RATE COEFFICIENTS AT 298 K FOR SO REACTIONS WITH 02, 03, AND NO2

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SO₂ photodissociation at 193 nm (ArF excimer laser) has been used to create SO radicals; the chemiluminescence from the SO + O₃ reaction has been used to follow the SO radical decay. Rate coefficients at 298 K of (1 07 ± 0.16) × 10⁻¹⁶, (1 06 ± 0 16) × 10⁻¹³, and (1 48 ± 0 20) × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ were measured for the reactions of SO with O₂, O₃, and NO₂, respectively.

1 Introduction

Crutzen [1] has suggested that the industrial release of OCS may significantly contribute to the sulfate layer in the stratosphere. In the stratosphere, OCS will be photodissociated to produce sulfur atoms, which are then oxidized to form SO radicals. SO is then oxidized to SO₂ by reaction with O₂ or O₃,

$$SO + O_2 \rightarrow SO_2 + O, \tag{1}$$

$$SO + O_3 \rightarrow SO_2 + O_2. \tag{2}$$

The room temperature rate of reaction (2) has recently been determined [2] as $(8.7 \pm 1.6) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹, in satisfactory agreement with the earlier work of Halstead and Thrush [3] who studied the reaction in the temperature range 275–320 K. Extrapolation of their results to a stratospheric temperature of 230 K gives a rate coefficient of 2.5×10^{-14} cm³ molecule⁻¹ s⁻¹.

Unfortunately, the situation for reaction (1) is much less satisfactory. No measurements have been made at room temperature or below. Breckenridge and Miller [4] have obtained an upper limit of 8 $\times 10^{-17}$ cm³ molecule⁻¹ s⁻¹ at 297 K. Extrapolations [5,6] of measurements at higher temperatures (>440 K) give rate coefficients of 1.3 and 2.2 $\times 10^{-17}$ cm³ molecule⁻¹ s⁻¹ at 297 K.

Because SO reacts very rapidly with several other stratospheric species (NO₂, OH, ClO) [7-9], it is im-

portant to measure the rate coefficients of reactions (1) and (2) from room temperature down to stratospheric temperatures. Only then will it be possible to estimate the perturbation in the chemistry of the stratosphere due to SO radicals. The work described below is the first measurement of the rate coefficient of reaction (1) at room temperature. In addition, we also remeasured the rate coefficient of reaction (2) at room temperature.

2. Experimental

Because the previous work [4] was limited to O_2 pressures of a few Torr, because of the nature of the afterglow systems used to generate the SO, the present work used ArF laser photodissociation of SO₂ to produce SO:

$$SO_2 + h\nu(193 \text{ nm}) \rightarrow SO(X^3\Sigma^-) + O(^3P).$$
 (3)

As far as the authors know, this is the first application of this technique to prepare SO and study its kinetics. At 193 nm, SO₂ has a high cross section $(1.1 \times 10^{-17} \text{ cm}^2)$ and there is insufficient energy to produce any excited states. The experiment could be done in the presence of several hundred Torr of O₂ because of the very weak absorption by O₂ at 193 nm (a value of $1.4 \times 10^{-22} \text{ cm}^2$ measured). Most experiments were performed with an SO₂ pressure of 30 mTorr, which produced half attenuation of the

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ArF beam over the 74 cm length of the cell.

The experiments were performed in a metal cell having three sets of orthogonal sidearms. One set, equipped with Brewster angle suprasil windows, transmitted the ArF laser radiation (Lambda Physik EMG 101) through the cell. The second set was equipped with a filter-photomultiplier combination, and the third set used a monochromator and photomultiplier to record emissions excited in the cell. A mercury lamp was mounted opposite the monochromator so that O₁ concentrations in the cell could be determined by 253.7 nm absorption. The output of the filtered photomultiplier was passed through an amplifierdiscriminator before being recorded on both a ratemeter-pen recorder system and an MCA (ND 100) used in the multichannel scaling mode The MCA was triggered from the excimer laser so that the temporal decay of emissions produced in the cell could be recorded. Then we made a semilog plot of intensity (counts in each channel) versus time using a log amplifier and a Hewlett–Packard X - Y recorder (model 7004B) with point plotting attachment. The filter-isolated emission was measured in the 410-500 nm region, although some measurements were also made in the 320-390 nm region. The cell was equipped with Baratron pressure gauges covering the 0-1, 0-100, and 0-1000 Torr ranges. The residence time of the gas in the cell was ≈ 10 s.

3. Results

In mixtures containing both SO_2 and O_2 a twocomponent decay was observed. The fast initial decay comes from the chemiluminescent reaction [10]

$$O + SO + M \rightarrow SO_2^*, \tag{4}$$

SO₂^{*}(
$$\widetilde{C}^{1}B_{2}, \widetilde{B}^{1}B_{1}, \widetilde{a}^{3}B_{1}$$
) → SO₂($\widetilde{X}^{1}A_{1}$)
+ hv(225–500 nm) (5)

For O₂ pressure \geq 50 Torr used in the present experiments, the lifetimes of the emitting states are $\leq 4 \mu s$ [11]. Hence, for the much longer-lived emission observed in these experiments, the decay of the emission is not determined by the lifetimes of the emitting states but instead is determined by the decay of the precursor species. The fast initial decay is mainly due

to the removal of O atoms by the reaction

$$0 + O_2 + M \rightarrow O_3 + M$$
 (M = O₂, He). (6)

The final slower decay arises from the chemiluminescent reaction

$$\mathrm{SO} + \mathrm{O}_3 \to \mathrm{SO}_2^* + \mathrm{O}_2,$$
 (7)

$$\mathrm{SO}_{2}^{*}(\widetilde{\mathrm{B}}^{1}\mathrm{B}_{1},\widetilde{\mathrm{a}}^{3}\mathrm{B}_{1}) \rightarrow \mathrm{SO}_{2} + h\nu(290-500 \text{ nm}), \qquad (8)$$

and predominantly reflects the much slower removal of SO. To remove any effects due to diffusive loss of O_3 , a small pressure of O_3 ($\approx 10 \text{ mTorr}$) was added to the SO_2/O_2 mixture.

The above scenario was confirmed in three major ways First, the initial decay was found to exhibit the predicted dependence on $[O_2]^2$, or $[O_2][M]$ for fixed O_2 and variable [M]. The decay rate was in good agreement with that expected [5] for reaction (6). Second, measurements in an SO₂/NO mixture with He buffer gave only a single decay (because no O_3 could be formed) with decay rates in good agreement with those expected for O + NO + He [12]. These measurements were made in the 320–390 nm region to avoid any interference from NO₂ chemiluminescence. Third, adding the small pressure of O_3 enhanced the intensity of the slow final decay with little effect on its decay rate.

Hence, to determine the rate coefficient for reaction (1), we measured the decay rate of the slower final component as a function of O_2 pressure. This



Fig. 1. SO decay rate versus O_2 . \triangle oxygen only; \circ oxygen + 100 Torr He; \square oxygen + 500 Torr He [SO₂] \approx 30 mTorr; [O₃] \approx 10 mTorr.



Fig 2. SO decay rate versus O_3 . [He] = 500 Torr; [SO₂] \approx 30 mTorr.

work represents the second study in which timeresolved observations on the SO_2 chemiluminescence from the $SO + O_3$ reaction have been used to obtain rate data [2] The results are shown in fig. 1. Data



Fig 3. SO decay rate versus NO₂. [He] = 100 Torr; [SO₂] \approx 30 mTorr; [O₃] \approx 20 mTorr.

were obtained for O_2 pressures up to 500 Torr in the presence of up to 500 Torr He. A rate coefficient of $(1.07 \pm 0.16) \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹ was determined for reaction (1) at 298 K. The measurements were made with two different grades of O_2 , 99.6 and 99.99%, to be sure that the observed SO removal was due to reaction (1) and not an impurity in the O_2 . As further confirmation of the technique and results obtained in this work, rate coefficients for reaction (2) and the reaction

$$SO + NO_2 \rightarrow SO_2 + NO$$
 (9)

have also been measured at 298 K. The results are shown in figs. 2 and 3 and give rate coefficients of $(106 \pm 0.16) \times 10^{-13}$ and $(1.48 \pm 0.20) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ for reactions (2) and (9) respectively.

4. Discussion

From fig 1 it is clear that there is no evidence for a three-body reaction. Hence, the rate coefficient for

$$SO + O_2 + M \rightarrow SO_3 + M$$
 (M = O_2 , He) (10)

is $\leq 10^{-36}$ cm⁶ molecule⁻² s⁻¹ and does not play a role in the stratospheric chemistry of SO. Perhaps this is not surprising because SO₃ is a symmetrical molecule and the reaction would involve both breaking the O-O bond and forming two S-O bonds. One might speculate on the possibility of three-body formation of an unsymmetrical SO O₂ molecule that could further react with O₂

$$SO + O_2 + M \rightarrow SO O_2 + M, \tag{11}$$

$$SO O_2 + O_2 \rightarrow SO_2 + O_3.$$
 (12)

Because no evidence for a three-body reaction is found it appears likely that $SO \cdot O_2$ is very weakly bound and reaction (12) does not occur.

Our rate coefficient for reaction (1) is slightly higher than the upper limit given by Breckenndge and Miller [4] and considerably higher than values obtained by extrapolation [5,6]. However, the two extrapolations are from measurements at much higher temperatures (440-2100 K) and are therefore of limited use in predicting rate coefficients at 287 K. Because of the low laser powers incident on the cell ($\leq 0.1 \text{ mJ}$ / pulse), the lack of dependence of the decay rates on SO_2 pressure (and hence SO density), and the pseudo first-order decays, contributions from processes second-order in SO such as

$$SO + SO + M \rightarrow (SO)_2 + M \tag{13}$$

with a rate coefficient [13] of 44×10^{-31} cm⁶ molecule⁻² s⁻¹ (for M = N₂) do not significantly contribute to the observed decays Although the possibility of an impurity in the O₂ appears to have been ruled out by the use of two different punties of O₂, final proof will come from comparing the measured activation energy of reaction (1) in this experiment with the activation energy of reaction (1) determined at higher temperatures (a fast reacting impurity would have a much lower activation energy). Such work is planned for the near future.

The rate coefficients for reactions (2) and (9) are in good agreement with recent measurements [2,7] of $(8.7 \pm 1.6) \times 10^{-14}$ and $(1 \ 3 \pm 0.10) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ respectively. For the NO₂ measurement it was found necessary to limit the O₃ addition to ≤ 20 Torr Higher O₃ additions gave rise to an apparently reduced rate coefficient, which probably reflects the removal of NO₂ by the reaction

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{14}$$

that has [12] a rate coefficient of $\approx 8 \times 10^{-17} \text{ cm}^3$ molecule⁻¹ s⁻¹.

It appears, therefore, that the technique described

above is capable of measuring rate coefficients of SO reactions relevant to stratospheric chemistry. Future work will be directed towards determining the temperature dependences of reactions (1) and (2) down to stratospheric temperatures.

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