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Rate constant of the gas phase reaction of SO₃ with H₂O

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The rate constants for the reaction of SO₃ with H₂O in He and in N₂ were measured at total pressures from 1–10 Torr in a flow tube at room temperature. The concentration of SO₃ was monitored by photofragment emission produced by 147 nm excitation. Dependencies of apparent reaction rates on wall conditions and reaction tube sizes were investigated. At total He pressures of 1–10 Torr, a value of $(5.7 \pm 0.9) \times 10^{-15}$ cm³/s was obtained for the upper limit of the homogeneous gas phase reaction rate constant. This rate value is more than two orders of magnitude lower than the previously published value, but it is consistent with the theoretical calculation provided in this paper.

I. INTRODUCTION

Acid rain is a major problem in atmospheric chemistry. The release of sulfur compounds into the air with their subsequent oxidation and conversion to sulfuric acid is recognized as the principal cause of acid rain; and SO_2 , produced by the combustion of fuels and by volcanic eruptions, is the major sulfur-containing species in polluted air. A reasonable chain mechanism for the oxidation of SO_2 to sulfuric acid has been proposed by Stockwell and Calvert^{1,2} as

 $SO_2 + OH + M \rightarrow HOSO_2 + M,$ (1)

 $HOSO_2 + O_2 \rightarrow HO_2 + SO_3, \tag{2}$

$$SO_3 + H_2O \rightarrow H_2SO_4. \tag{3}$$

The chain is continued by the reaction of HO₂ with NO to reform OH. By the Stockwell-Calvert mechanism, the amount of sulfuric acid formed is proportional to the amount of SO₂ released. An important step in the mechanism is the reaction of SO_3 with H_2O , which may occur in the gas phase and/or on the surfaces of aerosol particles. The rate constants of both routes could be important in assessing acid rain formation. Unfortunately, the rate constant for reaction (3) is not well established.³ Only one value has been reported: a rate constant of 9×10^{-13} cm³/s was obtained by Castleman et al.⁴ using a mass-spectroscopic method to monitor the decay of SO_3 in a very fast flow study. This rate constant⁴ is surprisingly fast for a reaction between two stable molecules. However, the rationale for such a fast rate was provided.^{5,6} The reaction proceeds via a vibrationally excited adduct (H₂O·SO₃) which rearranges spontaneously to H_2SO_4 .^{5,6} The product (H_2SO_4) and adduct ($H_2O \cdot SO_3$) geometries and the reaction energy surface were calculated by CNDO/2 methods⁵; and the results supported the vibrationally hot molecule reaction thesis. In their calculation⁵, an adduct stabilization energy of 15.2 kcal/mol (relative to $SO_3 + H_2O$) and an activation energy barrier for adduct rearrangement to sulfuric acid of 3.3 kcal/mol were obtained. RRKM calculations based on these frequencies and energetics for the spontaneous reaction rate constant of the adduct (i.e., vibrationally "hot" by 11.9 kcal/mol) gave rate constants more than three orders of magnitude faster than collisional stabilization rates at reaction pressures (0.01-0.1 Torr). The problem of very fast homogeneous gas phase reaction rates between SO₃ and H₂O, therefore, appeared to be well resolved. However, recent and more accurate ab initio calculations⁷ find that energy barriers between the $SO_3 \cdot H_2O$ adduct and sulfuric acid are significantly higher (i.e., between 23 and 31 kcal/mol, depending on the level of calculation). Hence, the thesis of vibrationally hot adduct molecule reactions is now less credible, and this in turn suggests that the rate constant of reaction (3) may be much slower than the original measurements indicated.

It has been pointed out that kinetic measurements of reaction (3) could be seriously affected by heterogenous reactions with adsorbed water on the walls.³ Remeasurements of the kinetics of reaction (3), therefore, are of considerable interest. In addition, because of the energy barrier changes as indicated by the *ab initio* results, recalculations of the **RRKM** spontaneous reaction rates of the vibrationally excited SO₃ \cdot H₂O adduct molecules are also needed.

In studying SO₃ gas phase kinetics, the handling and detection of SO₃ present major problems. Both SO₃ and H_2SO_4 are very corrosive; and, moreover, SO₃ reacts with water on walls and grease in joints to produce acidic products which attack O-rings and metals. It also reacts on the optical windows. These difficulties are best minimized by keeping SO₃ concentrations as low as possible. We have recently developed a simple and very sensitive detection method which is applicable to kinetic studies. The method, vacuum ultraviolet (VUV) stimulated photofragment emission (PFE)⁸, has been applied previously to the study of the HO₂ + O₃ reaction kinetics,⁹ and has now been applied to the study of the SO₃ + H₂O reaction. When SO₃ is excited

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FIG. 1. Schematic diagram of experimental apparatus.

by VUV photons at wavelengths shorter than 160 nm, it dissociates into $SO_2^* + O$, and then emits light from the SO_2 $(\tilde{B} \, {}^1B_1 \text{ and } \tilde{b} \, {}^3B_1 - \tilde{X} \, {}^1A_1)$ systems. The fluorescence cross section⁸ at 147 nm is about $1.5 \times 10^{-19} \text{ cm}^2$. With this PFE detection method, SO₃ can be detected at concentrations as low as 10^{10} molecules/cm³.

In this paper we report new and quite different results on the kinetics of the $SO_3 + H_2O$ reaction, including the effects of heterogeneous wall reactions on the kinetics. We also report RRKM calculations of the spontaneous reaction rate constants of the $SO_3 \cdot H_2O$ adduct as well as transition state estimates of the reaction (3) bimolecular rate constant. The calculated result is compared with experimental values obtained here and in the prior study.

II. EXPERIMENTAL

The schematic diagram of the experimental apparatus is shown in Fig. 1. The flow system consisted of a Pyrex cylindrical flow tube (2 in. outer diameter, 37 cm in length) with a concentric movable inlet (0.25 in. outer diameter Pyrex tube) in conjunction with a gas cell. To minimize surface effects, the outside of the inner inlet tube and the inside of the larger flow tube were coated with halocarbon wax. In some studies directed toward the investigation of wall effects a smaller (1 in. outer diameter) reaction tube was used both with and without halocarbon wax coating. The gas cell was a (3 in. outer diameter) stainless steel six-way cross. The reaction tube was connected vertically to the gas cell in order to avoid the accumulation of H₂SO₄ acid on the tube walls. A mechanical pump with a cold trap was used to drive the gas flow and SO₃ was detected by monitoring the SO₂ fluorescence from its 147 nm photolysis (i.e., by PFE). The light source was an Xe resonance lamp sealed with a MgF_2 window. The light entered the gas cell through the MgF_2 windows in a direction perpendicular to the reaction tube. A gas filter (1% of CH₄ in Ar at atmospheric pressure¹⁰) was used to cut off the 129.5 nm line of the Xe lamp. The light source intensity was monitored with a CsI photodiode (Hamamatsu R1187). The inside surfaces of the MgF₂ windows were constantly flushed by He to prevent deposits of SO₃ and H₂SO₄.

 SO_2 fluorescence from excitation of SO_3 was detected with a cooled photomultiplier tube (EMI 9558QB) at a direction perpendicular to both the light source and the reaction tube. A bandpass filter (Hoya U-350) transmitting in the 300–390 nm region was used to isolate the SO_2 emission bands. The signal from the PMT was processed by a photon counting system (ORTEC), and the experimental data of carrier gas flow rate, total gas pressure, light source intensity, and fluorescence intensity were simultaneously recorded by a microcomputer. To confirm that the observed signal originated from the photodissociation of SO_3 , the fluorescence was dispersed using a 0.25 m (Kratos GM 252) monochromator.

Water vapor (at room temperature) was mixed with either He or N₂ by bubbling the carrier gas through distilled water which was repeatedly degassed at liquid nitrogen temperature and stored in a stainless steel container. To achieve the desired concentration, the gas stream was further mixed with carrier gas before entering the reaction tube. The carrier gas flow rate was controlled by a mass flow controller (MKS), total pressure in the flow tube was monitored by a capacitance manometer, and total flow rate in each experimental run was measured by the pressure rise rate in a known volume. [H₂O] was calculated from the gas mixing ratio and was confirmed by the absolute [H₂O] value measured by photofragment emission. That is, the OH(A-X) emission intensity by the 129.5 nm photolysis of H₂O in He was calibrated with that of pure water as shown in Fig. 2. In



FIG. 2. Comparison of $[H_2O]$ determined by mixing ratio (square) and pure water (dot). $[H_2O]$ measured by the OH(A-X) fluorescence intensity by photolysis of H_2O at 129.5 nm.

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FIG. 3. Dispersed fluorescence spectra produced from the 147 nm photolysis of SO₃ in buffer gas N₂, (a) without water and (b) with water vapor of 10^{15} molecules/cm³. The monochromator resolution was 3.3 nm. Total pressure was 1.8 Torr with [SO₃] ~ 10^{14} molecules/cm³. (c) same as (a) except with an optical filter (Hoya U-350) placed in front of the monochromator entrance slit and the buffer gas being He.

the calibration procedure, the gas filter between the Xe lamp and the gas cell was changed to pure Ar or N₂ for transmission of both 129.5 and 147 nm lines. The threshold wavelength for the production of OH(A) from photoexcitation of H₂O is 137 nm.¹¹

Stabilized SO₃ (99%, Aldrich) was prepared as described in a previous paper.⁸ SO₃ vapor was diluted in He or N₂ and stored in a 5 ℓ Pyrex reservoir. Buffer gases of He (99.999%) and N₂ (99.999%) were used as delivered without further purification.

III. EXPERIMENTAL RESULTS

A. Detection of SO₃

The VUV excitation of SO₃ produces excited SO₂ from the fragmentation process,⁸

$$SO_3 + h\nu \rightarrow SO_2^* + O. \tag{4}$$

To exclude the possibility of emissions from some sources other than SO_2^* , the PFE spectrum obtained from the VUV excitation of SO_3 in N_2 , as shown in Fig. 3(a), was compared to that⁸ of pure SO_3 . They were similar. The broad semicontinuum is the singlet system and the structure is the triplet. When H_2O was added to the flow tube, the emission intensity decreased, but the emission spectrum was essentially unchanged as shown in Fig. 3(b). These results indicate that there is no additional emission from reaction products of $SO_3 + H_2O$, that is, SO_2^* is the sole emitter.

It is known that reaction (3) leads to sulfuric acid aerosol formation under certain conditions,¹² and that aerosol particles can scatter the visible light (450–600 nm) from the Xe lamp. Thus, a filter (U-350) was used to cut off this portion of light. When the filter was placed in front of the monochromator, the emission spectrum was modified as shown in Fig. 3(c). This filter was then placed in front of the PMT in the kinetic measurements to ensure that the observed emission originated solely from PFE. Also, the concentrations of both SO₃ and H₂O were limited to such low levels that aerosol scattered light was not noticeable. Thus, there was no interference to the PFE signal by scattered light.

The PFE intensity is described by

$$I_f = C\sigma_f[SO_3]I_0 \exp\left(-\sum_i \sigma_i n_i l\right) / \left(1 + \tau \sum_i n_i k_i\right),$$
(5)

where C is the detection efficiency, σ_f is the fluorescence cross section, I_0 is the light source intensity, l is the effective path length of the light source from the MgF₂ window to the center of the PMT view region, τ is the radiative lifetime of the excited SO^{*}₂, n_i is the concentration of a species *i*, σ_i is the absorption cross section of the species at 147 nm, and k_i is the quenching rate constant of SO^{*}₂ by the species.

The absorption cross sections of H_2O and SO_3 at 147 nm are 0.6 Mb¹¹ (1 Mb = 10⁻¹⁸ cm²) and 22 Mb,⁸ respectively, while the absorption cross section of H_2SO_4 is not known. The path length from the MgF₂ window to the PMT view region was about 13 cm, however, since the optical path was flushed by He, the effective optical path length was estimated to be less than 2 cm. Thus the light attenuation, represented by the exponential term in Eq. (5), is actually negligible. The denominator in Eq. (5) represents the reduction of the PFE intensity by the quenching of various gases. This term was held constant by maintaining all the gas concentrations constant. The relative concentration of SO₃ in the gas cell under these conditions is thus proportional to the PFE intensity.

In the experiments, initial concentrations of SO₃ were chosen on the order of 10^{12} molecules/cm³ so that a reasonable signal-to-noise ratio could be maintained, even when [SO₃] was decreased by a factor of 10 by reaction with water. The [SO₃] values were determined from the SO₃/He mixing ratios and also by the PFE intensities. In each measurement, all experimental parameters (linear flow velocity, total pressure, concentrations of reactants, and lamp intensity) were kept constant, except for the reaction time which was changed by moving the position of the SO₃/He injector tube. Since all the gas pressures, light attenuation and quenching factor were kept constant in each measurement, the decay in I_f was solely due to the decay of [SO₃] as a result of its reaction with water.

B. Reaction rate constant

The relative [SO₃] was measured as a function of reaction time for a fixed [H₂O]. When [SO₃] \leq [H₂O], the de-

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FIG. 4. Fluorescence intensity vs reaction distance. The total pressure was 1.55 Torr with He as buffer gas. The 2 in. outer diameter reaction tube was coated with halocarbon wax. The linear flow velocity was 52.3 cm/s, and the [H₂O] is in units of molecules/cm³.

cay of $[SO_3]$ can be represented by the pseudo-first-order (PSFO) approximation. The PSFO decay rate K is given by

$$K = k_3[H_2O] = -v \cdot d \left[\ln(I_f) \right] / dz, \tag{6}$$

where k_3 is the bimolecular rate constant of reaction (3), v is the linear flow velocity of reactants, and z is the reaction distance from the tip of the movable injector to the detection point of SO₃. Typical plots of $\ln(I_f)$ vs z for $[H_2O] = 0$, 3.23×10^{14} , and 6.87×10^{14} molecules/cm³ in He are shown in Fig. 4. Linear plots were observed for a wide range of $[H_2O]$ (5×10¹³-10¹⁵ molecules/cm³). Thus one can conclude that (1) the PSFO approximation holds under the experimental conditions, and (2) the interference of the [SO₃] measurement by other light, for example, possible emission from VUV excitation of H₂SO₄ and possible aerosol scattered light, is negligible. Typical PSFO decay rates vs [H₂O] are shown in Fig. 5 for He buffer gas and in Fig 6 for N_2 buffer gas. Experimental parameters are listed in Table I; data set 1 for He and data set 9 for N₂. In the figures, each data point represents the average K value, the error bar is the standard deviation, and the straight line is the least square fit. The rate constant of reaction (3) is obtained from the slope of the plot. The intercept of the plot represents the loss rate of SO_3 at the walls, which is approximately equal to the wall loss rate measured before introducing H2O into the reaction tube. The experimental data for various measure-



FIG. 5. Pseudo-first-order decay rates K vs $[H_2O]$ in He. Experimental parameters are listed in Table I, data set 1.

ments are summarized in Table I. The average reaction rate constant and error analysis are discussed below.

The flow velocity used in this experiment is quite slow because of the small reaction rate constant, and this slow flow velocity makes the experimental condition approach the applicable limitation of flow tube technique.¹³ It thus requires examining the possible effects¹³ of axial pressure gradient, radial concentration gradient, velocity gradient, and back diffusion. Based on the formula derived by Kaufman,¹³ the axial pressure gradient and velocity gradient are small in all measurements; therefore their effects on the measured reaction rate constants are negligible. In data sets 1 and 2 listed in Table I, the flow velocities are so small that a correction for the back diffusion is needed. This correction may increase the reaction rate constants for data sets 1 and 2 to values about 20% higher than those given in Table I. The corrected high values are more in line with other data measured at high flow velocities that do not require the correction of back diffusion. The radial concentration gradient for



FIG. 6. Pseudo-first-order decay rates K vs [H₂O] in N₂. Experimental parameters are listed in Table I, data set 9.

TABLE I.	Summary	of	experimental	data
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Data set	No of expts."	Total pressure (Torr)	Flow velocity (cm/s)	[H₂O] ^ь (10 ¹⁴)	K ₀ ° (s ⁻¹)	k_3 (10 ⁻¹⁵ cm ³ /s)
He as bu	ffer gas					
1	33	1.55	52.3	8.30	0.00	5.00 ± 0.88
2	19	1.62	63.1	5.80	1.13	4.68 ± 0.89
3	20	1.65	103.0	4.90	0.60	5.25 ± 0.84
4	15	1.64	170.1	5.60	1.25	6.05 ± 0.95
5	26	1.61	156.4	10.70	0.37	5.76 ± 0.85
6	20	1.62	117.0	10.50	1.34	5.59 ± 0.92
7	12	9.62	36.2	12.05	0.10	5.57 ± 0.88
8	19	9.20	49.3	7.98	1.38	5.78 ± 1.40
N_2 as but	fer gas					
- 9	21	1.71	73.6	11.26	0.91	5.85 + 0.89

^a One experiment means the determination of one pseudo-first-order decay rate.

^bThe highest [H₂O] used in the measurements in unit of molecules/cm³.

 $^{\circ}K_{0}$ is the intercept of the linear fit at $[H_{2}O] = 0$ which is equivalent to the wall loss rate.

data sets 1-6 is small because of low gas pressures, but it could be as high as 15% for data sets 7 and 8 because of pressures higher than 9 Torr. This radial concentration gradient could introduce the same amount of uncertainty for the measured reaction rate constants. Because of these additional uncertainties, the data sets 1, 2, 7, and 8 are not included in the average of the k_3 value.

The experimental conditions for the data sets 3–6 and 9 are within the applicable range of flow tube technique such that corrections for gradients and back diffusion are not required. The k_3 value averaged over these data is 5.7×10^{-15} cm³/s with an uncertainty of 0.9×10^{-15} cm³/s for a 95% confidence level. The possible systematic errors are $\pm 10\%$ for [H₂O] and $\pm 5\%$ for flow velocity, but the uncertainty associated with wall effect is difficult to estimate. The wall effect is further discussed in the next section.

It is worth noting that the $H_2O + SO_3$ reaction could form a weakly bound adduct.¹⁴ If the 147 nm excitation of the adduct can produce the same SO^{*} emission, then the adduct formation rate is not included in the present measurement. However, the emission from the adduct may not be large. From our extensive study of the quantitative molecular fluorescence spectroscopy, it is found that every molecule has its own distinct fluorescence excitation function and emission spectrum. The fluorescence quantum yield and fluorescence spectrum change from molecule to molecule. Even the $SO_3 \cdot H_2O$ adduct produces SO_2^* emission, the fluorescence quantum yield may be much smaller than that of SO_3 , because the adduct has more channels (other than the fluorescence channel) to dissipate the excitation energy. The possibility for the SO^{*}₂ emission from photoexcitation of the adduct is thus expected to be small.

C. Effect of heterogeneous reaction

Dramatic increases in PSFO decay rates were observed when the reaction tube was changed from 2 to 1 in. outer diameter. Also, surprisingly large K values were found when

the Pyrex reaction tube was not coated with halocarbon wax. The wall loss rate of SO₃ measured before introducing water into the uncoated reaction tube was as high as 40 s^{-1} . This is 5-7 times faster than the rates observed in the coated tube. When a small amount of water was added, the PSFO decay rate increased by an order of magnitude. This appeared to be a saturation level as further increases in water produced little additional rises in K. After the $SO_3 + H_2O$ experiment, the wall loss rate was measured again and found to be as fast as 400 s^{-1} . Even after flushing the reaction tube with He for a few hours, the wall loss rate remained very high. When the same 1 in outer diameter reaction tube was coated with halocarbon wax, the PSFO decay rate decreased by more than one order of magnitude. Similar high wall loss rates were observed for the 2 in. outer diameter reaction tube when it was not coated with halocarbon wax. At a fixed $[H_2O] = 1.7 \times 10^{14}$ molecules/cm³, K = 60 s⁻¹ was measured. After the water vapor was shut off, the wall loss rate maintained this same high value (60 s^{-1}) for an hour. The high wall loss rate is undoubtedly due to H₂O adsorption on the uncoated Pyrex wall, indicating that the heterogeneous reaction of SO_3 with absorbed H_2O on walls is extremely fast.

Halocarbon wax coating is commonly used for kinetic measurements of radicals because it is effective in reducing the wall decay rates of radicals. The wax may act by covering adsorption sites and lowering the sticking coefficients of species ordinarily strongly adsorbed. It is clear that the halocarbon coating employed in our experiment was effective in reducing the H_2O adsorption, because the wall loss rates did not change significantly before and after introducing water into the coated reaction tube. The best coating was obtained when the halocarbon wax was melted at high temperatures and coatings were made repeatedly.

The above observations clearly show that heterogeneity can play an important role in the $SO_3 + H_2O$ kinetics. For the results listed in Table I, the walls were coated with halocarbon wax such that the wall loss rates were less than 1.4 s^{-1} measured before and after each experiment. Since the wall loss rates are much smaller than the total loss rates of SO₃ reaction with H₂O (see Figs. 5 and 6), we believe that the measured reaction rate constant is close to the genuine homogeneous reaction rate constant. However, the possibility of wall effects in our measurements is still not excluded and our measured reaction rate constant should be considered an upper limit value.

The current result of $k_3 = (5.7 \pm 0.9) \times 10^{-15} \text{ cm}^3/\text{s}$ is much slower than the earlier published value⁴ of $(9.1 \pm 2.0) \times 10^{-13} \text{ cm}^3/\text{s}$. This difference is most likely caused by the wall effect. The earlier experiment⁴ used a fastflow apparatus that consisted of a cylindrical tube made of Pyrex glass or stainless steel of two different sizes. Their measured SO₃ loss rates did not depend on the tube size or material and that led them to attribute their measured value to homogeneous gas phase reaction. However, their observation may in fact be greatly affected by the heterogeneous reaction.

IV. THEORETICAL CALCULATION

The *ab initio* calculated energy surfaces⁷ of $SO_3 + H_2O$ reaction differ significantly from the surface obtained in the CNDO/2 calculation.⁵ The latter placed the SO₃ ·H₂O complex at a level 15.2 kcal/mol below that of the separated reactants and indicated a rather small barrier for reaction of the complex to sulfuric acid (i.e., $E \sim 3.3$ kcal/mol). By contrast, the ab initio calculations gave complex stabilization relative to SO₃ and H₂O between 20 and 28 kcal/mol, and gave energy barriers for complex reaction between 23 and 31 kcal/mol, depending on the level of calculation. The highest level, MP2(FC), set the complex stabilization at 21.4 kcal/mol and the zero point activation barrier to product formation from the complex of 23.2 kcal/mol (i.e., 1.8 kcal/ mol above the reactant zero point level). For comparison, the $CNDO/2^5$ and $MP2(FC)^7$ energy surfaces are shown in Fig. 7. The deeper potential well and higher energy barrier to



FIG. 7. Energy surfaces of the $SO_3 + H_2O$ reaction. The dashed line is given by Ref. 5 and the solid line is by Ref. 7.

products calculated for the complex by *ab initio* methods raises questions about the conclusions of the Castleman **RRKM** calculations (i.e., that reaction proceeds through vibrationally hot states of the complex directly to sulfuric acid and that collisional stabilization rates of the vibrationally hot complex molecules are much too slow to compete with this reaction).

By the mechanism of reaction (3), see Fig. 7, the experimental rate constant for SO₃ loss is given by

$$k_{3} = k_{a}(k_{f} + ZP)/(k_{b} + k_{f} + ZP),$$
(7)

where rate constants of the elementary steps are represented as averages. This equation assumes that molecules reacting through the transition state to the hot vibrational levels of the product (H_2SO_4) are all collisionally stabilized. Castleman's RRKM calculations confirm this assumption.

According to the CNDO/2 energy surface and Castleman's RRKM calculations, $k_f \gg k_b$ and $k_f \gg ZP$ (as $E_f \ll E_b$ and spontaneous reaction to sulfuric acid was calculated to be faster than collisional stabilization to the complex). Hence, $k_3 = k_a$, and this result is consistent with the high rate constant value observed by Castleman. However, according to the ab initio energy surface⁷ that has much higher activation energy barrier between the complex and sulfuric acid, it is not clear how the competing terms in the denominator of Eq. (7) compare. If either k_f or ZP are dominant, the rate constant expression reduces to $k_3 \sim k_a$ as deduced by Castleman et al. On the other hand, if k_b is dominant, k_3 $\sim k_a (k_f + ZP)/k_b$. We have repeated the RRKM calculations of the spontaneous reaction rates for the complex (k_{b} and k_{f}) using the MP2(FC) energy surface. The calculations were made in the standard manner of chemical activation systems¹⁵ employing the Beyer-Swinehart algorithm¹⁶ for direct count of quantum states. Vibration frequencies for the complex, the transition state to H_2SO_4 (TS_f) and the transition state for complex formation from SO₃ and H₂O (TS_b) are given in Table II. These frequencies are consistent with activation entropies, $S_f^{\dagger} = -4.6$ cal/deg and $S_b^{\dagger} = 11.1$ cal/deg, estimated by thermochemical kinetic methods¹⁷ for the complex reactions forward (to sulfuric acid) and back (to SO_3 and H_2O), respectively. Since it is well known that RRKM calculations are not sensitive to the exact choice of frequencies as long as they are consistent with activation entropies,¹⁵ we have made no special effort to obtain accu-

TABLE II. RRKM data input and output.

Input: Frequencies in (cm ⁻¹)							
Complex(SO ₃ ·H ₂ O):2(24 500),630,3(1200),3(550),4(280),1450,275							
$TS_{f}: 3500,2450,760,3(1200),4(550),725,575,2(1150)$							
$TS_{p}: 2(1390), 1070, 530, 2(500), 3655, 3755, 1595, 5(125)$							
$a_{(\text{He.complex})} = 0.20$ $a(\text{reactants,complex}) = 1.0$							
$e_{(\text{He,complex})} = 2.6$			e(reactants,complex) = 6.5				
Results:							
$k_f = 8.7 \times 10^6 \mathrm{s}^{-1}$							
$k_f / k_b = 6.3 \times 10^{-3}$							
$\beta ZP = 6.0 \times 10^5 \times P(\text{Torr}) \text{ s}^{-1}$							
P(Torr):	0.01	1.0	10.0	760			
k _f /βZP:	1.5×10 ³	15	1.5	1.9×10 ⁻²			

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rate frequency assignments. However, the assignments made are reasonable ones for the vibrational motions described. To estimate activation entropies, the assumptions were (1) that reaction to sulfuric acid has a reaction path degeneracy of six and proceeds via a "tight" transition state with the loss of one internal rotation (i.e., rotation of the H_2O vs SO_3 fragment in the complex), and (2) that the transition state for complex reaction back to reactants is "loose." Bond fission reactions, like the back reaction, typically have A factors in the $10^{16 \pm 1}$ range, ^{15,17} and the estimated 10^{15.6} s⁻¹ value is consistent with this range. The calculated average spontaneous decomposition rate for the forward reaction of the complex is $k_f = 8.7 \times 10^6$ s⁻¹, while collisional stabilization rates are about $\beta ZP(s^{-1}) = 6.0 \times 10^5$ $\times P(\text{Torr})$, where $\beta \sim 0.2$ for the collision efficiency of the He bath gas has been assumed. Thus our calculations indicate that decomposition and collisional stabilization rates are roughly equal at total pressures around 15 Torr. This translates into a calculated 60% increase in SO₃ loss rates (either by collisional stabilization to complex or reaction to H_2SO_4) for the 1–10 Torr total pressure range examined in this study. The considerably lower rate increases observed (i.e., zero within the experimental errors of $\pm 20\%$) essentially mean that the spontaneous decomposition rate constant (k_f) must be at least a factor of 3 or more faster than calculated. A complex stabilization energy 3 kcal or more less than the MP2(FC) value of 21.4 kcal would be sufficient to bring the calculations in line with experiment. The overall reaction (3), then, is calculated to be bimolecular (i.e., pressure independent within the stated errors, as observed) un-

der the 1-10 Torr total pressure conditions studied.

Because the zero point energy barrier to the reaction for the complex to sulfuric acid is so high (actually 1.8 kcal/mol above the zero point level of the reactants), reaction of the complex back to SO_3 and H_2O is much faster than its reaction forward to sulfuric acid. For reaction of hot complex molecules from energy levels above the activation energy barrier, our RRKM calculations found $k_f/k_b = 0.0063$, essentially independent of the complex stabilization energy. In addition, 20% of the complex molecules produced in the association reaction are formed at energy levels below the zero point energy barrier and are only capable of reacting back to reactants. Thus, by the ab initio energy surface, the experimental k_3 [by Eq. (7)] is estimated to be more than two orders of magnitude smaller than k_a . Thus it is clear that transition state species for the forward reaction (TS_f) are essentially in equilibrium with reactants. This is the assumption of transition state theory, hence straightforward transition state techniques¹⁷ can be employed to estimate the bimolecular reaction (3) rate constant. We have, accordingly, estimated the Arrhenius parameters of reaction (3) from the transition state theory relationships: $A_3 = rp_d$ $(ekT/h)e^{\Delta S^{\dagger}/R}$ atm⁻¹s⁻¹ and E_3 (pressure std state) $= (\Delta E_0^0 + (H_{300}^0 - H_0^0)^{\dagger} + RT)$ kcal/mol. The entropy and enthalpy content for the forward reaction transition state (TS_f) were calculated using the frequencies of Table II and the 3-21G(*) geometry of Ref. 7. Results are summarized below, where the 300 K thermodynamic values shown correlate vertically with the species SO₃, H₂O, TS, and H_2SO_4 , respectively.

	SO3 H	- H ₂ O	12	$\begin{pmatrix} O_2 S - OH \\ O - H \end{pmatrix}^{\dagger}$	→	H ₂ SO ₄ ,
S^{0} (cal/deg mol):	61.3	45.1		68.4		69.1;
$(H_{300}^0 - H_0^0)$ (cal/mol):	2770	2368		3164 ;		
ΔH_f^0 (kcal/mol):	- 93.2	- 57.1				— 177 .

Activation reaction changes are: $\Delta S^{\dagger} = -38.0$ cal/deg, $\Delta (H_{300}^0 - H_0^0)^{\dagger} = -1974$ cal, and $\Delta E_0^{\dagger} = 1800$ cal. Therefore, $A_3 = (6ekT/h)e^{-38.0/R} = 4.8 \times 10^5$ atm⁻¹ $s^{-1} = 5.3 \times 10^{-14}$ cm³/molecules s; E_3 (pressure std state) = 1800 + (-1974) + RT = 422 cal; E_3 (constant vol std state) = 422 + RT = 1018 cal; $k_3 = A_3 \cdot e^{-E3/RT}$ = 9.7 × 10⁻¹⁵ cm³/molecule s all at 300 K.

The estimated rate constant for reaction (3) is about a factor of 2 higher than the experimental value reported here. This is a reasonable good agreement considering that factor of 2 errors in A factors estimated by thermochemical methods are not unlikely¹⁷ and that the greatest potential source of error in the above estimate is clearly the calculated activation energy barrier. The good agreement between the calculated and the measured k_3 of this study lends support for the energy barrier (1.8 kcal/mol), and more important, for identification of the measured rate constant to be close to the homogeneous bimolecular gas phase reaction. Although present results support the spontaneous reaction of SO₃ with H₂O to sulfuric acid at pressures below 10 Torr (i.e., no total

pressure effect on the reaction rate), further studies on rate vs total pressure effects need to be made to determine the pressures at which collisional stabilization competes with spontaneous reaction of the hot complex and thereby to fix the stabilization energies of the $SO_3 \cdot H_2O$ complex.

VI. CONCLUSION

The reaction rate constants for the gas phase reactions of SO₃ + H₂O in He and N₂ were investigated using a flow system and a photofragment emission detection technique. The measured reaction rate constant at room temperature was found to be $(5.7 \pm 0.9) \times 10^{-15}$ cm³/s, independent of total pressure for He pressures in the range 1–10 Torr. Change in carrier gas from He to N₂ did not significantly effect the reaction rate constant. The present rate constant result is consistent with the theoretical RRKM rate constant based on the *ab initio* energy surface calculated by Chen and Plummer.⁷ Our value, however, is two orders of magnitude lower than the earlier value reported by Castleman *et al.*⁴ Heterogenous reaction of SO_3 with water on walls is extremely fast and can have a significant effect on the apparent reaction kinetics. This could be the reason for the difference between the present and former values.

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