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# Kinetic studies of the reaction of the SO radical with NO<sub>2</sub> and CIO from 210 to 363 K

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The rates of the reactions of the SO radical with NO<sub>2</sub> and ClO have been determined in a discharge flow system near 1 Torr pressure with detection of radical and molecular species using collisionfree sampling mass spectrometry. The rate constants were determined from the decay of SO radicals in the presence of an excess of NO<sub>2</sub> and ClO. The NO<sub>2</sub> reaction was studied between 210 and 363 K and found to be temperature invariant: SO + NO<sub>2</sub>  $\rightarrow$  SO<sub>2</sub> + NO;  $k_1 = (1.37 \pm 0.10) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>. Similarly, the ClO reaction was observed to be independent

of temperature in the interval from 248 to 363 K: SO + ClO $\rightarrow$ SO<sub>2</sub> + Cl;  $k_2 = (3.22 \pm 0.48) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>. Comparison is made with previous studies of these

reactions at room temperature and with other radical-radical reactions involving SO or ClO.

#### INTRODUCTION

The kinetics and mechanisms of the elementary reactions of the SO free radical are of considerable interest due to their role in such diverse areas as the upper atmosphere of Earth, the upper atmosphere of Venus, and high temperature combustion process. The two reactions studied here

$$SO + NO_2 \rightarrow SO_2 + NO$$
, (1)

$$SO + ClO \rightarrow SO_2 + Cl$$
 (2)

are considered in the NASA evaluation of data for use in modeling the stratosphere of Earth.<sup>1</sup> Both reactions provide routes for the oxidation of SO to  $SO_2$  in the upper atmosphere. Reaction (2) is particularly significant in that it has the potential for providing coupling between the chlorine and sulfur cycles in atmospheric systems.<sup>2,3</sup>

Considering the importance of these reactions in atmospheric phenomena, the paucity of rate data based on direct experiments is surprising. There are only two previous absolute, direct studies<sup>4,5</sup> of reaction (1) as well as an earlier study<sup>6</sup> which measured  $k_1$  relative to that for the reaction  $O + NO_2 \rightarrow O_2 + NO$ . Clyne and MacRobert<sup>4</sup> used the discharge flow-mass spectrometry technique at 295 K and obtained the value  $k_1 = (1.36 \pm 0.10) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>. More recently, Black *et al.*<sup>5</sup> determined  $k_1 = (1.48 \pm 0.20)$  $\times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> at 298 K in an experiment combining excimer laser photolysis of SO<sub>2</sub> and detection and monitoring of SO via the chemiluminescent reaction

$$SO + O_3 \rightarrow SO_2^* + O_2$$
. (3)

The discharge flow/chemiluminescence experiments of Clyne *et al.*<sup>6</sup> yield  $k_4/k_1 = 0.67$  where  $k_4$  refer to the rate of the reaction

$$O + NO_2 \rightarrow O_2 + NO.$$
 (4)

Using the recommended<sup>1</sup> value of  $k_4 = 9.3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , this ratio gives  $k_1 = 1.4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  in good agreement with the recent absolute measurements.

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In the case of reaction (2) there has been only a single previous determination of the rate constant. Clyne and Mac Robert,<sup>7</sup> again using the discharge flow-mass spectrometry technique, obtained the result  $k_2 = (2.3 \pm 0.6) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> at 295 K.

In the present experiments, absolute rate constants for reactions (1) and (2) have been measured using the discharge flow-mass spectrometry technique at 1 Torr pressure over the temperature intervals 210–363 K and 248–363 K, respectively. Given the good agreement among previous determinations of  $k_1$  at 298 K, the present study of this reaction at 298 K will serve as a check on the newly assembled apparatus. The present study represents the first determinations of these rate constants as a function of temperature. Thus these results, especially those at lower temperatures, will be particularly useful for models of the stratospheres of Earth and Venus. The absolute rate constant for the reaction of the SO radical with BrO is also being measured and these experiments will be described elsewhere.

## EXPERIMENTAL

The apparatus consists of a discharge flow system coupled via a collision-free sampling system to a quadrupole mass spectrometer. Figure 1 shows a schematic diagram of the system. A separate gas handling line was used to purify reagents and prepare standard mixtures for delivery to the flow tube.

#### **Discharge flow system**

The Pyrex flow tube (26 mm i.d., 50 cm long) incorporated an annular jacket for heating and cooling the flow tube and a movable Teflon injector (6 mm o.d.) for the addition of reagents such as NO<sub>2</sub> or ClO. Gas flows from the microwave discharges enter the flow tube through either or both side arms and were pumped at constant velocity ( $\bar{u} \le 1900$ cm s<sup>-1</sup>) along the tube and around a reentrant section near the first pinhole. The short region between the end of the flow tube and the first pinhole is not efficiently pumped. Typical flow conditions ranged from ~600  $\mu$ mol s<sup>-1</sup> at 363

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FIG. 1. Diagram of discharge flow/mass spectrometer system.

K to  $\sim 800 \,\mu\text{mol s}^{-1}$  at 210 K of He carrier gas at 1 Torr pressure. The side arms each contained a microwave discharge (2450 MHz) for generation of atomic and free radical species. The walls of the discharge used to form chlorine atoms were coated with H<sub>3</sub>PO<sub>4</sub> to minimize atom recombination. The discharge used to produce the SO radical was connected to a flow bypass system desribed below. The walls of this discharge tube as well as the walls of the flow tube itself were left uncoated.

The flow tube pressure was monitored at the center of the flow tube reaction zone using a capacitance manometer (MKS Baratron, model 222, 10 Torr head). Helium carrier gas flows and reagent flows ( $SO_2$ ,  $NO_2$ , NO,  $Cl_2$  all diluted in He) were measured by separate flow controllers (ASM International N.V., model AFC-260). Small corrections to the indicated flow rates for the dilute reagent flows were made to allow for the contribution of reagents to the heat capacity of the dilute mixtures.

The flow tube was cooled by pumping etyhyl alcohol through the jacket surrounding the tube. Cooling was provided by a low temperature bath/circulator (Neslab Instruments, Inc., model ULT-80). In a similar fashion heating was achieved with a mixture of ethylene glycol and water which was heated and circulated through the outer jacket by a high temperature bath/circulator (Neslab Instruments, Inc., Model EXACAL EX-250 HT). The temperature of the flow tube was measured with a thermocouple/indicator (Doric model DS-350) equipped with a copper-constantan thermocouple in contact with the cooling/heating jacket. The flow tube and jacket were insulated with several layers of "no drip" with a final layer of 15 mm thick foam rubber. Lines leading from the cooling and heating baths to the flow tube were similarly insulated. The difference between the bath temperature and flow tube temperature was always <10 °C. Temperature fluctuations at the flow tube were observed to be  $< \pm 1$  °C.

#### Sampling system and mass spectrometer

A two-stage stainless-steel collision free sampling system was designed and assembled based on those constructed by Clyne and co-workers.<sup>4,7-9</sup> Efficient collision-free sampling of the contents of the flow tube was achieved by use of two collinear pinholes which were 2 cm apart. Both pinholes were drilled in demountable stainless-steel disks, the first having a diameter of 1.5 mm and the second a diameter of 1.75 mm. The residual background pressure in the ion source was  $\sim 10^{-8}$  Torr. At a flow tube presure of 1 Torr the ion-source pressure was  $10^{-6}$  Torr with a background pressure in the mass spectrometer chamber of  $10^{-7}$  Torr.

The two differential stages were constructed of stainless steel and all flanges were sealed by copper gaskets. Each stage was pumped by a 6 in. diffusion pump (CVC PMC S-6B, nominal pumping speed 550 cm<sup>3</sup> s<sup>-1</sup>). Back streaming was minimized by the Dri-Cap shield incorporated into the pump design. Both pumps were filled with polyphenylether fluid (Convalex 010) which has a low backstreaming rate, a low vapor pressure ( $\sim 2 \times 10^{-9}$  Torr at 298 K) and is resistant to electron bombardment and thermal decomposition. A freon-cooled chevron baffle (CVC BC61C + BC016A) was incorporated into the first stage and an automatically filled liquid nitrogen trap added to the second stage in order to minimize contamination of the mass spectrometer and walls of the chamber resulting from back diffusion. A molecular-sieve foreline trap was used to trap rotary-pump oil.

A quadrupole mass spectrometer (Extranuclear Laboratories, Inc.) was used in conjunction with an off-axis channeltron multiplier. Signals were passed through an amplifier discriminator (EG&G Model 1182) and ion counting performed using a photon counter (EG&G Model 1109). The quadrupole head was housed within a liquid-nitrogencooled copper shroud. This shroud was used during experimental runs and reduced the background signal by an order of magnitude, thus increasing the detection limit of the mass spectrometer.

### Production and calibration of SO and CIO radicals

SO radicals were generated in a microwave discharge (2450 MHz) of dilute mixtures of 1% SO<sub>2</sub> in He using the method of Clyne and MacRobert.<sup>4,7</sup> The SO radicals are detected at m/e = 48. Since dissociative ionization of SO<sub>2</sub> results in the formation of SO<sup>+</sup> it is necessary to work at low electron energies, i.e., energies below the appearance potential for SO<sup>+</sup> from SO<sub>2</sub>, to prevent this contributing to the m/e = 48 peak. The literature value<sup>10</sup> for the latter is  $16.5 \pm 0.5$ eV and consequently all measurements were made at electron energies less than or equal to 16 eV. The lower limit to detection of SO was  $\sim 5 \times 10^9$  cm<sup>-3</sup> at a signal-to-noise ratio of 1:1. The discharge in SO<sub>2</sub> also produces smaller concentrations of O and S atoms which must be removed to prevent kinetic complications due to the occurrence of the rapid reactions  $O + NO_2^{-1}$  and  $S + NO_2^{-11}$  in the SO + NO<sub>2</sub> experiments and the rapid reaction  $O + ClO^{12}$  in the SO + ClO experiments. Removal of residual O and S from SO<sub>2</sub> discharge was accomplished using a discharge-bypass system<sup>4,7</sup> which takes advantage of the unreactive nature of the SO radical. The bypass system consisted of a 200 ml recombination volume positioned downstream from the discharge with a bypass at the other end of the volume which carried a much larger flow (factor of 5 to 10) than that through the discharge. This results in a long residence time ( $\sim 1$  s) in the recombination volume and allows sufficient time for removal of the reactive O and S atoms. Removal of O was evidenced by the complete quenching within the recombination volume of the blue chemiluminescence due to the reaction  $O + SO^{M} \rightarrow SO^{*}$  when the bypass flow was increased to 5 to 10 times the flow through the discharge. Absolute concentrations of the SO radical were determined using the rapid titration reaction  $SO + NO_2 \rightarrow SO_2 + NO^{4-7}$  and measuring the decrease in the concentration of NO2 upon complete removal of SO by excess NO<sub>2</sub>.

ClO radicals were generated in the flow tube by the rapid reaction  $^{13}$ 

Cl + Cl<sub>2</sub>O→ClO + Cl<sub>2</sub>;  

$$k = (7.8 + 0.8) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$

The Cl atom concentration ( $\sim 1 \times 10^{14}$  cm<sup>-3</sup>) allowed complete removal of Cl<sub>2</sub>O within 0.5 ms. Absolute concentrations of the ClO radicals were determined by converting ClO to NO<sub>2</sub> using the rapid reaction NO + ClO $\rightarrow$ NO<sub>2</sub> + Cl<sup>1</sup> and measuring the concentration of NO<sub>2</sub> formed. No decay of ClO in the absence of SO was observed indicating the absence of O atom impurities from the Cl<sub>2</sub>/He discharge.<sup>12</sup> Also no reaction between SO and Cl<sub>2</sub>O was observed.

# Reagents

Helium (99.999% Ideal Gas) was dried at 77 K using a molecular sieve trap. SO<sub>2</sub> (99.98% Matheson) and Cl<sub>2</sub> (99.9% Matheson) were degassed at 77 K. NO<sub>2</sub> (99.5% Matheson) was purified by adding O<sub>2</sub> followed by trap to trap distillation at 196 K to remove O<sub>2</sub> and NO. A small

correction ( < 5%) was made to the NO<sub>2</sub> flow rate to account for the rapid dissociation of the N<sub>2</sub>O<sub>4</sub> dimer. Cl<sub>2</sub>O was prepared *in situ* using a variation of the method of Shack and Lindahl.<sup>14</sup> Cl<sub>2</sub>/He mixtures were flowed ( $< 5 \mu$ mol s<sup>-1</sup>) through a 30×1 cm column of yellow MgO (99.9%, Mallinckrodt) which was heated to  $\approx 340$  K. The resultant Cl<sub>2</sub>O/Cl<sub>2</sub>/He mixture was then allowed to flow directly into the flow tube.

## RESULTS

Rate constants for reactions (1) and (2) were determined under pseudo-first-order conditions with  $[SO]_0 < [X]_0$ 



FIG. 2. Kinetics of the SO + NO<sub>2</sub> reaction at 298 K. (a) Typical first order logarithmic decay plots of SO in the presence of various excess concentrations of NO<sub>2</sub> ( $10^{12}$  cm<sup>-3</sup>): 0, 20.62; •, 8.52; and  $\blacktriangle$ , 6.39. (b) Summary plot of pseudo-first-order rate constant k' with [NO]<sub>2</sub> mean.

$$\ln\left(\frac{[SO]_0}{[SO]}\right) = k't = k [X]t.$$

The pseudo-first-order rate constant k' was corrected for axial diffusion of SO in the helium carrier gas. Also a small stoichiometric correction to [X] to allow for depletion of X was made:

$$[X]_{mean} = [X]_0 - [SO]_0/2$$
.

The rate constant for the SO + NO<sub>2</sub> reaction was determined over the temperature range 210-363 K with  $[NO_2]_0 > [SO]_0$ . NO<sub>2</sub> was added at reaction times ranging

TABLE I. Rate data for the  $SO + NO_2$  reaction.

from 2–20 ms. Table I summarizes the experimental conditions employed. The initial stoichiometries  $[NO_2]_0/[SO]_0$ ranged from 6 to 25. Figure 2(a) shows typical logarithmic decay plots of [SO] vs time which are linear over a tenfold decay of SO. An intercept was observed at each of the temperatures which extrapolates to a common origin at about -1.0 ms and was 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 have been seen in discharge flow-mass spectrometer systems previously.<sup>4,15</sup> Figure 2(b) shows the variation of the pseudo-

	Temp	[ <b>S</b> O]。	[NO <sub>2</sub> ]		k			
Run	(K)	$(10^{12} \text{ cm}^{-3})$	$(10^{12} \mathrm{cm}^{-3})$	$(s^{-1})$	$(10^{-11} \mathrm{cm}^3 \mathrm{s}^{-1})$			
<u> </u>	200	1.57	20.62	240	1 21			
2	298	1.57	17.24	275	1 31			
3		1.32	15 52	210	1 35			
4		1.32	13.75	189	1.35			
5		1.18	12.01	171	1.57			
6		1.16	10.80	148	1.44			
7		0.97	8 52	127	1.49			
8		0.95	7.62	106	1.39			
9		1.56	9.02	125	1.39			
10		1.56	12.92	174	1.34			
11		2 14	14 53	188	1.29			
12		2.14	13.55	172	1.27			
13		1.99	12.60	164	1.30			
14		1.85	11.77	160	1.36			
15		1.17	8.21	121	1.47			
16		1.42	8 99	132	1.47			
17		1.42	10.02	137	1 37			
18		1.55	10.80	150	1 38			
10		0.83	6 39	92	1.50			
17		mean value $= (1.3)$	$7 \pm 0.07 \times 10^{-11} \text{ cm}^3 \text{ s}$	$^{-1}(1\sigma)$	1.14			
20	363	0 44	10 38	123	1.25			
21	505	0.44	8.96	117	1 31			
21		0.40	7.21	88	1.22			
22		0.40	5.45	71	1 30			
24		0.39	3 68	51.6	1.60			
24		0.38	2.81	38.8	1 38			
26		0.38	4 57	63	1 38			
20		0.38	6.43	91	1.50			
2.		mean value $= (1.3)$	$3 \pm 0.07$ × 10 <sup>-11</sup> cm <sup>3</sup> s	$-1(1\sigma)$	1.12			
28	248	0.34	5.25	76	1.45			
29		0.35	6.08	91	1.50			
30		0.40	7.75	117	1.51			
31		0.34	6.94	103	1.48			
32		0.67	16.93	226	1.34			
33		0.60	15.27	223	1.46			
34		0.50	11.94	166	1.39			
35		0.40	8.60	120	1.40			
36		0.60	13.58	201	1.48			
37		0.47	10.26	143	1.39			
		mean value $= (1.4)$	$4 + 0.05 \times 10^{-11} \text{ cm}^3 \text{ s}$	$^{-1}(1\sigma)$				
38	210	0.62	11.13	142	1.28			
39		0.48	8.41	113	1.34			
40		0.40	8.45	107	1.27			
41		0.42	7.05	100	1.42			
42		0.41	5.65	76	1.34			
43		0.40	4.27	60	1.41			
44		0.66	4.29	61	1.42			
45		0.66	5.06	70	1.38			
46		0.81	7.30	96	1.32			
47		0.74	8.87	112	1.26			
48		1.00	10.30	134	1.30			
		mean value $= (1.3)$	$4 \pm 0.06$ ) × 10 <sup>-11</sup> cm <sup>3</sup> s	$(1\sigma)$				
overall mean value = $(1.37 \pm 0.07) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} (1\sigma)$								

first-order rate constant  $k'_1 = -d \ln[SO]/dt$  with  $[NO_2]_{mean}$  at 298 K and shows good second-order behavior. No intercept on the ordinate was observed at the temperatures employed. The rate constant was thus determined as a mean of the data and found to be invariant with temperature. The 48 determinations (Table I) gave a mean temperature independent value of  $k_1 = (1.37 \pm 0.07) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> (1 $\sigma$ ). Allowing for possible systematic error in flow rates, pressure, and reactant concentration gives the value



FIG. 3. Kinetics of the SO + ClO reaction. (a) Typical first-order logarithmic decay plots of SO at 298 K in the presence of various excess concentrations of ClO  $(10^{12} \text{ cm}^{-3}):\bullet, 1.44; \blacktriangle, 2.10; \blacksquare, 4.71; \text{ and O}, 7.44.$  (b) Summary plot of pseudo-first-order rate constant k' with [ClO] mean at 298, 248, and 363 K.

$$k_1 = (1.37 \pm 0.10) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$$
.

The rate constant for the SO + ClO reaction was measured over the temperature range 248-363 K with  $[ClO]_0 > [SO]_0$ . ClO was generated at reaction times from 2 to 20 ms. Initial stoichiometries  $[ClO]_0/[SO]_0$  ranged from 2 to 21. Figure 3(a) shows several typical logarithmic decay plots of [SO] vs time at 298 K which display good linearity over an order of magnitude decay in [SO]. As in the case of the  $SO + NO_2$  experiments, a similar dead time was observed. Figure 3(b) shows the dependence of the pseudofirst-order rate constant k' on [ClO] at 248, 298, and 363 K. Good second-order behavior is obtained with a small positive intercept of 22 s<sup>-1</sup>. The latter is attributed to loss of SO on the wall of the flow tube. The fact that the data from all three temperatures fit on a single line [Fig. 3(b)] suggests that the rate constant is independent of temperature in the range 248-363 K. This can also be seen in Table II which summarizes the results from 54 experiments. The rate constant was then determined from the slope of the line in Fig. 3(b) using least squares analysis. This gives a mean temperature independent value of

$$k_2 = (3.22 \pm 0.48) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}(1\sigma)$$
.

Efforts were made to extend the temperature range down to 210 K. Sensitivity for the SO radical was similar to that for experiments at the other temperatures. However sensitivity changes occurred during experimental runs resulting in nonlinear exponential decays. This was confirmed to be a sensitivity problem as the SO signal in the absence of CIO was lower at the end of the run than it was at the beginning.

## DISCUSSION

The value for  $k_1$  (298 K) obtained here, (1.37  $\pm 0.10$ )×10<sup>-11</sup> cm<sup>3</sup> s<sup>-1</sup>, is in excellent agreement with the recent absolute measurements of Clyne and Mac Robert,<sup>4</sup> (1.36  $\pm 0.10$ )×10<sup>-11</sup> cm<sup>3</sup> s<sup>-1</sup>, and Black *et al.*,<sup>5</sup> (1.48  $\pm 0.20$ )×10<sup>-11</sup> cm<sup>3</sup> s<sup>-1</sup>, as well as the earlier relative measurement of Clyne *et al.*<sup>6</sup> (1.4×10<sup>-11</sup> cm<sup>3</sup> s<sup>-1</sup>). The SO + NO<sub>2</sub> reaction thus serves as a reference reaction at 298 K and establishes the quantitative validity of the measurement of rate constants using the newly assembled discharge flow-mass spectrometry apparatus in our laboratory. The present experiments also demonstrate that the rate of reaction (1) is independent of temperature over the range 210– 363 K. This is not unexpected for a rapid reaction such as SO + NO<sub>2</sub>→SO<sub>2</sub> + NO.

Our results for the radical-radical reaction SO + ClO  $\rightarrow$ SO<sub>2</sub> + Cl may be compared with the only other measurement of this reaction. Clyne and MacRobert<sup>7</sup> used the same technique to obtain  $k_2 = (2.3 \pm 0.6) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>. Our mean value is somewhat higher,  $k_2(3.22 \pm 0.48) \times 10^{-11}$ cm<sup>3</sup> s<sup>-1</sup>, but the two values do overlap within the stated error limits. The temperature invariance of  $k_2$  observed in the present experiments is again not surprising, especially since  $k_2$  is at least twice as fast at  $k_1$  which was also found to be independent of temperature.

Our results for SO + ClO may also be compared to those for other radical-radical reactions involving SO or

ClO. Jourdain et al.<sup>16</sup> studied the reaction

$$SO + OH \rightarrow SO_2 + H$$
 (5)

and determined  $k_5$  (298 K) =  $(8.4 \pm 1.5) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>. This is a rapid reaction, its rate constant being 2 to 3 times faster than SO + ClO. The radical-radical reactions involving ClO with which our results for ClO + SO may be compared include: ClO + OH, ClO + HO<sub>2</sub>, and ClO + BrO. These reactions are 2.5 to 6 times slower than reaction (2),

having k (298 K) values of  $1.2 \times 10^{-11}$ ,  $5.0 \times 10^{-12}$ , and  $6.7 \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup>, respectively.<sup>1</sup> These reactions have either a slight negative temperature dependence (ClO + OH, ClO + HO<sub>2</sub>) or no measurable temperature dependence (ClO + BrO). This may be compared to the negligible temperature dependence observed in the present study for the reaction ClO + SO.

The results of the present temperature dependent study of the reactions of the SO radical with  $NO_2$  and ClO are

-

TABLE II. Rate data for the SO + ClO reaction.

	Temp.	[SO] <sub>0</sub>	[ClO]	$k'-k_{w}$	k		
Run	(K)	$(10^{12} \mathrm{cm}^3)$	$(10^{12} \text{ cm}^{-3})$	$(s^{-1})^{-1}$	$(10^{-11} \mathrm{cm}^3 \mathrm{s}^{-1})$		
1	298	0.71	3.18	90	2.83		
2		0.71	2.10	48	2.28		
3		0.64	3.97	115	2.90		
4		0.67	3.62	107	2.96		
5		0.25	5.27	210	4.10		
0		0.00	4./1	135	2.87		
/		0.09	5.32	157	2.95		
8		0.71	6.09	180	3.05		
19		0.65	0.59	210	3.19		
10		0.64	0.85	219	3.20		
11		0.03	/.44	234	3.15		
12		0.42	4.//	155	3.23		
13		0.42	7.09	182	3.13		
14		0.40	5.23	182	3.48		
15		0.44	3.78	135	3.37		
10		0.31	2.11	109	3.20		
19		0.35	3.11	100	3.21		
10		0.34	2.63	92	3.23		
20		0.31	2.41	07 71	2 20		
20		0.30	2.15	71 61	3.30		
21		0.28	1 20	45	3.02		
22		0.27	9.95	201	3.24		
23		0.42	3.00	131	3.29		
25		1.02	6 10	104	3.13		
26		1.02	7 27	241	3 31		
20		1.00	9.42	241	3.16		
28		1.10	12.92	405	3 13		
29		0.44	5 12	208	4.06		
30	248	0.51	1 76	53	3.01		
31	210	0.61	3 51	138	3 93		
32		0.64	3 21	125	3.89		
33		0.59	2.98	116	3.89		
34		0.55	2.59	99	3.87		
35		0.53	2.35	86	3.66		
36		0.51	2.13	73	3.43		
37		0.52	1.78	58	3.26		
38		0.51	1.41	41	2.91		
39		0.51	1.39	38	2.73		
40		0.51	1.16	29	2.50		
41		0.50	1.67	59	3.53		
42	363	0.83	1.15	30	2.56		
43		0.81	1.48	30	2.01		
44		0.80	1.69	40	2.36		
45		0.79	1.88	56	2.96		
46		0.77	2.20	68	3.09		
47		0.80	2.28	77	3.39		
48		0.75	2.56	80	3.11		
49		0.75	2.73	115	4.21		
50		0.76	3.27	126	3.85		
51		0.77	3.77	140	3.71		
52		0.76	2.35	81	3.46		
53		0.75	2.30	76	3.32		
54		0.76	1.95	62	3.16		
mean value = $(3.22 \pm 0.48) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} (1\sigma)$							

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particularly applicable to the chemistry of the upper atmospheres of Earth and Venus. The lack of an observed temperature dependence for the rate constants of these reactions means that these data can confidently be employed in models describing such low temperature (200–270 K) atmospheric systems.<sup>2,3</sup> A better understanding of the role of SO in the atmospheric chemistry of Earth and Venus depends on measurements of rate parameters for the pertinent SO reactions at stratospheric temperatures.

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