Reaction Probability of N_2O_5 on Aqueous Aerosols

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The reaction probability, γ, of N_2O_5 (to form HNO_3) with monodisperse $NH_3/H_2SO_4/H_2O$ aerosols has been measured in a flow tube reactor at atmospheric pressure. Experiments were performed at temperatures of 274 and 293 K and at relative humidities of 1–76%. It appears that the presence of a liquid phase is necessary for reaction. With NH_4HSO_4 aerosol, γ values are nonzero, even below the deliquescence point of the pure salt, and show a gradual increase with increasing relative humidity up to constant values of 0.05 and 0.09 for 293 and 274 K, respectively. Experiments with aerosols of varied NH_3/H_2SO_4 ratios suggest that evaporation of NH_3 from the NH_4HSO_4 aerosols creates excess H_2SO_4 on the surface. This can take up water vapor to provide the reactant for N_2O_5 below the deliquescence point of NH_4HSO_4. The present observations are consistent with the reaction of N_2O_5 with moist aerosols being a major removal mechanism for odd nitrogen and a major source of HNO_3 in the nighttime troposphere. The same reaction on H_2SO_4 aerosols may be of significance in the stratosphere.

INTRODUCTION

The importance of oxides of nitrogen (NO and NO_2) in atmospheric chemistry is well recognized. For example, these oxides play a major role in the generation of tropospheric ozone. Also, the gas phase reaction of NO_2 with HO radicals has been identified as a major source of nitric acid. However, the mechanisms by which NO and NO_2 are converted to HNO_3 and eventually removed from the atmosphere by wet or dry deposition are still not fully established. It is known that, at night, O_3 oxidizes NO to NO_2 and, if sufficient O_3 is present, the oxidation proceeds to NO_3. NO_3 and NO_2 exist in rapid equilibrium with N_2O_5. Observed nighttime concentrations of NO_3 imply that there must be some unidentified sink for NO_3 or N_2O_5. The loss in clean tropospheric air suggests that there is a well-mixed, long-lived scavenger for NO_3 [Noxon et al., 1978; Noxon, 1983]. Although possible scavengers have been suggested which involve homogeneous reactions of NO_3 [Winer et al., 1984; Johnston et al., 1986; Atkinson et al., 1986], a meaningful evaluation of the extent of their involvement is impossible at this time.

Russell et al. [1986] concluded that if the slow homogeneous reaction of N_2O_5 with H_2O had a rate constant as large as 1.3×10^{-21} cm^3 molecule^{-1} s^{-1}, it would be the dominant source of tropospheric HNO_3, even under relatively dry desert conditions. This rate constant would imply an N_2O_5 lifetime of the order of 1 hour. The reaction of N_2O_5 with aerosols could easily be much faster than this [Heikes and Thompson, 1983]. The homogeneous reaction of N_2O_5 with H_2O is almost certainly slower than assumed by Russell et al.; only upper limits to the rate constants have been measured. The most recent determination has found an upper limit of 2.7×10^{-22} cm^3 molecule^{-1} s^{-1} [Sverdrup et al., 1987]. Thus it is possible that the heterogeneous reaction between N_2O_5 and H_2O is much more important than the corresponding homogeneous reaction. This reaction may be an important source of HNO_3 in the troposphere.

The observed tropospheric loss rate for NO_3 is often more than an order of magnitude larger than the "background" value observed by Noxon [1983]. These observations have

been summarized by Atkinson et al. [1986]. They imply that if the loss is due to a reaction of N_2O_5, the N_2O_5 lifetimes must range from hundreds to tens of thousands of seconds. These rates are too fast to be accounted for by the homogeneous reaction of gaseous N_2O_5 with H_2O vapor. This has led to the suggestion that the hydrolysis of N_2O_5 to HNO_3 on the surfaces of particles or drops may account for the loss [Heikes and Thompson, 1983; Lazrus et al., 1983; Richards, 1983]. In fact, Platt et al. [1984] have observed a strong dependence of the scavenging rate on relative humidity. This would be qualitatively consistent with the removal of N_2O_5 by reaction with water in aqueous aerosols formed at high humidities.

The results of several model calculations have shown that the reaction of N_2O_5 with aqueous aerosol may well be fast enough to be important in the troposphere. The rate of reaction of a gas with a particle may be expressed in terms of the reaction probability, γ, which is the fraction of collisions of gas molecules with the surface which result in reaction. The calculations of Heikes and Thompson [1983] show that a reaction probability of 0.1 and a very low particle number density of 10^3 particles cm^{-3} gives a lifetime of thousands of seconds. Number densities encountered in the atmosphere can be much greater than this. We also note that the heterogeneous reaction of N_2O_5 might be expected to depend on the amount of water picked up by the particles. This depends on the relative humidity, not the absolute water vapor concentration. Since temperatures are lower at night, the relative humidity is generally higher.

The heterogeneous reaction of N_2O_5 with water has also been suggested in other contexts. Cadle et al. [1975] have suggested that N_2O_5 might hydrolyze on stratospheric aerosols; they found a large effect for this reaction in a model in which they set $\gamma = 1$. Evans et al. [1985] have proposed that this reaction, taking place in polar stratospheric clouds, plays a role in forming the Antarctic "ozone hole." Austin et al. [1986] have argued that wintertime variations in stratospheric HNO_3 concentrations require an as yet unidentified source of HNO_3. They propose that the heterogeneous reaction of N_2O_5 with H_2O, with γ as low as 10^{-3}, could be this source. Chameides [1986] has included heterogeneous reactions of N_2O_5 and NO_3 in a model of nighttime cloud chemistry. Sticking coefficients of 0.01 and 0 were considered. It was found that these reactions could be a major source of HNO_3 in clouds. Chang [1986] has modeled precipitating clouds
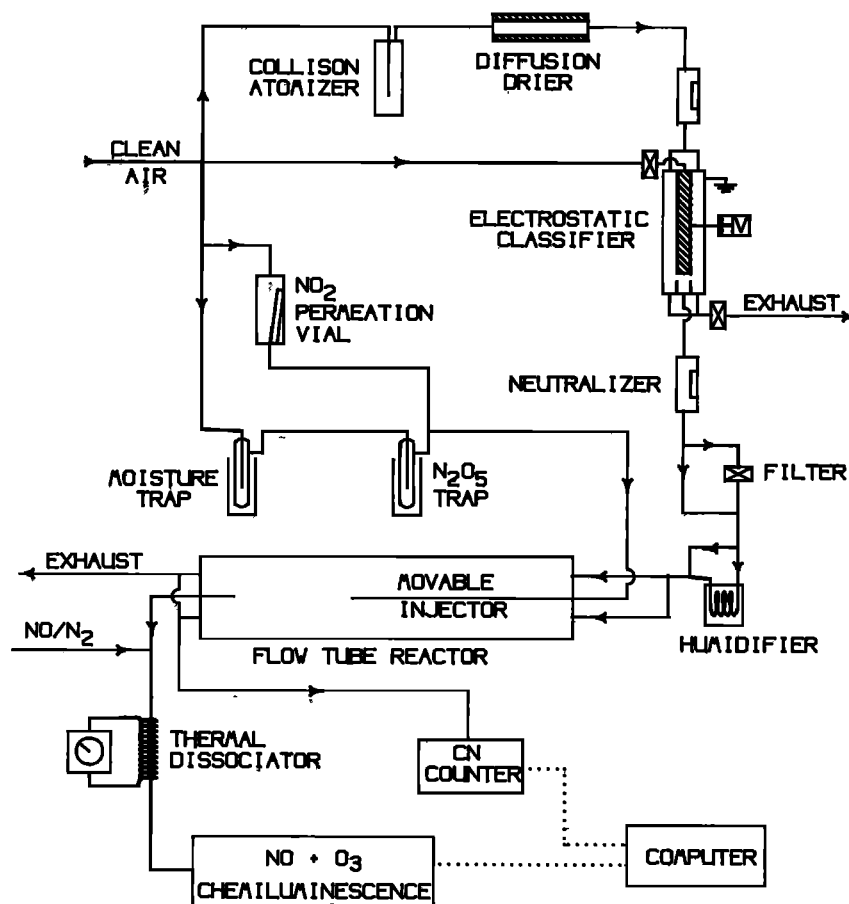
Fig. 1. Flow diagram of the experimental apparatus.

using N_2O_5 reaction probabilities with cloud droplets varying from 1 to 10^{-3}. He found that the model results were sensitive to this parameter and that this reaction could be a significant source of nitrate.

The calculations mentioned above considered a wide range of possible values for the reaction probability for N_2O_5 with liquid surfaces. This was made neccessary by the lack of experimental data on this reaction. A study of the reaction on relatively dry sulfuric acid ($<5\%$ H_2O) at room temperature [Baldwin and Golden, 1979; Baldwin, 1982] yielded a lower bound for γ of 3.8×10^{-5}. Another, similar, study gave a result 2 orders of magnitude larger [Rossi et al., 1987]. Brouwer et al. [1986] found a reaction probability of 3×10^{-3} on dry charcoal and 5×10^{-3} on charcoal in the presence of a small partial pressure of H_2O. The low water activity of these experiments casts doubt upon their applicability to atmospheric conditions. Harker and Strauss [1981] found values of 1×10^{-4} at 263 K and 5×10^{-5} at 221 K for the reaction probability on frozen H_2SO_4/H_2O solutions. They measured somewhat larger values of 3×10^{-4} at 233 K and 1×10^{-4} at 249 K on liquid solutions. Using an indirect method, Verhees [1986] found a reaction probability of 8×10^{-6} on wet NaCl and $MgCl_2$ aerosols. If γ is much less than 10^{-3}, then the reaction of N_2O_5 with aqueous aerosol must be an unimportant source of HNO_3. This would leave the nighttime loss of N_2O_5 unexplained.

We report here an experimental measurement of γ for N_2O_5 on aqueous aerosols with a composition more typical of those found in the atmosphere. We have directly measured the

decay of N_2O_5 in the presence of a monodisperse, submicron aerosol. Most measurements were made using NH_4HSO_4, typical of tropospheric aerosols [Charlson et al., 1978]. Additional experiments were performed with aerosol composition varying from $(NH_4)_2SO_4$ to H_2SO_4. The particles are sufficiently small that the rate of reaction is directly proportional to the reaction probability and the total surface area of the particles.

EXPERIMENTAL METHOD

A diagram of the experimental apparatus is shown in Figure 1. The rate constants were measured at atmospheric pressure in a flow tube equipped with a movable injector. The flow tube has a diameter of 7.5 cm, is 140 cm long, and has a jacket through which liquid can be circulated for temperature control. Because of the high pressure at which the tube is operated, there will be a significant radial concentration gradient. The conversion of distance into time therefore requires the use of a velocity which is larger than the plug flow velocity [Brown, 1978; Keyser, 1984]. For ideal laminar flow, the appropriate velocity is 1.6 times the plug flow velocity. As we have discussed previously [Mozurkewich et al., 1987], the flow in this tube probably has some convective mixing. We have therefore used a flow velocity of 1.3 ± 0.3 times the plug flow velocity, as has been done previously [Mozurkewich et al., 1987; Ferguson et al., 1969]. A total flow of 4.0 L min^{-1} (all flows are referred to 0.80 atm and 293 K) was used for these experiments. A few experiments were carried out with flows
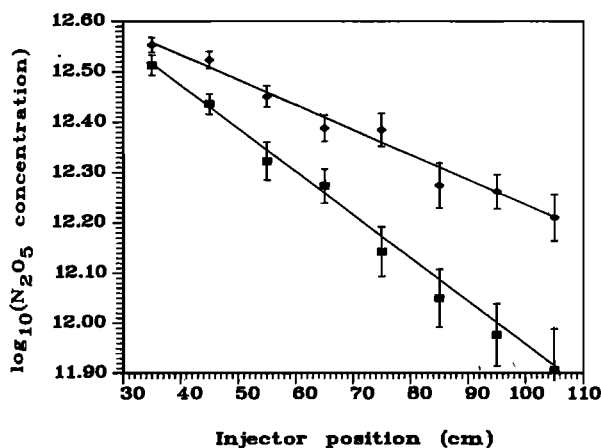
Fig. 2. Example first-order decay plots showing $\log_{10}[N_2O_5$ concentration] versus distance at 293 K and 55% relative humidity. Upper data set is with no aerosol particles. Lower data set is for an aerosol number density of 3.3×10^4 particles cm^{-3} and a particle radius of 93.9 nm. The correction for the presence of larger, doubly charged particles increases the total surface area by 18%. Lines are from a weighted least squares fit.

ranging from 2 to 5 L min^{-1}; the results did not depend on flow rate.

An Aadco clean air supply was used to provide clean, dry air for the experiments. The method of producing a monodisperse aerosol has been described previously [Mozurkewich et al., 1987]. Briefly, a solution of NH₄HSO₄ in water was placed in a Collison atomizer, where a polydisperse aerosol of liquid droplets was formed. The NH₄HSO₄ solution was prepared from Dilute-it analytical concentrates (J. T. Baker) of NH₄OH and H₂SO₄ and deionized water. The water is removed in a diffusion dryer and a monodisperse fraction of the crystalline particles was separated using an electrostatic classifier (TSI, model 3071), also called a differential mobility analyzer (DMA). The DMA was operated at a sheath air to aerosol flow ratio of about 5:1, yielding a spread of radii about the mean of ±13% [Knutson and Whitby, 1975].

After leaving the DMA, the particles were passed through a neutralizer to remove most of the charge. The flow was split into two steams, with one passed through a filter to adjust the number density. These were then recombined. A measured fraction of this flow was then saturated with water vapor in a humidifier. This consists of 1 m of GoreTex tubing immersed in deionized water in a closed vessel held at the temperature of the flow tube. The humidifier is capable of saturating a flow of up to 3 L min^{-1}, with little change in particle number density. The performance of the humidifier was checked using a dewpoint hygrometer (EG&G model 911). The humid and dry airflows were then recombined and admitted to the flow tube.

A second flow, amounting to one tenth of the total, entered the tube through the movable injector. The injector was a 1/4-inch tube, closed at the end, with six radial holes. A portion of this was directed through a trap containing a molecular sieve adsorbant. This trap was placed in a dry-ice/ethanol bath (about 193 K). The flow was then passed through a trap containing solid N₂O₅ placed in a dry-ice/chloroform slush bath (about 205 K). The N₂O₅ was prepared according to the method of Cantrell et al. [1987]. The remainder of the injector flow was passed over a NO₂ permeation vial (Thermedics, Incorporated). Typical initial mixing ratios of N₂O₅ and NO₂ in the flow tube were about 200 and 500 ppb, respectively.

Under these conditions the equilibrium dissociation of N₂O₅ is less than 1% at the highest temperature (293 K) used in these experiments. Some experiments were carried out without adding any NO₂. This had no effect on the observed decay rate; hence N₂O₅, and not NO₃, was the active reactant in this system. The variation of N₂O₅ concentration with the rate of the gas flow in the N₂O₅ trap indicated that the gas was saturated with N₂O₅.

The particle number density was measured using a single particle condensation nucleus counter (TSI model 3760), which sampled a portion of the flow tube exhaust. The radii of the dry particles could be calculated from the operating conditions of the DMA [Knutson and Whitby, 1975]. The absolute radii were checked using monodisperse latex spheres (Seragen Diagnostics) and found to agree within the stated accuracy for the spheres (a few percent). The radii of the drops at a given relative humidity (RH) were then calculated using the radius ratios determined in the tandem DMA experiments described below.

Since the DMA classifies particles according to electrical mobility rather than size, there are some particles carrying a double charge, with radii larger than that of the singly charged particles. The fraction of doubly charged particles was determined by measuring the size distribution of the atomizer output and assuming a Boltzmann charge distribution [Liu and Pui, 1974]. A suitable correction (typically 10–15%) to the calculated particle surface area was then made.

The concentration of N₂O₅ was determined using the method of Fahey et al. [1985]. A flow of 0.5 cm³ s^{-1} of a mixture of 8.6 ppm NO in N₂ was added to a 16 cm³ s^{-1} sample from the flow tube. This was then passed through a 40-cm length of 1.0 cm ID quartz tubing heated to about 375 K. At this temperature the N₂O₅ rapidly dissociates, and the NO₃ formed reacts with NO. The amount of NO remaining is then measured using the standard chemiluminescent reaction with ozone. For typical N₂O₅ concentrations used in these experiments, between 10 and 75% of the NO was consumed. We found that the amount of NO consumed did not depend on the concentration of NO used, as long as the NO concentration was sufficiently large. Before the flow was admitted to the NO instrument, it was drawn through nylon and particle filters. The N₂O₅ concentration was found to fluctuate somewhat with time; this was the major source of scatter in measuring the decays. We believe that these fluctuations were due to variations in the temperature of the slush bath.

AEROSOL REACTION RATES

In a typical experiment the N₂O₅ concentration was measured with the injector placed at several different positions in the flow tube. Only the central 70 cm of the tube was used. In the upstream portion of the tube, laminar flow is being established [Goldstein, 1965], and the flow is equilibrating at the temperature of the experiment. Immediately downstream of the injector, there is a region of nonexponential decay [Gormley and Kennedy, 1949] as the N₂O₅ mixes, and a steady concentration profile is established. By not moving the injector too close to the sampling area, effects due to this region are held constant. Before and after measuring the decay, the N₂O₅ flow was turned off and the NO signal level measured.

The concentration versus distance data were then plotted on a semilog plot and fit to an exponential decay by weighted least squares. This yielded a psuedo-first-order rate constant. Example first-order decays are shown in Figure 2. Loss of
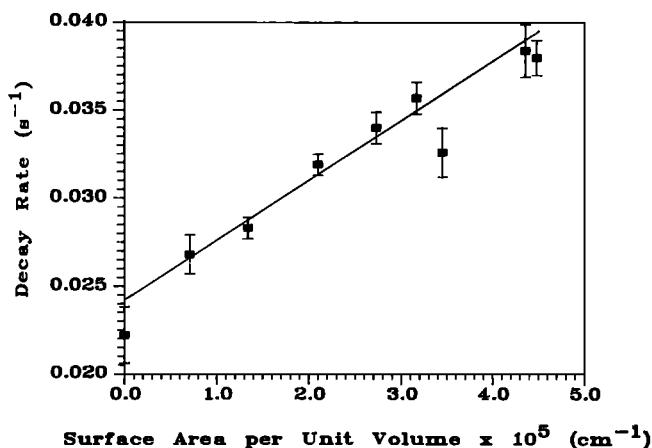
Fig. 3. Example plot of psuedo-first-order decay rate versus aerosol surface area per unit volume. Data are for 293 K and 55% relative humidity.

N_2O_5 to the walls of the flow tube were observed in the absence of any aerosol. This loss increased with increasing relative humidity in the flow, so it was probably due to reaction with water vapor. The loss rate is much too large to be due to homogeneous reaction with water vapor.

For each temperature and relative humidity, eight to 10 first-order decays were measured. These included one or more experiments without particles as well as a number of experiments with varying particle radii and number densities. For each series of decays, three different particle sizes, with wet radii ranging from about 40 to 100 nm, were used. The maximum number density (about 2.5×10^5 cm^{-3}) was achieved at about 40 nm. Using particles with radii less than this resulted in too little aerosol surface area to achieve measurements of reasonable accuracy. The falloff in number density became severe above 100 nm; also, double-charging effects become large in this region. The 40- to 100-nm size range was also a convenient choice for our use, because effects due to surface curvature [Lewis et al., 1961] and diffusion limitation [Fuchs and Sutugin, 1970] are only a few percent in this region. Two or three different number densities were used with each particle size.

The resulting first-order decays were then plotted versus aerosol surface area per unit volume, as shown in Figure 3. This is analogous to the second-order plots normally used in gas phase kinetic studies. A straight line was fit to these data, and the wall loss rate constant (intercept) and second-order rate constant (slope) were determined. The wall loss rate became very large at higher humidities. The second-order rate constant, k_2, is related to the reaction probability, γ, by the equation $k_2 = \gamma v/4$, where v is the mean molecular speed of N_2O_5.

An examination of the residuals from the second-order plots showed a weak dependence on particle size. The direction of the trend implies that larger particles have larger values of γ. This effect could only be separated from the statistical uncertainty when all of the residuals (140 points) were considered collectively. As a result, we cannot quantify this effect. It could be an artifact due to systematic nonlinearities in measuring particle radii or number densities.

The results for γ as a function of relative humidity and temperature are summarized in Table 1 and Figure 4. For experiments at 293 K it is seen that γ is very small when dry

TABLE 1. N_2O_5 Reaction Probabilities for 1:1 NH_3/H_2SO_4 Ratio in Atomizer Solution

RH, %	274 K	293 K
1	0.006 ± 0.007	0.009 ± 0.002
12	0.024 ± 0.008	0.020 ± 0.005
25	0.022 ± 0.008	0.035 ± 0.005
34	0.055 ± 0.024	0.025 ± 0.010
45	0.060 ± 0.009	0.051 ± 0.006
55	0.099 ± 0.020	0.056 ± 0.010
66	0.079 ± 0.008	0.050 ± 0.007
76	0.101 ± 0.023	0.039 ± 0.012

Uncertainties are twice the standard deviation.

air (<2% RH) is used, increases rapidly up to a humidity of 40%, the deliquescence point, and then levels off at a value of about 0.05. At 274 K the behavior is qualitatively similiar; values of γ are similiar at low RH, but at this temperature they level off at a higher value, about 0.09. It should be noted that the uncertainty in the flow characteristics mentioned above results in a systematic uncertainty of ±20% in these values. Preliminary results had been obtained at 283 K. Because of changes in the experimental procedure, these results are not quantitatively comparable. However, they do show the same qualitative behavior.

The observed dependence of γ on RH for NH_4HSO_4 aerosols was not anticipated. NH_4HSO_4 has a deliquescence point of 39.7% RH (293 K). In theory it should not pick up water below this humidity; above it the crystal should dissolve entirely [Tang and Munkelwitz, 1977]. We expected a sharp change in the reaction probability at this deliquescence point. Obviously, our observations (Figure 4) do not match these expectations. In order to understand this behavior, we carried out the aerosol deliquescence experiments described in the following section.

AEROSOL DELIQUESCENCE PROPERTIES

By using two DMA's in tandem (TDMA technique) it is possible to resolve changes in aerosol radii as small as 0.3% [Radar and McMurry, 1986]. We used this method to study the tendency of NH_4HSO_4 aerosols to pick up water. DMA flow ratios of 9:1 were used in these experiments in order to get higher resolution. The experiments were carried out at room temperature, typically 295 K.
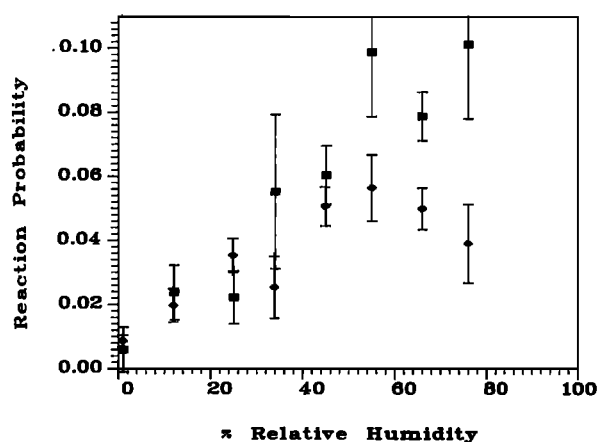

Fig. 4. Reaction probability as a function of relative humidity at 274 K (squares) and 293 K (diamonds). Error bars are twice the standard deviations.
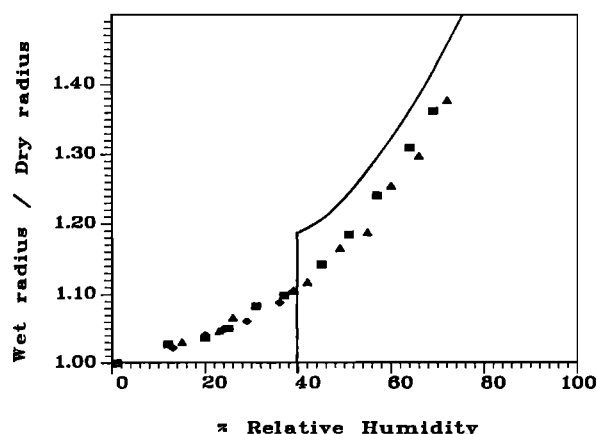
Fig. 5. Aerosol wet-to-dry radius ratio as a function of relative humidity. The atomizer solution contained a 1:1 NH_3/H_2SO_4 ratio: solid curve, calculated [*Tang and Munkelwitz*, 1977]; squares indicate dry radius equal to 33.3 nm; triangles, dry radius equal to 55.9 nm; diamonds, dry radius equal to 75.3 nm.

As in the kinetics experiments described earlier, an aerosol was produced in an atomizer, dried, and a monodisperse fraction was selected using DMA 1. The sheath airflow exiting from this DMA was filtered and a portion was humidified. This flow was then combined with the monodisperse aerosol flow. The combined flow entered a dead volume with a residence time of 6 s to allow the aerosol to equilibrate. Particles in this size range should equilibrate with water vapor on a time scale of 10 ms; bypassing the dead volume did not affect the results. A portion of this flow was then admitted to DMA 2 as the aerosol flow; the rest was filtered and used for the sheath airflow. In this manner the flows in both DMAs were kept equal, and the humidities of the sheath and aerosol flows were kept the same. The aerosol output of DMA 2 was sent to the condensation nuclei (CN) counter and a portion of the sheath air output was passed through the dew-point hygrometer.

In these experiments DMA 1 was set to a fixed voltage and the particle number density was measured as DMA 2 was scanned through a series of voltages. The resulting size distribution was then analyzed by the method of *Rader and McMurry* [1986]. Values of the flow ratio parameter determined from fitting the size distribution agreed well with the measured values. The particle radius was calculated from the voltage at which the peak number density occurred. There was a systematic deviation of about 1% in the particle radii measured by the two DMAs. This difference has no effect on the results described below, since these are based entirely on measurements made with the second DMA at various humidities.

The experiments were repeated for a series of relative humidities, initial particle sizes and initial particle compositions. Results are shown in Figure 5. When the atomizer contains a 1:1 NH_3/H_2SO_4 ratio (NH_4HSO_4), the growth of particles is very different from that reported by *Tang and Munkelwitz* [1977]. A significant amount of water is picked up below the deliquescence point. In contrast, for a ratio of NH_3 to H_2SO_4 of 2:1 ($(NH_4)_2SO_4$), no growth occurs, as expected. Behavior similiar to that shown in Figure 5 was noted by *Charlson et al.* [1974].

Although the vapor pressure of NH_3 over a saturated solution of NH_4HSO_4 is very small (less than 10^{-10} atm), the evaporation lifetime from drops in our size range is only a few

minutes. Thus it is entirely possible that a small but significant fraction (a few percent) of the NH_3 may evaporate in the time it takes the particle to crystalize. If this occurs, there will be a layer of H_2SO_4 on the surface of the resulting crystal; this will readily pick up water even at low RH. We believe that this accounts for the deliquescence behavior seen here.

In order to test this explanation, we carried out experiments in which the atomizer contained a solution with an NH_3 to H_2SO_4 ratio of 1.25:1.0. The idea was to insure that no free sulfuric acid would form, even if some NH_3 were to evaporate. As seen in Figure 6, the aerosol produced from this solution deliquesces at the expected RH. However, the amount of water picked up at higher humidities is somewhat less than that expected theoretically (solid curve). This deviation cannot be explained by the Kelvin effect (vapor pressure increase due to surface curvature; *Lewis et al.* [1961]), since the data presented in Figure 5 show that the same radius ratios are obtained for particles with radii varying by more than a factor of 2. The Kelvin effect for the smallest particles would be more than double that for the largest particles employed here.

We believe that the discrepancies between the theoretical and measured values in Figure 6 are due to nonsphericity of the crystalline particles. The DMA sorts particles according to electrical mobility. This is related to particle size by means of the aerodynamic drag on the particle. A nonspherical particle will have greater drag than a spherical particle of the same volume. It will therefore appear to have a greater "radius" when sized by the DMA. For sufficiently small particles, which will be randomly oriented, the drag is proportional to the surface area [*Dahneke*, 1973]. The particles considered here will be reasonably near this limit. The data in Figure 6 can be explained if the dry, crystalline particles have a surface area 20% greater than a sphere of the same volume. Such a value is reasonable; it is slightly less than the value for a cube. In calculating the aerosol surface areas, we used the measured ratios of the solution droplet to dry particle radii.

In order to obtain deliquescence behavior typical of NH_4HSO_4, it was necessary to increase the NH_4^+ concentration by 25%. This does not imply that 25% of the NH_3 in the 1:1 solution evaporates. As the NH_4^+ concentration increases, the pH of the solution increases rapidly. Hence the NH_3 vapor pressure, and the rate of NH_3 evaporation, also increases rapidly.
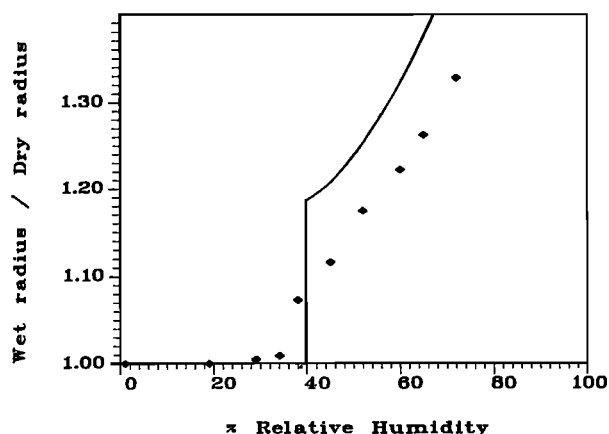

Fig. 6. Aerosol wet-to-dry radius ratio as a function of relative humidity. The atomizer solution contained a 1.25:1 NH_3/H_2SO_4 ratio: solid line, calculated [*Tang and Munkelwitz*, 1977]; points, dry radius equal to 55.4 nm.

TABLE 2. Comparison of N_2O_5 Reaction Probabilities at 293 K for Various NH_3/H_2SO_4 Ratios in the Atomizer Solution

RH, %	NH_4/H_2SO_4	Reaction Probability
25	1.00	0.035 ± 0.005
25	1.02	0.021 ± 0.011
25	2.00	<0.003
30	1.25	0.012 ± 0.004
34	1.00	0.025 ± 0.010
35	1.25	0.013 ± 0.005
45	0.98	0.053 ± 0.008
45	1.00	0.051 ± 0.006
45	1.02	0.041 ± 0.037
42	1.25	0.022 ± 0.014
48	1.25	0.031 ± 0.011
55	1.00	0.056 ± 0.010
60	2.00	0.043 ± 0.005
66	1.00	0.050 ± 0.007
70	1.25	0.040 ± 0.006
76	1.00	0.039 ± 0.012

Uncertainties are twice the standard deviation.

REACTIONS ON AEROSOLS OTHER THAN NH_4HSO_4

As described earlier, the aerosol deliquescence properties depend on the NH_3/H_2SO_4 ratio. We therefore decided to examine the effect of this ratio on γ. A summary of results from these experiments, along with some data from Table 1 for comparison, are given in Table 2. It is seen that very small (2%) changes in the NH_3/H_2SO_4 ratio change γ by less than the experimental uncertainty. However, a 25% increase in NH_4^+ significantly reduces γ at both low and high humidities. The sharp onset of deliquescence, observed in the TDMA experiments, is still not seen in the behavior of γ. This may be due to the greater time available for evaporation in the flow tube experiment relative to the TDMA experiment.

This possibility was further examined by using an $(NH_4)_2SO_4$ solution in the atomizer. In this case, no reaction ($\gamma < 0.003$) was observed at 25% RH. However, a significant reaction rate ($\gamma = 0.043 \pm 0.005$) was observed at 60% RH. This would seem to indicate that evaporation of NH_3 leaves the aerosol with a composition between that of ammonium bisulfate (NH_3 to H_2SO_4 ratio of 1:1, deliquescence point at 40% RH) and letovicite (NH_3 to H_2SO_4 ratio of 1.5:1, deliquescence point at 67% RH). That a large fraction of NH_3 would evaporate from this aerosol is reasonable. As the NH_4^+ concentration increases, the pH, and therefore the NH_3 vapor pressure, increases rapidly.

Because of the high vapor pressure of NH_3 over $(NH_4)_2SO_4$, we decided to add NH_3 to the vapor phase in order to suppress evaporation from the solution and therefore insure that the particles remained crystalline above the deliquescence point of NH_4HSO_4. The method of NH_3 addition was based on the work of Dasgupta and Dong [1986]. The distilled water in the humidifier was replaced with a solution consisting of 0.025 M KH_2PO_4, 0.026 M Na_2HPO_4, and 0.0035 M NH_4OH. We estimate that this produced a gas phase NH_3 mixing ratio of about 100 ppb. The addition of gas phase NH_3 produced an increased rate of wall loss, especially at higher relative humidities. We measured reaction probabilities of 0.017 ± 0.012 at 44% RH and 0.042 ± 0.014 at 50% RH.

The vapor pressure of added NH_3 should be more than sufficient to insure that the NH_3 to H_2SO_4 ratio is at least

1.5:1. Thus at first glance it would appear that these results imply that reaction of N_2O_5 occurs on dry particles. However, since both HNO_3 and NH_3 are present in this system, we expect to form NH_4NO_3, which deliquesces at 65% RH [Stelson and Seinfeld, 1982]. A mixture of letovicite and NH_3NO_3 should deliquesce at a lower RH than either salt alone. As a result, this experiment was inconclusive.

As noted earlier, we believe that the reaction probabilities measured at relative humidities below 40% are due to a thin layer of H_2SO_4 on the surface of the aerosol. Furthermore, several previous experiments involving N_2O_5 reaction probabilities [Harker and Strauss, 1981; Baldwin and Golden, 1979; Rossi et al., 1987] have been on H_2SO_4 surfaces. We therefore decided to measure γ on H_2SO_4 aerosols; the results are shown in Table 3. We limited the experiments to 10% RH in order to minimize the potential for corrosion of the equipment. The experiments of Baldwin and Golden [1979] and Rossi et al. [1987] were done with very dry H_2SO_4. The liquid solutions used by Harker and Strauss had a composition corresponding to about 10% RH. We determined the ratio of the particle radius at 10% RH to that in dry air by a TDMA experiment similiar to those described above.

From the data in Table 3, we see that the temperature dependence of γ is similiar to that on NH_4HSO_4, but perhaps slightly weaker. There seems to be little dependence on RH. This is not entirely due to inadequate drying of the H_2SO_4 droplets in the diffusion dryer, since the TDMA experiment showed growth at 10% RH. Thus there must be a significant difference in the aerosol water content at the two humidities. This implies that the rate-determining step is not reaction with water but is some preliminary step, such as

$$N_2O_5(aq) \rightarrow NO_3^-(aq) + NO_2^+(aq)$$
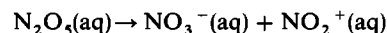
For NH_4HSO_4 aerosols the presence of H_2O is necessary in order that there be a liquid phase. We also see from Table 3 that γ is larger on H_2SO_4 than on NH_4HSO_4. This implies that the drop in γ at low RH, seen in Figure 4, is due to the small liquid volume, not a change in composition of the liquid.

Harker and Strauss [1981] have reported values for γ on H_2SO_4/H_2O liquid surfaces for an H_2O mole fraction of 32%, corresponding to roughly 10% RH. They found $\gamma = 3 \times 10^{-4}$ at 233 K and 1×10^{-4} at 249 K. Thus the sign of their temperature dependence is the same as ours, but the values of γ are several orders of magnitude lower. They also found lower values for γ and a positive activation energy for frozen H_2O/H_2SO_4 surfaces at temperatures of 221–263 K.

Baldwin and Golden [1979] report a lower bound for γ on relatively dry ($<5\%$ H_2O) H_2SO_4 surfaces of 3.8×10^{-5}. Using a similiar method, Rossi et al. [1987] report a value an "order of magnitude" larger than the value 3.2×10^{-4} which they found for $ClNO_3$. It is not clear from that paper whether this is also a lower bound. The value is, however, intermediate between our results and those of Harker and Strauss. A low value on relatively dry H_2SO_4 is not inconsistant with our observed lack of relative humidity dependence. We would

TABLE 3. N_2O_5 Reaction Probabilities on H_2SO_4 Aerosols

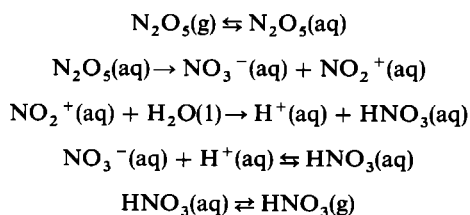| RH, %	274 K	293 K
1	0.139 ± 0.013	0.108 ± 0.048
10	0.139 ± 0.005	0.093 ± 0.006

Uncertainties are twice the standard deviation.

expect that when the water content becomes sufficiently small, the rate-determining step would change from the ionization step to the subsequent reaction with H_2O.

CONCLUSIONS

N_2O_5 reacts with H_2O in NH_4HSO_4 aerosol particles. At 293 K the reaction probability, γ, is about 0.05 for humidities above the deliquescence point of 40% RH. At 274, K γ increases to 0.09 at these humidities. At lower humidities the values of γ drops off. An aerosol containing a liquid phase is required for these reactions to take place at an appreciable rate.

We propose the following mechanism for this reaction. N_2O_5 is known to form an ionic crystal [Cotton and Wilkinson, 1980] and to dissociate into ions when dissolved in neat HNO_3 [Robinson and Stokes, 1959]. We therefore expect that when N_2O_5 dissolves in water, it will dissociate to NO_2^+ and NO_3^-, both of which will react readily in water to form HNO_3:

$$N_2O_5(g) \leftrightarrows N_2O_5(aq)$$

$$N_2O_5(aq) \rightarrow NO_3^-(aq) + NO_2^+(aq)$$

$$NO_2^+(aq) + H_2O(1) \rightarrow H^+(aq) + HNO_3(aq)$$

$$NO_3^-(aq) + H^+(aq) \leftrightarrows HNO_3(aq)$$

$$HNO_3(aq) \rightleftarrows HNO_3(g)$$

That the first step is rate limiting is indicated by the fact that the reaction probability is higher on H_2SO_4 aerosols with a low water activity. Both the dissociation of N_2O_5 and its reevaporation from solution should be very rapid; the reaction probability reflects the competition between these two processes. Diffusion into the drop is much slower; as a result, the reaction takes place almost entirely in a thin layer near the surface, and the loss of N_2O_5 is therefore proportional to surface area. A meaningful quantitative analysis of these processes is not possible because of a lack of data on the relevant Henry's law constants, diffusion coefficients, and reaction rate constants.

The reaction probability becomes gradually smaller at low humidities because, below the deliquescence point of NH_4HSO_4, there is only a thin layer of liquid on the surface of the particle. This is probably a result of a small excess of H_2SO_4 formed as NH_3 evaporates from the NH_4HSO_4 aerosol solution. When this layer becomes thin enough that the N_2O_5 can diffuse uniformly throughout the solution (saturate it), the rate of reevaporation becomes faster. The observation that γ decreases as the temperature increases may result from a larger increase with temperature in the rate of evaporation than in the rate of dissociation.

N_2O_5 also reacts on sulfuric acid aerosols at low humidities. The reaction probability is somewhat larger than on NH_4HSO_4 aerosols, has a similar temperature dependence, and does not seem to depend on relative humidity.

As noted in the introduction, most other work on the reaction probabilities of N_2O_5 has been carried out at very low water activities. The exception is the work of Verhees [1986], who reports low values of only 8×10^{-6} at 78% RH on NaCl and $MgCl_2$ aerosols. At this RH these salts are expected to form solution droplets. We have no explanation for the apparent discrepancy between our results and those of Verhees. However, we note that his data appear to be unusual in that

he also found a very low reaction probability (10^{-9}–10^{-8}) on his reactor walls, even at RH up to 78%. From the data of Morris and Niki [1973], we estimate reaction probabilities for N_2O_5 on the walls of 4×10^{-6} at 20% RH, dropping to $< 10^{-7}$ on dry walls. This estimate uses the reasonable assumption that the major portion of the reaction which they observed was due to wall loss. Our wall loss data implies a similar reaction probability at these humidities. At RH greater than 70%, we find wall reaction probabilities in excess of 10^{-5}, much larger than those reported by Verhees.

The reaction of N_2O_5 with aqueous aerosol may well be significant in the atmosphere. Taking γ in the range of 0.05–0.1, as observed here, aerosol number densities of 10^3–10^5 cm^{-3}, typical of the troposphere, and the reasonable size distributions used by Heikes and Thompson [1983], we find that N_2O_5 lifetimes vary between about 30 s and 2 hours. These are about an order of magnitude faster than needed to explain nighttime loss of NO_3 [Atkinson, 1986]. The reaction probabilities on natural aerosols may be lower due to some of the aerosols being nonhygroscopic (soot or soil dust, for example) or due to the presence of organic films on the aerosols [Gill et al., 1983]. The unexplained scavenger for NO_3 in the nighttime atmosphere may well be moist aerosol particles. The values of γ that we have measured for H_2SO_4 aerosols (Table 3) are well in excess of those that produce significant effects on the stratospheric HNO_3 concentrations in the model of Austin et al. [1986].

REFERENCES

Atkinson, R., A. M. Winer, and J. N. Pitts, Jr., Estimation of nighttime N_2O_5 concentrations from ambient NO_2 and NO_3 radical concentrations and the role of N_2O_5 in night-time chemistry, Atmos. Environ., 20, 331–339, 1986.

Austin, J., R. R. Garcia, J. M. Russell III, S. Solomon, and A. F. Tuck, On the atmospheric photochemistry of nitric acid, J. Geophys. Res., 91, 5477–5485, 1986.

Baldwin, A. C., Reactions of gases on prototype aerosol particle surfaces, in Heterogeneous Atmospheric Chemistry, Geophys. Monogr. Ser., vol. 26, edited by D. R. Shryer, pp. 99–102, AGU, Washington, D. C., 1982.

Baldwin, A. C., and D. M. Golden, Heterogeneous atmospheric reactions: Sulfuric acid aerosols as tropospheric sinks: Science, 206, 562–563, 1979.

Brouwer, L., M. J. Rossi, and D. M. Golden, Reaction of N_2O_5 with H_2O on carbonaceous surfaces, J. Phys. Chem., 90, 4599–4603, 1986.

Brown, R. L., Turbular flow reactors with first-order kinetics, J. Res. Natl. Bur. Stand., 83, 1–8, 1978.

Cadle, R. D., P. Crutzen, and D. Ehhalt, Heterogeneous chemical reactions in the stratosphere, J. Geophys. Res., 80, 3381–3385, 1975.

Cantrell, C. A., J. A. Davidson, R. E. Shetter, B. A. Anderson, and J. G. Calvert, Reactions of NO_3 and N_2O_5 with molecular species of possible atmospheric interest, J. Phys. Chem., 91, 6017–6021, 1987.

Chameides, W. L., Possible role of NO_3 in the nighttime chemistry of a cloud, J. Geophys. Res., 91, 5331–5337, 1986.

Chang, T. Y., Estimates of nitrate formation in rain and snow systems, J. Geophys. Res., 91, 2805–2818, 1986.

Charlson, R. J., A. H. Vanderpol, D. S. Covert, A. P. Waggoner, and N. C. Ahlquist, $H_2SO_4/(NH_4)_2SO_4$ background aerosol: Optical detection in St. Louis region, Atmos. Environ., 8, 1257–1267, 1974.

Charlson, R. J., D. S. Covert, T. V. Larson, and A. P. Waggoner, Chemical properties of tropospheric sulfur aerososls, *Atmos Environ.*, *12*, 39–53, 1978.

Cotton, F. A., and G. Wilkinson, *Advanced Inorganic Chemistry*, 4th ed., pp. 427–428, John Wiley, New York, 1980.

Dahneke, B. E., Slip correction factors for nonspherical bodies, II, Free molecule flow, *Aerosol Sci.*, *4*, 147–161, 1973.

Dasgupta, P. K., and S Dong, Solubility of ammonia in liquid water and generation of trace levels of standard gaseous ammonia, *Atmos. Environ.*, *20*, 565–570, 1986.

Evans, W. F. J., C. T. McElroy, and I. E. Galbally, The conversion of N_2O_5 to HNO_3 at high latitudes in winter, *Geophys. Res. Lett.*, *12*, 825–828, 1985.

Fahey, D. W., C. S. Eubank, G. Hubler, and F. C. Fehsenfeld, A calibrated source of N_2O_5, *Atmos. Environ.*, *19*, 1883–1890, 1985.

Ferguson, E. E., F. C. Fehsenfeld, and A. L. Schmeltekpoft, Flowing airglow measurements of ion-neutral reactions, in *Advances in Atomic and Molecular Physics*, vol. 5, edited by D. R. Bates, pp. 1–57, Academic, San Diego, Calif., 1969.

Fuchs, N. A., and A. G. Sutugin, *Highly Dispersed Aerosols*, Butterworth, Stoneham, Mass, 1970.

Gill, P. S., T. E. Graedel, and C. J. Weschler, Organic films on atmospheric aerosol particles, fog droplets, cloud droplets, raindrop and snowflakes, *Rev. Geophys.*, *21*, 903–920, 1983.

Goldstein, S., *Modern Developments in Fluid Dynamics*, pp. 299–308, Dover, New York, 1965.

Gormley, P. G., and M. Kennedy, Diffusion from a stream flowing through a cylindrical tube, *Proc. R. Irish Acad.*, *52*, 163–169, 1949.

Harker, A. B., and D. R. Strauss, Kinetics of the heterogeneous hydrolysis of dinitrogen pentoxide over the temperature range 214–263 K, *Fed. Aviat. Admin. Publ. FAA-EE-81-3*, Rockwell Int. Sci. Cent., Thousand Oaks, Calif., 1981.

Heikes, B. G., and A. M. Thompson, Effects of heterogeneous processes on NO_3, HONO, and HNO_3 chemistry in the troposphere, *J. Geophys. Res.*, *88*, 10,883–10,895, 1983. (Correction, *J. Geophys. Res.*, *89*, 11,829, 1984.)

Johnston, H. S., C. A. Cantrell, and J. G. Calvert, Unimolecular decomposition of NO_3 to form NO and O_2 and a review of N_2O_5 /NO_3 kinetics, *J. Geophys. Res.*, *91*, 5159–5172, 1986.

Keyser, L. F., High-pressure flow kinetics. A study of the OH + HCl reaction from 2 to 100 torr, *J. Phys. Chem.*, *88*, 4750–4758, 1984.

Knutson, E. O. and K. T. Whitby, Aerosol classification by electric mobility: Apparatus, theory, and applications, *J. Aerosol Sci.*, *6*, 443–451, 1975.

Lazrus, A. L., P. L. Haagenson, G. L. Kok, B. J. Huebert, C. W. Kreitzberg, G. E. Likens, V. A. Mohnen, W. E. Wilson, and J. W. Winchester, Acidity in air and water in a case of warm frontal precipitation, *Atmos. Environ.*, *17*, 581–591, 1983.

Lewis, G. N., M Randall, K. S. Pitzer, and L. Brewer, *Thermodynamics*, 2nd ed., McGraw-Hill, New York, 1961.

Liu, B. Y. H., and D. Y. H. Pui, Equilibrium bipolar charge distribution of aerosols, *J. Colloid Interface Sci.*, *49*, 305–312, 1974.

Morris, E. D., Jr., and H. Niki, Reaction of dinitrogen pentoxide with water, *J. Phys. Chem.*, *77*, 1929–1932, 1973.

Mozurkewich, M., P. H. McMurry, A. Gupta, and J. G. Calvert, Mass accommodation coefficient for HO_2 radicals on aqueous particles, *J. Geophys. Res.*, *92*, 4163–4170, 1987.

Noxon, J. F., NO_3 and NO_2 in the mid-Pacific troposphere, *J. Geophys. Res.*, *88*, 11,017–11,021, 1983.

Noxon, J. F., R. B. Norton, and W. R. Henderson, Observation of atmospheric NO_3, *Geophys. Res. Lett.*, *5*, 675–678, 1978.

Platt, U. F., A. M. Winer, H. W. Biermann, R. Atkinson, and J. N. Pitts, Jr., Measurement of nitrate radical concentrations in continental air, *Environ. Sci. Technol.*, *18*, 365–369, 1984.

Rader, D. J., and McMurry, P. H., Application of the tandem differential mobility analyzer to studies of droplet growth or evaporation, *J. Aerosol Sci.*, *17*, 771–787, 1986.

Richards, L. W., Comments on the oxidation of NO_2 to nitrate—Day and night, *Atmos. Environ.*, *17*, 397–402, 1983.

Robinson, R. A., and R. H. Stokes, *Electrolyte Solutions*, 2nd ed., pp. 377–380, Butterworth, Stoneham, Mass., 1959.

Rossi, M. J., M. Ripudaman, and D. M. Golden, Heterogeneous chemical reaction of chlorine nitrate and water on sulfuric acid surfaces at room temperature, *Geophys. Res. Lett.*, *14*, 127–130, 1987.

Russell, A. G., G. R. Cass, and J. H. Seinfeld, On some aspects of nighttime atmospheric chemistry, *Environ. Sci. Technol.*, *20*, 1167–1172, 1986.

Stelson, A. W., and J. H. Seinfeld, Relative humidity and temperature dependence of the ammonium nitrate dissociation constant, *Atmos. Environ.*, *16*, 983–992, 1982.

Sverdrup, G. M., C. W. Spicer, and G. F. Ward, Investigation of the gas phase reaction of dinitrogen pentoxide with water vapor, *Int. J. Chem. Kinet.*, *19*, 191–205, 1987.

Tang, I. N., and H. R. Munkelwitz, Aerosol growth studies, III, Ammonium bisulfate aerosols in a moist atmosphere, *J. Aerosol Sci.*, *8*, 321–330, 1977.

Verhees, P., On the atmospheric chemistry of NO_2–O_3 systems, Ph.D. thesis, Wageningen Agric. Univ., Wageningen, The Netherlands, 1986.

Winer, A. M., R. Atkinson, and J. N. Pitts, Jr., Gaseous nitrate radical: Possible nighttime atmospheric sink for biogenic organic compounds, *Science*, *224*, 156–159, 1984.

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