Reactive Uptake of N_2O_5 by Aerosol Particles Containing Mixtures of Humic Acid and Ammonium Sulfate[†]

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The kinetics of reactive uptake of N_2O_5 on submicron aerosol particles containing humic acid and ammonium sulfate has been investigated as a function of relative humidity (RH) and aerosol composition using a laminar flow reactor coupled with a differential mobility analyzer (DMA) to characterize the aerosol. For single-component humic acid aerosol the uptake coefficient, γ, was found to increase from 2 to 9×10^{-4} over the range 25−75% RH. These values are 1−2 orders of magnitude below those typically observed for single-component sulfate aerosols (*Phys. Chem. Chem. Phys.* **2003**, *5*, 3453−3463;[1] *Atmos. Environ.* **2000**, *34*, 2131−2159[2]). For the mixed aerosols, γ was found to decrease with increasing humic acid mass fraction and increase with increasing RH. For aerosols containing only 6% humic acid by dry mass, a decrease in reactivity of more than a factor of 2 was observed compared with the case for single-component ammonium sulfate. The concentration of liquid water in the aerosol droplets was calculated using the aerosol inorganic model (for the ammonium sulfate component) and a new combined FTIR-DMA system (for the humic acid component). Analysis of the uptake coefficients using the water concentration data shows that the change in reactivity cannot be explained by the change in water content alone. We suggest that, due to its surfactant properties, the main effect of the humic acid is to reduce the mass accommodation coefficient for N_2O_5 at the aerosol particle surface. This has implications for the use of particle hygroscopicity data for predictions of the rate of N_2O_5 hydrolysis.

1. Introduction

The heterogeneous hydrolysis of N_2O_5, reaction R1, within aerosol particles and cloud droplets to yield HNO_3 is the dominant removal channel for nitrogen oxides at night.[3]

$$N_2O_5(g) + H_2O(liq) \xrightarrow{\text{aerosol}} 2HNO_3(aq) \qquad (R1)$$

This reaction converts reactive nitrogen oxide compounds (NO_x) into a longer-lived reservoir species HNO_3, which can then be removed from the atmosphere via wet or dry deposition. Because NO_x concentrations strongly influence the rate of tropospheric O_3 formation, the rate of N_2O_5 hydrolysis has an important role in determining the oxidative capacity of the troposphere.[4]

Initial studies of this reactive uptake process showed that under stratospheric conditions, significant loss could occur to acidic aerosol particles. Reactive uptake coefficients, γ, defined as the probability of irreversible loss from the gas phase with reference to the gas-phase collision frequency with the aerosol surface, were measured for sulfuric acid aerosol over the range 225−293 K by Fried et al.[5] Efficient uptake was found, with uptake coefficients on the order of 0.1.

The impact of N_2O_5 hydrolysis under tropospheric conditions was first estimated by Dentener and Crutzen, using $\gamma = 0.1$. It was found that the inclusion of heterogeneous N_2O_5 hydrolysis decreased NO_x and O_3 levels by 45% and 10%, respectively, compared with values obtained considering only gas-phase chemistry.[4] Although Dentener and Crutzen used $\gamma = 0.1$ and considered only sulfate aerosol, their study has motivated much of the subsequent laboratory measurements of reactive uptake and work aimed at improving global models to take into account heterogeneous reactions.

Reactive uptake of N_2O_5 has been measured on a number of inorganic substrates over a range of temperatures and relative humidities,[1,2,6−10] and has been shown to be a function of, among other parameters, composition, particle size and phase. For pH-neutral or mildly acidic aerosols, γ increases with increasing relative humidity (RH), implying a dependence of the rate of reaction on the liquid water content of the aerosols.[1,2,11] Furthermore, at a given RH, this hydrolysis reaction proceeds much more quickly on supersaturated liquid droplets than on solid particles.[1,11]

The recent study by Evans and Jacob[12] takes account of the dependence of γ on relative humidity, temperature and aerosol substrate. The model contains five types of aerosol: mineral dust, sulfate (assumed to be present as ammonium sulfate), organic carbon, black carbon and sea salt, and γ for reactive uptake of N_2O_5 is parametrized using recent laboratory data from Hallquist et al.,[1] Kane et al.[2] and Thornton et al.[11]

Using this parametrization, a global mean γ of 0.02 was found, much lower than the $\gamma = 0.1$ used previously in global models. Relative to the model of Tie et al.,[13] in which $\gamma = 0.1$ for all aerosols, increases were observed in the calculated mass-averaged tropospheric NO_x, O_3, and OH of 7%, 4%, and 8%

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respectively, and better agreement between these values and climatological observations was noted.

The study of Evans and Jacob therefore points to the need to carry out further laboratory studies to more accurately parametrize the rate of N_2O_5 hydrolysis on tropospheric aerosols. In light of this, our primary motivation is to address the lack of experimental data for the rate of N_2O_5 hydrolysis onto aerosols containing organics. At the time of writing, there are only three studies in the literature that report uptake of N_2O_5 by aerosols with an organic component.

Thornton et al.[11] found that malonic acid aerosol showed behavior similar to inorganic aerosols such as $(NH_4)_2SO_4$ and NH_4HSO_4. γ for solid malonic aerosol was less than 0.001; for aqueous malonic acid aerosol, γ was 0.002 at 10% RH and increased with RH to $\sim$0.03 at RH = 50−70%. In a follow up paper, Thornton and Abbatt[14] showed that the presence of millimolar levels of hexanoic acid reduced γ on artificial seawater at 70% RH from $\sim$0.025 to 0.008 ± 0.004. They attributed this effect to the partitioning of hexanoic acid to the gas−aerosol interface at a surface coverage of approximately a monolayer. A similar reduction of γ in the presence of an organic film was reported by Folkers et al.[15] In their study, $\sim$15 nm thick organic films (formed by the in situ ozonolysis of α-pinene) were found to reduce γ on NH_4HSO_4 aerosol by a factor of 5.

In the model of Evans and Jacob,[12] malonic acid is used to represent all organic aerosol. However, malonic acid only represents a small fraction of the organic compounds found in atmospheric aerosol. These organic compounds cover a huge range of sizes, solubilities and functional groups and are likely to have very different effects on the hydrolysis of N_2O_5.

In this study, we extend our previous work on the phase transitions of aerosols containing humic acid and ammonium sulfate[16] to consider the reactivity of these aerosols with respect to N_2O_5 hydrolysis. Following the recommendations of Fuzzi et al.,[17] humic acid was chosen as a model compound for the humic-like substances that are present in the water-soluble organic aerosol fraction.

We present uptake coefficients for N_2O_5 hydrolysis on aerosols containing mixtures of humic acid and ammonium sulfate measured using an aerosol flow tube. We have also developed a new technique combining FTIR with an SMPS system to measure the water mass content of aerosols and this technique is used to determine the water content of single-component humic acid aerosol. In our previous paper, we showed that the water content of the mixed humic acid−ammonium sulfate aerosols could be predicted by assuming the inorganic and organic components did not interact. Thus our measurements of the water content of single-component humic acid aerosol, combined with the water content of ammonium sulfate aerosol as given by the aerosol inorganic model (AIM),[18−20] can be used to calculate the water content of the mixed aerosols. This allows us to test the degree to which γ for N_2O_5 hydrolysis can be predicted on the basis of a knowledge of the water content of the aerosol particles alone.

2. Experimental Methods

Kinetic experiments were carried out using an atmospheric pressure aerosol flow tube in which the contact time between the aerosol and the N_2O_5 is controlled by a sliding injector. The system has been described in our previous papers[1,7] but will be described again here as several modifications have been made.

A schematic of the flow system is shown in Figure 1. Aerosols were generated from bulk aqueous solutions using a commercial atomizer (3076, TSI). The bulk solutions were made up from mixtures of humic acid (sodium salt, Aldrich) and ammonium sulfate (99.98%, Fisher) in distilled water and filtered to remove the majority of insoluble components.

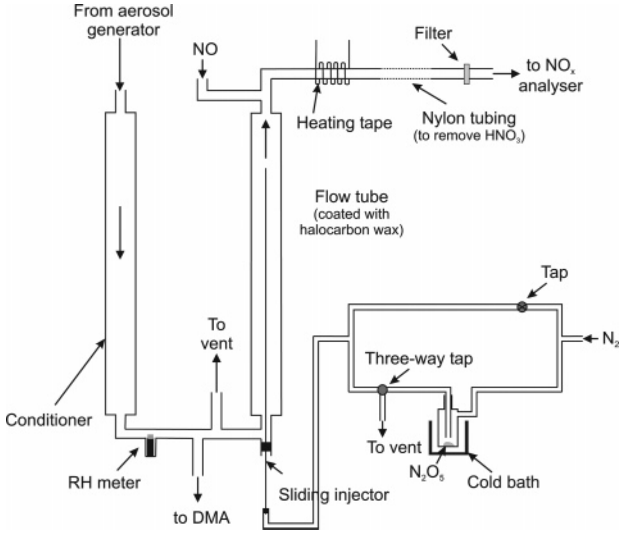

Figure 1. Aerosol flow tube system used to measure uptake coefficients for N_2O_5 hydrolysis on aerosol particles.

Part of the aerosol flow from the atomizer enters the aerosol flow tube system via a diffusion dryer (residence time $\sim$30 s), which reduces the relative humidity (RH) to <2% and the discard flow is sent to a dump line. The dryer consists of a clear channel surrounded by silica gel (Breckland Scientific) and can be bypassed if required. The RH of the aerosol stream is adjusted by the addition of a flow of humidified nitrogen and monitored using a Vaisala Humitter 50Y probe. Prior to entering the main flow tube, the aerosol stream is passed through a tube of length 90 cm and diameter 4.5 cm, which acts as a conditioner to allow the particles to reach equilibrium. The main aerosol flow tube has an internal diameter of 3.2 cm and a length of 50 cm. Typical bulk flow rates are 1.4 cm s^{-1}.

2.1. Aerosol Characterization. The aerosol size distribution was measured using a scanning electrical differential mobility analyzer (DMA) system (Hauke EMS VIE-08) with a Faraday cup electrometer detector (FCE, Hauke, Model FCE 08/A). During a single scan, the DMA measures particle mobility diameters in the range 20−1000 nm with measurements being made at 35 size bins over 5 min; between two and four scans are averaged to obtain the size distribution during a kinetic run. The sheath air flow is humidified to the same RH as the aerosol flow to prevent changes in particle size during sampling.

The aerosol size distribution for a 1:1.5 HA:AS (by mass) aerosol obtained at 50% RH using the DMA is shown in Figure 2. The maximum in this number distribution occurs at 88 nm. Corresponding maxima in the surface area distribution and the volume distribution are 307 and 598 nm, respectively, and the total aerosol surface area is 0.23 $m^2\ m^{-3}$. Total aerosol surface areas for the experiments described in this work varied from 0.12 to 0.50 $m^2\ m^{-3}$.

2.2. N_2O_5 Production and Delivery. N_2O_5 is synthesized prior to use from the reaction of NO with excess ozone in a flow system. The N_2O_5 produced is trapped and stored at 195 K. During kinetic experiments, the solid N_2O_5 is held in a coldfinger placed in a cold bath (Huber CC180) at 213 K and a flow of dried nitrogen (between 25 and 50 cm^3 (STP) min^{-1} depending on the required N_2O_5 concentration) is passed

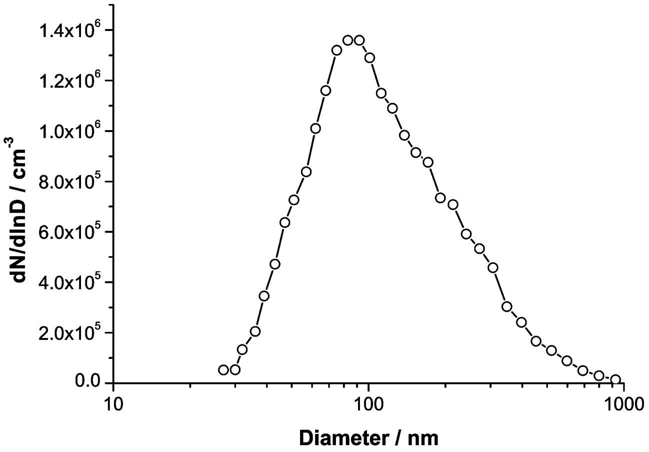

Figure 2. Aerosol size distribution as obtained using the DMA for a 1:1.5 HA:AS (by mass) aerosol at 50% RH.

through the trap to entrain the N_2O_5 into the gas stream. N_2O_5 enters the aerosol flow tube by means of a stainless steel sliding injector lined with 3.2 mm i.d. Teflon tube. The end of the injector is fitted with a Teflon “pepper pot” containing 16 small pinholes to enhance the mixing of this stream with the main gas flow passing down the flow tube. The flow tube was coated internally with halocarbon wax to minimize loss of N_2O_5 to the walls.

2.3. N_2O_5 Detection. N_2O_5 is detected indirectly by thermal decomposition followed by gas-phase titration of the product NO_3 with NO. A slow flow of NO (100 ppmv in N_2) is added to the gas stream just before the exit port of the flow tube. The flow rate is adjusted using a needle valve to give an NO concentration of approximately 500 ppbv in the mixing region at the end of the flow tube. On exiting the flow tube, the gas stream passes through a glass tube heated to ~400 K where the N_2O_5 decomposes via

$$N_2O_5 \rightarrow NO_2 + NO_3 \tag{R2}$$

The lifetime of N_2O_5 with respect to thermal decomposition at 400 K is 1.1×10^{-3} s,[21] and the residence time in the converter is ~0.19 s so it can be assumed that all the N_2O_5 has decomposed after passing through the converter.

The NO_3 reacts with the excess NO to produce NO_2, reaction R3. The NO concentration in the absence of N_2O_5 can be measured by bypassing the cold trap, and the N_2O_5 concentration

$$NO_3 + NO \rightarrow 2NO_2 \tag{R3}$$

is simply derived from the difference between the NO concentration in the presence and absence of N_2O_5.

The NO concentration is determined using a commercial NO_x analyzer (Thermo Environmental Instruments, 42C). To facilitate faster response times, the averaging circuitry is bypassed and the raw signal from the instrument photomultiplier tube is fed directly to a digital data logger (PICO technology). This output voltage showed a linear response to mixtures of known flows of NO and N_2 over the range 0−2000 ppbv NO.

To prevent degradation of the NO_x analyzer by the aerosol particles or HNO_3, a filter (Whatman Polycap TF) was placed in the sample line and ~60 cm of nylon tubing was placed between the converter and the NO_x analyzer to adsorb any gaseous HNO_3 produced during the reaction or from the vaporization of the aerosol particles.

2.4. Experimental Procedure and Data Analysis. The loss of N_2O_5 to the aerosol is determined by changing the position of the sliding injector (to vary the contact time between the N_2O_5 and the aerosol) while monitoring the change in N_2O_5 concentration.

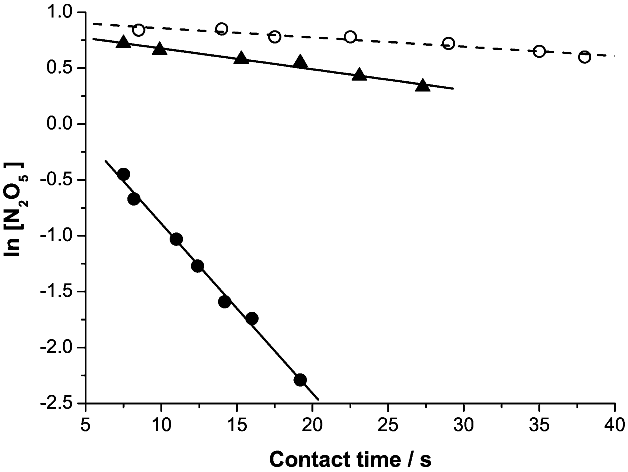

Figure 3. First-order plot for the loss of N_2O_5 to the flow tube walls in the absence of aerosol (open circles) and loss of N_2O_5 in the presence of ammonium sulfate aerosol (filled circles) and humic acid aerosol (filled triangles) at 50% RH. The lines show linear fits to the data from which the values for the first-order rate coefficients are calculated.

For our flow tube system with a linear flow velocity of 1.4 cm s^{-1}, the Reynolds number is 29 and thus the flow can be considered to be laminar after 5 cm.[22] The time for diffusional mixing of the N_2O_5 with the aerosol stream is estimated to be ~5 s.[22] Consequently, kinetic data are collected for contact times of 5−40 s. Baseline NO readings are taken before and after each kinetic run and, as N_2O_5 is also irreversibly lost to the flow tube walls, N_2O_5 loss is measured in both the presence and absence of aerosol.

Figure 3 shows N_2O_5 decays in the presence (solid lines) and absence (dotted line) of aerosol. First-order decay is observed in all cases. The first-order rate coefficients, k_w for loss in the absence of aerosol and k_a for loss in the presence of aerosol, are determined from the slope of these lines. If required, the initial N_2O_5 concentration can be estimated from the y-intercept. Figure 3 also shows that loss to ammonium sulfate aerosol (circles) is much greater than loss to the humic acid aerosol (triangles).

The uptake coefficient for loss of N_2O_5 to the flow tube walls, γ_w, is given by

$$\gamma_w = \frac{2k'_w r}{\nu} \tag{1}$$

where k'_w is the first-order rate coefficient for N_2O_5 loss to the flow tube walls (corrected for nonplug flow conditions and the effects of axial and radial diffusion using the method of Brown[23]), r is the flow tube radius and ν is the mean molecular speed of the gas-phase N_2O_5 molecules.

Values for γ_w at different RH are shown in Figure 4, which shows that γ_w increases with RH and that the variability in values obtained also increases with RH. Similar behavior was seen in work carried out in our laboratory previously.[7] However, the values for γ_w shown in Figure 4 are lower than earlier measurements by approximately a factor of 2.

This reduction in γ_w was achieved by employing an alternative approach to coating the walls with halocarbon wax. Previously, the walls were coated by dissolving the halocarbon wax in a solvent (dichloromethane), coating the walls with this solution and allowing the solvent to evaporate. Now the wax is

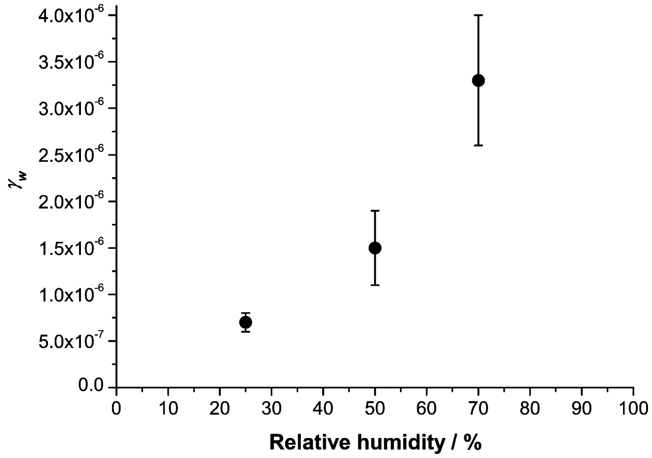

Figure 4. Variation of γ_w with RH obtained for a flow tube coated by directly melting halocarbon wax onto the flow tube walls. Values of γ_w at each RH were determined by taking the average of values for k_w obtained over several days, with the error bars showing the standard deviation from the mean.

directly melted onto the flow tube walls using a heat gun. This second method gave lower values for the loss of N_2O_5 to the flow tube walls, k_w, which were reproducible over the period of a day's experiment.

Reducing the loss of N_2O_5 to the flow tube walls has several advantages. It is not possible to obtain reproducible measurements of the N_2O_5 concentration in the mixing region, i.e., for contact times of less than 5 s. At low initial N_2O_5 concentrations and high values for k_w, most of the N_2O_5 is lost in this mixing region making accurate measurements of k_w difficult as the NO concentrations in the region where measurements can be made approach the baseline NO concentration.

Mentel et al.[8] have shown that uptake onto aerosols containing nitrate (at concentrations of approximately 20 mol kg^{-1}) is up to an order of magnitude lower than uptake onto sulfate aerosols. This "nitrate effect" introduces a possible experimental artifact as, during N_2O_5 hydrolysis, the product NO_3^- can build up in the aerosol droplets. To reduce the problems associated with the nitrate effect, experiments should be carried out under conditions of low initial N_2O_5 concentrations and high particle volume.

The reduction in k_w allowed experiments to be carried out at lower initial N_2O_5 concentrations, between approximately 300 and 600 ppbv for the experiments described in this work. No dependence of γ on the initial N_2O_5 concentration was seen in any of our experiments, suggesting that uptake is not subject to inhibition due to the nitrate effect.

The reduction in k_w also meant that the loss to unreactive aerosols could be better distinguished from loss to the walls allowing low values for γ to be determined more accurately. The detection limit for γ depends on the available aerosol surface area but is around 1×10^{-4} for $k_w \sim 0.005$ s^{-1}.

The first-order rate coefficient for loss of N_2O_5 to the aerosol particles, k_{het}, is defined by

$$k_{het} = \gamma \frac{\nu}{4} S_a \qquad (2)$$

where S_a is the surface area of the aerosol particles per unit volume as calculated from the DMA measurements, ν is the mean molecular speed of the N_2O_5 gas molecules and γ is the uptake coefficient. k_{het} is found from the first-order loss rate coefficients in the absence of aerosol, k_w, and in the presence of aerosol, k_a, using the procedure described by Brown.[23] In the corrections, the gas-phase diffusion coefficient for N_2O_5 was assumed to be 0.10 cm^2 s^{-1}, as calculated by Hu and Abbatt.[6]

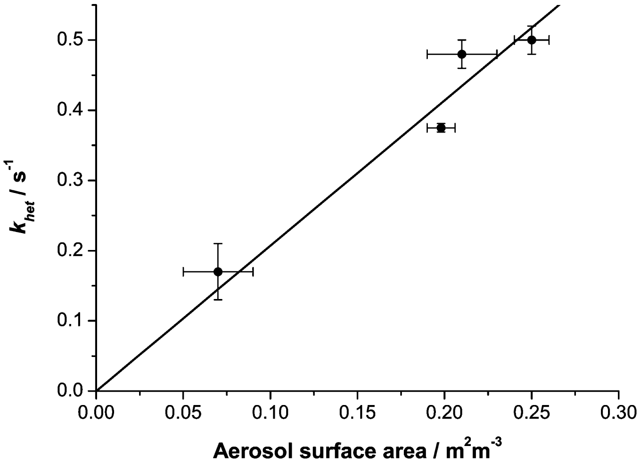

Figure 5. Aerosol surface area, S_a, versus the corrected first-order rate coefficient for loss of N_2O_5 to the aerosol, k_{het}. The uptake coefficient, γ, can be calculated from the gradient of this plot.

Figure 5 shows a plot of the retrieved k_{ket} versus S_a. In the absence of systematic errors, such a plot should be a straight line through the origin with a gradient of $\gamma(\nu/4)$.

The uptake coefficient for a number of determinations of γ for N_2O_5 hydrolysis onto a particular aerosol at a particular RH can be derived in two ways: (a) from the weighted mean of the individual determinations or (b) from the gradient of a plot of k_{het} versus S_a. The choice of procedure was dictated by the fact that for some experimental systems, it was not possible to vary the surface area over a wide enough range to obtain a value for γ using the second method. However, when this was possible, values for γ derived using these two alternative methods agreed within the calculated errors.

2.5. Water Content of Humic Acid Aerosol. The water content of aerosols containing various combinations of inorganic ions can be determined using AIM.[18,19] Although models including organic components are being developed,[24,25] there is currently no thermodynamic model that can be used to determine the water content of an aerosol containing a large organic molecule such as humic acid. The water content of mixed aerosols can often be described using the Zvanovskii–Stokes–Robinson (ZSR)[26] approximation that the individual components do not interact and hence take up water independently.[27] Our previous paper on the growth of aerosols containing humic acid and ammonium sulfate showed that this model could be applied for aerosols containing these compounds.[16] Thus, once the water content of single-component humic acid is known, then the ZSR approximation can be used to determine the water content of aerosols containing mixtures of humic acid and ammonium sulfate.

We have developed a technique for determining the water content of aerosols using a combined FTIR-DMA system. The system will be described in more detail in a later paper so the description given here is brief. The basis for the technique is the calibration of the IR absorption due to condensed-phase water using an aerosol for which the liquid water content is known, in this case ammonium sulfate. The resulting calibration curve can then be used to determine the liquid water content of aerosols that are currently not included in thermodynamic models such as AIM.

IR spectra are recorded using an FTIR spectrometer and the aerosol size distributions measured using an SMPS system consisting of a TSI Model 3080 Electrostatic Classifier with a

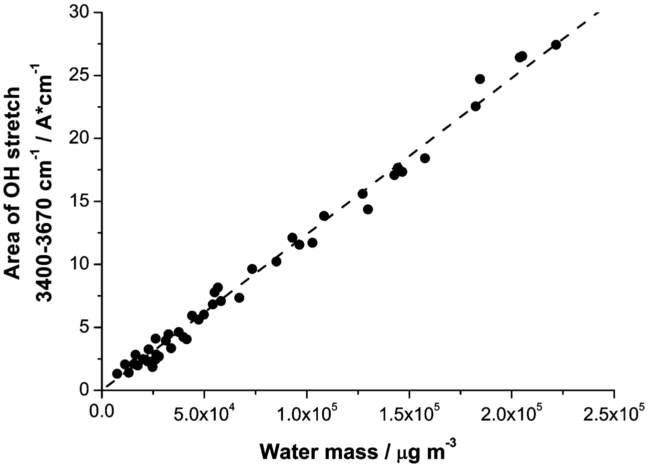

Figure 6. Calibration curve relating the absorption due to condensed phase water to the water mass.

TSI Model 3081 Long DMA and a TSI Model 3010 Condensation Particle Counter. The AFT-FTIR system has been described elsewhere.[28,29] The RH in the flow tube is calculated from the IR spectra using a separate calibration curve, based on the integration of gas-phase water lines in the range 1691−1710 cm^{-1} and the absorption due to condensed-phase water is quantified by integrating the area from 3400 to 3670 cm^{-1}. FTIR alone cannot provide quantitative values for the total amount of aerosol but absorptions due to the aerosol can be calibrated to a total aerosol mass if the aerosol size distribution is simultaneously measured by the SMPS system.

An analysis of the IR spectra of ammonium sulfate aerosol was used to construct a calibration curve relating the absorption due to condensed-phase water (3400−3670 cm^{-1}) to the water mass. The total dry mass of aerosol was calculated from the volume distribution (as measured by the SMPS) using a density of 1.77 g cm^{-3} and correlated with the sulfate absorption mode, 1000−1200 cm^{-1}. IR spectra were taken over the range 0−90% RH. The mass of ammonium sulfate at each RH was calculated using the data from the SMPS and the area of the sulfate absorption mode. The water mass fraction of the ammonium sulfate aerosol at each RH was taken from AIM and converted to a total water mass based on the total amount of ammonium sulfate contained within the aerosol. The resulting calibration curve showed a linear correlation between the aerosol water mass and the area 3400−3670 cm^{-1}, Figure 6.

The correlation was tested for malonic acid aerosol, generated from a 1 wt % solution. As a significant portion of the aerosol volume occurred in particles >1 μm in diameter, which were not measured by the DMA, the distribution was fitted to a log-normal function and this corrected volume distribution used to calculate the total aerosol mass using a density of 1.63 g cm^{-3}. This mass was correlated with the carbonyl absorption mode (1813−1550 cm^{-1}). The water mass fraction over a range of RH was calculated using the calibration plot shown in Figure 6 and agreed with bulk solution measurements.[29]

3. Results

3.1. Aerosol Composition. The composition of the aqueous solutions used to generate internally mixed humic acid and ammonium sulfate aerosols was determined using the method described in our previous paper.[16] A small quantity of each solution was dried and the wt % of N, C, and H determined (Microanalysis, Department of Chemistry, University of Cambridge). Elemental analysis was also carried out on the single-component humic acid and ammonium sulfate solutions.

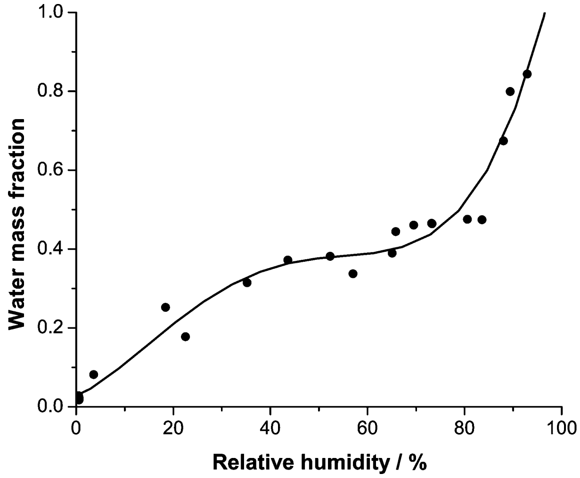

Figure 7. Mass fraction of water as a function of RH for single-component humic acid aerosol. The line shows a fourth-order polynomial fit to the data.

TABLE 1: Summary of the Elemental Analysis Data Used To Determine the Ratios (by Mass) of Humic Acid (HA) to Ammonium Sulfate (AS) Present in the Filtered Solutions

		elemental analysis			ratio	
solution	wt % solid	wt % C	wt % H	wt % N	HA	AS
HA	0.8	40.8	2.8	0.5	1	−
AS	1.3	0	5.9	21.2	−	1
Mix 1	1.7	15.5	4.2	11.5	1	1.5
Mix 2	2.1	6.2	4.9	16.4	1	5
Mix 3	2.0	15.9	4.2	11.5	1	11
Mix 4	1.7	12.5	4.4	13.1	1	15

Elemental analysis results for the solutions used in these experiments are summarized in Table 1. Errors in the measured wt % are estimated to be ±1% based on the variation in the results from separate analyses of the same dried solutions. In subsequent sections, aerosols formed from these solutions will be referred to by their mass ratios of humic acid to ammonium sulfate (i.e., HA:AS).

3.2. Aerosol Water Content. The water content of single-component humic acid aerosol was determined using the combined FTIR−SMPS system described in section 2.5. IR absorption spectra of humic acid aerosols between 0 and 90% RH were analyzed for both the mass of humic acid (calculated from the dry volume distributions using a density of 1.1 g cm^{-3} for humic acid (Sigma Aldrich Technical Services) and the area 1400−1000 cm^{-1}) and mass of water (calculated from the area 3400−3670 cm^{-1} and the calibration curve derived from the analysis of ammonium sulfate aerosol). These data are used to construct a water mass content curve as a function of RH, Figure 7.

The growth factors for the single-component humic acid aerosol were taken from our measured TDMA growth curve.[16] Although this curve was measured for aerosol particles first dried to RH < 2%, it was assumed that no hysteresis behavior would be observed, an assumption that is supported by the lack of hysteresis observed with FTIR spectroscopy.[16] The growth factors for the single-component ammonium sulfate aerosol were taken from Seinfeld and Pandis.[30] Growth factors for the mixed aerosols at a particular RH, G_M, were determined using

$$G_M = (\epsilon_O G_O{}^3 + \epsilon_{IN} G_{IN}{}^3)^{1/3} \qquad (3)$$

where G_O is the hygroscopic growth factor of the organic particles, G_{IN} is the hygroscopic growth factor of the inorganic

TABLE 2: Growth Factors, G_M, and Water Concentrations, $[H_2O]$, for the Humic Acid (HA) and Ammonium Sulfate (AS) Aerosols Studied in This Work.

aerosol	RH/%	G_M	$[H_2O]$/M
HA	25	1.07	15.8
	50	1.09	25.4
	75	1.11	32.4
1:1.5 HA:AS	25	1.04	17.2
	50	1.14	28.5
	70	1.23	36.4
1:5 HA:AS	25	1.02	17.2
	50	1.18	27.9
	70	1.30	36.0
1:11 HA:AS	25	1.01	17.7
	50	1.19	27.8
	70	1.32	36.0
1:15 HA:AS	25	1.01	16.5
	50	1.19	28.0
	70	1.33	35.6
AS	25	1.00	0
	50	1.20	27.8
	60	1.28	30.4
	70	1.35	35.3

particles, ϵ_O the organic volume fraction and ϵ_{IN} the inorganic volume fraction. This expression assumes that the inorganic and organic components take up water independently, i.e., the Zvanovskii−Stokes−Robinson (ZSR) approximation, and that the volumes are additive.[26,30]

To convert our mass fractions to volume fractions, densities of 1.77 and 1.1 g cm^{-3} were used for the ammonium sulfate and humic acid components, respectively. The density of the mixed particles was assumed to be the weighted average of the density of the individual components. Calculated values for G_M were used to determine the aerosol volume at a particular RH assuming an initial dry aerosol diameter of 100 nm.

The water mass fraction of ammonium sulfate aerosols and humic acid aerosols at different RHs was determined using AIM and the humic acid water content curve (Figure 7), respectively. The mass of water absorbed by the aerosol particles was converted into a water concentration (in molar) using the aerosol particle volume determined from the hygroscopic growth factors.

Our previous studies of the phase transitions of mixed humic acid and ammonium sulfate aerosols showed that the ammonium sulfate component is crystalline at 25% RH.[16] In determining the water concentration in the mixed aerosols at 25% RH, it was assumed that the particle consisted of a solid ammonium sulfate core surrounded by humic acid and water. Growth factors and water concentrations for the aerosols studied in this work are summarized in Table 2.

3.3. Kinetic Measurements. Uptake coefficients, γ, for N_2O_5 hydrolysis were measured for single-component humic acid aerosol and four aerosols containing different mixing ratios of humic acid and ammonium sulfate. Experiments were also carried out on single-component ammonium sulfate aerosol for comparison with the literature data. For each system, experiments were carried out at three different RHs: 25%, 50%, and 70%. For all experiments at 25% RH, the aerosol stream was passed through the diffusion dryer prior to entering the flow tube system; the dryer was bypassed in the experiments carried out at 50 and 70% RH.

The deliquescence relative humidity (DRH) for a single-component ammonium sulfate aerosol is (80 ± 2)% RH and the efflorescence relative humidity (ERH) is (34 ± 2)% RH.[16,28] Ammonium sulfate particles are therefore expected to be solid for experiments carried out at 25% RH and supersaturated droplets for experiments carried out at 50 and 70% RH where the dryer is bypassed.

TABLE 3: Uptake Coefficients for N_2O_5 Hydrolysis, γ, Obtained for Aerosols Containing Humic Acid (HA) and Ammonium Sulfate (AS).

aerosol	RH/%	$10^4\gamma$[a]	$10^4\alpha$[b]	V_a/S_a/nm[c]	no. of determinations
HA	25	1 ± 1	1 ± 1	53	3
	50	3 ± 1	3 ± 1	54	5
	75	10 ± 4	10 ± 4	49	5
1:1.5 HA:AS	25	5 ± 2	5 ± 2	60	5
	50	3 ± 2	3 ± 2	61	6
	70	14 ± 2	14 ± 2	62	2
1:5 HA:AS	25	3.3 ± 0.8	3.4 ± 0.8	60	4
	50	8 ± 2	8 ± 2	61	5
	70	23 ± 8	24 ± 8	65	5
1:11 HA:AS	25	7 ± 1	7 ± 1	46	3
	50	31 ± 6	34 ± 6	54	4
	70	80 ± 20	90 ± 20	69	5
1:15 HA:AS	25	6.3 ± 0.4	6.5 ± 0.4	61	4
	50	40 ± 10	50 ± 10	67	5
	70	83 ± 6	99 ± 6	69	4
AS	25	57 ± 6		44	4
	50	150 ± 30	320 ± 30	46	5
	60	160 ± 20	290 ± 20	56	6
	70	190 ± 20	390 ± 20	50	7

[a] Weighted mean of all determinations; errors are calculated from the standard deviation of the individual determinations. [b] Calculated assuming a volume-limited process, eq 4. [c] Determined from the DMA measurements.

In our previous study of the phase transitions of aerosol containing humic acid, we showed that single-component humic acid aerosol showed no efflorescence or deliquescence behavior.[16] Thus, these particles are expected to be in the liquid phase under all experimental conditions.

The addition of humic acid to an ammonium sulfate aerosol decreased the DRH of the ammonium sulfate component (down to 62% for a 1.5:1 HA:AS mixture) and increased the ERH (up to 48% for a 1.5:1 HA:AS mixture).[16] The mixed aerosols were also shown to contain liquid water below the DRH of the ammonium sulfate component. For the mixed aerosol systems, the aerosol particles are therefore expected to be partially solid at 25% RH (as the ammonium sulfate component will have crystallized) and supersaturated droplets at 50% and 70% RH.

3.3.1. Uptake onto Single-Component Ammonium Sulfate Aerosol. Uptake coefficients obtained for ammonium sulfate aerosol are shown in Table 3. Uptake onto the solid particles at 25% RH is much slower than the uptake onto the supersaturated droplets at RH ≥ 50% where γ increases with increasing RH. Figure 8 compares data from this work with recent values for uptake onto submicron-sized ammonium sulfate aerosol from the literature showing our data are in good agreement with previous studies. Up until RH ≈ 50%, there is a general increase in γ with increasing RH. However, above 50% RH, there are two differing trends; the data of Kane et al.[2] show a continuing increase of γ with increasing RH whereas that of Hallquist et al.[1] suggest that γ is independent of RH in this region. Our data show a continuing increase in γ with increasing RH. However, within the experimental errors, the data point at 70% RH is in agreement with the measurements of both Hallquist et al.[1] and Kane et al.[2]

3.3.2. Uptake onto Aerosols Containing Humic Acid. Uptake coefficients obtained for aerosols containing humic acid are given in Table 3 and shown as a function of RH in Figure 9. This figure shows that the reactivity of the mixed aerosols increases with increasing RH and with increasing ammonium sulfate mass fraction. The variation of γ with humic acid mass fraction at these three different RHs is shown in Figure 10, which shows that the reactivity of the ammonium sulfate aerosol is significantly reduced even with only 6% humic acid by mass. It should be noted that the value for single-component humic

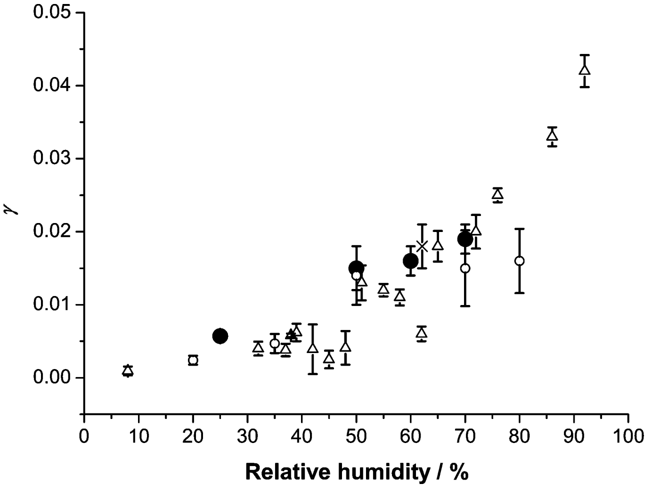

Figure 8. Uptake coefficients for N_2O_5 hydrolysis, γ, versus RH for ammonium sulfate aerosol: filled circles, this work; open circles, Hallquist et al.;[1] triangles, Kane et al.;[2] cross, Folkers et al.[15]

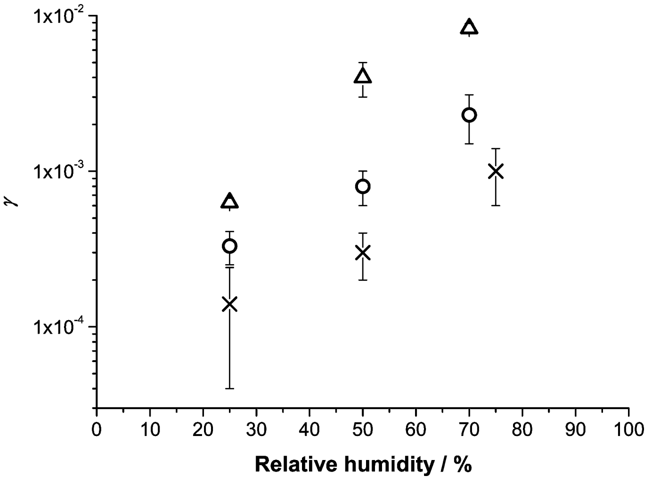

Figure 9. Uptake coefficient for N_2O_5 hydrolysis, γ, versus RH for humic acid (crosses), 1:5 HA:AS (circles), and 1:15 HA:AS (triangles) aerosols.

acid quoted at 70% RH was measured at 75% RH. However, it is expected that the variation in γ over this RH range is small and within the errors of our measurements.

4. Discussion

Uptake coefficients have been determined for aerosols containing mixtures of humic acid and ammonium sulfate. Values of γ between 1×10^{-4} and 8×10^{-3} were obtained with the lowest values obtained for conditions of low RH and high humic acid mass fractions. Generally, uptake coefficients for aerosols containing humic acid are an order of magnitude below those measured for single-component sulfate aerosols under similar conditions.[1,2] Trends observed of increasing γ with increasing ammonium sulfate mass fraction and increasing RH should also be noted.

At first sight, it might be expected that the reactivity of the mixed aerosol could be calculated as a mass- or volume-weighted average of the uptake coefficients of the single-component aerosols. However, we found that it was not possible to reproduce the measured values for γ for the mixed aerosols on either basis, and there was a particularly large decrease in uptake for the smallest humic acid mass fractions.

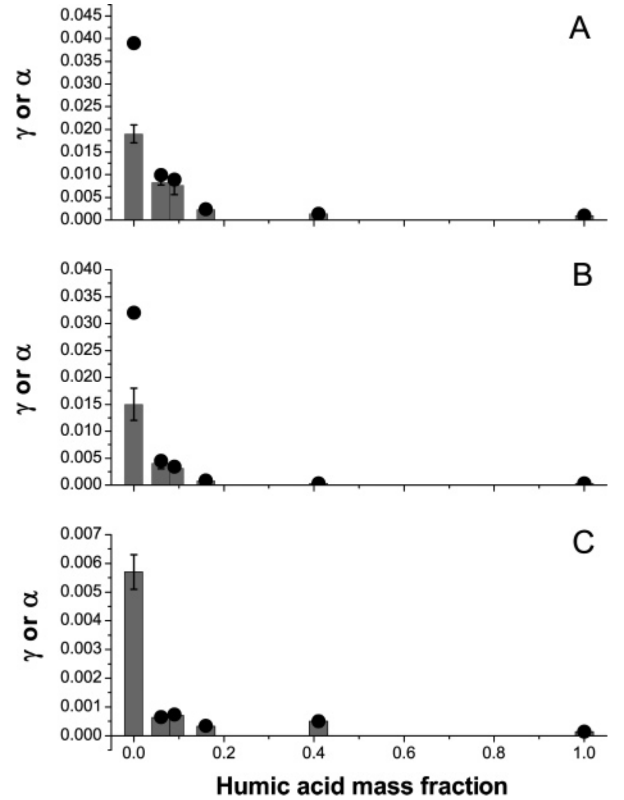

Figure 10. Experimental uptake coefficients for N_2O_5 hydrolysis, γ (bars), and mass accommodation coefficients as calculated using eq 4 (filled circles) versus humic acid mass fraction at 70% RH (A), 50% RH (B) and 25% RH (C).

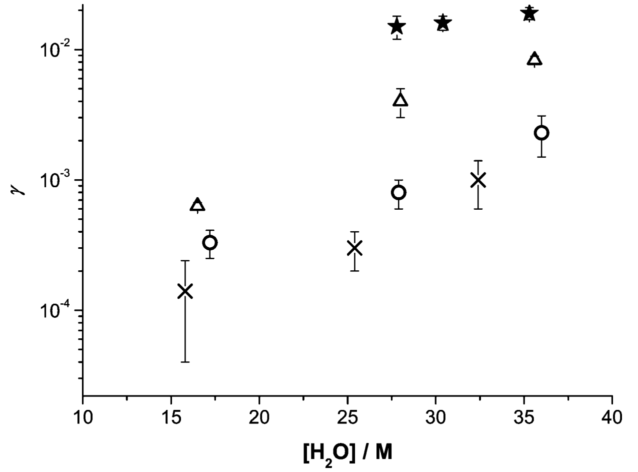

Figure 11. Uptake coefficient for N_2O_5 hydrolysis, γ, versus water concentration, $[H_2O]$, for humic acid (crosses), 1:5 HA:AS (circles), and 1:15 HA:AS (triangles) aerosols. Data for single-component ammonium sulfate aerosols (stars) are shown for comparison.

Figure 11 shows the variation of γ with liquid water concentration. Different uptake coefficients are observed for aerosol with similar water concentrations and it is apparent that, for these systems, aerosol reactivity cannot be explained solely on the basis of aerosol water content.

In the following discussion, we examine the uptake coefficients using the resistance model described by Kolb et al.[31] and Davidovits et al.[32] According to this model, when the rate of reaction in solution is slow relative to that of diffusion, uptake becomes limited by the aerosol volume and γ is given by

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{\nu}{4HRTk^{\mathrm{I}}}\frac{S_a}{V_a} \tag{4}$$

where α is the mass accommodation coefficient, ν is the mean molecular speed of the gas-phase N_2O_5 molecules, H is the Henry's law constant, R is the gas constant, T is the temperature, k^I is the pseudo first-order rate coefficient for reaction in solution, S_a is the aerosol surface area and V_a is the aerosol volume.

For the hydrolysis of N_2O_5 on the weakly acidic aqueous aerosols considered in this work, we assume that reaction occurs in solution with water alone. Although direct reaction with the functional groups of the various humic acid molecules is possible, it is considered to have a much lower rate than that of reaction with the water molecules that are present in excess.

Following the study of Thornton and Abbatt of the reactive uptake of N_2O_5 by malonic acid aerosols,[14] the following mechanism for hydrolysis of is adopted: N_2O_5 is first accommodated into an aqueous surface layer and then reacts to form a hydrated intermediate,

$$N_2O_5(aq) + H_2O(liq) \rightleftharpoons [H_2ONO_2]^+(aq) + NO_3^-(aq) \quad (R4)$$

Further reaction of the intermediate with H_2O yields HNO_3 and H_3O^+ via

$$[H_2ONO_2]^+(aq) + H_2O(liq) \rightarrow HNO_3(aq) + H_3O^+(aq) \quad (R5)$$

Thornton and Abbatt[14] suggest that for aqueous malonic acid aerosol with water activity less than 0.4 (RH < 40%), reaction R5 becomes rate limiting, but at RH > 50%, either mass accommodation or the formation of the intermediate, R4, becomes rate limiting.

The rate of reaction in the condensed phase can therefore be identified with that of either reaction R4 or reaction R5, both of which involve water. It is therefore reasonable to assume that the rate of reaction scales linearly with water concentration,

$$k^I = k^{II}[H_2O] \quad (5)$$

where k^{II} is the second-order rate coefficient for reaction in solution and $[H_2O]$ is the concentration of water in the aerosol droplets.

In the following analysis, we use our measured uptake coefficients and the resistance model[31,32] to calculate the mass accommodation of N_2O_5 at the particle surface under the assumption that it is the dependence of α on the humic acid content that controls the rate of reactive uptake. Indeed, the recent studies of both Folkers et al.[15] and Thornton and Abbatt[14] show a reduction of γ for N_2O_5 hydrolysis in the presence of organic films and possess qualitative similarities with our work. Folkers et al.[15] attributed their results to either a smaller Henry's law coefficient or mass accommodation coefficient, thus a slower initial solvation of N_2O_5 in the droplets. It is possible that a large organic molecule with surfactant properties, such as humic acid, could affect the rate of N_2O_5 hydrolysis in the same way.

In our analysis we take $T = 298$ K and $H = 2$ M atm^{-1} [3,9] and assume that only water and N_2O_5 are involved in the rate-determining step for reaction within the aerosol particle. Thus, $k^{II} = 2.6 \times 10^4$ M^{-1} s^{-1}, as measured by Thornton et al.,[11] independent of the aerosol substrate.

The mass accommodation coefficient, α, was calculated using eq 4, and water concentrations were taken from Table 2. The retrieved values for α are given in Table 3 and shown as a function of humic acid mass fraction at different RHs by the filled circles in Figure 10.

For single-component ammonium sulfate aerosol, a value of $\alpha \approx 3.3 \times 10^{-2}$ was obtained, which was approximately constant over the RH range 50−70%, similar to that for uptake of N_2O_5 onto pure water where $\gamma = 0.03 \pm 0.01$.[33] Using our analysis method, no value for α can be calculated at 25% RH as ammonium sulfate is crystalline under these conditions and therefore the concentration of liquid water in the particles is zero.

For all aerosols containing humic acid, calculated values of α were between 1×10^{-4} and 1.0×10^{-2}. α was found to increase with increasing RH, and to decrease with increasing humic acid mass fraction. A large reduction in α results from only a small mass fraction of humic acid. As noted above, this cannot be accounted for by changes in V_a/S_a or $[H_2O]$ in eq 4 and it is apparent that, at high HA mass fractions or low RH, $\alpha \approx \gamma$ implying that uptake is limited by mass accommodation at the particle surface.

Humic acids are known to have surfactant properties and have been shown to from micelles in aqueous solution.[34,35] Kiss et al.[36] have measured the surface tension of humic-like substances (HULIS) extracted from tropospheric aerosol. The surface tension of the aqueous solutions was decreased by 24−42 compared with that for pure water with organic matter present at a concentration of about 1 g L^{-1}. They also found that the addition of HULIS to ammonium sulfate solution, enhanced the surface tension lowering effect of the organic constituent. This was explained by the interaction of the ammonium sulfate and the HULIS: the inorganic component, when present in high concentration, forces the organic surfactants to the air−water interface, thus causing a surfactant enriched layer on the surface.

We suggest that the presence of this organic layer reduces the mass accommodation coefficient for N_2O_5 at the particle surface. As the amount of liquid water associated with the particles increases with increasing RH,[16] the increase in surface water likely assists the accommodation of N_2O_5. Thus α increases with increasing RH.

Of course, whether a process is limited by the aerosol volume or surface area depends on the competition between reaction and diffusion in the liquid droplet and the droplet size. This is best quantified by the reacto-diffusive parameter, q, as defined by

$$q = r\sqrt{\frac{k^I}{D_l}} \quad (6)$$

where r is the particle radius and D_l is the liquid-phase diffusion coefficient. Assuming a value of k^{II} as above, and $D_l = 1 \times 10^{-5}$ cm^2 s^{-1},[3,11] reacto-diffusive lengths between 30 and 50 nm were calculated, giving values of q between 2 and 3. Under such conditions, volume-dependent uptake is a reasonable approximation.

However, it is possible that in the presence of a large organic molecule such as humic acid may reduce D_l. As the reacto-diffusive length, l, decreases with decreasing D_l, a significant reduction in D_l may cause the reaction to become limited not by volume as above but by the available aerosol surface area.[31,32] However, for D_l within a range of between 10^{-6} and 10^{-5} cm^2 s^{-1} chosen to simulate both a more solidlike and more liquid film, as used by Folkers et al.,[15] the surface-limited uptake model does not adequately represent our data.

It is possible that a combined reduction in α and D_l could account for our observed uptake coefficients and that uptake is not adequately represented by either extreme of volume- or surface-limited uptake. Furthermore, other physico-chemico parameters may also be affected by the presence of the humic acid, e.g., the Henry's law constant as noted by Folkers et al.[15] Until such time as these data become available, the reduction in uptake coefficient is best explained, albeit tentatively, by a reduction in the mass accommodation coefficient, α.

5. Conclusions and Atmospheric Implications

Uptake coefficients have been determined for aerosols containing mixtures of humic acid and ammonium sulfate. The observed trends in γ could not be explained with reference to the liquid water content of the aerosols alone. An analysis was performed using the resistance model[31,32] to obtain further information on the effect of humic acid on parameters such as the mass accommodation coefficient at the surface of the aerosol particles and the rate of N_2O_5 diffusion through the liquid droplet. It was found that a reduction in the liquid-phase diffusion coefficient, though possible, is unlikely to be sufficient to account for the observed decrease in uptake.

By assuming that the bimolecular rate coefficient for reaction in solution, k^{II}, was independent of the aerosol substrate, we calculated mass accommodation coefficients, α, from the measured values for γ by assuming a volume-dependent uptake process. α was found to decrease with increasing humic acid mass fraction and to increase with increasing RH. We attribute this to a surfactant property of the humic acid. At low RH and high humic acid mass fractions, mass accommodation at the surface appears to be the rate-limiting step in the uptake process.

In the only modeling study to account for the variation of γ for N_2O_5 hydrolysis with temperature, RH and aerosol composition, Evans and Jacob,[12] chose to use data for γ on malonic acid aerosol from Thornton et al.[11] to represent all organic aerosol. Thornton et al.[11] found that uptake coefficients onto malonic acid aerosols were comparable with uptakes measured on single-component inorganic aerosol. Our data, along with that of Folkers et al.,[15] show that aerosols consisting of high molecular weight, oxygenated organic molecules show uptake coefficients of up to a factor of 42 lower than that of single-component inorganic aerosols such as NH_4HSO_4 and $(NH_4)_2SO_4$ and that γ is also reduced on internally mixed organic/inorganic aerosols. One implication of these results is that N_2O_5 hydrolysis may occur at significantly slower rates on aged atmospheric aerosol and aerosol from polluted regions, which tend to contain a higher proportion of high molecular weight oxygenated organic material.[37]

Much work has been carried out recently into the study of the hygroscopic growth and phase transitions of aerosols containing organic species,[27] and data from these experiments are now beginning to be included into thermodynamic models.[24,25] However, this work has shown that γ for N_2O_5 hydrolysis cannot be predicted on the basis of the water content of aerosols alone and that the nature of the organic must be taken into consideration. More experimental data on aerosols containing a wide variety of both insoluble and soluble organic species are needed before N_2O_5 hydrolysis on these aerosols can be effectively parametrized and incorporated into global models.

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