 295 K. For the radical-radical reaction SO + ClO we found $k_3 = (3.22 \pm 0.48) \times 10^{-11}$ cm⁻³ s⁻¹, again independent of temperature from 248 to 363 K. This is in moderate agreement with the 295 K result of Clyne and MacRobert.⁵ This paper⁵ also reports the only previous study of the SO + BrO reaction. The reaction was studied at 295 K in a discharge flow system with SO in excess; the decay of BrO and the formation of SO₂ were followed by collision-free sampling to a mass spectrometer. Although BrO removal was observed to occur at a rate comparable to that for SO₂ formation, quantitative measurement of the decay of BrO was not possible due to low sensitivity for BrO (10^{11} cm⁻³ for a signal-tonoise ratio S/N = 1) and variation in the sensitivity, possibly due to heterogeneous loss processes in the sampling system.⁶ Based on limited data obtained by following the rate of formation of SO₂, a lower limit of $k_1 > 4 \times 10^{-11}$ cm³ s⁻¹ was reported.

The present experiments employ essentially the same technique as Clyne and MacRobert⁵ but with considerably improved stability and sensitivity $(3 \times 10^9 \text{ cm}^{-3} \text{ for BrO}$ and $2 \times 10^9 \text{ cm}^{-3}$ for SO at S/N = 1). Quantitative measurements were made of the decay of SO under conditions of excess BrO and also of the decay of BrO with SO in excess. This yields two independent measures of k_1 at 298 K.

EXPERIMENTAL

Details of the apparatus and technique employed in kinetic studies of the reactions of the SO radical have been described in a previous publication.¹ In summary, a Pyrex discharge-flow system was linked via a two-stage collision-free sampling system to a quadrupole mass spectrometer (Extranuclear Laboratories, Inc.). Typical flow conditions were $650 \mu mol s^{-1}$ of He carrier gas at 1 Torr pressure. Helium carrier gas flows and reagent flows (SO₂, Br₂, O₂, NO, NO₂ all diluted in He) were measured by separate flow controllers (ASM International N.V., model AFC 260).

Ground state SO radicals were generated in a microwave discharge (2450 MHz) of dilute mixtures of 1% SO₂ in He. The SO radicals were detected at m/e = 48 using low electron energies (<16 eV) in order to suppress interference from the dissociative ionization of SO₂. Removal of residual O and S atoms was accomplished using a discharge-bypass system.^{1,2} Absolute concentrations of SO were determined using the rapid titration reaction SO + NO₂ \rightarrow SO₂ + NO and measuring the decrease in [NO₂] or the increase in [SO₂] upon complete removal of SO by excess NO₂. At a

^{*)} NAS/NRC Postdoctoral Research Associate.

^{b)} Present address: Dept. of Chemistry, The University of Birmingham, P.O. Box 363, Birmingham B15 2TT, United Kingdom.

signal-to-noise ratio (S/N) equal to 1, the concentration of SO was $\sim 2 \times 10^9$ cm⁻³.

BrO radicals were generated in the flow tube by the rapid reaction 7 :

O + Br₂→BrO + Br,

$$k_4 = (1.4 \pm 0.2) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}.$$
 (4)

Ground state $O({}^{3}P)$ atoms were formed as a byproduct from the SO₂ discharge or produced in a separate discharge from a dilute O₂/He mixture. The former source was used for the experiments with SO in excess ([SO]₀>[O]₀ in the SO₂ discharge and therefore [SO]₀>[Br]₀) while the latter source was used for experiments with BrO in excess. A large excess of Br₂(~10¹⁴ cm⁻³) was added through the movable teflon injector to the flow of O(³P) atoms in the flow tube. This large excess ensures rapid formation of BrO (1 to 2 milliseconds) and also prevented loss of BrO via the rapid reaction⁷:

$$O + BrO \rightarrow Br + O_2, k_5 = 3.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}.$$
 (5)

The BrO radicals were detected at m/e = 97 using electron energies of ~ 20 eV. Absolute concentrations of BrO were determined using the titration reaction⁸:

BrO + NO
$$\rightarrow$$
Br + NO₂,
 $k_6 = 2.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, (6)

and measuring the [NO₂] formed. A lower limit to detection of BrO was $\approx 3 \times 10^9$ cm⁻³ at a signal-to-noise ratio of 1:1.

Helium (Ideal Gas Products, 99.999%) was passed through a molecular sieve trap at 77 K before entering the flow tube. SO₂ (Matheson, 99.98%) and Br₂ (Baker Chemicals, 99.9%) were degased at 77 K. O₂ (Matheson UHP, 99.99%) was used without purification. NO (Matheson, 99%) was purified by fractional distillation at 140 K. NO₂ (Matheson, 99.5%) was purified by adding O₂ followed by trap-to-trap distillation at 196 K to remove O₂ and NO. A small correction (<5%) was made to the NO₂ flow rate to account for the rapid dissociation of the N₂O₄ dimer which occurred between the flow controller and the flow tube.

RESULTS

The reaction of SO with BrO was studied under pseudofirst-order conditions using two different methods. In method I, BrO was in excess and the course of the reaction was followed by monitoring the decay of SO with reaction time (i.e., distance from the movable injector to the pinhole). This is the approach used in our study of the SO + ClO reaction.¹ In method II, SO was used in excess and the decay of BrO is monitored as a function of time. This is similar to the experiments of Clyne and MacRobert⁵ which gave a lower limit for k_1 .

The pseudo-first-order rate equation for a reaction

 $A + B \xrightarrow{k} products,$

where $[B]_0 > [A]_0$ is given by

 $\ln([\mathbf{A}_0]/[\mathbf{A}]) = k[\mathbf{B}]t.$

Small stoichiometric corrections to [B] were made to allow for the depletion of B during the course of the reaction

$$[\mathbf{B}]_{\text{mean}} = [\mathbf{B}]_0 - 1/2[\mathbf{A}]_0$$



FIG. 1. Kinetics of the SO + BrO reaction under conditions of excess BrO. (a) Typical first-order logarithmic decay plots of SO: \blacksquare : [BrO]_{mean} = 0.45×10^{12} cm⁻³, O: [BrO]_{mean} = 1.66×10^{12} cm⁻³, \blacktriangle : [BrO]_{mean} = 1.76×10^{12} cm⁻³, \spadesuit [BrO]_{mean} = 2.62×10^{12} cm⁻³. (b) Summary plot of pseudo-first-order rate constant k' with [BrO]_{mean}.

The pseudo-first-order rate constant is given by $k'_{obs} = k[B]_{mean}$. Corrections were made to k'_{obs} to allow for axial diffusion of SO and BrO radicals in the carrier gas by means of the equation

$$k' = k'_{obs} \left[1 + (D/v^2) k'_{obs} \right],$$

where k' is the corrected first-order rate constant, D is the diffusion coefficient, and v is the flow velocity. Diffusion coefficients for SO and BrO were determined using the method of Lewis *et al.*⁹

BrO in excess

BrO was generated at reaction times from 2 to 15 ms. Initial $[BrO]_0/[SO]_0$ stoichiometries were low due to the necessity of keeping $[BrO]_0$ low to limit the removal of BrO via the fast disproportionation reaction¹⁰

BrO + BrO
$$\rightarrow$$
 products,
 $k_7 = 2.7 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}.$
(7)

It was necessary in some experiments to make a small correction to $[BrO]_{mean}$ to allow for the removal of BrO via reaction (7). Figure 1(a) shows typical logarithmic decay plots of $[SO]_0/[SO]$ vs time, which display good linearity up to about an order of magnitude decay in [SO].

An intercept was observed which extrapolates to a common origin at about -1.0 ms and is assigned to a dead time in the sampling system. Similar dead times due to inefficient pumping between the end of the flow tube and the first pinhole were observed in our studies of SO + NO₂ and SO-+ ClO¹ and have been noted previously in other discharge flow-mass spectrometer systems.^{2,5,11,12} Figure 1(b) shows the dependence of the pseudo-first-order rate constant k' on [BrO]_{mean} based on the results from 26 experiments.

Good second-order behavior is demonstrated by the fact that the plot of k' vs $[BrO]_{mean}$ is linear. A small positive intercept of 12 s^{-1} is observed which is attributed to the loss of SO on the wall of the flow tube. The bimolecular rate constant was determined from the slope of the line in Fig. 1(b) using least squares analysis. This gives a mean value at 298 K of $(6.64 \pm 1.33) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} (1\sigma)$.

To allow for possible systematic error due to the low values of $[BrO]_0/[SO]_0$, the larger than usual correction due to the rapid BrO + BrO reaction, and possible error in the [BrO] calibration, we quote the value from Method I as

$$k_1 = (6.6 \pm 2.0) \times 10^{-11} \,\mathrm{cm}^3 \,\mathrm{s}^{-1}$$
.

SO in excess

Unlike the previous method, no correction for the occurrence of the SO + SO (8) reaction was necessary since the rate of this reaction has been shown to be very slow $(k_8 < 3 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1})$.^{2,13} SO was added at reaction times from 2 to 15 ms and initial stoichiometries $[SO]_0/[BrO]_0$ were varied from 4 to 10. Typical logarithmic decay plots of [BrO] vs time are displayed in Fig. 2. Table I summarizes the results of a total of nine experiments performed with SO in excess. The mean value of the rate constant from these experiments is $(4.76 \pm 0.80) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} (1\sigma)$. Allowing for possible systematic error in reactant concentration



FIG. 2. Kinetics of the SO + BrO reaction under conditions of excess SO. Plot of ln BrO signal vs time. \blacksquare : [SO]_{mean} = 2.17×10¹² cm⁻³. \blacksquare : [SO]_{mean} = 5.93×10¹² cm⁻³.

TABLE I. Results for SO + BrO \rightarrow SO₂ + Br under conditions of excess SO.

$[BrO]_0/10^{11} \text{ cm}^{-3}$	$[SO]_{mean}/10^{12} \text{ cm}^{-1}$	$-3 k'/s^{-1}$	$k/10^{-11} \mathrm{cm}^3 \mathrm{s}^{-1}$
7.09	4.14	149	3.60
7.99	3.45	170	4.93
5.55	3.76	177	4.71
5.35	3.04	159	5.23
5.35	2.83	142	5.02
3.35	2.17	94	4.33
3.73	2.36	133	5.63
3.00	2.04	121	5.93
5.80	5.93	203	3.42
Mean valu	$e = (4.76 \pm 0.80) \times$	$10^{-11} \mathrm{cm}^3$	$s^{-1}(1\sigma)$

gives the Method II value

 $k_1 = (4.8 \pm 1.6) \times 10^{-11} \,\mathrm{cm}^3 \,\mathrm{s}^{-1}.$

DISCUSSION

We have used two methods to determine the rate constant for the reaction $SO + BrO \rightarrow SO_2 + Br$. Each had its own advantages and disadvantages. Method I with BrO in excess gave good first-order SO decays over a good range of [BrO], but the stoichiometry was low resulting in poorer first-order conditions, and a significant correction to [BrO] was required due to loss via BrO + BrO. The experiments using Method II with SO in excess had better first-order conditions and required no corrections for the occurrence of SO + SO, but the BrO decay plots showed more scatter and the experiments were more difficult to perform. This could have been due to the more reactive nature of BrO compared to SO, making it more difficult to monitor BrO decays quantitatively.

The results from the two methods are in moderate agreement. Given the limitations inherent in each method, we see no reason to prefer one over the other. We therefore quote the simple mean of the two values as the recommended rate constant at 298 K,

$$k_1 = (5.7 + 2.0) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1},$$

where the quoted uncertainty is the larger of the uncertainties associated with the two separate determinations.

Our result for k_1 is consistent with the lower limit of 4×10^{-11} cm³ s⁻¹ derived by Clyne and MacRobert⁵ from experiments under conditions very comparable to our Method II (SO in excess). Our result for SO + BrO may also be compared to those for other reactions involving SO. The pertinent reactions of SO include SO + NO₂, SO + ClO, and SO + OH. All are fast reactions involving oxidation of SO to SO₂ with rate constants (298 K) of 1.4×10^{-11} cm³ s^{-1} , 1-4 3.2 × 10⁻¹¹ cm³ s⁻¹, 1 and 8.4 × 10⁻¹¹ cm³ s⁻¹, 14 respectively. Our value for SO + BrO ($k = 5.7 \times 10^{-11} \text{ cm}^3$ s^{-1}) shows that the rate of this SO reaction is intermediate in this series, being several times faster than that for NO₂ or ClO, but somewhat slower than the reaction with OH. Since the reactions $SO + NO_2$ and SO + ClO have been shown to be independent of temperature from 210 to 363 K and 248 to 363 K, respectively,¹ it may be expected that the faster reactions SO + OH and SO + BrO will also show little or no temperature dependence. The reactivity of the SO radical is

TABLE II. Comparison of kinetic data of SO, NO, and O atoms.^a

x	k(SO + X)	k(NO + X)	k(O + X)
0,	1.0×10^{-13} (Ref. 15)	1.8×10^{-14} (Ref. 16)	8.0×10^{-15} (Ref. 17)
OC10	1.9×10^{-12} (Ref. 5)	3.4×10^{-13} (Ref. 18)	5.0×10^{-13} (Ref. 18)
NO ₂	1.4×10^{-11} (Ref. 1-4)	•••	9.5×10^{-12} (Ref. 19)
CIO	3.2×10^{-11} (Ref. 1)	1.7×10^{-11} (Ref. 8)	4.2×10^{-11} (Ref. 20)
BrO	5.7×10^{-11} (this work)	2.1×10^{-11} (Ref. 8)	3.0×10^{-11} (Ref. 7)
OH	8.4×10^{-11} (Ref. 14)	1.5×10^{-11} (Ref. 21)	3.1×10^{-11} (Ref. 22)

^a Rate constants at 298 K in units cm³ s⁻¹. Note that for the OH + NO reaction the high pressure limiting rate constant is quoted.

similar to that of NO and O atoms with respect to their reaction with O_3 , ^{15–17} OCIO, ^{5,18} NO₂, ^{1–4,19} CIO, ^{1,8,20} BrO, ^{7,8} and OH. ^{14,21,22} As can be seen from Table II, the reactions of SO are faster than those for NO and O (except for CIO + O) and that the trend in reactivity is similar, with the rate constant increasing in the order $O_3 < OCIO < NO_2 < CIO$, BrO, OH.

Finally, it may be noted that the reaction $SO + BrO \rightarrow SO_2 + Br$ is of interest for models of the upper atmosphere of the Earth. It provides one of the routes for oxidation of SO to SO_2 in the atmosphere.²³ This reaction also has the potential for being one of the few reactions to provide coupling between atmospheric sulfur cycles and atmospheric bromine cycles. Similar roles for the analogous SO + ClO reaction have been proposed for the atmosphere of the Earth²⁴ and Venus.²⁵

ACKNOWLEDGMENT

This work was supported by the NASA Upper Atmosphere Research Program.

¹J. Brunning and L. J. Stief, J. Chem. Phys. 84, 4371 (1986).

- ²M. A. A. Clyne and A. J. MacRobert, Int. J. Chem. Kinet. 12, 79 (1980).
 ³G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. 90, 55 (1982).
- ⁴M. A. A. Clyne, C. J. Halstead, and B. A. Thrush, Proc. R. Soc. Ser. A **295**, 355 (1966).

- ⁵M. A. A. Clyne and A. J. MacRobert, Int. J. Chem. Kinet. **13**, 187 (1981). ⁶A. J. MacRobert, Ph.D. thesis, Queen Mary College, University of Lon-
- don, 1981. ⁷M. A. A. Clyne, P. B. Monkhouse, and L. W. Townsend, Int. J. Chem.
- Kinet. 8, 425 (1976).
- ⁸G. W. Ray and R. T. Watson, J. Phys. Chem. 85, 2955 (1981).
- ⁹R. S. Lewis, S. P. Sander, S. Wagner, and R. T. Watson, J. Phys. Chem. 84, 2009 (1980).
- ¹⁰S. P. Sander and R. T. Watson, J. Phys. Chem. 85, 4000 (1981).
- ¹¹J. Brunning, J. Chem. Soc. Faraday Trans. 2 81, 663 (1985).
- ¹²M. A. A. Clyne, A. J. MacRobert, T. P. Murrells, and L. J. Stief, J. Chem. Soc. Faraday 2 80, 877 (1984).
- ¹³R. I. Martinez and J. T. Herron, Int. J. Chem. Kinet. 15, 1126 (1983); J. T. Herron and R. E. Huie, Chem. Phys. Lett. 76, 322 (1980).
- ¹⁴J. L. Jourdain, G. LeBras, and J. Combourieu, Int. J. Chem. Kinet. 11, 569 (1979).
- ¹⁵G.Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett. **90**, 55 (1982).
- ¹⁶G. W. Ray and R. T. Watson, J. Phys. Chem. **85**, 1673 (1981); J. V. Michael, J. E. Allen, Jr., and W. D. Brobst, *ibid.* **85**, 4109 (1981).
- ¹⁷P. H. Wine, J. M. Nicovich, R. J. Thompson, and A. R. Ravishankara, J. Phys. Chem. 87, 3948 (1983).
- ¹⁸P. P. Bemand, M. A. A. Clyne, and R. T. Watson, J. Chem. Soc. Faraday Trans. 1 69, 1356 (1973).
- ¹⁹P. P. Bernand, M. A. A. Clyne, and R. T. Watson, J. Chem. Soc. Faraday Trans. 2 70, 564 (1974).
- ²⁰J. J. Margitan, J. Phys. Chem. 88, 3638 (1984).
- ²¹C. Anastasi and I. W. M. Smith, J. Chem. Soc. Faraday Trans. 2 74, 1056 (1978).
- ²²W. H. Brune, J. J. Schwab, and J. G. Anderson, J. Phys. Chem. 87, 4503 (1983).
- ²³W. B. DeMore, JPL Publication No. 85-37, 1985.
- ²⁴W. B. DeMore and Y. L. Yung, Science 217, 1209 (1982).
- ²⁵Y. L. Yung and W. B. DeMore, Icarus 51, 199 (1982).