

# Kinetics and Thermodynamics of the Gas Phase Reaction $\text{SO}_3 + \text{NH}_3 + \text{N}_2 \leftrightarrow \text{H}_3\text{NSO}_3 + \text{N}_2$

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The kinetics of the gas phase reaction  $\text{SO}_3 + \text{NH}_3 + \text{N}_2 \leftrightarrow \text{H}_3\text{NSO}_3 + \text{N}_2$  were studied with a flow reactor coupled to a chemical ionization mass spectrometer for detection of  $\text{SO}_3$  and  $\text{H}_3\text{NSO}_3$ . The rate coefficient for the association reaction  $\text{SO}_3 + \text{NH}_3 + \text{N}_2$  was measured as a function of temperature (280–340 K) and pressure (20–80 Torr of  $\text{N}_2$ ). Analysis of the  $\text{SO}_3$  decay and  $\text{H}_3\text{NSO}_3$  appearance at higher temperatures yielded rate coefficients for  $\text{H}_3\text{NSO}_3$  decomposition and the enthalpy of the reaction  $\text{SO}_3 + \text{NH}_3 \leftrightarrow \text{H}_3\text{NSO}_3$ :  $\Delta H_{298\text{K}}^\circ = -24 \pm 1 \text{ kcal mol}^{-1}$ .

## Introduction

The dominant loss mechanism for  $\text{SO}_3$  in the atmosphere is reaction with gas phase water to produce sulfuric acid.<sup>1–3</sup> The association reaction of  $\text{SO}_3$  with ammonia (eq 1) typically



accounts for less than  $10^{-4}$  of the  $\text{SO}_3$  loss in the atmosphere.<sup>3,4</sup>  $\text{H}_3\text{NSO}_3$  appears to have an unusually strong affinity for  $\text{H}_2\text{SO}_4$ , and it has been proposed that the association of  $\text{H}_3\text{NSO}_3$  and  $\text{H}_2\text{SO}_4$  may be an important step in the formation of aerosol in the atmosphere despite the low concentrations of  $\text{H}_3\text{NSO}_3$ .<sup>4</sup>

The stability of  $\text{H}_3\text{NSO}_3$  is not well established. High-level calculations by Wong et al. predict that  $\text{H}_3\text{NSO}_3$  is bound by about 19 kcal mol<sup>-1</sup> relative to  $\text{NH}_3$  and  $\text{SO}_3$ .<sup>5</sup> Lovejoy and Hanson<sup>4</sup> report that the  $\text{H}_3\text{N}-\text{SO}_3$  bond enthalpy is greater than 20 kcal mol<sup>-1</sup>, based on the observation of exponential  $\text{SO}_3$  decays in excess  $\text{NH}_3$  at room temperature.

The theoretical work by Wong et al.<sup>5</sup> predicts that gas phase  $\text{H}_3\text{NSO}_3$  is a zwitterion with significant electron donation from the N to S leading to a large dipole moment of 6.6 D. Wong et al.<sup>5</sup> also predict that gas phase  $\text{H}_3\text{NSO}_3$  has a significantly longer (about 0.1 Å) N–S bond than the solid form. Canagaratna et al.<sup>6</sup> have measured the microwave spectrum of gas phase  $\text{H}_3\text{NSO}_3$  and find that the structure agrees very well with the theoretical predictions of Wong et al.<sup>5</sup> They also confirm that  $\text{H}_3\text{NSO}_3$  is a zwitterion with about 0.4 electrons transferred from N to S.

Shen et al.<sup>7</sup> reported the first kinetic measurements for the reaction  $\text{SO}_3 + \text{NH}_3$ . They measured a rate coefficient of  $(6.9 \pm 1.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  in 1–2 Torr of He with a flow reactor and photofragment-emission detection of  $\text{SO}_3$ . Lovejoy and Hanson<sup>4</sup> have recently reported measurements of the pressure dependence of the association rate coefficient and observation of the  $\text{H}_3\text{NSO}_3$  product.

In the present work, the kinetics of the loss of  $\text{SO}_3$  in the presence of  $\text{NH}_3$  are measured as a function of temperature (280–343 K) and pressure (20–80 Torr of  $\text{N}_2$ ). At elevated temperatures (383–402 K) the decomposition of  $\text{H}_3\text{NSO}_3$  is observed, and equilibrium constants for reaction 1 are measured. These data yield the temperature dependence of the  $\text{SO}_3 + \text{NH}_3$  reaction near the low-pressure limit and the heat of formation

of  $\text{H}_3\text{NSO}_3$ . The implications of these results to the understanding of the atmospheric chemistry of  $\text{H}_3\text{NSO}_3$  are discussed.

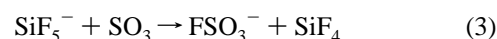
## Experimental Section

The kinetics of the reaction of  $\text{SO}_3$  with  $\text{NH}_3$  were studied by monitoring the concentration of  $\text{SO}_3$  at the exit of a laminar flow reactor as a function of the contact distance between  $\text{SO}_3$  and  $\text{NH}_3$ .  $\text{SO}_3$  was monitored with chemical ionization mass spectrometry.<sup>3</sup> The reactor was a Pyrex cylinder 50 cm long with a 1.62 cm internal diameter. The temperature of the reactor was controlled by circulating temperature-regulated fluid through copper tubing soldered to an insulated copper sleeve surrounding the reactor. The reactor temperature was measured with a thermocouple mounted on the end of a movable inlet. The temperature gradient was less than 2 K along the reaction zone for the conditions of the present work.  $\text{SO}_3$  was generated near the end of the movable inlet by oxidizing  $\text{SO}_2$  on a hot nichrome filament in the presence of  $\text{O}_2$ , as described previously.<sup>3</sup> Ammonia was added to the reactor at the upstream end along with the main flow of  $\text{N}_2$ . Mixtures of  $\text{NH}_3$  in  $\text{N}_2$  were prepared in 12 L Pyrex bulbs by adding measured pressures of  $\text{NH}_3$  and  $\text{N}_2$ . The reactor pressure was measured with a capacitance manometer and gas flows were measured with mass flow meters. The mass flow meters were calibrated with a wet test meter or by measuring the rate of change of pressure in a calibrated volume.

The CIMS ion–molecule reactor was operated at 5 Torr with about a 0.1 s contact time with the  $\text{SO}_3$  reactor effluent.  $\text{SO}_3$  was detected by using the following reactions<sup>3,8</sup>



and

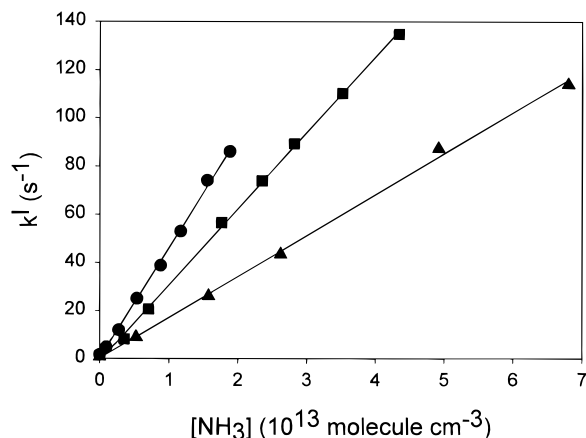


$\text{H}_3\text{NSO}_3$  was detected by using



Initial  $\text{SO}_3$  concentrations in the neutral flow reactor ranged from about  $(1-10) \times 10^9 \text{ molecule cm}^{-3}$ . The  $\text{NH}_3$  concentration was typically at least 50 times larger than  $[\text{SO}_3]$  so that

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**Figure 1.** First-order rate coefficient for SO<sub>3</sub> loss as a function of [NH<sub>3</sub>] and temperature. Circles = 280 K, 41.4 Torr. Squares = 301 K, 41.0 Torr. Triangles = 334 K, 40.6 Torr.

**TABLE 1: Summary of SO<sub>3</sub> + NH<sub>3</sub> Rate Coefficients**

<i>p</i> (N <sub>2</sub> ) (Torr)	<i>T</i> (K)	<i>v</i> <sup>a</sup> (cm s <sup>-1</sup> )	[NH <sub>3</sub> ] <sub>max</sub> (10 <sup>12</sup> molecules cm <sup>-3</sup> )	no. of <i>k</i> <sup>l</sup> measmnts	<i>k</i> <sub>f</sub> <sup>b</sup> (10 <sup>-12</sup> cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> )
20.5	280	391	53	7	2.76 (0.06)
20.1	298	423	81	8	1.90 (0.10)
21.1	317	445	124	9	1.34 (0.14)
20.2	317	441	118	6	1.35 <sup>c</sup> (0.08)
20.5	341	472	133	8	0.87 <sup>c</sup> (0.05)
41.4	280	197	19	8	4.58 (0.16)
41.0	301	214	43	8	3.16 (0.06)
41.0	319	237	72	7	2.30 (0.14)
40.6	334	240	68	6	1.70 (0.08)
40.0	343	247	88	6	1.47 (0.10)
81.3	280	100	4.9	6	8.2 (0.3)
79.8	300	107	7.1	7	5.04 (0.34)
80.4	320	113	13	8	3.47 (0.22)

<sup>a</sup> Average reactor flow velocity. <sup>b</sup> 95% confidence levels for precision are indicated in parentheses. <sup>c</sup> SiF<sub>5</sub><sup>-</sup> reagent ion.

the SO<sub>3</sub> loss was pseudo first order in SO<sub>3</sub>. The Reynolds number for the neutral reactor flow was about 75.

## Results and Discussion

Rate coefficients were measured by monitoring the concentration of SO<sub>3</sub> at the exit of the flow reactor as a function of the contact distance with NH<sub>3</sub> for a range of NH<sub>3</sub> concentrations. The NO<sub>3</sub><sup>-</sup>HNO<sub>3</sub> reagent ion was used for the majority of the measurements. At temperatures below 350 K the SO<sub>3</sub> decays were exponential, as expected for a first-order process, and as observed previously.<sup>4</sup> First-order SO<sub>3</sub> loss rate coefficients were extracted from the decays by using the Brown algorithm.<sup>9</sup> First-order rate coefficients are plotted as a function of the concentration of NH<sub>3</sub> for a range of temperatures in 40 Torr of N<sub>2</sub> in Figure 1. The slopes of these plots yield the effective second-order rate coefficients for SO<sub>3</sub> + NH<sub>3</sub>. All of the measured association rate coefficients are listed in Table 1. The quoted errors are the 95% confidence levels for precision only. The overall uncertainty in the rate coefficients is estimated to be ±20%. The room temperature rate coefficients measured in this work are in excellent agreement with the previous measurements of Lovejoy and Hanson,<sup>4</sup> but are about 100 times smaller than the original measurement by Shen et al.<sup>7</sup> Heterogeneous loss of SO<sub>3</sub>, possibly related to the relatively high levels of SO<sub>3</sub>, may have influenced the Shen et al.<sup>7</sup> measurement.

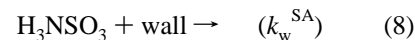
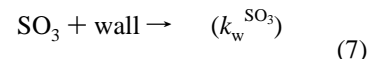
The pressure and temperature dependence of the rate coefficient for a three-body reaction may be described by the Troe formalism<sup>10</sup>

$$k(M, T) = \left( \frac{k_0(T)[M]}{1 + \frac{k_0(T)[M]}{k_\infty(T)}} \right) 0.6^y \quad (5)$$

$$y = \left( 1 + \left[ \log \left( \frac{k_0(T)[M]}{k_\infty(T)} \right) \right]^2 \right)^{-1}$$

where  $k_0(T) = k_0^{300}(T/300)^{-n}$  and  $k_\infty(T) = k_\infty^{300}(T/300)^{-m}$ . A fit of the  $k(M, T)$  data (Table 1) to eq 5, including the previous measurements<sup>4</sup> at 295 K, gives  $k_0^{300} = (3.6 \pm 0.4) \times 10^{-30}$  cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>,  $k_\infty^{300} = (4.3 \pm 1.2) \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>, and  $n = 6.1 \pm 1.0$ , with  $m$  fixed equal to zero. The errors reflect an estimated 20% uncertainty in the measured rate coefficients. The fit results changed by less than 10% for  $0 < m < 3$ . The assumption that the high-pressure limiting rate coefficient is independent of temperature (i.e.  $m = 0$ ) is reasonable considering that the high-pressure limit rate coefficient is large at room temperature and the temperature dependence of  $k_\infty$  is generally weak (see, for example, ref 10).

At temperatures above 380 K the unimolecular decomposition of H<sub>3</sub>NSO<sub>3</sub> into SO<sub>3</sub> + NH<sub>3</sub> competed efficiently with the association reaction, and the SO<sub>3</sub> decays were not simple exponentials (see Figure 2). For these conditions the SO<sub>3</sub> decay and H<sub>3</sub>NSO<sub>3</sub> appearance were modeled to extract the rate coefficient for decomposition of H<sub>3</sub>NSO<sub>3</sub>. The kinetics were modeled with the following mechanism



For this mechanism [SO<sub>3</sub>] and [H<sub>3</sub>NSO<sub>3</sub>] are described by

$$[\text{SO}_3] = \frac{[\text{SO}_3]_0}{a - b} [(a + c)\exp(at) - (b + c)\exp(bt)] \quad (9)$$

and

$$[\text{H}_3\text{NSO}_3] = \frac{k_f[\text{NH}_3][\text{SO}_3]_0}{a - b} [\exp(at) - \exp(bt)] \quad (10)$$

where

$$a = 0.5[(d^2 - 4e)^{1/2} - d]$$

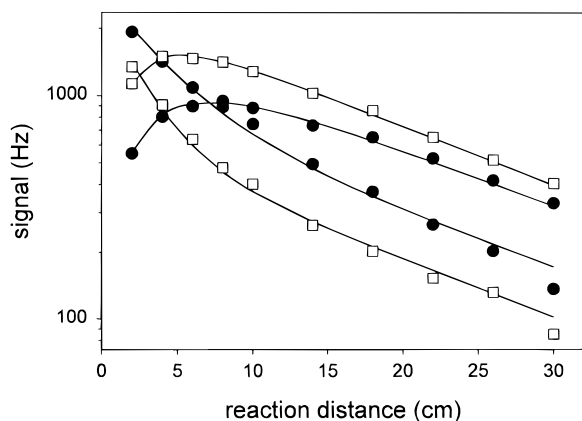
$$b = -0.5[(d^2 - 4e)^{1/2} + d]$$

$$c = k_r + k_w^{\text{SA}}$$

$$d = k_f[\text{NH}_3] + k_r + k_w^{\text{SO}_3} + k_w^{\text{SA}}$$

$$e = k_w^{\text{SA}}k_f[\text{NH}_3] + k_r k_w^{\text{SO}_3} + k_w^{\text{SA}}k_w^{\text{SO}_3}$$

The SO<sub>3</sub> decay and H<sub>3</sub>NSO<sub>3</sub> appearance were fit simultaneously to these equations with  $k_f$  fixed at the value extrapolated from the lower temperature data. The reaction time was calculated using the relationship  $t = z/(1.7v)$  where  $z$  is the reaction distance and  $v$  is the average flow velocity.<sup>4</sup> The rate coefficient for SO<sub>3</sub> wall loss was fixed at the value measured in the absence of NH<sub>3</sub>. This value was always within 10% of the diffusion-limited value, implying that the SO<sub>3</sub> reaction probability with the reactor wall was greater than 10<sup>-3</sup>. The nonlinear regression variables included the first-order H<sub>3</sub>NSO<sub>3</sub>



**Figure 2.**  $\text{SO}_3$  and  $\text{H}_3\text{NSO}_3$  signals ( $\text{NO}_3\text{-SO}_3$  and  $\text{H}_2\text{NSO}_3\text{-HNO}_3$ ) as a function of reaction distance and  $[\text{NH}_3]$ . Reactor conditions:  $v = 288 \text{ cm s}^{-1}$ , 393 K, 40.0 Torr of  $\text{N}_2$ . Squares:  $[\text{NH}_3] = 9 \times 10^{13} \text{ molecule cm}^{-3}$ . Circles:  $[\text{NH}_3] = 1.8 \times 10^{14} \text{ molecule cm}^{-3}$ . Solid lines are fits to the data as described in the text. Fit results are listed in Table 2.

**TABLE 2: Summary of  $\text{SO}_3 + \text{NH}_3 + \text{N}_2 \leftrightarrow \text{H}_3\text{NSO}_3 + \text{N}_2$  Equilibrium Measurements**

$p(\text{N}_2)$ (Torr)	$T$ (K)	$k_f$ ( $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	$[\text{NH}_3]$ ( $10^{13} \text{ molecule cm}^{-3}$ )	$v$ ( $\text{cm s}^{-1}$ )	$k_r$ ( $\text{s}^{-1}$ )	$\Delta H^\circ$ (kcal $\text{mol}^{-1}$ )
40.8	393	7.4	5	281	44	-24.0
40.8	393	7.4	9	281	41	-24.1
40.8	393	7.4	18	281	38	-24.1
40.4	402	6.5	12	295	97	-23.8
40.4	402	6.5	12	295	94	-23.9
40.4	402	6.5	25	295	117	-23.7
40.0	393	7.3	18	288	41	-24.1
40.0	393	7.3	9	288	37	-24.2
40.3	383	8.3	9	279	22	-24.1
40.3	383	8.3	6	279	20	-24.1
40.3	383	8.3	2	279	21	-24.1
40.6	393	7.4	10	280	33	-24.3
40.6	393	7.4	14	280	38	-24.1
40.6	393	7.4	19	280	39	-24.1
40.6	393	7.4	13	280	40	-24.1
79.1	383	13	9	138	33	-24.1
79.1	383	13	19	138	48	-23.8
79.1	383	13	5	138	35	-24.0
79.1	383	13	14	138	47	-23.8
41.0	393	7.4	9	272	36	-24.2
41.0	393	7.4	14	272	41	-24.1
41.0	393	7.4	5	272	35	-24.2

decomposition rate coefficient  $k_r$ , the  $\text{H}_3\text{NSO}_3$  wall loss ( $k_w^{\text{SA}}$ ), and the CIMS sensitivity for  $\text{SO}_3$  relative to  $\text{H}_3\text{NSO}_3$ . A set of experimental  $\text{SO}_3$  and  $\text{H}_3\text{NSO}_3$  profiles and the simultaneous fits to eqs 9 and 10 are presented in Figure 2. All the equilibrium measurements are summarized in Table 2. The rate coefficient for wall loss of  $\text{H}_3\text{NSO}_3$  was consistently about 40% less than the diffusion-limited value, implying that at these elevated temperatures the wall reaction probability for  $\text{H}_3\text{NSO}_3$  was reduced and/or evaporation of  $\text{H}_3\text{NSO}_3$  was important. The fitted wall loss rate coefficients for  $\text{H}_3\text{NSO}_3$  varied by less than about 20% for the range of  $\text{NH}_3$  concentrations used in this work. The CIMS sensitivities for  $\text{H}_3\text{NSO}_3$  and  $\text{SO}_3$  were a function of the concentration of  $\text{HNO}_3$  in the ion-molecule reactor. For the conditions of the present work, the CIMS was typically 1–3 times more sensitive to  $\text{H}_3\text{NSO}_3$  than  $\text{SO}_3$ .

The equilibrium constant could only be measured over a limited range of temperatures because of the very strong temperature dependence of the rate coefficient for decomposition of  $\text{H}_3\text{NSO}_3$ . Therefore, the reaction enthalpy was derived by using a third-law analysis. The entropy of  $\text{H}_3\text{NSO}_3$  was calculated from experimental<sup>6</sup> and theoretical<sup>5</sup> structural pa-

**TABLE 3: Predicted  $\text{H}_3\text{NSO}_3$  Decomposition Lifetimes for Tropospheric Conditions**

pressure (Torr)	$T^a$ (K)	$k_f$ ( $10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )	$k_r$ ( $\text{s}^{-1}$ )	$\text{H}_3\text{NSO}_3$ decomp lifetime (s)
760	281	2.2	$9 \times 10^{-3}$	110
405	254	2.3	$1.1 \times 10^{-4}$	9100
195	222	2.5	$1.4 \times 10^{-7}$	$7 \times 10^6$

<sup>a</sup> On the basis of a model atmosphere for 40° N in March (ref 15).

rameters and scaled vibrational frequencies.<sup>5</sup> The entropies of  $\text{SO}_3$  and  $\text{NH}_3$  were taken from the literature.<sup>11</sup> These values yielded an entropy change for the formation of  $\text{H}_3\text{NSO}_3$  (reaction 1) of  $-0.036 \text{ kcal mol}^{-1} \text{ K}^{-1}$  for  $250 \text{ K} < T < 400 \text{ K}$ . Calculations also showed that the change in heat capacity for reaction 1 is negligible for  $300 \text{ K} < T < 400 \text{ K}$  ( $|\Delta C_p| < 1 \text{ cal mol}^{-1} \text{ K}^{-1}$ ), so that  $\Delta H^\circ$  is essentially independent of temperature between 300 and 400 K.

In the equilibrium experiments, data were taken in the entrance and mixing region immediately downstream of the  $\text{SO}_3$  moveable source (see Figure 2). It should be noted that at lower temperatures  $\text{SO}_3$  decays were linear in this region, even though the radial velocity and concentration gradients are not expected to be fully developed until about 5–10 cm downstream of the inlet.<sup>12</sup> On the basis of the poorly defined reaction time at short reaction distances, the uncertainties in the measured equilibrium constants are estimated to be about a factor of 2. This yields a reaction enthalpy for  $\text{SO}_3 + \text{NH}_3 \leftrightarrow \text{H}_3\text{NSO}_3$  of  $\Delta H_{298\text{K}}^\circ = -24 \pm 1 \text{ kcal mol}^{-1}$  and a heat of formation for  $\text{H}_3\text{NSO}_3$  of  $\Delta H_{298\text{K}}^\circ = -129.6 \pm 1.0 \text{ kcal mol}^{-1}$ , where the standard state is 1 atm. This experimental  $\text{H}_3\text{N-SO}_3$  bond enthalpy is about 4 kcal  $\text{mol}^{-1}$  larger than the theoretical value.<sup>5</sup>

### Atmospheric Implications

The lifetime of  $\text{H}_3\text{NSO}_3$  with respect to unimolecular decomposition for several conditions of pressure and temperature characteristic of the troposphere are listed in Table 3. Other potential atmospheric loss processes for  $\text{H}_3\text{NSO}_3$  include scavenging by aerosol and clustering with  $\text{H}_2\text{SO}_4$ . The heterogeneous reaction probability for  $\text{H}_3\text{NSO}_3$  is probably near unity. In this case the lifetime of  $\text{H}_3\text{NSO}_3$  with respect to aerosol scavenging will range from seconds in clouds to many hours in clean air.<sup>13</sup> Assuming a very efficient reaction with  $\text{H}_2\text{SO}_4$  and ambient  $[\text{H}_2\text{SO}_4]$  ranging from  $10^6$  to  $10^7 \text{ molecule cm}^{-3}$ ,<sup>14</sup> yields a lifetime of  $\text{H}_3\text{NSO}_3$  with respect to clustering with  $\text{H}_2\text{SO}_4$  of about  $10^3\text{--}10^4 \text{ s}$ . This analysis shows that the unimolecular decomposition of  $\text{H}_3\text{NSO}_3$  is most important in the lower troposphere for clean conditions. In the free troposphere the dominant loss processes for  $\text{H}_3\text{NSO}_3$  are probably scavenging by aerosol and clustering with  $\text{H}_2\text{SO}_4$ . In order to understand the role of  $\text{H}_3\text{NSO}_3$  in the nucleation of atmospheric particles, the kinetics of production and decomposition of clusters of the form  $\text{H}_3\text{NSO}_3(\text{H}_2\text{SO}_4)_x$  are needed.

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