Heterogeneous Uptake of Gaseous N_2O_5 by $(NH_4)_2SO_4$, NH_4HSO_4, and H_2SO_4 Aerosols

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The heterogeneous uptake of gaseous N_2O_5 by ammonium sulfate [$(NH_4)_2SO_4$], ammonium bisulfate [NH_4HSO_4], and sulfuric acid [H_2SO_4] aerosols as a function of relative humidity has been investigated at room temperature and atmospheric pressure. Ammonium-containing aerosols were generated by a constant-output atomizer and conditioned by passing through a diffusion dryer. Sulfuric acid aerosols were produced by the homogeneous reaction of SO_3 and H_2O in a borosilicate vessel. Addition of a dry or wet N_2 flow controlled the relative humidity (RH) of these aerosol flows. Using a chemical ionization mass spectrometer (CIMS) for N_2O_5 concentration monitoring and a scanning mobility particle spectrometer (SMPS) for aerosol characterization, reaction probabilities (γ) in the range of 0.001 to 0.1 for the uptake of N_2O_5 were determined as a function of RH. The results are expressed as follows: $\gamma[(NH_4)_2SO_4] = 2.79 \times 10^{-4} + 1.30 \times 10^{-4} \times (RH) - 3.43 \times 10^{-6} \times (RH)^2 + 7.52 \times 10^{-8} \times (RH)^3$, $\gamma[NH_4HSO_4] = 2.07 \times 10^{-3} - 1.48 \times 10^{-4} \times (RH) + 8.26 \times 10^{-6} \times (RH)^2$, and $\gamma[H_2SO_4] = 0.052 - 2.79 \times 10^{-4} \times (RH)$. We suggest that the water content and phase in the ammonium-containing aerosols control the reactivity of N_2O_5 while liquid-phase ionic reactions primarily dominate the uptake in sulfuric acid aerosols.

Introduction

The heterogeneous uptake of gaseous N_2O_5 by sulfuric acid aerosols

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad (1)$$

is one of the most important atmospheric processes in controlling OH and NO_x concentrations, and thus determining the ozone balance in the upper troposphere and lower stratosphere.[1,2] Reaction 1 converts the reactive nitrogen oxides (NO_x) into the reservoir species HNO_3, which is then recycled back to NO_x by the reaction with OH radicals and the photolytic process, or removed from the atmosphere by deposition.

In a global troposphere model, Dentener and Crutzen[3] have adopted a reaction probability (γ) of 0.1 for ammonium bisulfate aerosol as a typical aerosol in the atmosphere. They found the decreases of yearly averaged NO_x, O_3, and OH levels of 49%, 9%, and 9% with respect to values obtained by considering gas-phase reactions only. Dentener and Crutzen[3] have also calculated the impact by using a smaller reaction probability of 0.01 and the decreases of NO_x, O_3, and OH are still very high, being 40%, 4%, and 3%, respectively. These calculations suggest that the magnitude of γ for reaction 1 is also of fundamental importance in global tropospheric chemistry.

Sulfuric acid aerosol is produced from gas-phase processes of sulfur-bearing compounds and also from volcanic emissions. Under lower stratospheric conditions, the aerosol may consist entirely of sulfuric acid. In the middle and upper troposphere, however, reactions of sulfuric acid aerosols with ammonia lead to the neutralized forms of sulfate aerosols: ammonium bisulfate and ammonium sulfate.[4] The properties of these aerosols, including deliquescence and efflorescence, under varying atmospheric conditions of relative humidity (RH) and temperature, have been thought to be important in heterogeneous chemistry.[4,5]

The heterogeneous reaction of N_2O_5 with sulfuric acid has been investigated extensively in aerosols,[6−10] droplet,[11] and bulk surfaces[12,13] in the temperature range of 200−300 K. The results at room temperature have been reviewed recently[14,15] and found to be in excellent agreement among these investigations. For this reason we have performed some experiments to check the reliability of our recently developed aerosol reactor as shown in the Experimental Section. For ammonium bisulfate aerosols, Mozurkewich and Calvert[6] have measured the γ values as a function of relative humidity from 1 to 76% and demonstrated the peak reactivity of ∼0.05 at ∼55%. In a previous investigation Hu and Abbatt[9] have determined the reaction probability being 0.04−0.05 at 50−69% and decreasing to a value of ∼0.02 at 83−94% for ammonium sulfate aerosol. Since the data basis is rather limited, we feel the confirmation of these two sets of data on ammonium-containing sulfate aerosols in the range of relative humidity from 1 to 100% is necessary.

Because of the importance of this reaction in the atmosphere, we have undertaken a series of experiments to measure reaction probabilities for these aerosols using an aerosol flow-reactor that is interfaced to a chemical ionization mass spectrometer. In the following sections we will describe the preparation and measurement of aerosols, the procedures used to determine reaction probability, and the potential impact of our results on atmospheric chemistry.

Experimental Method

The apparatus used in these experiments is composed of two main sections. The first section includes a brief discussion of the generation and characterization of the various sulfate aerosols under investigation. The second section describes the instruments needed to introduce and measure N_2O_5. The components of each section are discussed along with the treatment relevant to data analysis.

Aerosol Generation and Characterization. Figure 1 shows the components of the experimental setup used to control aerosol

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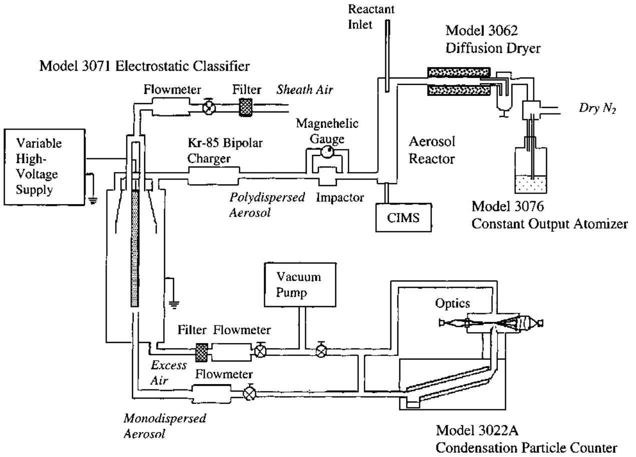

Figure 1. Schematic diagram of generation and measurement of ammonium-containing sulfate aerosols.

formation and measurement. Ammonium sulfate (J. T. Baker, 99.4%) and ammonium bisulfate (E M Science, 99.8%) aerosols were formed by using a constant output atomizer (TSI, model 3075) filled with 0.1%-by-mass solutions in distilled water. This dilution provided sufficient aerosol output for uptake measurements without blocking such aerosol measurement instruments such as the regulating valves and inlet impactor.

Aerosols were produced by the expansion of compressed, dry N_2 through an orifice, which then atomized liquid drawn from the reservoir. The N_2 carrier passed through a molecular sieve trap in order to remove the impurities. Large droplets impacted upon the wall of the atomizer and returned to the reservoir, while a fine spray of particles left the generator. This flow was then passed through a diffusion dryer (TSI, model 3062), which was used to partially control the relative humidity of the final aerosol flow and to allow large aerosol particles settling to the wall, providing a more repeatable particle size distribution. Further change of the aerosol humidity was achieved by adding water vapor or dry N_2 flows to the aerosol stream. Relative humidity was measured at the bottom of the flow reactor with a fast-response, digital hygrometer (VWR, model 35519-041), which was protected from irreversible aerosol coating on the sensor surface by a tube filter (Balston, DFU-9930-05 DF), inserted into the exit tube of the flow reactor. It is noted that the relative humidity measurements were performed in the absence of N_2O_5 in order to prevent the contamination of the sensor element.

Sulfuric acid aerosols were produced by a different method than that described above (not shown in Figure 1) and based solely on SO_3 hydrolysis. The first step in aerosol production was the mixing of SO_3 vapor and moisturized N_2 streams into a glass reactor, allowing reaction and nucleation. SO_3 was supplied from fuming sulfuric acid (Aldrich, 26−29.5% SO_3) in a N_2 carrier. This aerosol stream then passed into a condensation chamber containing sulfuric acid (prepared from concentrated sulfuric acid, J. T. Baker, 96.2%) of known composition. The residence time in this chamber was long enough to allow aerosol particles reaching equilibrium in the exchange of water vapor above the solution. The time required to reach equilibrium varies greatly as a function of temperature and composition, limiting the range of aerosols that could be produced by this source.

The characterization of aerosols was identical regardless of aerosol type and composition. Following passage through the flow reactor, the aerosol flow was channeled into an electrostatic classifier (TSI, model 3071A). After exposure to a ^{85}Kr bipolar charger, aerosol particles were selected according to their electrical mobility before being passed to a condensation particle counter (TSI, model 3022A). By scanning the classifier voltage and measuring the particle sizes at those voltages, a particle distribution was obtained. Since particle separation depends on electrical mobility and not particle size, a correction to the particle distribution must be made to account for multiply charged aerosols. A typical data of sulfate aerosol from this setup is shown in Figure 2. From this information, a variety of properties of the aerosol can be calculated, including total particle density, surface area, and aerosol volume, with particular interest in the surface area-to-volume ratio of the aerosol flow. It should be noted that the calculation using the SMPS software is based on the assumption that the aerosols are spherical.

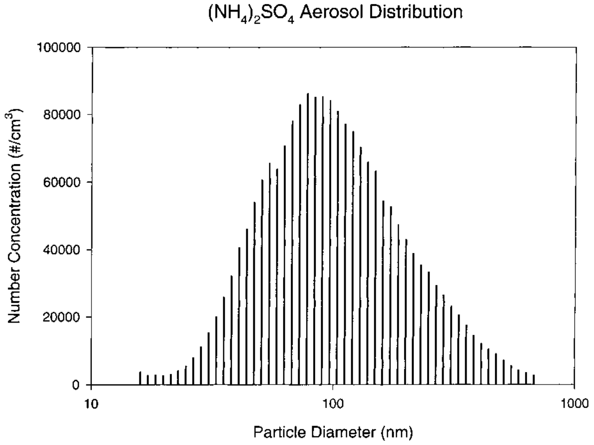

Figure 2. Typical size distribution of ammonium sulfate aerosols. Data shown are from 0.1 wt % ammonium sulfate with 92% RH and are corrected for multiple charging of particles. The mean diameter is 0.12 μm and the geometric standard deviation is 1.965. The surface area density is 0.0016 cm^2/cm^3.

To ensure that aerosol size distribution measured after exposure to the flow tube was indeed the same as those generated during atomization or reaction, the aerosol size distribution was measured either through the flow tube or through a ∼0.5 cm diameter conductive silicon tube under otherwise identical conditions. The silicon tube has a much smaller volume (∼17 cm^3) than the flow tube (∼1000 cm^3), thus residence time in the tubing was significantly reduced, eliminating possible size changes occurring during transit in the flow tube. Particle sizes were measured at 25, 60, and 90% RH. In each case, the surface area-to-volume ratios of the aerosol flow were less than 5% variation from each other, with no clear trend in the difference. Thus, we conclude that the aerosol loss in the reactor is negligible.

An additional concern in particle measurement was possible size changes associated with the mixing of the aerosol stream with sheath air in the electrostatic classifier. To test this, experiments were performed using the usual room air sheath inlet (RH 42%) or encasing the inlet in a dry N_2 flow to achieve ∼0% RH (measured by hygrometer). Experimental data were then collected for aerosols at RH of 17, 47, and 95%. As in the case of adjusting aerosol residence time, there was little effect observed by modifying the sheath gas humidity, indicating that the size distribution data reported by our instruments is an accurate reflection of particle sizes in the reaction cell.

Flow Reactor and N_2O_5 Measurement. The experimental setup for the reaction probability measurement is shown schematically in Figure 3. The central component is the atmospheric pressure flow reactor. The reactor is a 130-cm long Pyrex tube with an inner diameter of 2.5 cm suspended vertically. Although equipped with a jacket to allow cooling of

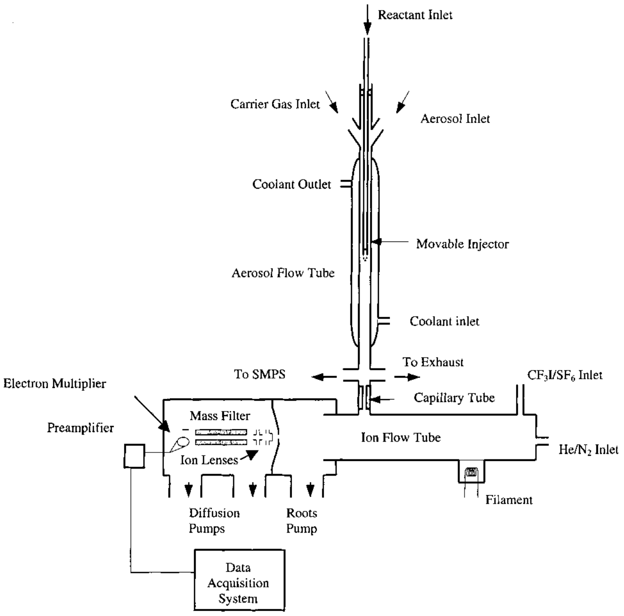

Figure 3. Schematic diagram of aerosol flow reactor. The reactor interfaces to both an aerosol measurement apparatus shown in Figure 1 and a chemical ionization mass spectrometer.

the tube, all experiments reported herein were conducted at room temperature (295 ± 1 K).

N_2O_5 was synthesized at 295 K by the reaction NO_2 with O_3 in an O_2 carrier and was collected in a Pyrex vessel at 196 K. The sample was further purified with distillations in order to remove impurities. O_3 was prepared by using an electrical discharge tube. During the experimental run, N_2O_5 was kept at 213 to 237 K in a methanol chiller (Haake, model A80). A movable stainless steel inlet ran through the central axis of the flow tube, allowing addition of N_2O_5 at variable distances. A separate inlet carried the aerosol and N_2 mixture into the tube. All flow sources had bypass valves to remove chemicals as needed without changing the total flow conditions.

Total flow rates in the tube varied between 1.0 and 2.5 L/min, allowing the reaction to take place under laminar flow conditions (Reynolds number Re = 60−150). After passing through the flow tube, the reactant stream was channeled either into the electrostatic classifier or through a glass capillary for N_2O_5 detection by mass spectroscopy, with excess gas vented into the exhaust hood.

Detection of N_2O_5 was accomplished by chemical ionization mass spectrometry using CF_3I as the ionizing gas.[12,16] In the ion flow-tube, CF_3I passed over a rhenium ribbon, which was heated by a direct current of 8−10 A, to produce I^- ions. The subsequent reaction of I^- with N_2O_5 produced NO_3^-. The detection sensitivity is about 1×10^{11} molecule cm^{-3} (S/N = 1, 1 s integration in the aerosol reactor). The product for reaction 1, HNO_3, was also monitored by the reaction $I^- + HNO_3 + M \rightarrow I^-{\cdot}(HNO_3) + M$. The advantage in this experimental method is that it can distinguish between N_2O_5 and HNO_3 through the selective ion−molecule reactions. Flow rates of CF_3I and N_2 carrier gas were regulated to reach a final pressure of ~0.15 Torr in the ion flow-tube. Initial N_2O_5 concentrations in the aerosol reactor were varied in the range of $\sim 5 \times 10^{12}$ to $\sim 2 \times 10^{14}$ molecule cm^{-3} in the uptake experiments. However, there was no observed difference in reaction probability.

Data Collection and Treatment. The first step in determining the reaction probability of N_2O_5 by sulfate aerosols is the calculation of the first-order decay rate, *k*. A typical experiment measures the concentration of N_2O_5 at several injector positions. The change of N_2O_5 concentrations is given in the following equation:

$$d[N_2O_5]/dt = -k[N_2O_5]A \tag{2}$$

where *A* is the surface area density (or the surface-to-volume ratio) for sulfate aerosol. All measurements began 25 cm from the bottom of the flow reactor to ensure a laminar flow being fully developed (without the effects of turbulent mixing). The slope aquired by the change in concentration vs time is the first-order decay rate for a given experiement. Reaction times are determined from the injector position and flow velocity according to the relationship $t = l/v$ where v is the flow velocity (cm/s) and l is the length of the stainless steel injector position relative to the starting position (cm).

The calculated decay rates, *k*, are then corrected for axial and radial diffusion effects in the flow tube according to the treatment reported in the literature.[17−19] The corrected decay rate is designated to be k_c. In the data analysis the gas-phase diffusion coefficient of N_2O_5 in N_2 [20] is estimated using the relationship

$$D_g = (63.92/p) \times (T/293)^{1.94} \tag{3}$$

where *p* is the pressure (Torr) and *T* the temperature (K) of the reactor. Typically, the correction for diffusion effects is less than 10% and hence the estimation of diffusion coefficient does not cause any significant error in the determination of reaction probability.

From the corrected decay rates, k_c, the reaction probability for a selected aerosol can be determined. A simple and straightforward estimate of the uptake coefficient can be made by using the aerosol size distribution

$$\gamma = \frac{4k_c}{A\omega} \tag{4}$$

where *A* is the surface area density of aerosols measured by SMPS and ω the mean molecular velocity of N_2O_5. However, all of the data shown in the next section are analyzed by a more complete method developed directly from the SMPS data,[21]

$$k_c = \sum_i k(r_i) = \sum_i \frac{\gamma N_i \omega \pi r_i^2}{1 + \gamma\left(\dfrac{0.75 + 0.283Kn_i}{Kn_i(Kn_i + 1)}\right)} \tag{5}$$

and the Knudsen number

$$Kn_i = 3Dg/\omega r_i \tag{6}$$

is calculated for various particle radii (r_i) of aerosols shown in Figure 2. Typically, the difference in γ values determined by eqs 4 and 5 is less than 10−20% for the results shown in the next section. It should be noted that we assume the shape of aerosol is spherical in the data treatment. While the assumption is true for liquid-phase aerosol, but it may underestimate the surface area density of dry, solid sulfate aerosols. Further discussion on this point will be given in the next section.

Results and Discussion

Figure 4 shows typical changes in N_2O_5 signal as a function of reaction time. As described above in the Experimental Section, reaction time is calculated from changes in the injector position and flow rates. The plot allows the calculation of the

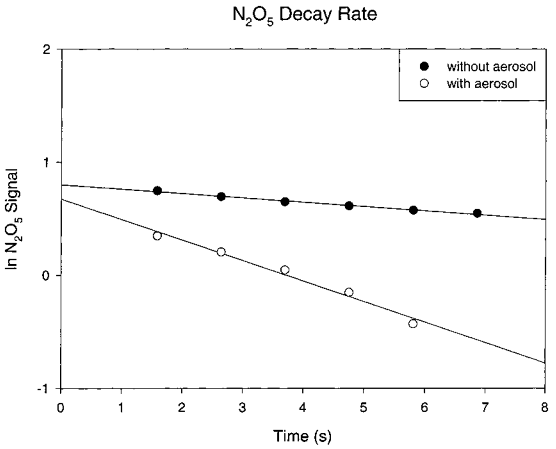

Figure 4. Typical N_2O_5 decay profiles with and without aerosol flow. Aerosols are generated from 0.1 wt % ammonium bisulfate at 39% RH. The experimental conditions are: p(total) = 723 Torr, T = 294 K, v = 7.6 cm/s, surface area density = 8.6×10^{-4} cm^2/cm^3, and [N_2O_5] ~ 1.5×10^{14} molecules/cm^3.

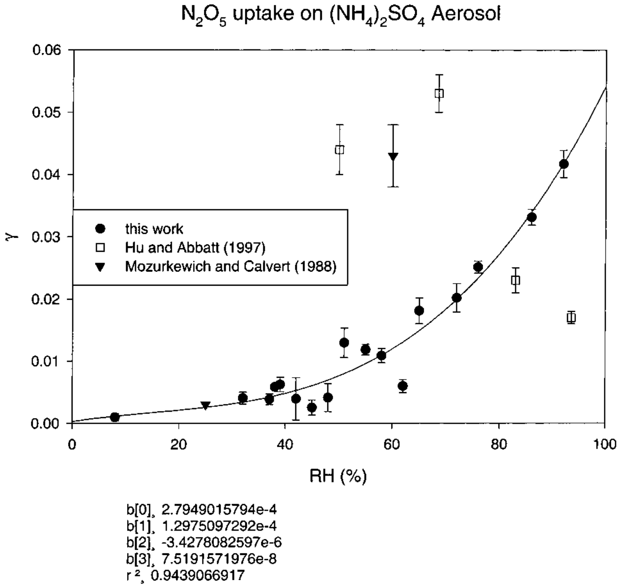

Figure 5. Reaction probability measurements for N_2O_5 hydrolysis on ammonium sulfate aerosol as a function of relative humidity. The uncertainty represents one standard deviation of our data.

TABLE 1: Reaction Probability Determinations for the Uptake of N_2O_5 on Ammonium Sulfate Aerosols (The uncertainty represents one standard deviation.)

RH (%)	γ	uncertainty
8	9.4×10^{-4}	5.9×10^{-4}
32	4.0×10^{-3}	9.6×10^{-4}
37	3.8×10^{-3}	8.5×10^{-4}
38	5.8×10^{-3}	2.5×10^{-4}
39	6.2×10^{-3}	1.2×10^{-3}
42	3.9×10^{-3}	3.4×10^{-3}
45	2.5×10^{-3}	1.2×10^{-3}
48	4.1×10^{-3}	2.3×10^{-3}
51	0.013	2.4×10^{-3}
55	0.012	8.7×10^{-4}
58	0.011	1.1×10^{-3}
62	6.0×10^{-3}	1.0×10^{-3}
65	0.018	2.1×10^{-3}
72	0.020	2.3×10^{-3}
76	0.025	9.6×10^{-4}
86	0.033	1.3×10^{-3}
92	0.042	2.2×10^{-3}

first-order decay of N_2O_5 under given conditions (k = slope). The upper curve (solid circles) indicates the decay of N_2O_5 without aerosol present, while the open circles represent the uptake of N_2O_5 by sulfate (in this case, ammonium bisulfate). To properly correct for the increased decay of N_2O_5 in various RH conditions, the first-order decay rates as a function of RH in the absence of aerosol are determined throughout the experiment. The reaction probabilities on the wall of the reactor, $\gamma_w = 2rk_c/\omega$ (r was defined as the radius of the flow reactor, 1.25 cm), were determined to be in the range of $\sim 2 \times 10^{-6}$ at low RH to $\sim 1 \times 10^{-5}$ at high RH. The overall decay rate was then corrected for the wall contributions, yielding only decay rate caused by sulfate aerosol. This value is then corrected for axial and radial diffusion as described above. From this value, the reaction probability can be determined. This procedure is adopted in every experiment discussed in the following sections.

Ammonium Sulfate. The uptake of N_2O_5 on ammonium sulfate aerosols is shown in Figure 5 and also listed in Table 1. The uptake on dry aerosols (under the condition of less than 40% RH) is found to be relatively small, <0.01. As the humidity increases above 50% RH, N_2O_5 uptake increases from ~0.01 to ~0.04 at 92% RH. The polynomial fit of the data gives

$$\gamma[(NH_4)_2SO_4] = 2.79 \times 10^{-4} + 1.30 \times 10^{-4} \times (RH) - 3.43 \times 10^{-6} \times (RH)^2 + 7.52 \times 10^{-8} \times (RH)^3 \quad (7)$$

Our results are supported by comparison to the phase transition of ammonium sulfate aerosols described by Tang and Munkelwitz[22] and Xu et al.[23] The aerosol has an efflorescence point near 40% RH at 25 °C, above which the water content increases steadily and below which particles are completely dry. As our particles are formed in a wet environment and subsequently dried, the expected water content is expected to match these results. The closeness of the uptake data to the evaporation profile of ammonium sulfate suggests that the water content of the aerosol controls the N_2O_5 uptake. It is further noted that the reaction primarily takes place with thin liquid water on the surface of solid aerosols (≤40% RH). On the other hand, the hydrolysis may occur throughout the volume of liquid-phase aerosols (>40% RH).

In the data treatment using eq 5 we assume the ammonium sulfate aerosols are spherical. At humidity greater than 40% RH, the sulfate aerosols are in liquid form and the assumption is correct. But, under dry conditions (<40% RH) the aerosols become solid and the crystal structure of ammonium sulfate is orthorhombic. Since the surface area density on the basis of this crystal structure is greater than that using the spherical assumption, the γ values we report in Table 1 and Figure 5 may be smaller.

Data for uptake on ammonium sulfate collected by Hu and Abbatt[9] are represented with square symbols in Figure 5. Our data does not match the trend of these results with RH, but does fall within the same range of γ value (0.02−0.05) at high RH. A limited set of data reported by Mozurkewich and Calvert[6] are also shown in Figure 5 (solid triangles). Their result at 25% RH is in excellent agreement with out data at low RH. However, their data at 60% RH, needing to be reduced by ~15% because of a small error in the data treatment,[6,7] is still substantially greater than our data. The source of the discrepancy is unknown, but probably associated with the preparation and conditions of the aerosols.

Ammonium Bisulfate. Experiments similar to the above were also performed for ammonium bisulfate aerosols. The results are shown in Figure 6 and also tabulated in Table 2. The uptake of N_2O_5 increases steadily as the water content increases. Again

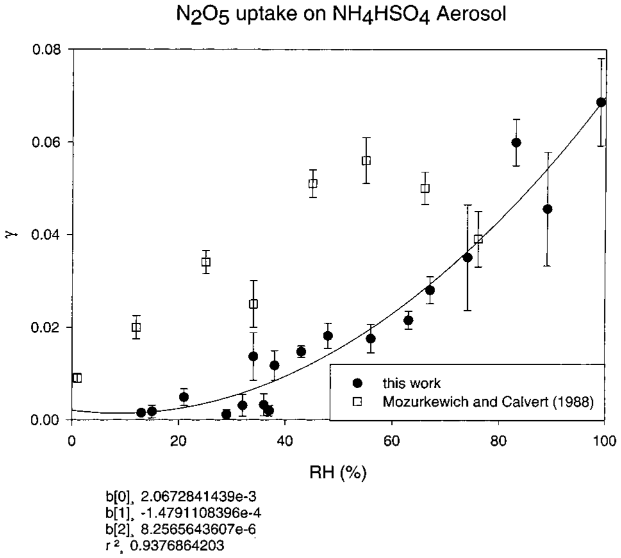

Figure 6. Reaction probability measurements for N_2O_5 hydrolysis on ammonium hydrogen sulfate aerosol as a function of relative humidity. The uncertainty represents one standard deviation of our data.

TABLE 2: Reaction Probability Determinations for the Uptake of N_2O_5 on Ammonium Bisulfate Aerosols (The uncertainty represents one standard deviation.)

RH (%)	γ	uncertainty
13	1.5×10^{-3}	4.2×10^{-4}
15	1.8×10^{-3}	1.4×10^{-3}
21	4.8×10^{-3}	1.8×10^{-3}
29	1.1×10^{-3}	1.0×10^{-3}
32	3.1×10^{-3}	2.3×10^{-3}
34	0.014	5.2×10^{-3}
36	3.2×10^{-3}	2.4×10^{-3}
37	1.9×10^{-3}	1.1×10^{-3}
38	0.012	3.2×10^{-3}
43	0.015	1.3×10^{-3}
48	0.018	2.7×10^{-3}
56	0.018	3.1×10^{-3}
63	0.022	1.9×10^{-3}
67	0.028	2.9×10^{-3}
74	0.035	0.011
83	0.060	5.1×10^{-3}
89	0.046	0.012
99	0.069	9.5×10^{-3}

we use the polynomial fit of our data, and the result gives

$$\gamma[NH_4HSO_4] = 2.07 \times 10^{-3} - 1.48 \times 10^{-4} \times (RH) + 8.26 \times 10^{-6} \times (RH)^2 \quad (8)$$

The trend of reaction probability versus RH follows the water activity of the ammonium bisulfate at room temperature.[22-24] The observation suggests that hydrolysis is the dominant step in the uptake of N_2O_5. A kinetic study was previously investigated at 293 K by Mozurkewich and Calvert.[6] The trend in their data matches ours fairly well, but with somewhat larger γ values overall. It should be noted, however, that subsequent work by this group finds these values should be ~15% smaller,[6,7] which would bring the two studies somewhat closer to agreement.

Sulfuric Acid. The reactive uptake on sulfuric acid aerosols has been examined extensively by a number of groups previously,[6-13] thus our examination was kept quite limited, mainly for the confirmation of these previous results using our apparatus. The data are shown in Figure 7 and also listed in Table 3. Our data corresponds reasonably well with published value[6-11] of N_2O_5 uptake at lower relative humidity (RH < 25%). If we exclude the data (shown in open circles) by Mozurkewich and Calvert[6] because the data analysis is in error,[6,7] we derive a fit for all data by linear regression:

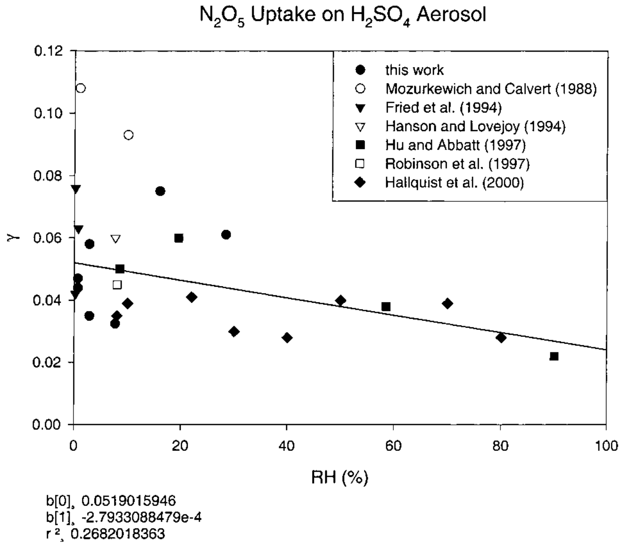

Figure 7. Reaction probability measurements for N_2O_5 hydrolysis on sulfuric acid aerosol as a function of relative humidity.

TABLE 3: Reaction Probability Determinations for the Uptake of N_2O_5 on Sulfuric Acid Aerosols

RH (%)	H_2SO_4 (wt %)	g
0.7	81	0.044
0.7	81	0.047
2.9	76	0.058
2.9	76	0.035
7.7	70	0.033
16.0	63	0.075
28.4	55	0.061

$$\gamma[H_2SO_4] = 0.052 - 2.79 \times 10^{-4} \times (RH) \quad (9)$$

The reaction probability on H_2SO_4 aerosol shows only a weak dependence upon the relative humidity, in contrast to those on ammonium-containing aerosols as shown in the previous sections. The results reported here suggest that the reaction mechanism in the uptake of N_2O_5 by these sulfate aerosols is substantially different. Detailed discussion is given in the following section.

Reaction Mechanisms. The comparison of N_2O_5 uptake in ammonium-containing sulfate aerosols with that of water is shown in Figure 8. It appears that $\gamma[NH_4HSO_4]$is slightly greater than $\gamma[(NH_4)_2SO_4]$ over the wide range of RH from 10 to100%. Within experimental error, each set of data approaches the uptake value of water ($\gamma \sim 0.05$).[14,25] The previous evaluation[14] quoted the error limit at a factor of 2. However, the most recent evaluation[15] suggests that the γ value for water is ~0.022 at 295 K. It is noted that the water content of aerosol strongly affects the activity of N_2O_5 uptake as described in the previous section. This is consistent with the suggestion of Mentell et al.,[26,27] who studied N_2O_5 uptake on Na^+-neutralized sulfate aerosols. In addition, the γ value for ammonium bisulfate is slightly greater than that of ammonium sulfate, possibly due to the phase change in ammonium sulfate aerosol at 40−80% RH or the presence of a small quantity of H^+ in the ammonium bisulfate aerosol.

Recently Robinson et al.[11] postulated a simple reaction mechanism for the uptake of N_2O_5 on sulfuric acid aerosols

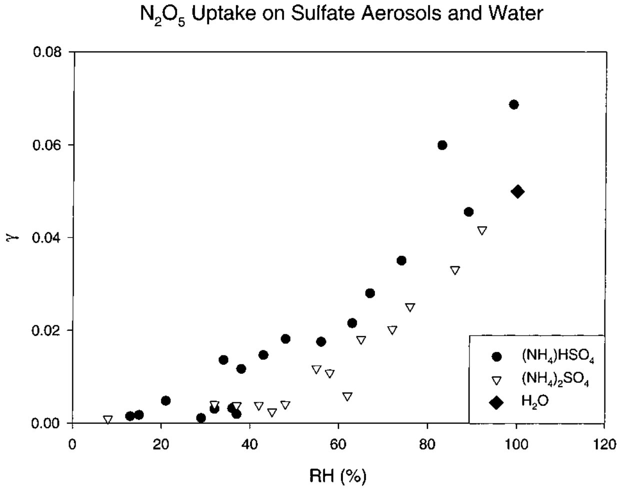

Figure 8. Comparison of reaction probability measurements for N_2O_5 on water, ammonium bisulfate, and ammonium sulfate aerosols as a function of relative humidity.

and bulk substrates for a wide range of acid composition and temperature, using a single consistent set of accommodation coefficient (α) and liquid-phase reaction parameters (H^*, D_l, and k_l). The mechanism includes the following steps:

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \tag{10}$$

$$N_2O_5 + H^+ \rightarrow HNO_3 + NO_2^+ \tag{11a}$$

$$NO_2^+ + H_2O \rightarrow HNO_3 + H^+ \tag{11b}$$

This model is highly successful in explaining the temperature dependence from 200 to 300 K and also the composition dependence from 40 to 80 wt %. However, the result for H_2SO_4 aerosol is in contrast with those for ammonium-containing sulfate aerosols as shown in Figures 5−7. Perhaps, the shortage of H^+ in ammonium-containing sulfate aerosols inhibits the reaction step (eq 11a). Thus the hydrolysis step (eq 10) provides the limiting step for the reactive uptake.

Atmospheric Implications. On the basis of the result for ammonium bisulfate at 50−100% RH, the γ value is about 0.02−0.06 at 294 K. We use the temperature dependence reported for ammonium bisulfate aerosol[6] and for sulfuric acid aerosol[10,11] and estimate that the γ value could increase up to a factor of 3 at lower temperatures between 260 and 280 K if ammonium bisulfate droplet remains as a supercooled liquid. Thus, for the theoretical study of the global tropospheric chemistry we recommend the uptake coefficient of 0.1 to be used in the model calculation. According to the model of Dentener and Crutzen[3], the decreases of NO_x, O_3, and OH are 49%, 9%, and 9%, respectively, due to the effect of reaction 1 as compared to that using gas-phase reactions alone.

Conclusions

The reaction probabilities of N_2O_5 on ammonium sulfate and ammonium bisulfate aerosols are strongly dependent on the relative humidity (or the water content of aerosols) at room temperature. Hydrolysis is believed to be the dominant reaction step. For sulfuric acid aerosols, however, the reaction probability decreases slightly as the relative humidity increases and we believe that ionic reactions apparently play an important role.

At 50−100% RH, the γ values for ammonium bisulfate aerosols are in the range 0.02 to 0.06. Thus, reaction 1 is very efficient in converting NO_x to HNO_3 in the atmosphere. Using a γ value of 0.1 after adopting the temperature dependence of reaction probability, reaction 1 has an important effect on the concentrations of NO_x, O_3, and OH in the global troposphere as suggested by Dentener and Crutzen[3].

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