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Reactive Uptake of Trimethylamine into Ammonium Nitrate Particles

Julie A. Lloyd, Katherine J. Heaton, and Murray V. Johnston*

Chemistry and Biochemistry Department, University of Delaware, Newark, Delaware 19716

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The reaction of trimethylamine (TMA) vapor with a polydisperse distribution of ammonium nitrate particles (20−500 nm dia.) was studied in a flow tube reactor with particle analysis by laser desorption (1064 nm) 70 eV electron ionization (EI) in an ion trap time-of-flight (IT-TOF) aerosol mass spectrometer. When the TMA vapor concentration was very high, essentially complete exchange of TMA for ammonia in the particles was achieved. When the TMA vapor concentration was lower (~500 ppb for a reaction time of 23 s), partial exchange was observed, and the initial reactive uptake coefficient was estimated to be on the order of 2 × 10^{-3} at 20% RH. This value suggests that measurable exchange is possible in the atmosphere when particles are exposed to an amine concentration on the order of 1 ppb for a few hours. The effects of particle size, water content, and amine molecular structure on uptake remain to be elucidated.

Introduction

Alkyl amines are emitted into air from industrial processes such as sewage treatment and waste incineration,[1] vehicle exhaust,[2] marine sources,[3] biomass burning, and animal husbandry.[4] Amines are most prevalent in regions of intense agricultural operations where the concentrations of individual compounds can exceed 1 ppb, with trimethylamine (TMA) usually in greatest abundance.[4] Rate constants for the reaction of mono-, di-, and trimethylamines with hydroxyl radicals are on the order of $2.2-6.5 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1},[5] and those with ozone are on the order of $1.7-7.8 \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1}.[6] These relatively rapid reactions give amines a lifetime on the order of hours in ambient air. Despite the relatively fast removal rate, several studies have detected amines in the particle phase[7,8] as well as within aqueous fog and rain drops.[9] Amines have also been linked to particle nucleation events in a study at a boreal forest in Finland, where dimethylamine was found in particles during particle formation and growth events.[10]

Amines can lead to particle formation and growth in two main ways. First, amine salts can be formed in an analogous manner to ammonia

$$NR_{3(g)} + HNO_{3(g)} \rightarrow R_3NHNO_{3(s)} \quad (1)$$

$$2NR_{3(g)} + H_2SO_{4(g)} \rightarrow (R_3NH)_2SO_{4(s)} \quad (2)$$

Amine salts have been studied experimentally by mixing the respective vapors in a smog chamber.[7] A recent theoretical study has suggested that amines are likely to enhance sulfuric acid−water nucleation more effectively than ammonia.[11] Second, amines can be oxidized to produce secondary organic aerosol, which has been the subject of recent smog chamber studies.[12−14]

The main sources of alkyl amines are also sources of ammonia. Ambient ammonia concentrations are somewhat higher than amines, on the order of 0.1−10 ppb, and highly dependent on the proximity to the source.[15] While amine and ammonia ambient concentrations are often correlated, little work has been done to study the interplay between the two in salt formation. In particular, it is important to understand how amine molecules exchange into pre-exisiting ammonium salts. In this study, we consider the exchange of TMA for ammonia in ammonium nitrate particles. Ammonium nitrate constitutes a significant fraction of ambient particulate matter, exceeding 50% in some locations.[16] Its formation is favored by low temperature and high relative humidity (RH),[17] and ambient concentrations can exhibit strong diurnal variations.[18] Similar characteristics have been noted for ambient amine salt formation.[7]

Experimental Section

The experimental setup used to study the reaction of trimethylamine (TMA) vapor with ammonium nitrate particles is shown in Figure 1. TMA vapor was produced by flowing air over a solution of TMA in water. Ammonium nitrate aerosol was generated with a commercial constant output atomizer. The TMA and aerosol flows were mixed in a flow tube reactor whose design is given elsewhere.[19] The reactor length corresponded to a residence time of 23 s, and the initial mass concentration of ammonium nitrate aerosol was ~160 μg/m^3. Diffusion driers were used to maintain a relative humidity (RH) of ~20% inside of the reactor. The aerosol flow exiting the reactor was split to a commercial scanning mobility particle sizer (SMPS) for particle size distribution measurements, a home-built ion trap time-of-flight (IT-TOF) aerosol mass spectrometer[20] for chemical composition measurements, and waste. The IT-TOF mass spectrometer was operated in the infrared laser desorption (LD, 1064 nm) 70 eV electron ionization (EI) mode. Additional

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* To whom correspondence should be addressed. Email: mvj@udel.edu. Phone: 302-831-8014. Fax: 302-831-6335.

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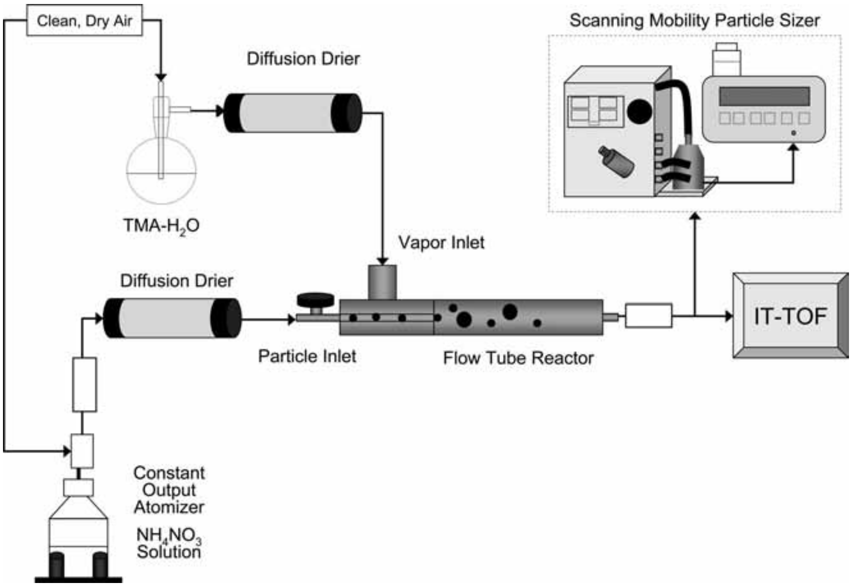

Figure 1. Experimental setup for flow tube kinetics.

experimental details are given in Supporting Information along with typical size distributions for the reactant ammonium nitrate aerosol (Figure S1).

Since instrumentation was not available to directly measure the TMA concentration in the reactor, the following experiment was performed to obtain an estimate. The ammonium nitrate solution in Figure 1 was replaced with a solution of nitric acid in water and mixed in the reactor with TMA vapor generated from a 4.5 x10^{-4} M solution. When the two vapors mixed, TMA−nitrate particles were formed, and the concentration of TMA vapor originally introduced into the reactor was determined from the volume concentration of TMA−nitrate particles. Further aspects of this experiment are discussed in the Results and Discussion section.

Results and Discussion

Figure 2a shows the LD-EI mass spectrum of ammonium nitrate particles that were passed through the flow tube reactor with dry, clean air. The mass spectrum is dominated by 17, 30, and 46 *m*/*z* corresponding to NH_3^+, NO^+, and NO_2^+, respectively. Ion signal at these *m*/*z* values is not surprising since ammonium nitrate would be expected to produce the respective gas-phase molecules when vaporized with a pulsed infrared laser beam. Interestingly, there is no direct evidence for formation of HNO_3 from the laser desorption process. The small amount of ion signal at *m*/*z* values not associated with fragment ions of the gas-phase molecules is from the background.

Figure 2b shows the LD-EI mass spectrum after exposing the ammonium nitrate aerosol to TMA vapor generated from the 45 wt % reagent solution. The high solution concentration gave such a high vapor concentration that complete exchange of TMA for ammonia occurred. The mass spectrum in Figure 2b still shows ions associated with nitrate at 30 and 46 *m*/*z*. However, the ion signal at 17 *m*/*z* is completely missing and replaced by 15, 42, 58, and 59 *m*/*z*. These latter ions are prominent in the 70 eV EI NIST library spectrum[21] for gas-phase TMA. It should be noted that the library spectrum for TMA includes significant ion signal at 30 *m*/*z*, and it is likely that this ion in Figure 2b includes contributions from both TMA and nitrate. The 59 *m*/*z* ion, prominent in both Figure 2b and the library spectrum, most likely arises from self-chemical ionization. Since the TMA vapor concentration in this experiment far exceeds the molar concentration of ammonium nitrate aerosol, it is not surprising that essentially complete exchange has occurred

$$NH_4NO_{3(s)} + C_3H_9N_{(g)} \rightarrow NH_{3(g)} + C_3H_9NHNO_{3(s)} \quad (3)$$

Concurrent with the mass spectrum change from Figure 2a to b were SMPS measurements showing a three-fold increase in the aerosol volume along with a shift of the number distribution to a larger particle diameter (see Figure S1, Supporting Information). The volume change was used to estimate the density of the transformed TMA−nitrate particles. First, the volume concentration of the original ammonium nitrate aerosol was converted to a molar concentration based on the assumption that the ammonium nitrate particles were spherical with a density of 1.7 g/cm^3. Second, the molar concentration of ammonium nitrate before exchange was assumed to be equivalent to the molar concentration of TMA−nitrate after exchange. Third, the calculated molar concentration and measured volume concentration of TMA−nitrate after exchange were combined with the molecular weight to estimate the density. The density obtained from this calculation, 0.80 g/cm^3, assumes a spherical particle morphology. A literature value for the density of trimethylaminium nitrate was not found for comparison; however, this value is similar to the density of the reagent TMA solution, 0.83−0.88 g/mL at 20 °C. Such a low density for the TMA−nitrate product is surprising given that previous measurements have shown the organic amine−nitrate salts to have a higher density than the free base amine.[12] It is possible that the procedure used to determine the density was subject to artifacts such as water in the particle phase, sorption of additional TMA to the particle surface beyond what was needed to exchange all of the ammonia, fission of larger particles into multiple smaller particles during exchange, or nonspherical morphology of the original and/or transformed particles.

Reactive uptake of TMA into ammonium nitrate particles was semiquantitatively studied by performing the exchange reaction at a low TMA concentration. Unexchanged ammonium nitrate aerosol was analyzed first to confirm that the signal intensity ratio was at background. Next, TMA vapor was added to the flow tube by bubbling air through a 4.5 × 10^{-7} M TMA

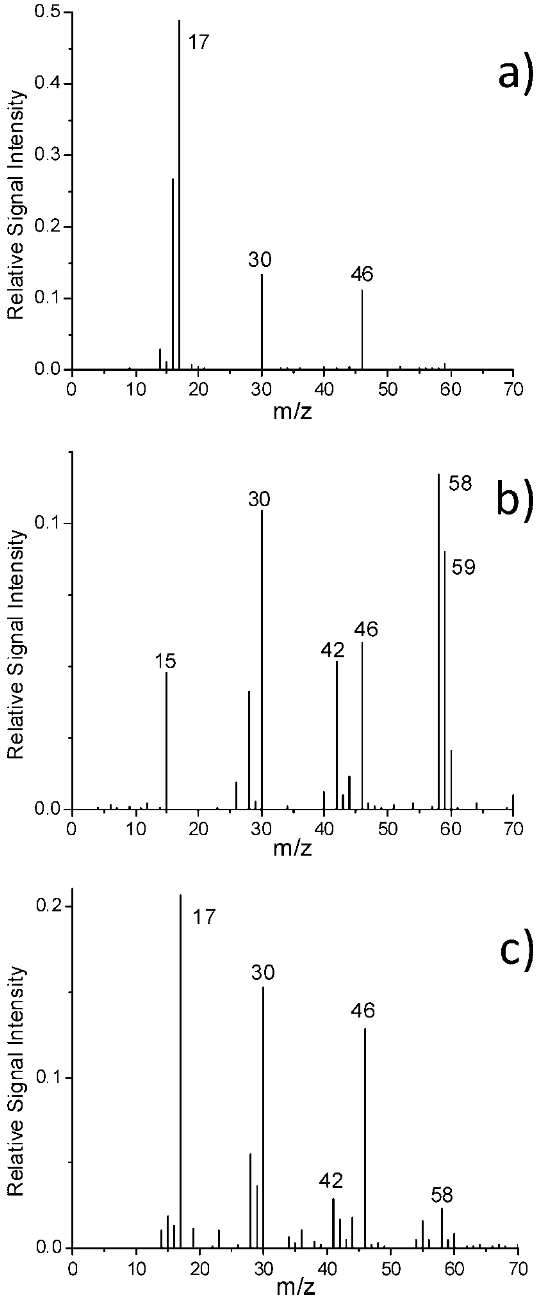

Figure 2. LD-EI mass spectra of ammonium nitrate particles a) unexchanged, b) after exposure to TMA vapor produced from a 45 wt % solution, and c) after exposure to TMA vapor produced from a 5×10^{-4} M solution.

solution. At this level, no exchange was detected in the LD-EI mass spectrum, in other words the mass spectrum was equivalent to that in Figure 2a. The concentration of the TMA solution was successively increased by factors of 10 until exchange was observed. For each new TMA solution, the TMA vapor was flowed through the system for 1.5 h to ensure stabilization of the TMA vapor concentration in the reactor. It was found that partial exchange, defined as both a measurable increase in the 42, 58, and 59 *m/z* ion intensities (TMA) and decrease in the 16 and 17 *m/z* intensities (ammonia) relative to the 46 *m/z* intensity (nitrate), first occurred with the use of a 4.5×10^{-4} M TMA solution. Figure 2c shows the LD-EI mass spectrum obtained from the 4.5×10^{-4} M experiment. Increasing the solution concentration to 4.5×10^{-3} M or above gave a mass spectrum similar to that in Figure 2b.

Determination of an uptake coefficient requires knowledge of the original TMA vapor concentration. The TMA vapor concentration produced from the 4.5×10^{-4} M TMA solution was determined by mixing TMA and nitric acid gas flows in the reactor to produce TMA–nitrate particles. The experiment is described more completely in the Experimental Section. The volume concentration of TMA–nitrate particles produced in this manner was found to be invariant with the concentration of nitric acid in the solution used to generate the vapor, suggesting that nitric acid was in large excess and that essentially all of the TMA was taken up into particles. From the volume concentration of TMA–nitrate aerosol produced from this reaction and the density estimated previously, the TMA vapor concentration for the experiment in Figure 2c was estimated to be ~500 ppb. This vapor-phase concentration of TMA is much greater than the amount of TMA taken up into the ammonium nitrate particles; therefore pseudo-first-order kinetics can be assumed. The rate of TMA exchange into the ammonium nitrate particles is given by

$$\frac{\mathrm{d}[\mathrm{TMA}]}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathrm{NH}_4^+]}{\mathrm{d}t} = k_\mathrm{I} t \tag{4}$$

where $k_\mathrm{I} = k_\mathrm{II}[\mathrm{TMA}]_0$. The pseudo-first-order rate constant, k_I, is given by

$$k_\mathrm{I} = \frac{-\ln\left(\dfrac{[\mathrm{NH}_4^+]_t}{[\mathrm{NH}_4^+]_0}\right)}{t} \tag{5}$$

where $[\mathrm{NH}_4^+]_t$ is the ammonium concentration in the particles at $t = 23$ s, $[\mathrm{NH}_4^+]_0$ is the ammonium concentration in the particles at $t = 0$, and t is the reaction time of 23 s. The concentration ratio in eq 5 can be expressed in several ways

$$\frac{[\mathrm{NH}_4^+]_t}{[\mathrm{NH}_4^+]_0} = \left(\frac{[\mathrm{NH}_4^+]}{[\mathrm{NO}_3^-]}\right)_t = 1 - \left(\frac{[\mathrm{TMA}]}{[\mathrm{NO}_3^-]}\right)_t \tag{6}$$

The ammonium to nitrate concentration ratio for Figure 2c can be estimated from the relative intensities of the corresponding ions in the mass spectra, assuming that the relative intensities in Figure 2a correspond to a concentration ratio of 1. Similarly, the TMA to nitrate concentration ratio for Figure 2c can be estimated from the relative intensities of the corresponding ions, assuming that the relative intensities in Figure 2b correspond to a concentration ratio of 1. In either case, an additional assumption is needed that the signal intensity ratio varies linearly with the concentration ratio. These two estimates for the concentration ratio are then used to calculate k_I. Once k_I is known, the initial reactive uptake coefficient (γ_0) averaged over the entire particle size distribution can be determined[19]

$$\gamma_0 = \frac{k_\mathrm{I}\, \mathrm{NH_4NO_3}_{,\mathrm{tot.mol}}}{\mathrm{NH_4NO_3}_{,\mathrm{tot.SA}}\, v[\mathrm{TMA}]_0} \tag{7}$$

where $\mathrm{NH_4NO_3}_{,\mathrm{tot.mol}}$ is the number of moles of ammonium nitrate particles per unit volume across the entire particle size distribution at the beginning of the reaction, $\mathrm{NH_4NO_3}_{,\mathrm{tot.SA}}$ is the surface area of ammonium nitrate particles per unit volume across the entire particle size distribution at the beginning of the reaction (both parameters determined from SMPS), v is the average molecular speed of TMA, and $[\mathrm{TMA}]_0$ is the vapor-phase concentration. The value of γ_0 determined by this approach is $(2 \pm 2) \times 10^{-3}$. The large relative error arises from (1) variations in the ion signal intensity ratio when replicates are performed and (2) differences in the concentration ratio determined by the two methods (eq 6). The γ_0 determination may also be subject to systematic error arising from the procedure used to estimate the density of the TMA−nitrate product and/or assumptions made in converting the ion signal intensity ratio to the TMA to nitrate concentration ratio. For these reasons, the value of γ_0 determined in this work should be regarded only as an order of magnitude estimate.

To the authors' knowledge, there are no reported values for reactive uptake coefficients of TMA onto either wet or dry nitrate particles. Others have studied the uptake of ammonia onto water,[22,23] sulfuric acid,[24] and ice.[25] For water, the values range from 0.006 to 0.3, depending on temperature and pH.[22] The uptake coefficient for TMA exchange into ammonium nitrate at 20% RH determined here is somewhat below this range. It is important to note that the uptake was determined for particles over a wide size distribution of ~20−500 nm. It is not known if the uptake is dependent on particle size and, therefore, which mechanism appears to be limiting (e.g., reaction at the particle surface or reaction within the entire particle). It is also not known how the water content influences uptake. Ammonium nitrate is hygroscopic, and significant particulate water would be expected even at 20% RH. A previous study has shown that the small amount of surface water on sodium chloride particles at 20% RH is sufficient to enhance the uptake by orders of magnitude over a dry, crystalline surface.[19]

One additional experiment was performed where ammonia and TMA vapors were comixed with ammonium nitrate particles by generating vapor from a solution containing 6.5×10^{-2} M ammonia along with 5×10^{-4} M TMA. The relative concentrations of TMA and ammonia vapors produced in this experiment (10-fold difference) were typical of the relative concentrations found in ambient air. The mass spectrum obtained from this experiment (not shown) is the same as that in Figure 2c within experimental error. This result indicates that exchange is not affected by an excess amount of ammonia vapor. Finally, it should be noted that an uptake coefficient on the order of 2×10^{-3} suggests that measurable exchange is possible in the atmosphere even at low RH when ammonium nitrate particles are exposed to an amine concentration on the order of 1 ppb for a few hours. Future work is needed to more accurately determine the uptake coefficient over a wide range of compounds and elucidate the effects of particle size and water content on uptake.

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Supporting Information Available: Additional details of the experimental setup, instrumentation, and data analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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