Uptake of gas-phase alkylamines by sulfuric acid

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Recent field and experimental studies have suggested that acid-base reactions of alkylamines may play an important role in secondary aerosol formation. We investigated the heterogeneous chemistry of ethylamine (EA), diethylamine (DEA) and triethylamine (TEA) on liquid H_2SO_4 (1 wt%–80 wt%). Irreversible reactive uptakes were observed for all three alkylamines. The reactive uptake coefficients (γ) of alkylamines increased with the acid concentration, and the γ value for DEA appeared to increase slightly faster than that of EA and TEA. The potential roles in secondary aerosol formation of different alkylamines are briefly discussed.

heterogeneous chemistry, alkylamine, flow tube, sulfuric acid, secondary aerosol

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Low molecular weight alkylamines are emitted by a variety of widespread anthropogenic and biogenic sources, such as in industrial emissions and car exhaust [1–3], air samples from cattle feedlots [4,5], and waste incinerators and sewage treatment plants [6]. They constitute an important class of environmental pollutants due to their toxic and odorous properties. A number of short chain alkylamines have been detected in marine, rural and urban atmospheres in the gas phase [7], particle phase [8], and aqueous fog and rain drops [9].

Recently, the reactivity of alkylamines has received attention for its potential important role in secondary aerosol formation. Although the relative importance of amines as a source of particulate organic nitrogen remains unclear, field studies suggest that organic nitrogen species could form an appreciable fraction of organic aerosol mass [10–16]. Tan et al. [16] found that organic amines were present in all particulate matter from one episodic event of elevated levels of particulate matter below $2.5\ \mu\text{m}$ (PM_{2.5}) in an urban environment. Mäkelä et al. [12] observed a strong positive correlation between new particle formation events and the

concentrations of dialkylammonium sulfate or bisulfate in remote boreal forest studies. In another study [17], the concentrations of dialkylammonium were found to be 10 times higher than those of the corresponding monoalkylammonium salt in aerosol samples collected over a major bovine source. Facchini et al. [18] reported dimethyl- and diethylammonium salts were the most abundant organic species detected in fine marine particles, and represented on average 11% of the secondary organic aerosol fraction.

In an effort to evaluate the aerosol forming potential of alkylamines in the atmosphere, only a few studies have investigated the atmospheric reaction processes of amines. Alkylamines absorb light at wavelengths below 250 nm and thus do not undergo photolysis in the troposphere [1]. Both acid-base reactions between amines and acids (i.e. nitric and sulfuric acid) are commonly present in the atmosphere and oxidation of amines appear to play roles in the formation of organic nitrogen containing particles [19]. Murphy et al. [20] performed chamber research to investigate particulate formation from amines and reported that primary and secondary amines produced salts and that tertiary amines produced non-salt secondary organic aerosols in yields of

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5%–23% via reactions with OH and ozone. Smog chamber research showed that the lower bound reaction rate constant of trimethylamine with nitrate radical was estimated to be $4.4 \times 10^{-16} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ with a 65% conversion rate to the aerosol phase [21]. Using thermodynamic modeling, Barsanti et al. [22] suggested that acid-base reactions between amines and acids could play an important role in organic salt formation, which contribute to the growth of new particles.

Intriguingly, although alkylammonium salts may be important contributors to secondary aerosol formation, only high-concentration dialkylammonium salts were detected in both BIOFLUX [23] and ambient samples. Explanations for these interesting observations have been proposed. These emphasized that high concentrations of dialkylammonium salts in the aerosol phase might be due to selective accumulation of dialkylamines by acid [18]. To our knowledge, only heterogeneous uptake of methylamine, dimethylamine, and trimethylamine on 59 wt%–82 wt% H_2SO_4 and between 243 and 283 K have been reported recently [24]. The uptake of alkylamines over a wider acidity range on H_2SO_4 has not been investigated. Knowledge of the uptake of different alkylamines on H_2SO_4 solution is also important in view of a recent suggestion [25] that amines are likely to effectively enhance neutral and ion-induced sulfuric acid-water nucleation in the atmosphere.

Thus, the major goals of this research were to: (i) describe the implementation of a rotated wetted-wall reactor (RWW) combined with a differentially pumped single-photo ionization (SPI) time of flight mass spectrometer (TOFMS), which was designed for studies on the heterogeneous absorption and reaction; (ii) to investigate the uptake of gas-phase ethylamine (EA), diethylamine (DEA) and triethylamine (TEA) on aqueous sulfuric acid solutions over the composition range of 1 wt%–80 wt%.

1 Experimental

The experiments were performed using a RWW-SPI-TOFMS improved from the custom-built equipment used in an earlier study (Figure 1) [26]. The RWW consisted of a glass cylindrical flow reactor equipped with an external glass jacket similar to that in a previous work [27] for thermostating and a rotatable inner cylinder (length $L=30$ cm; inner radius $r=1.25$ cm) for supporting the liquid film. Small volumes ($V_{\text{liq}}=3\text{--}3.5$ mL) of water or sulfuric acid solution were placed in the inner cylinder, which was rotated (5–10 r/min) to maintain a thin film on the wall. The film for 3.5 mL of solution was approximately 0.015 cm thick. Mixing and saturation of the solutions and wetting of the wall were facilitated by the presence of a glass stirring bar (29 cm length, 0.17 cm diameter) that rested on the bottom of the rotating cylinder. To reduce water evaporation from the solution in the rotating cylinder, pure nitrogen car-

Figure 1 Schematic diagram of experimental setup.

rier gas was admitted through a reservoir holding the same H_2SO_4 solution before entering the reactor from a sidearm inlet. This ensured that the acid composition was not modified during the experiments. Organic compounds seeded in the nitrogen carrier gas were introduced into the main flow of the reactor through a movable glass injector centered in the rotating cylinder. For 80 wt% H_2SO_4 solution experiments, pure nitrogen carrier gas was replaced by pure helium. The movable injector allowed for adjustment of the contact time between the gas and liquid surfaces. Most of the measurements were performed with a total flow rate of $400\text{--}620 \text{ cm}^3 \text{ min}^{-1}$ at standard temperature and pressure (STP, 273 K and 1 atm, 1 atm=1.013 Pa), a total pressure of 20–31 Torr (4.8 Torr for 80 wt% H_2SO_4 solution experiments, 1 Torr = 1.333×10^2 Pa), and temperature of 298 K.

Uptake of alkylamine on the acid solution was studied by monitoring variations in the alkylamine concentration in the gas-phase. The concentration of alkylamine was monitored by sampling the flow with a differentially pumped SPI-TOFMS. Alkylamine was ionized by a 118-nm laser, which was generated by focusing the third harmonic (355 nm, ~ 30 mJ/pulse, 10 Hz) of a Nd:YAG laser in a tripling cell that contained a 250 Torr argon/xenon (10/1) gas mixture. At the end of the cell, a MgF_2 lens (83 mm focal length at 118 nm) was used to focus the generated 118 nm laser. The spot size of the ionization laser light at the ionization area was about 1 mm. To separate the generated 118 nm laser beam from the 355 nm fundamental beam, a MgF_2 prism (apex angle=6°) was inserted into the laser beams. In this case, the mass signal is produced by ionization purely from the 118 nm laser radiation with low power (approximately 1 $\mu\text{J/pulse}$ and 5 ns pulse duration). In this work, 20 times signal averaging was used (signal-to-noise ratio>10:1). The alkylamines EA, DEA and TEA were monitored by their molecular ions at $m/z = 45, 73$ and 101, respectively.

EA (70%, aqueous solution, Alfa Aesar), DEA and TEA (99%, Alfa Aesar), and sulfuric acid (96 wt%–98 wt%, Beijing Chemical Reagents Company) were used without further purification. To avoid the introduction of water vapor in the reaction gas when using the EA aqueous solution, standard mixtures of the alkylamine in N_2 (0.5%–1%) were individually prepared by injecting each compound into an

evacuated 15 L glass flask for its saturated vapor pressure and pressurizing with pure nitrogen to $P=3$ atm. All carrier flows were monitored with calibrated electronic mass flow meters (Seven Star D08-1D/ZM, Beijing, China). H_2SO_4 solutions were prepared by mixing 96 wt%–98 wt% H_2SO_4 solution with 18 M Ω cm deionized water. The acid compositions of these solutions were determined accurately by titration with known NaOH solutions before and after each experiment.

2 Results and discussion

For uptake investigations the injector was placed in a downstream position ($L=0$ cm in Figure 1) where the liquid was not exposed to the reactive gas. This was used to obtain the initial concentration of alkylamine in the system, S_0 . The injector was then moved upstream to expose the liquid to the gas (maximum exposure $L=30$ cm) and obtain the concentration of alkylamine after exposure to H_2SO_4 solution (S). The uptake of alkylamine by the H_2SO_4 solution was indicated by the difference between S_0 and S . The first-order rate coefficient for removal of the alkylamine from the gas phase, k_{obs} (s^{-1}), was calculated from the S_0 and S values, as

$$\ln\left(\frac{S}{S_0}\right) = -k_{\text{obs}}L/v_{\text{ave}}, \quad (1)$$

where L is the contact distance between the gas and the liquid (1–20 cm), and v_{ave} is the average carrier flow velocity. k_{obs} was determined by placing the injector at various positions in the reactor. The surface rate constant for removal of the organic compound from the gas phase, $k_{\text{gas-surface}}$, can be determined by correcting k_{obs} for diffusion [28–30]

$$\frac{1}{k_{\text{gas-surface}}} = \frac{1}{k_{\text{obs}}} - \frac{1}{k_{\text{diff}}}, \quad (2)$$

$$k_{\text{diff}} = \frac{3.66D_1}{r^2}, \quad (3)$$

where r (cm) is the radius of the reactor and D_1 ($\text{cm}^2 \text{s}^{-1}$) is the diffusion coefficient, which can be calculated from Fuller-Schettler-Giddings correlation. The uptake coefficient, γ , is determined as the probability of irreversible alkylamine loss per collision with H_2SO_4 solution surface [31],

$$\gamma = \frac{4k_{\text{gas-surface}}V}{\omega A}, \quad (4)$$

where ω is the mean molecular speed of the reactant gas molecule, V is the volume of the reaction zone, and A is the geometric area of the exposed acid solution.

Uptake measurements (Figure 2) were performed by exposing a certain length of the sulfuric acid solution to the alkylamine vapor while monitoring the alkylamine signal using SPI-TOFMS. Adsorption and desorption to/from the

Figure 2 Typical experimental profiles. (a) Reactive uptake of EA on 60 wt% H_2SO_4 solution (EA exposure to acid at 1, 3, 5, 7 and 10 cm, respectively), observed at 45 amu. (b) Reactive uptake of DEA on 40 wt% H_2SO_4 solution (DEA exposure to acid at 1, 3, 5, 10 and 7 cm, respectively), observed at 73 amu. (c) Reactive uptake of TEA on 20 wt% H_2SO_4 solution (TEA exposure to acid at 2, 5, 8, 11 and 14 cm, respectively), observed at 101 amu.

liquid phase were evident from a decreased or increased alkylamine signal, respectively. The uptake of alkylamines was investigated over a wide range of sulfuric acid compositions, 1 wt%–80 wt% H_2SO_4 . Irreversible reactive uptakes were observed for all three alkylamines. The uptake displayed a steady-state feature. Replacing the injector at its initial position did not lead to a desorption peak, which indicates that the absorbed amine reacted irreversibly with H_2SO_4 to form alkylammonium sulfates [32]. This type of uptake is referred to as reactive throughout this manuscript. All alkylamines behaved in a similar manner in the uptake experiments, which suggests that reactive uptake occurs for all gas-phase alkylamines by H_2SO_4 solutions (1 wt%–80 wt%) under our experimental conditions.

Figure 3 illustrates the loss of DEA as a function of the injector distance. In the series of uptake experiments with 1 wt%–80 wt% H_2SO_4 solution, the reactive uptake coefficient of alkylamine (Table 1, Figure 4) was determined from the plot of $\ln[S/S_0]$ versus the contact distance between

Figure 3 DEA signal as a function of injector distance for 20wt%–60 wt% H_2SO_4 solution.

Figure 4 Reactive uptake coefficients of EA, DEA and TEA, as a function of sulfuric acid acidity.

Table 1 Reactive uptake coefficient measurements of EA, DEA and TEA in H_2SO_4 solution^{a)}

H_2SO_4 (wt%)	g ($\times 10^{-2}$)		
	EA	DEA	TEA
80	0.89 ± 0.19	2.40 ± 0.25	0.69 ± 0.16
60	0.67 ± 0.12	1.40 ± 0.21	0.35 ± 0.12
40	0.33 ± 0.14	0.36 ± 0.08	0.23 ± 0.017
20	0.24 ± 0.12	0.26 ± 0.09	0.18 ± 0.042
1	0.14 ± 0.009	0.25 ± 0.07	0.16 ± 0.015

a) Each point is the average of at least three measurements, and the error corresponds to one standard deviation (σ).

the gas and the liquid. All alkylamine signals were found to decrease linearly in these plots according to eq. (1). As all decays followed pseudo-first order kinetics, we obtained the first-order decay rate (k_{obs}) from the slope using a linear regression method. After correcting for the effects of diffusion, the uptake coefficient was determined using eq. (4). As the acid concentration increased, the uptake coefficient of each alkylamine also increased. The γ value for DEA appeared to increase slightly faster than those for the other species. Compared with the uptake of ammonia in H_2SO_4 solutions [33,34], the measured uptake coefficients of EA, DEA and TEA are about 50–100 times smaller. As organic substituents, alkylamines are expected to have smaller Henry's law constants and mass accommodation coefficients than ammonia, which may possibly explain the dif-

ferences in the uptake coefficients between ammonia and alkylamines in H_2SO_4 solutions [35]. In a similar manner to ammonia, the observed positive dependence of alkylamine uptake coefficient on sulfuric acid concentration can be explained by an increase in the Henry's law constant and mass accommodation coefficient with acidity [33,34]. The trends of Henry's law constants and mass accommodation coefficients with acidity may be dissimilar for the different organic substituent alkylamines, so further research in this area is required to interpret the different rates of increase of the uptake coefficients for alkylamines with the acidity.

3 Conclusions

To illustrate the atmospheric importance of the uptake of alkylamines in sulfuric acid aerosols, we need to understand the loss mechanisms and their rates for typical atmospheric conditions. It is thought that the major reactions of alkylamines in the gas phase involve oxidation by atmospheric oxidants such as OH and O_3 . Atkinson [36] reported rate constants for the reactions of OH (k_{OH}) with various alkylamines on the order of 2×10^{-11} – $9 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$. This leads to atmospheric lifetimes on the order of approximately 3–13 h assuming an OH concentration of $1 \times 10^6 \text{ molecules cm}^{-3}$.

Experimental data from the present study allow for an estimation of the rate of loss of alkylamines due to their reaction with sulfuric acid. The lifetimes of the alkylamines before uptake on sulfuric acid can be estimated as $\tau = 4/\gamma\omega\sigma$, where ω is the mean molecular speed of alkylamines and σ is the area density ($2 \times 10^{-7} \text{ cm}^2/\text{cm}^3$ [37]) of atmospheric sulfate aerosol. In the upper troposphere, sulfate aerosols are mainly composed of 40 wt%–80 wt% sulfuric acid [38,39], and these atmospheric H_2SO_4 concentrations were assumed in earlier calculations of methanol [40] and acetone [41] loss rates. Consequently, the γ values of alkylamines with 60 wt%–80 wt% H_2SO_4 (Table 1) were adopted in our calculations. This leads to atmospheric lifetimes of 8–14 h for DEA, 17–23 h for EA, and 32–64 h for TEA. If the γ values of the alkylamines with <20 wt% H_2SO_4 solution are adopted, the atmospheric lifetimes of the alkylamines are more than 3 d.

The calculations are somewhat crude, but it can be concluded that the acid-base reaction with high acidity sulfuric acid (60 wt%–80 wt%) is one of the loss mechanisms of alkylamines. The calculation assumes that DEA may be easily removed from the surfaces of sulfuric acid aerosols under ambient conditions. Hence, it is likely that the heterogeneous reactions of DEA have an important role in secondary aerosol formation for the accumulation of diethylammonium sulfates by high acidity sulfuric acid in the aerosol phase. However, the reaction of alkylamines with low acidity sulfuric acid (<20 wt%) in the upper troposphere is expected to be negligible.

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