

Heterogeneous Chemistry of Alkylamines with Sulfuric Acid: Implications for Atmospheric Formation of Alkylaminium Sulfates

LIN WANG, VINITA LAL,
ALEXEI F. KHALIZOV, AND
RENYI ZHANG*

Department of Atmospheric Sciences and Department of
Chemistry, Texas A&M University, College Station, Texas 77843

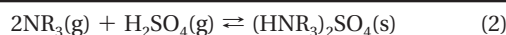
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The heterogeneous interaction of alkylamines with sulfuric acid has been investigated to assess the role of amines in aerosol growth through the formation of alkylaminium sulfates. The kinetic experiments were conducted in a low-pressure fast flow reactor coupled to an ion drift-chemical ionization mass spectrometer (ID-CIMS). The measurements of heterogeneous uptake of methylamine, dimethylamine, and trimethylamine were performed in the acidity range of 59–82 wt % H_2SO_4 and between 243 and 283 K. Irreversible reactive uptakes were observed for all three alkylamines, with comparable uptake coefficients (γ) in the range of 2.0×10^{-2} to 4.4×10^{-2} . The measured γ value was slightly higher in more concentrated sulfuric acid and at lower temperatures. The results imply that the heterogeneous reactions of alkylamines contribute effectively to the growth of atmospheric acidic particles and, hence, secondary organic aerosol formation.

Introduction

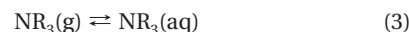
Aliphatic amines are emitted from a variety of humans-related sources, including animal husbandry, sewage treatment, waste incineration, industrial activities (1, 2), and vehicle exhaust (3). It has also been suggested that in the remote areas the metabolism and degradation of proteins (4) and bubble bursting at the air-sea interface (5) contribute to the atmospheric burden of aliphatic amines. Low molecular weight alkylamines are highly volatile, and the ambient concentrations of individual gas-phase alkylamines, from rather sparse measurements, range from 0.3–4.2 ng m^{-3} in the marine atmosphere of Hawaii (6) to 231–562 $\mu\text{g m}^{-3}$ in a location near a commercial dairy (7).

In the atmosphere, aliphatic amines undergo oxidation by OH and NO_3 radicals and O_3 (1, 8, 9), leading to the formation of organic nitrogen-containing species, which can be partitioned to the particle phase (8–11). With a strong organic base, amines react with nitric acid and sulfuric acid, and all three species are in equilibrium with particulate aminium nitrate and aminium sulfate salts, according to reversible reactions 1 and 2 (10, 11).



The equilibrium of these two reactions depends on temperature, relative humidity, and particle acidity (11, 12).

In addition to contributing to growth of existing atmospheric particles, low molecular weight alkylamines have been implicated in new particle nucleation and growth. Theoretical calculations suggest that the formation of the amine- H_2SO_4 cluster is thermodynamically favored (13), and the formation of aminium salts can potentially contribute to new particle growth (14). Recently, Wang et al. (15) have shown in laboratory experiments that heterogeneous reactions of gaseous alkylamines on H_2SO_4 nanoparticles result in formation of alkylaminium sulfates and particle growth. The heterogeneous reaction of gaseous alkylamines involves several steps, including partitioning of amines into the liquid phase governed by the Henry's law constant (reaction 3) and liquid phase reaction 4 leading to the formation of aminium ions.



The occurrence of the heterogeneous reaction of alkylamines in the atmosphere is supported by chemical composition analysis of atmospheric nanoparticles formed from nucleation (16).

The heterogeneous reaction between gas-phase alkylamines and acidic sulfate aerosols also alters the chemical composition and physical properties of particles, including acidity and hygroscopicity. Quantitative modeling of formation and growth rates of atmospheric secondary organic aerosols requires knowledge of accurate uptake coefficients of alkylamines in acidic particles, which are currently unavailable.

In this study, we have investigated heterogeneous uptake of methylamine, dimethylamine, and trimethylamine on H_2SO_4 solution in the acidity range of 59–82 wt % and between 243 and 283 K. The kinetic experiments were conducted in a low-pressure fast flow reactor coupled to an ion drift-chemical ionization mass spectrometer (ID-CIMS). Methylamine, dimethylamine, and trimethylamine are the simplest alkylamines and have been previously identified in ambient air (6). A comparison of the uptake coefficients among the three methyl-substituted amines yields insight into the effect of alkyl group substitution on the heterogeneous reaction rate. Atmospheric implications of the present results to formation of secondary organic aerosols are discussed.

Experimental Section

The uptake measurements were performed in a laminar-flow reactor coupled to ID-CIMS, similarly to our previous work (17–19). Only a brief description of the experimental procedures is described in this paper. As shown in Figure 1, the Pyrex reactor was 50 cm long and with an internal radius of 1.25 cm. Aqueous H_2SO_4 solution was placed into a Pyrex vessel, which was recessed to form a trough that was 20 cm in length, 2.0 cm in width, and 0.7 cm in depth. The temperature of the flow reactor was controlled by flowing SYLTherm heat transfer fluid through the outer jacket of the reactor using a Neslab ULT-80 circulator and was monitored by a thermocouple. All carrier flows were monitored with calibrated electronic mass flow meters (Millipore

* Corresponding author e-mail: zhang@ariel.met.tamu.edu.

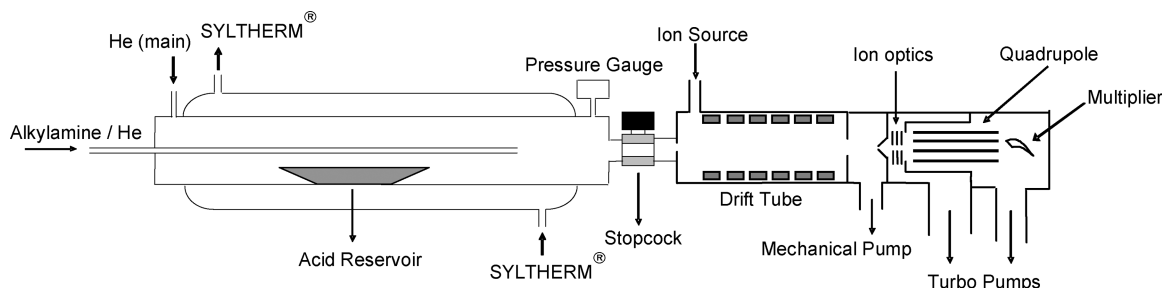


FIGURE 1. Schematic representation of the laminar-flow reactor coupled to ID-CIMS.

Tylan 260 Series). The flow reactor was operated under laminar flow conditions at a total pressure of about 1.3 Torr and a flow velocity of 800–1100 cm s⁻¹.

Methylamine (CH₃NH₂, Aldrich, ≥ 98%), dimethylamine ((CH₃)₂NH, Aldrich, ≥ 99%), and trimethylamine ((CH₃)₃N, Aldrich, ≥ 99%) were used as received without further purification. Mixtures of individual alkylamines in He (50–100 ppm) were prepared by two-step dilution, which involved introducing the alkylamine vapor of a known partial pressure into an evacuated 2 L glass bulb, pressurizing the bulb with He to ~500 Torr, depressurizing to ~5 Torr, and repressurizing with He to ~900 Torr. To eliminate the drop in the alkylamine/He flow during the uptake experiments, a fresh mixture was prepared after ~20% of alkylamine in the bulb was used. The alkylamine vapor in He was introduced into the flow reactor through a movable injector, and its partial pressure in the reactor was on the order of 10⁻⁶ to 10⁻⁷ Torr.

H₂SO₄ solutions were prepared by dilution of 96% H₂SO₄ (ACS reagent, Aldrich) with deionized water (18 mΩ•cm). The acid reservoir was changed for each experiment, and the composition of the acid was checked before and after each experiment by titration with standard NaOH solution (0.105 N, Aldrich). During the experiment, water vapor was added to the flow reactor to minimize changes in the acid composition (20). Since the water vapor pressure of sulfuric acid solution increased with increasing temperature and decreasing sulfuric acid concentration (20), only concentrated H₂SO₄ solutions (59–82 wt % H₂SO₄) between 243 and 283 K were studied to avoid a significant change in the acid concentration in our uptake experiments.

Details of the ID-CIMS instrumentation have been described previously (21, 22). Alkylamines were detected according to the proton transfer reaction with H₃O⁺



where X and XH⁺ denote alkylamines and their corresponding protonated forms, respectively. Methylamine, dimethylamine, and trimethylamine were monitored at their protonated peaks, [CH₃NH₂ + H]⁺ (*m/z* = 32), [(CH₃)₂NH + H]⁺ (*m/z* = 46), [(CH₃)₃N + H]⁺ (*m/z* = 60), respectively. The measured protonated alkylamine signal intensities were corrected for the instrumental background, which was typically less than 4% of the corresponding alkylamine signals. During the uptake measurements, H₃¹⁸O⁺ isotope ion was monitored to account for the variation in the protonated alkylamine signal intensity due to minor fluctuation in the reagent ion signal.

Uptake of gas-phase species by a planar liquid surface can be modeled by a coupled diffusion-reaction equation (23, 24). The uptake coefficient, γ , is calculated from the first-order rate coefficient (*k*) of alkylamine signals (25)

$$\gamma = \frac{4k(V)}{\omega(A)} \quad (6)$$

where *V* is the volume of the flow reactor, *A* is the geometric area of the exposed acid, and ω is the mean thermal speed of the alkylamine molecule. The value of *k* is related to the change in the gas-phase concentration of the reactive molecule before and after exposure to sulfuric acid by

$$k = \frac{u}{L} \ln \left(\frac{I_0}{I_t} \right) \quad (7)$$

where *u* is the carrier gas flow velocity (cm s⁻¹), *L* is the injector position (i.e., the contact distance between the gas and liquid), *I*₀ is the initial alkylamine signal before uptake by H₂SO₄, and *I*_{*t*} is the signal at a given reaction time (corresponding to a given injector position). We did not account for radial gas-phase diffusion since a symmetrical, cylindrical tube was not used in our uptake experiments. There is currently no analytical solution for gas-diffusion correction for a semicircular shape tube used in our experiments. Using gas-diffusion coefficients for amines in He calculated by Fuller-Schettler-Giddings equation, we estimated an uncertainty of about 20% associated with gas-diffusion correction for the semicircular shape tube.

Results and Discussion

Uptake experiments were performed by exposing a length of the acid surface to the alkylamine vapor while monitoring the alkylamine signal using the ID-CIMS. Figure 2a shows that uptake of trimethylamine in 59 wt % H₂SO₄ at 283 K is irreversible. A steady-state flow of trimethylamine was first established with the tip of the movable injector placed downstream the vessel containing a H₂SO₄ aqueous solution. The trimethylamine concentration in the gas phase dropped instantly when the injector was withdrawn upstream to expose a 1-cm length of the H₂SO₄ solution surface to the trimethylamine vapor. No recovery in the trimethylamine signal was observed on the time scale of the exposure. Terminating the exposure by sliding the injector downstream resulted in a recovery of the trimethylamine signal to its original level. No desorption peak was observed, indicating that the absorbed amine reacted irreversibly with H₂SO₄ to form alkylaminium sulfates (15). The similar behaviors were observed in all alkylamine uptake experiments, suggesting an irreversible uptake of alkylamine vapor by aqueous H₂SO₄ solution under our experimental conditions.

The measurements of uptake coefficients were conducted by observing the decay of alkylamine signal as a function of the alkylamine reaction time with the H₂SO₄ solution surface. Figure 2b illustrates a typical profile of the decay in the alkylamine signal upon exposure to 69 wt % H₂SO₄ at 283 K at various injector positions. The injector was successively withdrawn over the H₂SO₄ solution surface to the distance of 0.5, 3.0, and 7.5 cm. Successive decay of the trimethylamine signal was evident upon each withdrawal of the injector. At the end of the experiment, the injector was pushed back to its original position, and a full recovery of the signal was observed.

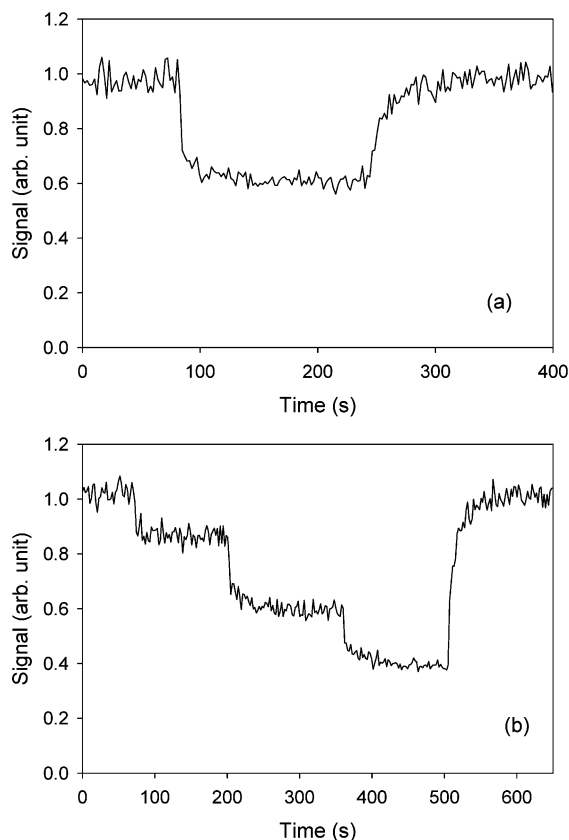


FIGURE 2. Temporal profiles of the protonated trimethylamine signal. (a) The injector was withdrawn to expose a 1 cm length of 69 wt % sulfuric acid, with $T = 283$ K, $P_{\text{total}} = 1.39$ Torr, and $u = 1108$ cm s⁻¹. (b) The injector was successively withdrawn for a total of 7.5 cm length of 59 wt % sulfuric acid, with $T = 283$ K, $P_{\text{total}} = 1.39$ Torr, and $u = 946$ cm s⁻¹.

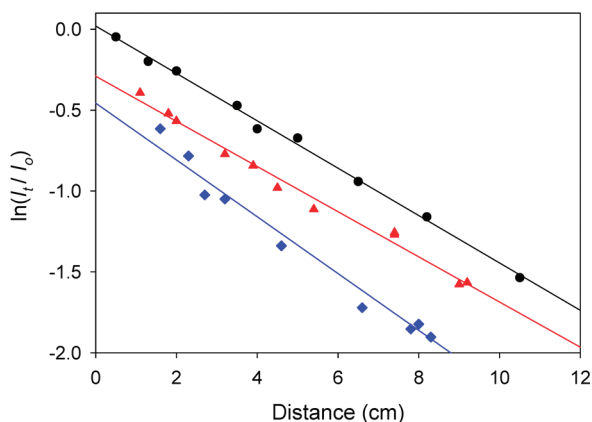


FIGURE 3. Alkylamine signal as a function of the injector position. The blue diamonds represent the measurement of methylamine vapor exposed to 82 wt % sulfuric acid, with $T = 283$ K, $P_{\text{total}} = 1.34$ Torr, and $u = 1109$ cm s⁻¹; the red triangles represent the measurement of dimethylamine vapor exposed to 82 wt % sulfuric acid with $T = 283$ K, $P_{\text{total}} = 1.30$ Torr, and $u = 1147$ cm s⁻¹; the black circles represent the measurement of trimethylamine vapor exposed to 80 wt % sulfuric acid with $T = 283$ K, $P_{\text{total}} = 1.36$ Torr, and $u = 1045$ cm s⁻¹.

The first-order decay of the alkylamine signal was plotted against the reaction distance for each uptake experiment condition. Figure 3 depicts typical alkylamine signal decays upon exposure to H₂SO₄ solution as a function of the injector position. The black circles, red triangles, and blue diamonds represent measurements for trimethylamine, dimethylamine,

and methylamine, respectively, under similar experimental conditions, i.e., 80–82 wt % H₂SO₄, $T = 283$ K, $P_{\text{total}} = 1.30$ –1.36 Torr, and $u = 1045$ –1147 cm s⁻¹. It is evident that all three decays followed the first-order kinetics. The first-order rate constants were determined from the slope of the linear regression of each data set, and the uptake coefficients were computed from the obtained first-order rate constants. Since the mean thermal speeds of the three alkylamines vary up to 40% under similar experimental conditions, a larger first-order rate constant, i.e., a larger slope in Figure 3, does not necessarily reflect a larger uptake coefficient.

Table 1 summarizes the measurements of uptake coefficients for methylamine, dimethylamine, and trimethylamine exposed to various H₂SO₄ solutions. The uptake coefficients are in the range of 0.020–0.039 for methylamine (62–82 wt % H₂SO₄ and 243–283 K), 0.025–0.044 for dimethylamine (62–82 wt % H₂SO₄ and 243–283 K), and 0.022–0.043 for trimethylamine (59–80 wt % H₂SO₄ and 243–283 K). The uncertainty represents scatter in the data during the measurements at the two standard deviation level and is not an estimate of systematic errors. We estimated that systematic uncertainty in our measured rate constants was within $\pm 30\%$, taking into account possible sources of error in the measurements of gas flow rate, temperature, and pressure, and gas-phase diffusion correction.

Among the three alkylamines, the uptake coefficients for dimethylamine and trimethylamine are generally comparable and slightly larger than those for methylamine under similar conditions of wt % H₂SO₄ and temperature. The difference in the uptake coefficients for methylamine, dimethylamine, and trimethylamine is rather insignificant and likely within the uncertainty of the measurements. The measured uptake coefficients for methylamine, dimethylamine, and trimethylamine are about 20 times smaller than that for the uptake of ammonia in H₂SO₄ solutions, which increases as a function of acid concentration and reaches unity at >55 wt % H₂SO₄ (26, 27). Since the proton affinity is the smallest for ammonia, followed by methylamine, dimethylamine, and trimethylamine (28), the rate of proton transfer cannot explain the differences in the uptake coefficients between ammonia and alkylamines in H₂SO₄ solutions. It is possible that the smaller uptake coefficients for alkylamines are attributed to the effect of the Henry's law constants (26), which are expected to be smaller than that for ammonia, because of the organic substituent.

The measured uptake coefficients for methylamine, dimethylamine, and trimethylamine in our experiments increase with increasing acid concentration (Figure 4) and decreasing temperature (Figure 5), similarly to ammonia (27, 29). For each alkylamine, the temperature dependence of γ is less pronounced in more concentrated H₂SO₄ solutions, as depicted in Figure 5 for methylamine. In concentrated H₂SO₄, the uptake is governed by the mass accommodation coefficient (30), since the rates of dissolution and reaction of alkylamines in the bulk acidic solution are faster than the mass accommodation. Hence, the observed positive dependence of γ with sulfuric acid concentration can be explained by an increase in the mass accommodation coefficient with acidity (27, 29). The role of a surface specific reaction of alkylamines with H⁺ ions near the gas–liquid interface is not currently known due to the lack of uptake coefficient data over a wide range of pH values (27). The dependence of the uptake coefficient on acidity for alkylamines is likely to be similar to that of ammonia in H₂SO₄ solutions; the uptake coefficient of ammonia was only dependent on the Henry's Law constant with a pH value from 7 to 10 but was dominated by the acid-based reaction for the pH value smaller than 7 (27, 29). On the other hand, the observed negative temperature dependence of γ can be partially

TABLE 1. Measured Uptake Coefficients γ for Alkylamines in H_2SO_4^a

alkylamines	H_2SO_4 (wt %)	γ ($\times 10^{-2}$)				
		283 K	273 K	263 K	253 K	243 K
methylamine	62	2.0 ± 0.2	2.1 ± 0.3	3.1 ± 0.5	2.8 ± 0.2	3.3 ± 0.2
	71	2.0 ± 0.3	2.9 ± 0.5	2.6 ± 0.5	3.5 ± 0.3	3.5 ± 0.5
	82	3.2 ± 0.5	3.3 ± 0.3	3.9 ± 0.5	2.8 ± 0.3	3.9 ± 0.5
dimethylamine	62	3.0 ± 0.6	3.0 ± 0.3	3.3 ± 0.5	3.2 ± 0.4	3.5 ± 0.3
	71	2.5 ± 0.4	3.0 ± 0.3	3.2 ± 0.3	3.0 ± 0.4	3.6 ± 0.3
	82	3.2 ± 0.3	3.1 ± 0.3	3.0 ± 0.4	3.2 ± 0.4	4.4 ± 0.3
trimethylamine	59	2.2 ± 0.2	2.7 ± 0.2	2.3 ± 0.2	3.0 ± 0.3	3.4 ± 0.2
	69	2.7 ± 0.8	2.5 ± 0.2	3.3 ± 0.2	3.4 ± 0.3	4.3 ± 0.5
	80	3.5 ± 0.2	3.0 ± 0.1	3.8 ± 0.5	3.2 ± 0.2	4.3 ± 0.4

^a Each point in the table corresponded to at least three separate uptake experiments, and for each uptake experiment at least two measurements at varied gas–liquid contact distances were performed. The error corresponds to two standard deviations (2σ) for all measurements.

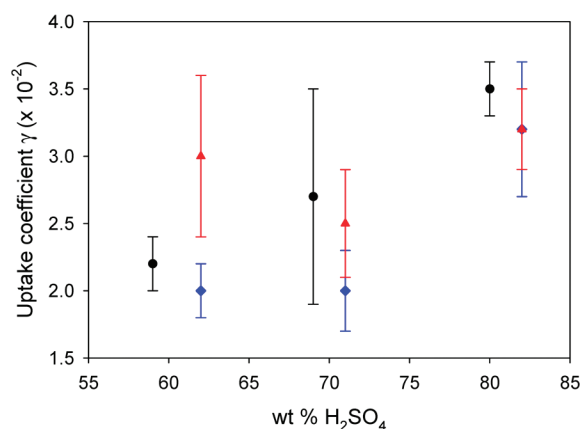


FIGURE 4. Uptake coefficient, γ , as a function of sulfuric acid concentration at 283 K. The blue diamonds, red triangles, and black circles represent the measurements of methylamine, dimethylamine, and trimethylamine, respectively.

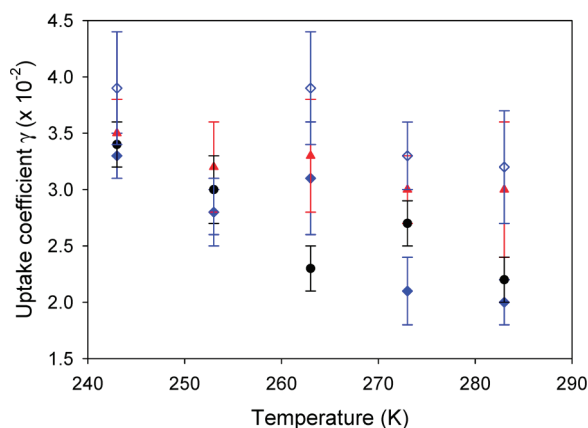


FIGURE 5. Uptake coefficient, γ , as a function of temperature. The solid and open blue diamonds represent the measurements of methylamine vapor exposed to 62 wt % and 82 wt % sulfuric acid, respectively; the solid red triangles represent the measurement of dimethylamine vapor exposed to 62 wt % sulfuric acid; the solid black circles represent the measurement of trimethylamine vapor exposed to 59 wt % sulfuric acid.

explained by the negative temperature dependence of the mass accommodation coefficient (26, 29).

Atmospheric Implications

Our measured uptake coefficients suggest that the heterogeneous reaction of alkylamines leads to efficient growth of acidic particles and, hence, alteration of their composition,

especially during new particle formation events or in the upper troposphere where the acidity of sulfate particles is likely to be concentrated (20). Neutralization of sulfuric acid particles by amines may also affect heterogeneous reactions of organic carbonyls (15), which are produced in large quantity from photochemical oxidation of anthropogenic and biogenic hydrocarbons (31–33). For instance, using the uptake coefficient measured at 283 K, we estimate that it takes ~ 20 min for 1 ppb dimethylamine to completely neutralize a 60 wt % sulfuric acid particle (at 17% relative humidity) of a 100 nm diameter. Our measurements suggest that the uptake coefficients of amines decrease slightly as the acidity decreases. In the lower troposphere, the particulate sulfuric acid is rather diluted, and the uptake of amines in less acidic aqueous droplets can be smaller. Furthermore, the concentrations of amines are expected to be an order of magnitude lower than that of ammonia (0.1–10 ppb) in the atmosphere, except perhaps in the immediate vicinity of amine emission sources (11). Considering a higher ambient concentration and larger uptake coefficient for ammonia than those for amines, it is plausible that fresh H_2SO_4 particles will be dominantly neutralized by ammonia when both ammonia and amines are present in the atmosphere. However, amines can displace ammonium cations in ammonium nitrate, ammonium bisulfate, and ammonium sulfate particles (11, 34, 35), leading to accumulation of aminium cations in the particle phase. Complete exchange of ammonia in clusters (smaller than 3 nm) by amine is expected to occur within several seconds to minutes in ambient atmosphere (34), while exchange of ammonia in 20–500 nm particles is measurable within a few hours (35). Field measurements showed that dimethylammonium and diethylammonium salts were detected in aerosols collected during new particle formation events in boreal forest (36), over a major bovine source (2), in marine air masses (37, 38), and in an urban area (39), while corresponding primary and tertiary aminium ions were not present or in concentrations a factor of 10 lower than those of the corresponding secondary ammonium ions. Our measured uptake coefficients indicate comparable values for methylamine, dimethylamine, and trimethylamine on concentrated sulfuric acid. By analogy, the uptake coefficients for ethylamine, diethylamine, and triethylamine are expected to be comparable. A previous measurement of emission of aliphatic amines from animal husbandry suggested a lower emission rate for dimethylamine than those for methylamine and trimethylamine (40). Hence, it is likely that selective accumulation of dialkylammonium in the particle phase is due to favored thermodynamic equilibrium of secondary aminium salts in less acidic aqueous droplets (11).

Since the surface tension and equilibrium vapor pressure are highly elevated for nanoparticles (< 20 nm) (15, 41), care

must be taken when applying the uptake coefficients measured on bulk surfaces in our study to nucleation mode particles. Full understanding of the gas/particle kinetics related to aerosol nucleation and growth will require extension of the uptake measurements to those nanoparticles.

Acknowledgments

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