Uptake of Gaseous Alkylamides by Suspended Sulfuric Acid Particles: Formation of Ammonium/Aminium Salts

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ABSTRACT: Amides represent an important class of nitrogen-containing compounds in the atmosphere that can in theory interact with atmospheric acidic particles and contribute to secondary aerosol formation. In this study, uptake coefficients (γ) of six alkylamides (C₁ to C₆) by suspended sulfuric acid particles were measured using an aerosol flow tube coupled to a high resolution time-of-flight chemical ionization mass spectrometer (HRTToF-CIMS). At 293 K and <3% relative humidity (RH), the measured uptake coefficients for six alkylamides were in the range of (4.8−23) × 10⁻⁴. A negative dependence upon RH was observed for both N-methylformamide and N,N-dimethylformamide, likely due to decreased mass accommodation coefficients (α) at lower acidities. A negative temperature dependence was observed for N,N-dimethylformamide under <3% RH, also consistent with the mass accommodation-controlled uptake processes. Chemical analysis of reacted sulfuric acid particles indicates that alkylamides hydrolyzed in the presence of water molecules to form ammonium or aminium. Our results suggest that multiphase uptake of amides will contribute to growth of atmospheric acidic particles and alter their chemical composition.

1. INTRODUCTION

Amides refer to a category of nitrogen-containing organic compounds with a general formula of R₁C(O)NR₂R₃ (R₁, R₂, and R₃ = a hydrogen atom or an alkyl group). They are directly emitted from various sources, including biomass burning,1 cooking,2 combustion,2 animal husbandry,3 sewage treatment,4 and industrial manufacture processes of lubricants, inks, and many other products.5 In addition to the primary emission sources, amides can be generated in situ in the atmosphere as well. For example, amides are products formed from the gas-phase reactions of amines with OH and NO₃ radicals and ozone6−9 and from OH radical-initiated reactions of 2-aminoethanol.10,11 Amides can also be formed via atmospheric accretion reactions of organic acids with amines or ammonia.12 In addition, reactions of particulate amines with stabilized Criegee intermediates or secondary ozonides will lead to the formation of amides.13

Gaseous amides have been detected close to their sources. Leach et al. measured over 4000 pptv (parts per trillion by volume) of dimethylformamide (DMF) near waste and sewage operations.4 Large emissions (4.21 g kg⁻¹) of acetamide (AA) were detected from peat fires burning.13 Formamide (FA) was detected as a degradation product of 2-aminoethanol emitted from an industrial carbon capture facility.13 In addition to measurements of amides near the emission sources, Yao et al. recently reported the detection of C₁⁻ to C₆⁻amides in the urban atmosphere of Shanghai using a high resolution time-of-flight chemical ionization mass spectrometer (HRTToF-CIMS).14 up to hundreds of pptv of amides, and even peak concentrations of 8700 pptv for C₆-amides, were observed in urban Shanghai.

The detection of high concentrations of amides in the ambient air urges a complete understanding on their atmospheric transformation. Previous studies reported that amides can undergo reactions with atmospheric oxidants including OH and NO₃ radicals, O₃, and Cl atoms,5,17 leading to nitrogen-containing products that can contribute to the formation of secondary aerosols.20 On the other hand, acetamide was found to only have a very weak enhancement capability on sulfuric acid nucleation.23 Nevertheless, amides are expected to interact with acids since they are prone to accept protons. Indeed, previous studies suggest that amides would hydrolyze via the AO₂⁻ mechanism in acidic media in the presence of water molecules, giving rise to the formation of ammonium or aminium.24,25 Therefore, amides likely interact with atmospheric acidic particles, especially newly formed sulfuric acid particles with a high acidity, and alter their physicochemical properties.

Received: June 21, 2017
Revised: September 6, 2017
Accepted: September 14, 2017
Published: September 14, 2017

DOI: 10.1021/acs.est.7b03175
In this study, we investigated uptake of six alkylamides by suspended sulfuric acid particles in an aerosol flow tube coupled to a HRTof-CIMS using protonated ethanol reagent ions. The influences of temperature (293–355 K) and relative humidity (≤3–80% RH) on uptake coefficients were studied as well to elucidate the rate-determining step during the uptake processes. In addition to kinetic measurements, we analyzed the chemical composition of sulfuric acid particles exposed to FA or DMF at different RH to elucidate the detailed reaction pathway. Atmospheric implications of our study are discussed.

2. MATERIALS AND METHODS

The experimental system for the uptake measurements is illustrated schematically in Figure 1. The aerosol flow tube is made of Pyrex glass with an inner diameter of 8 cm and a total length of 1.2 m. The inlet of the flow tube is characterized with two side-injectors for introduction of gases, and a stainless-steel injector of 8 mm inner diameter that is situated along the tube’s centerline for introduction of aerosols. The outlet of the flow tube is connected to online instruments to monitor the progress of uptake experiments. Temperature and RH were monitored using RH/temperature probes (model HMP110, Vaisala Inc., Finland). The majority of experiments were performed at room temperature (293 K). However, there were a set of experiments during which temperatures were regulated between 293 and 355 K by heating the aerosol flow tube with a heating tape.

In this study, a pure air generator (model 737, AADCO Instruments Inc.) was passed through a commercial constant output atomizer (TSI 3076) that was filled with a diluted H₂SO₄ solution to produce suspended sulfuric acid particles. The outflow was then directed to multiple silica gel dryers to reduce the RH to less than 3%. In case of experiments at a high RH, the aerosol flow was then mixed with a 100% RH flow of typically 0.1 slpm was passed through the glass tube to entrain the corresponding alkylamide into the gas flow, and then directed into the aerosol flow tube through one side injector. In order to reduce the wall loss of gaseous alkylamides, a Teflon layer was coated on the inner wall of the aerosol flow tube and the outer wall of the stainless-steel injector.

The other side injector was retained for a pure air flow rate in the aerosol flow tube constant throughout one experiment when the aerosol flow was bypassed from the aerosol flow tube.

Gaseous alkylamides (C₁ to C₃) were generated using homemade permeation sources. FA (≥ 99.5%, Sigma-Aldrich), AA (≥99%, Sigma-Aldrich), N-methylformamide, (MF, ≥99%, Sigma-Aldrich), propanamide (PA, ≥97%, Sigma-Aldrich), N-methylacetamide (MA, ≥ 99%, Sigma-Aldrich), and DMF (≥ 99%, Sigma-Aldrich) were used as received without further purification. The permeation tube was placed in a glass tube with an inner diameter of 2.5 cm that was immersed in a constant temperature liquid bath. An ultrahigh purity (UHP) nitrogen (≥99.9999%, Pujing Specialty Gases Factory, China) flow of typically 0.1 slpm was passed through the glass tube to entrain the corresponding alkylamide into the gas flow, and then directed into the aerosol flow tube through one side injector.

An aerodyne HRTof-CIMS that allows mass spectrometric measurements with high sensitivity and high mass resolution was used to monitor the concentrations of gaseous alkylamides during the uptake experiments. The instrumentation has been described in details in previous studies. In this work, we used protonated ethanol as reagent ions due to its higher proton affinity (185.6 kcal mol⁻¹) compared to that of water (165.2 kcal mol⁻¹) and therefore more selectivity for.
detecting species whose proton affinities are even higher (e.g., >196 kcal mol\(^{-1}\) for alkylamides\(^{1}\)).

Alkylamides were detected through the following ion-molecule reaction:

\[
\begin{align*}
(C_2H_5OH)_x H^+ + R_n C(O)NR_2R_3 & \rightarrow (C_2H_5OH)_y R_n C(O)NR_2R_3 H^+ + (n - y) C_2H_5OH
\end{align*}
\]

where \(n = 1, 2, 3; j = 0, 1; R_n C(O)NR_2R_3\) donates alkylamides; and \((C_2H_5OH)_y R_n C(O)NR_2R_3 H^+\) donates the protonated alkylamides and their clusters with ethanol. Concentrations of alkylamides were in the range of hundreds of pptv to a few ppbv, estimated using the calibration coefficients from a previous study.\(^{16}\) Note that the measured signal intensities for protonated alkylamides were then corrected by subtracting the instrumental background, which was generally less than 7% of the initial signal intensities of the alkylamides in all of our uptake experiments.

The chemical composition of sulfuric acid particles after exposure to FA or DMF was analyzed by HRTToF-CIMS that was interfaced to a Filter Inlet for Gases and AEROsols (FIGAERO). Briefly, FIGAERO-HRTToF-CIMS provides unperturbed measurements of gaseous samples while collecting particles on a PTFE filter via an entirely separate sampling port.\(^{32}\) Analysis of collected particles was conducted via thermal desorption by heated UHP N\(_2\). Note that, before filter collection, we specifically directed the aerosol sample flow through a cylindrical diffusion scrubber filled with activated charcoal to remove the redundant gaseous alkylamides. Particle loss in the scrubber was negligible. The typical collection time for the aerosol flow was 10 min.

Uptake of a gas-phase species by a liquid surface can be treated by a diffusional and reactional equation.\(^{33}\) The observed first-order rate coefficient \(k_{obs}\) is derived from the observed decay in the absence and presence of sulfuric acid aerosols, as given in eq 1:

\[
k_{obs} = \frac{u}{L} \ln \left( \frac{I_0}{I} \right)
\]

where \(u\) is the carrier gas flow velocity (cm s\(^{-1}\)), \(L\) is the contact distance between the gaseous alkylamide and suspended sulfuric acid particles, \(I_0\) is the initial signal intensity of the alkylamide and \(I\) is the signal intensity of the alkylamide after a reaction time of \(t\) (corresponding to a contact distance of \(L\)). The uptake coefficient \(\gamma\) is then determined using eq 2:

\[
\gamma = \frac{4 k_{p}}{S \omega_{amide}}
\]

where \(k_p = k_{obs} - k_w\) is the first-order rate coefficient for loss of alkylamides onto the suspended aerosol particles, \(S\) is the total aerosol surface area-to-volume ratio of the aerosol flow obtained with the SMPS, \(\omega_{amide}\) is the average molecular speed of the alkylamide in the gas phase, and \(k_w\) is the first-order rate coefficient for alkylamides’ loss to the flow tube wall that is determined in the same manner as \(k_{obs}\) in the absence of particles. \(k_w\) is generally larger at higher RH, and a \(k_w\) of < 0.0017 s\(^{-1}\) for DMF was measured at 293 K and ~80% RH. The values of \(k_w\) were much smaller than those of \(k_p\) in the same experiment in this study. The extent of the uptake can be varied by either changing the contact distance, or changing the aerosol surface area-to-volume ratio.

3. RESULTS AND DISCUSSION

**Uptake Measurements.** Alkylamide uptake experiments were performed by measuring the decay of the gaseous alkylamide. Figure 2 shows a typical profile of the decay in the alkylamide signal upon exposure to H\(_2\)SO\(_4\) particles at 293 K and < 3% RH, using FA as an example. We first established a stable signal of FA with the aerosol flow being bypassed from the aerosol flow tube. Subsequently, as we introduced H\(_2\)SO\(_4\) particles into the aerosol flow tube and exposed them to gaseous FA, a sharp decrease in the signal of FA was observed. When we bypassed H\(_2\)SO\(_4\) particles again, the concentration of FA recovered to its original level, indicating that the uptake by suspended H\(_2\)SO\(_4\) particles was responsible for the observed loss. FA was bypassed at 2700 s to establish an instrumental background for the gas phase FA. Analogous profiles were observed in all uptake experiments in this study.

Figure 3 plots the first-order rate coefficients \(k_p\) of FA (red triangles), MF (blue circles), and DMF (black squares) as a function of \((S \omega_{amide})/4\) under virtually identical experimental conditions.
conditions, that is, RH < 3% and T = 293 ± 1 K. The error bar represents one standard deviation that is a result of measurement uncertainties. With a correction of wall losses, such plots should be straight lines through the origin. Excellent $R^2$ values were obtained, being 0.99, 0.98, and 0.99 for FA, MF, and DMF, respectively. As shown in eq 2, the linear regression of each data set in Figure 3 yields an uptake coefficient $\gamma$. Similar plots were obtained for all of our uptake experiments.

Table 1 summarizes our measured uptake coefficients of six different alkylamides ($C_1$ to $C_3$) over a range of RHs and temperatures. Uptake coefficients of FA, MF, MA, and DMF were measured to be $(4.8 \pm 0.1) \times 10^{-2}$, $(12 \pm 1) \times 10^{-2}$, $(23 \pm 1) \times 10^{-2}$, and $(14 \pm 1) \times 10^{-2}$, respectively, at 293 K and < 3% RH. Attempts to measure the uptake coefficients of AA and PA at the same temperature were unsuccessful due to their relatively low volatility. To cope with this problem, we performed measurements of these two alkylamides at an elevated temperature (338 K) by heating the aerosol flow tube with a uniformly wrapped heating tape. The measured uptake coefficients were $(4.9 \pm 0.6) \times 10^{-2}$ for AA and $(5.0 \pm 0.6) \times 10^{-2}$ for PA, respectively. By assuming the same temperature dependence for the uptake coefficients of AA and PA as that for DMF that will be discussed in the next section, we derived uptake coefficients of $(9.6 \pm 0.6) \times 10^{-2}$ and $(9.7 \pm 0.6) \times 10^{-2}$, respectively, for AA and PA at 293 K and < 3% RH (Table 1). The two calculated uptake coefficients and those acquired experimentally for the other four alkylamides generally coincide with the relative values of their proton affinities as listed in Table 1. On the other hand, the measured uptake coefficient for MA is higher than the estimated one for AA, indicating that the steric hindrance of the ethyl substituent in the AA molecules might counteract the proton affinity, since the specific structure of a molecule could be directly related to its capacity to interact with a surface.

**Uptake As a Function of Relative Humidity.** The measured uptake coefficients on a logarithmic scale of MF and DMF by suspended $H_2SO_4$ particles at 293 K are plotted as a function of RH, as shown in Figure 4. Both MF and DMF exhibit a large negative humidity dependence, of which the former one is more remarkable. The MF uptake coefficient decreases from $(12 \pm 1) \times 10^{-2}$ to $(0.10 \pm 0.12) \times 10^{-2}$ between < 3% and 50% RH, whereas the uptake coefficient of DMF decreases from $(14 \pm 1) \times 10^{-2}$ to $(0.13 \pm 0.08) \times 10^{-2}$ between < 3% and 50% RH, whereas the uptake coefficient of

**Figure 4.** Uptake coefficient $\gamma$ as a function of RH for N-methylformamide (MF) and N,N-dimethylformamide (DMF) at $T = 293 \pm 1$ K and $L = 65$ cm. The olive-green line is an estimation of $H_2SO_4$ concentration calculated using water vapor pressure data over aqueous sulfuric acid solution. The error bar represents one standard deviation.
DMF decreases from \((14 \pm 1) \times 10^{-2}\) to \((0.13 \pm 0.08) \times 10^{-2}\) between < 3% and 80% RH.

The overall uptake of gaseous molecules on aerosols is a sequence of coupled processes including accommodation, diffusion in the bulk phase involving either liquid or solid phases, and reaction in the bulk phase.\(^{38-37}\) Since a general solution of such equations cannot be obtained, an approximate equation based on a resistant model is used for expressing \(\gamma\).\(^{38-40}\) In this study, the uptake coefficient for alkylamides upon sulfuric acid aerosols can be expressed as

\[
1 = \frac{1}{\gamma} = \frac{1}{\alpha} + \frac{1}{\Gamma_{\text{rxn}} + \Gamma_{\text{sol}}},
\]

where \(\alpha\) is mass accommodation coefficient, \(\Gamma_{\text{sol}}\) is the resistance due to solubility limitation, and \(\Gamma_{\text{rxn}}\) is the resistance due to reactions in the bulk phase. The terms on the right side of eq 3 represent the gas-to-particle transfer and the coupled reaction-diffusion processes in the bulk, respectively.

Within the relative humidity studied in this work, the concentration of sulfuric acid is in the range of 27–75 wt % \(\text{H}_2\text{SO}_4\), calculated using water vapor pressure data over aqueous sulfuric acid solution.\(^{41-45}\) In concentrated \(\text{H}_2\text{SO}_4\), the uptake of alkylamides is governed by mass accommodation,\(^{46}\) since the rates of dissolution and reaction are faster than the mass accommodation. Previous studies on uptake of ammonia by \(\text{H}_2\text{SO}_4\) solutions\(^{44,46}\) and uptake of alkylamines by \(\text{H}_2\text{SO}_4\) solutions\(^{47}\) also showed similar conclusions. Hence, the negative humidity dependence of the uptake coefficient \(\gamma\) is likely due to decreased mass accommodation coefficients \(\alpha\) at lower acidities.\(^{44,46,47}\)

**Uptake As a Function of Temperature.** The temperature dependence of the multiphase uptake of DMF by suspended sulfuric acid particles has been investigated under RH < 3% and within a temperature range of 293–355 K. As shown in Table 1, the uptake coefficients of DMF by sulfuric acid particles decrease from \((14 \pm 1) \times 10^{-2}\) to \((5.3 \pm 0.2) \times 10^{-2}\) with the temperature increasing from 293 to 355 K, showing a negative dependence upon temperature.

As discussed in the previous section, the uptake of alkylamides by sulfuric acid particles under RH < 3% is governed by the mass accommodation coefficient. Hence, the temperature dependence of uptake coefficient \(\gamma\) here is in fact a temperature dependence of mass accommodation coefficient \(\alpha\). A thermodynamic model has been developed for the mass accommodation process based on the critical cluster theory.\(^{40,48}\)

In this model, surface dynamics of the gas uptake process is viewed from the perspective of nucleation theory. The impinging gas-phase molecule \((n_\text{g})\) initially strikes the particle surface and becomes a loosely bound surface species \((n_\text{s})\) that participates in the nucleation process. If such a molecule becomes part of a critical sized cluster \((n_\text{c}^*)\), it will serve as a center for further condensation and will grow/aggregate in size until it merges with the bulk phase. The temperature dependence of \(\alpha\) is expressed in terms of an experimentally observed Gibbs free energy, \(\Delta G_{\text{obs}}\), according to

\[
\frac{\alpha}{1 - \alpha} = \frac{k_{\text{des}}}{k_{\text{sol}}} = \exp \left( \frac{-\Delta G_{\text{obs}}}{RT} \right),
\]

where \(k_{\text{des}}\) is the rate of desorption from the surface, \(k_{\text{sol}}\) is the rate of transfer of molecules from the surface into the bulk phase, \(\Delta G_{\text{obs}} = \Delta H_{\text{obs}} - T \Delta S_{\text{obs}}\) is the Gibbs free energy barrier of the transition state between the gaseous species \((n_\text{g})\) and the critical cluster \((n_\text{c}^*)\), and \(\Delta H_{\text{obs}}\) and \(\Delta S_{\text{obs}}\) represent the enthalpy and entropy changes during the accommodation, respectively.

In Figure 5, the natural log of \(\gamma/(1-\gamma)\) is plotted as a function of \(1/T\) using our uptake coefficients for DMF. It is evident from the plot that our data fit the model fairly well, indicating the observed temperature dependence is consistent with a mass accommodation-controlled multiphase uptake. \(\Delta H_{\text{obs}}(\text{DMF}) = -(13.04 \pm 2.40) \text{ kJ mol}^{-1}\) and \(\Delta S_{\text{obs}}(\text{DMF}) = -(57.57 \pm 7.46) \text{ J K}^{-1} \text{ mol}^{-1}\) are derived from the slope and the intercept of the plot, respectively. The values of \(\Delta H_{\text{obs}}\) and \(\Delta S_{\text{obs}}\) are always negative\(^{40,48-50}\) reflecting that the mass accommodation process is always favored in terms of enthalpy, and that the dissolution of a trace gas into the aerosol corresponds to an entropy primarily contributed from the critical cluster binding energy and surface tension. The enthalpy and entropy changes for DMF in our study are smaller than those reported for NH\(_3\) that were obtained from the uptake measurements in a droplet train flow reactor at pH 1, with \(\Delta H_{\text{obs}}(\text{NH}_3) = -37.76 \text{ kJ mol}^{-1}\) and \(\Delta S_{\text{obs}}(\text{NH}_3) = -150.27 \text{ J mol}^{-1} \text{ K}^{-1}\) (ref 46). From the critical cluster theory, the capacity of a gas molecule to participate in the aggregation process with solvent molecules defines the ease of the gas molecule’s incorporation into bulk phase. This capacity is directly related to properties of both the solvent and the gas molecule, and in a way can be reflected by the magnitudes of the two parameters, \(\Delta H_{\text{obs}}\) and \(\Delta S_{\text{obs}}\) that is, gas molecules with smaller \(\Delta H_{\text{obs}}\) and \(\Delta S_{\text{obs}}\) are more capable of forming a critical cluster.\(^{40}\) Therefore, a higher solvent acidity in our study and a higher proton affinity of DMF (212.1 kcal mol\(^{-1}\))\(^{51}\) than that of NH\(_3\) (204.0 kcal mol\(^{-1}\))\(^{52}\) can probably explain the observed difference in \(\Delta H_{\text{obs}}\) and \(\Delta S_{\text{obs}}\) between DMF and NH\(_3\). It is not surprising that alkylamides with higher proton affinities tend to have larger uptake coefficients, just as summarized previously in Table 1, since they are likely to be more actively bond to sulfuric acid molecules and easier to enter the bulk phase. On the other hand, care should be taken to extrapolate this dependence to the temperature outside the range and to other five alkylamides, although the critical cluster model fits the data set of DMF reasonably well.

**Product Analysis.** Here, we analyzed the chemical composition of sulfuric acid particles after exposure to FA or
DMF to elucidate the detailed reaction pathway within the particles. The experiments were performed under both wet and dry conditions, and by attaching a FIGAERO inlet to HRTof-CIMS.

Figure 6a depicts a typical temporal profile for experiments conducted under 50% RH. We first established a stable FA signal, and then introduced suspended H₂SO₄ particles into the flow tube. Between 21 and 72 min, the aerosol flow was directed through a denuder to remove the redundant FA, with a simultaneous particle collection between 62 and 72 min by the FIGAERO inlet. The chemical composition of collected H₂SO₄ particles was analyzed using FIGAERO-HRTof-CIMS between 72 and 115 min.

Since protonated ethanol reagent ions were used, it is not surprising to observe the signal of protonated FA, which exhibits a double-peak thermogram in the plot. The first and narrower peak corresponds to FA molecules that strike the aerosol surface and becomes a loosely bound surface species (n₁) whereas the second peak at higher temperature corresponds to FA molecules that have been tightly interconnected and incorporated into the bulk liquid (n₂). In addition, NH₄⁺ was observed. The temporal profile of NH₄⁺ from our collected H₂SO₄ particles coincided with that of NH₄⁺ from an authentic NH₄HSO₄ solution analyzed by FIGAERO-HRTof-CIMS with the same thermal program (the blue line in the zoomed-in plots on the top right of Figure 6a), indicating the formation of ammonium salts during the uptake process. The results suggest that under 50% RH, the uptake of gaseous FA involves primarily two processes: the mass accommodation, and the hydrolysis of FA in the acidic particles followed by formation of ammonium.

As for experiments conducted under dry condition (Figure 6b), only two peaks of protonated FA were observed, and NH₄⁺ was not found, indicating that hydrolysis of FA did not occur during the uptake under dry condition. This phenomena is consistent with previous findings that three water molecules are required to participate in the hydrolysis of one amide molecule. Since there was hardly any water in suspended H₂SO₄ particles at < 3% RH, hydrolysis of FA would not tend to happen.

Analogically, hydrolysis of DMF was not observed for uptake experiments at < 3% RH, whereas (CH₃)₂H₂N⁺, as a hydrolysis product from DMF according to the A₃/2 mechanism, was identified at 90% RH uptake experiments.

4. ATMOSPHERIC IMPLICATIONS

Our measurements of the multiphase uptake of six alkylamides by suspended sulfuric acid particles allow us to assess the contribution of multiphase chemistry to the atmospheric loss processes of gaseous amides. Assuming a sulfuric acid aerosol population with a total surface area of 5 × 10⁷ μm² cm⁻³ and an average diameter of 100 nm that corresponds to ~14 μg m⁻³ mass loading, the predicted lifetime of DMF with respect to multiphase loss on sulfuric acid aerosols at 298 K and 54% RH (~41 wt % H₂SO₄) is around 4 h. On the other hand, a 24 h daytime average global OH radical concentration of 10⁶ molecules cm⁻³ (ref. 51) and a reported rate constant of (1.4 ± 0.3) × 10⁻¹² cm³ molecule⁻¹ s⁻¹ for the OH radical-initiated reaction with DMF at 298 K18 leads to a lifetime of ~0.8 day for DMF. The lifetimes of DMF against NO₃ radicals and Cl atoms are 0.5 and 6 days, respectively, using a 12 h average nighttime NO₃ radical concentration of 5 × 10⁷ molecules cm⁻³ (ref. 52) and an average global chlorine concentration of 10⁴ molecules cm⁻³ (ref. 53). These estimates suggest that multiphase uptake of amides by acidic aerosols could be more competitive than gaseous oxidation in terms of atmospheric loss for DMF.

Furthermore, we have measured the uptake coefficients of MF and DMF by suspended sulfuric acid particles at 293 K and 58 wt % H₂SO₄. Using the temperature dependence for DMF
obtained in our study, we derive that uptake coefficients of MF and DMF at 283 K are 0.71 × 10^{-2} and 1.4 × 10^{-2}, respectively. In a previous experimental study on uptake of three alkyamines (C_{n} to C_{2}) by sulfuric acid at 283 K, uptake coefficients of (2.0 ± 0.2) × 10^{-2}, (3.0 ± 0.6) × 10^{-2}, and (2.2 ± 0.2) × 10^{-2} were obtained for methylamine (by 62 wt% H_{2}SO_{4}), dimethylamine (by 62 wt% H_{2}SO_{4}), and trimethylamine (by 59 wt% H_{2}SO_{4}), respectively. Clearly, under similar temperature and acidity, the estimated uptake coefficients for alkylamides here are smaller compared to those for alkylamines. Nevertheless, ambient concentrations of amines in urban Shanghai were reported to be at least an order of magnitude higher than those of amines. Hence, amides could compete with amines to react with acidic particles in places where concentrations of atmospheric amides are higher than those of amines. On the other hand, the water content of ambient acidic particles is presumably larger than that of the concentrated sulfuric acid particles used in our study, fulfilling the requirement for the presence of water in the particle. As a result, hydrolysis of amides is expected to occur with the formation of ammonium and aminium, adding more complexity to track particles' evolution.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.7b03175.

Additional information regarding the surface area-weighted size distributions of sulfuric acid particles (PDF)

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ACKNOWLEDGMENTS

This study was financially supported by the National Key R & D Program of China (2017YFC0209505), National Natural Science Foundation of China (No. 21222703, 21561130150, 41575113, and 91644213) and the Cyrus Tang Foundation (No. CTF-FD2014001). L.W. thanks the Royal Society-Newton Advanced Fellowship (NA140106).

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