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A Stop-Flow Time-of-Flight Mass Spectrometry Kinetics Study. Reaction of Ozone with Nitrogen Dioxide and Sulfur Dioxide

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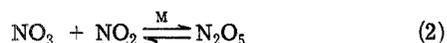
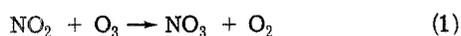
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Rate constants for the reaction of ozone with nitrogen dioxide have been determined over the temperature range 260–343°K. The technique employed was that of stop-flow TOF mass spectrometry. All measurements were carried out using nitrogen dioxide in large excess over ozone, 10 to 1 or greater. Over the indicated temperature range the data could be fit to the simple Arrhenius expression $k_1 = (9.01 \pm 0.81) \times 10^{-14} \exp(-4824 \pm 230 \text{ cal mol}^{-1}/RT)$. Units are $\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. A more limited investigation of the analogous reaction between ozone and sulfur dioxide indicated that this reaction was extremely slow, having a k value $\leq 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ at 300°K.

Introduction

The mechanism for conversion of NO_2 to N_2O_5 via reaction with O_3 is now considered to be important to our understanding of atmospheric nitrogen chemistry. The reaction has been found to occur in two steps²



In spite of the apparent importance of this reaction, there appears to be significant disagreement on the value of the rate constant at 298°K²⁻⁶ and only very limited temperature dependence data.² Due to this fact, we have initiated a new investigation of reaction 1 using the relatively new technique of stop-flow time-of-flight mass spectrometry. The temperature range covered was 260–343°K. The results obtained in the present study are compared with literature values as available.

Experimental Section

A schematic diagram of the stop-flow time-of-flight mass spectrometer system is shown in Figure 1. The principal components of this system are (1) two 2-l. sample bulbs, one filled with an O_3 -He mixture, the other with NO_2 -He; (2) a solenoid valve on each of two flow lines, the opening and closing time being controlled by a timer switch; (3) a Pyrex temperature jacketed reaction cell fitted

with a molecular leak; and (4) a time-of-flight mass spectrometer for purposes of monitoring O_3 or NO_2 as a function of time. Details on each of these components are given below.

The 2-l. sample bulbs were typically filled to a total pressure of 15 Torr and could be used for five or six experiments without a significant change in pressure ($\sim 7\%$). In most experiments the total pressure in the reaction cell was 3 Torr. To minimize the problem of photodecomposition, the NO_2 sample bulb was blackened and all experiments were carried out without direct overhead room lighting.

The stainless steel solenoid valves were operated through a timer control box whose range was variable from 0.1 to 10 sec. In most experiments carried out in this study, a 0.5-sec opening cycle was employed. Flow conditions, especially mixing times, were determined by using sample bulbs containing test mixtures of Ar-He and O_2 -He. In these tests, the mixing time was defined by the time required for the minor gases Ar and O_2 to reach 95% of their maximum ion intensity as measured on a high-speed visicorder print out. These mixing tests were performed at several different temperatures and over a concentration range of Ar and O_2 which overlapped the concentrations of NO_2 and O_3 employed. With the timer control set at 0.5 sec (uncertainty $\pm 10\%$), the observed mixing time was typically < 1 sec. For a setting of 3 sec, a mixing time of < 5 sec was observed.

The Pyrex reaction cell was 1.5 in. in diameter and 3.5 in.

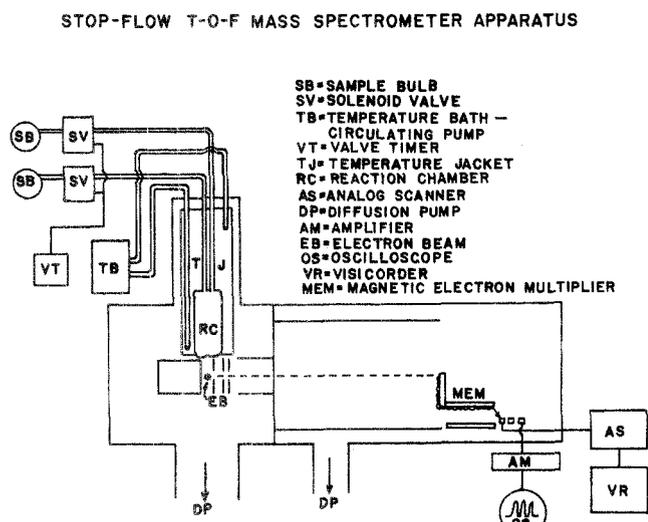


Figure 1. Schematic drawing of the stop-flow TOF mass spectrometer system.

in length. Surrounding the entire reaction cell was a temperature jacket through which either a heating or cooling fluid could be circulated. The temperature of the heating or cooling fluid was controlled through the use of a Lauda Model K-4/R temperature controller-circulator. In all cases, the temperature was maintained to within $\pm 0.5^\circ$. To ensure that the reactant gases were temperature equilibrated before mixing, the temperature jacket on the reaction cell was extended ~ 4.5 in. above the top of the cell. Both flow lines were made to pass through this extended temperature jacket (see Figure 1). The molecular leak on the Pyrex cell was approximately 95μ in diameter and was positioned 2.5 cm above the electron beam of the mass spectrometer.

The mass spectrometer used in this study was a Bendix Model 14 time-of-flight instrument which was updated with a Mark IV retro-fit kit. The instrument was also modified to include a differential pumping station on the ion source, permitting operating pressures in the reaction cell as high as 10 Torr. (Typically, the ion source region was held at a pressure of 10^{-5} Torr or lower and the flight tube was operated at pressures of less than 2×10^{-6} Torr.) A final modification consisted of the installation of a predynode gating module which was used to eliminate any possible saturation of the electron-magnetic multiplier by the diluent gas He. The print out for the mass spectrometer was a Honeywell visicorder. In all experiments, the electron beam energy of the mass spectrometer was set at either 20 or 70 eV.

In a typical experiment 3–21 mTorr of O_3 was mixed with 40–400 mTorr of NO_2 . The concentration of NO_2 was in all cases 10–50 times greater than that of O_3 ; hence, the observed kinetics were pseudo-first order throughout the reaction. The exact initial concentration of NO_2 in an experimental run was determined from test runs made immediately before and after an experiment. In these test runs only NO_2 and He were injected into the reaction cell. The agreement between these two measurements was typically 6% or better. Calibration of the mass spectrometer for NO_2 was carried out at least twice a day; however, in general, it was found that the day to day variation in the sensitivity of the instrument for NO_2 was 3% or less. The concentration of NO_2 used in calculating the absolute bimolecular rate

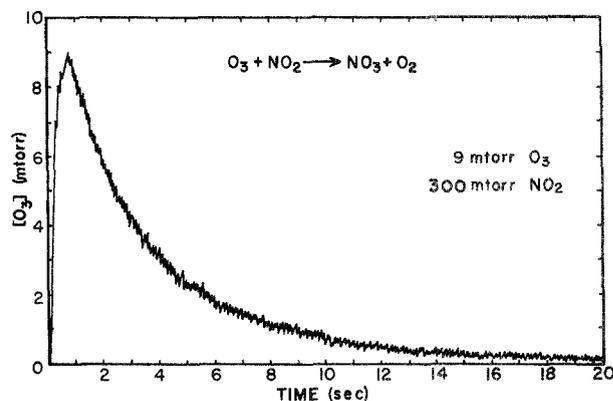


Figure 2. Typical O_3 decay curve in the presence of NO_2 : $[O_3] = 9$ mTorr, $[NO_2] = 300$ mTorr.

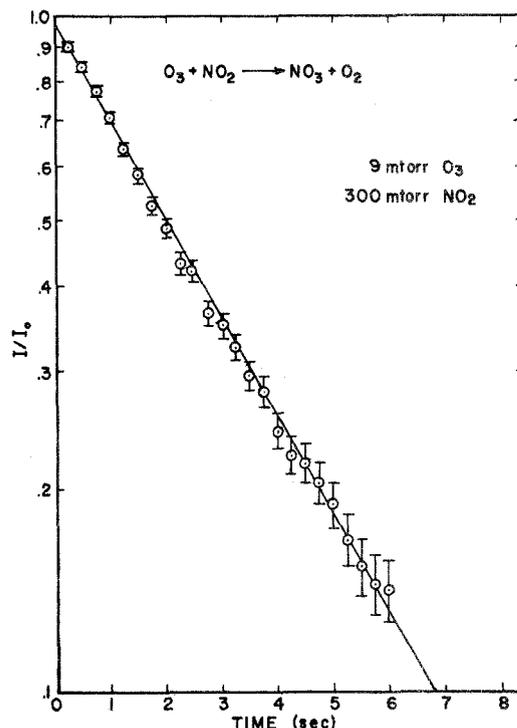


Figure 3. First-order plot of the O_3 decay curve shown in Figure 2.

constant was taken as the average of the initial and final concentrations. The final concentration of NO_2 was determined by taking a stoichiometric factor of 2 for the number of NO_2 molecules consumed per O_3 molecule reacted.⁷ It should be pointed out, however, that since the change in NO_2 concentration was small in a given experiment, the calculated bimolecular rate constant was rather insensitive to the value of the stoichiometric factor chosen.

A typical O_3 decay curve is shown in Figure 2, and the corresponding semilogarithmic plot showing first-order kinetic behavior is illustrated in Figure 3. The major uncertainties in these experiments were those resulting from the evaluation of the average concentration of NO_2 ($\pm 4\%$), and the graphical determination of the first-order rate constant from Figure 3, $\pm 5\%$. The probable error in individual measurements is therefore on the order of $\pm 7\%$. (The loss of reactants due to diffusion out of the reaction cell was negligible when compared to the loss rate due to reaction.)

Materials used in this study included Ultra-High Purity Gold labeled oxygen (99.95%) and helium (99.999%) sup-

TABLE I: Rate Constants for the Reaction of Ozone with Nitrogen Dioxide

<i>T</i> , °K	[O ₃], mTorr	[NO ₂], mTorr	<i>k</i> ₁ , sec ⁻¹	<i>k</i> , cm ³ molecule ⁻¹ sec ⁻¹
260	6	109	0.039	(9.13 ± 0.72) × 10 ⁻¹⁸
	10	150	0.053	
	12	206	0.072	
	18	260	0.095	
	12	336	0.106	
278	4	110	0.059	(1.51 ± 0.12) × 10 ⁻¹⁷
	11	181	0.097	
	8	202	0.115	
	16	275	0.138	
	16	313	0.165	
	8	332	0.169	
	24	364	0.195	
303	6	79	0.092	(3.42 ± 0.27) × 10 ⁻¹⁷
	4	108	0.111	
	6	131	0.150	
	8	158	0.185	
	8	175	0.194	
	8	253	0.280	
	8	332	0.374	
	12	333	0.361	
	24	347	0.371	
	8	364	0.400	
	8	406	0.460	
323	4	74	0.122	(5.41 ± 0.43) × 10 ⁻¹⁷
	8	130	0.210	
	8	179	0.310	
	8	199	0.308	
	24	224	0.367	
	8	248	0.414	
	30	338	0.532	
	30	338	0.532	
343	13	95	0.217	(8.15 ± 0.65) × 10 ⁻¹⁷
	4	139	0.341	
	15	165	0.384	
	23	194	0.434	
	30	267	0.606	

plied by the Matheson Co. These gases were used without further purification. Ozone was made by passing pure oxygen through an Orec Corp. ozonator at a flow rate of 14 cc/min. The ozone was trapped and stored on silica gel in a glass vessel at the temperatures of a trichloroethylene-Dry Ice slush bath. A uv analysis of the ozone at 2600 Å (ϵ 130 cm⁻¹ atm⁻¹) indicated a typical purity level of 94%. Matheson nitrogen dioxide was used after being mixed with a large excess of oxygen to convert traces of nitric oxide to nitrogen dioxide. Repeated degassings at 77 and 195°K were then used to remove the unreacted O₂. An infrared analysis of the purified NO₂ showed the NO level to be <0.05%.

Pressure measurements in the range of 1–1000 mTorr were made using an MKS type 90H Baratron head. Higher pressures were measured either with a dibutylphthalate oil manometer or a Wallace & Tiernan absolute pressure gauge. At the bulb pressures used in these experiments (>100 mTorr), both the precision and accuracy of the pressure measurements were 2% or better.

The possible formation of the dimer,⁸ N₂O₄, *i.e.*



was considered for all temperatures employed in this study. Corrections were applied to the average value of the [NO₂] whenever the magnitude of such corrections approached the 2% level.

Results and Discussion

The experimental data collected at temperatures of 260, 278, 303, 323, and 343°K are given in Table I. The bimolecular rate constants reported here were determined from the

slope of a plot of the pseudo-first-order rate constant *vs.* the NO₂ concentration (see Figure 4). At 303°K, the bimolecular rate was (3.42 ± 0.27) × 10⁻¹⁷ cm³ molecule⁻¹ sec⁻¹. Variations in the total pressure by a factor of 4 had no effect on the measured value of *k*₁. Figure 4 and Table I also show that changes in the concentration of O₃ from 4 to 30 mTorr produced no deviation in the *k*₁ *vs.* [NO₂] plot. In addition, Figure 4 indicates the absence of any significant quantities of reactive impurity (*e.g.*, NO) since all the plots of the pseudo-first-order rate constant against NO₂ extrapolated through zero.

Although the rate of formation of products from this reaction (NO₃ and N₂O₅) was of considerable interest (particularly with regard to an evaluation of the stoichiometric factor) the absence of parent ions for both NO₃ and N₂O₅ made these experiments impractical.

Over the temperature range of 260–343°K a least-squares fit of the data gave an Arrhenius expression of the form (see Figure 5)

$$k_{\text{bi}} = (9.01 \pm 0.81) \times 10^{-14} \times \exp(-4824 \pm 230 \text{ cal mol}^{-1}/RT)$$

Units are in cm³ molecule⁻¹ sec⁻¹. The error limits quoted above are for the temperature range of 260–343°K and are the standard errors from a least-squares treatment of the data. Outside the indicated temperature range, the errors in *A* and *E* were determined from a consideration of the maximum and minimum slopes which could be drawn through the error bars of the data presented in Figure 5.

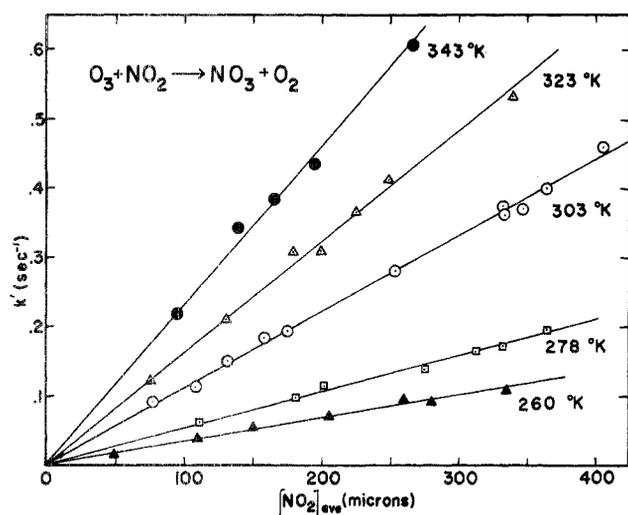


Figure 4. A plot of the pseudo-first-order rate constant vs. $[\text{NO}_2]$; ●, 343°K, △, 323°K, ○, 303°K, □, 278°K, and ▲, 260°K.

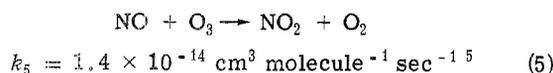
These errors were $\pm 2.7 \times 10^{-14}$ in A and ± 368 cal mol $^{-1}$ in the value of E .

Possible sources of systematic error in this experiment include decomposition of NO_2 on the walls of the sample bulbs and flow lines, and wall reactions in the reaction cell proper. As indicated in the Experimental Section of this paper, all NO_2 storage vessels in the laboratory were blackened and room lights were left off. Also, the entire network of storage bulbs flow lines and reaction cell were fabricated from Pyrex glass. In no case, was any evidence found which might have suggested the importance of wall reactions.

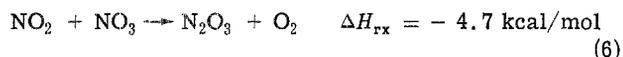
As discussed earlier, in the reaction of ozone with nitrogen dioxide the simple two step mechanism 1 and 2 has generally been accepted as correct⁴⁻⁶ and, thus, leads one to assign a value of 2 for the stoichiometric factor, $\Delta[\text{NO}_2]/\Delta[\text{O}_3]$. Several attempts have been made to evaluate this number^{3,6,9} but the uncertainties in these measurements still leave some doubt as to whether this number is actually 2 or possibly slightly lower. A stoichiometric number of less than 2 might result from reaction 2 not going to completion or from reaction 1 giving products different from those indicated, e.g.



Reaction 4 could then be followed by the very fast reaction



If the reaction sequence 4 and 5 were important, ozone would be catalytically converted to O_2 with little or no change in the concentration of NO_2 , $\Delta[\text{NO}_2]/\Delta[\text{O}_3] \approx 0$. Another reaction possibility is the process



In this case, the stoichiometric number would again be 2 provided that the N_2O_3 had a chemical lifetime long compared to the kinetic sampling time. All indications are, however, that N_2O_3 is very short lived. In the study reported here all experiments were carried out with a large excess of NO_2 , and the decay of O_3 under pseudo-first-order conditions was used to evaluate the bimolecular rate constant for reaction 1.

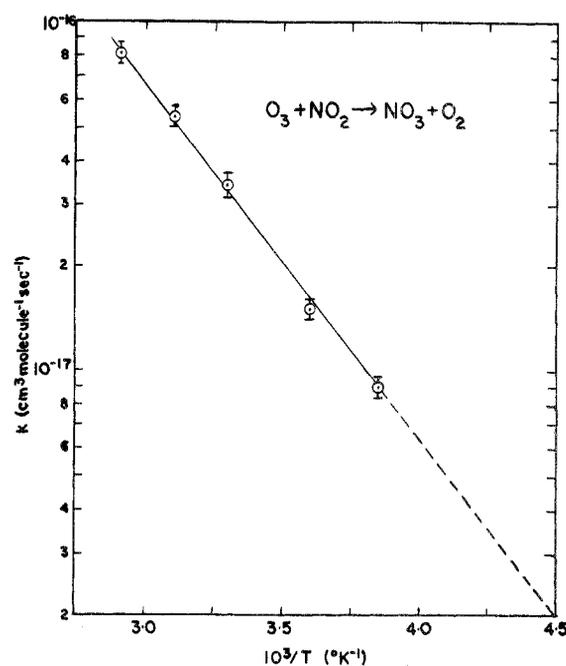


Figure 5. An Arrhenius plot for the reaction $\text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{O}_2$. Each data point is based on from 5 to 11 experiments at each temperature.

Evidence indicating the absence of any complex secondary reactions was found in the well-behaved first-order decays of O_3 (see Figure 2), the observed linear second-order plots shown in Figure 4, and the observed linear Arrhenius plot (over the temperature range of 260–343°K) seen in Figure 5.

Johnston and Yost² were the first to investigate reaction 1 in an effort to determine the bimolecular rate constant. They employed a stop-flow technique which involved monitoring the decay of the NO_2 photometrically. In this study, no stoichiometry factor was determined; however, a previously measured value⁹ was cited to account for their observations. They obtained a rate constant of 6.1×10^{-17} cm 3 molecule $^{-1}$ sec $^{-1}$ at 298°K and an activation energy of 7.0 ± 0.6 kcal mol $^{-1}$ over a temperature range of 16°. Their room temperature results are approximately two times higher than those reported here, and the activation energy is about 1.5 times larger. Ford, Doyle, and Endow³ measured the value of k_1 using a stirred flow reactor with photometric detection of O_3 . Their average value of $3.3 \times 10^{-17 \pm 2}$ cm 3 molecule $^{-1}$ sec $^{-1}$ is in good agreement with ours.

More recently, studies have been reported by Ghormley, Ellsworth, and Hochanadel,⁵ Wu, Morris, and Niki,⁶ and Stedman and Niki.⁴ These investigations were all carried out at $\sim 300^\circ\text{K}$. Stedman and Niki⁴ used a stirred flow reactor with chemiluminescent detection of O_3 . Wu, *et al.*,⁶ employed both chemiluminescent detection and long path infrared analysis. In the first study⁴ a value of $6.5 \pm 50\% \times 10^{-17}$ cm 3 molecule $^{-1}$ sec $^{-1}$ was measured for k_1 . Wu, *et al.*,⁶ using two experimental methods, obtained an average value of $(4.40 \pm 0.65) \times 10^{-17}$ cm 3 molecule $^{-1}$ sec $^{-1}$. Although the first measurement is nearly 50% higher than the second, the results do agree within the expressed experimental uncertainties. In the investigation by Ghormley, *et al.*,⁵ a flash photolysis absorption spectroscopy technique was employed in which NO was generated *via* reactions



and

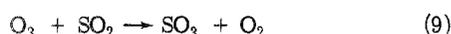


followed by the production of NO₂ from process 5. In this experimental system, the half times for reactions 5 and 1 differed by nearly a factor of 500, thus, making it rather easy to time resolve these processes experimentally. The value of k_1 obtained in the above study was $3.14 \pm 0.50 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. A summary of all rate data published on reaction 1 is given in Table II. From this compilation, it is seen that the k values from the three most recent studies of reaction 1 (including the present one) are all in good agreement within the quoted experimental uncertainties. The average value calculated for k_1 from this data set is $3.50 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ at 300°K.

As pointed out in the Introduction, previous to this investigation the temperature dependence of k_1 had only been examined over the limited temperature range 286–302°K. The value of E_{act} quoted in that work² was $\sim 7 \text{ kcal mol}^{-1}$ or a factor of 1.5 times higher than reported here. An examination of the possible impact these new results might have on atmospheric modeling studies shows that in the lower troposphere the rate of conversion of NO₂ to N₂O₅ will be approximately 2 times slower than previously calculated. In the stratosphere, at temperatures of 215°K, the rate of conversion of NO₂ will be nearly 1.5 times faster than calculated from the earlier rate expression of Johnston. (The crossover point for the two rate expressions occurs at about 240°K.)

Near the completion of this study these authors learned of a new investigation by Johnston¹⁰ in which the temperature dependence of k_1 was examined over the temperature range 298–230°K. Preliminary results from this study indicate an activation energy of $\sim 4900 \text{ cal mol}^{-1}$ in excellent agreement with the value reported here.

In a follow-up study of the reaction of ozone with nitrogen dioxide, these authors briefly investigated the analogous reaction of ozone with sulfur dioxide



In this case, an examination of the literature revealed only a qualitative statement about the rate constant for this reaction, indicating that the process was very slow.¹¹ In this investigation of reaction 9, experiments were carried out at both 300 and 360°K, using $\sim 200 \text{ mTorr}$ of O₃ and 20 mTorr of SO₂. The reaction's progress was therefore followed by observing the pseudo-first-order decay of SO₂. Only at 360°K could a significant reaction be detected. On the

TABLE II: Summary of Reported Rate Measurements on the Reaction
NO₂ + O₃ → NO₃ + O₂

$T, ^\circ\text{K}$	$k, \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$	Ref
286–302	$9.8 \times 10^{-12} \exp(-7000 \pm 600 \text{ cal mol}^{-1}/RT)$	2
298	3.3×10^{-17}	3
298	$6.5 \pm 50\% \times 10^{-17}$	4
298	$3.14 \pm 0.50 \times 10^{-17}$	5
298	$(4.40 \pm 0.65) \times 10^{-17}$	6
268–231	$1.23 \times 10^{-13} \exp(-4900/RT)$	10
260–343	$(9.76 \pm 0.54) \times 10^{-14} \exp(-4824 \pm 280 \text{ cal mol}^{-1}/RT)$	This work

basis of the observed decay rate a rate constant of approximately $10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ was calculated at 360°K. Assuming at least a 10 kcal mol^{-1} activation energy for this process, the rate constant at 300°K is expected to be $\leq 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. Although such a low k value suggests that heterogeneous reactions may have influenced these measurements, it is nonetheless clear that the value reported still represents an upper limit for the homogeneous reaction. It is thus apparent that reaction 9 will not be of any atmospheric significance either in the natural atmosphere or under smog conditions.

Note Added in Proof. Very recently new experiments have been carried out on the SO₂–O₃ system using the technique of stop-flow uv spectroscopy. At 300°K the rate constant measured was $k \leq 2 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, in good agreement with the mass spectrometry work.

References and Notes

- (1) Acknowledgment is made by this author to the National Science Foundation RANN program (Grant No. GI-36338X) and the Climatic Impact Assessment Program, Office of the Secretary, Department of Transportation, for their support of this research.
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