Effect of Relative Humidity on Aerosol Generation through Experiments at Low Concentrations of Gaseous Nitric Acid and Ammonia

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Abstract

Particle generation of ammonium nitrate from gaseous nitric acid and ammonia at low concentrations (100-600 ppbv) was investigated using a flow-type reactor with a silanized inner wall for deactivation. The particle number concentration of the generated aerosols was maximum at a constant relative humidity (RH) of around 60% in experiments at different gas concentrations. The RH of 60% coincides with the deliquescence relative humidity (DRH) of ammonium nitrate, and the physical state of particles is thought to be different below and above DRH. The size distribution of the particles was greatly affected by the RH. The NH_4NO_3 content in the wet particles was measured and compared with the value derived from the hydration-dehydration cycle. This report provides a simple and convenient method to generate NH_4NO_3 particles.

Keywords: Deliquescence relative humidity; Ammonium nitrate; Particle generation.

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INTRODUCTION

Atmospheric aerosols are attracting attention because of their use as a global material through their generation, conversion and removal processes, as well as their impact on the climate due to the effect of the changing albedo (Charlson and Wigley, 1994). Atmospheric aerosols are classified into primary particles and secondary particles. There are many uncertain areas (particle generation and growth mechanisms, chemical component, gas-particle balance, etc.) especially with secondary particles, which are generated by gas-to-particle conversion in the atmosphere. Most secondary particles are fine particles ($d_p < 1$ µm) and their lifetime in the atmosphere is sufficient to contribute to a number of physical and chemical processes.

Ammonium nitrate is a major component of atmospheric aerosols, and secondary NH_4NO_3 particles from the reaction of gaseous HNO_3 with NH_3 in the atmosphere have been reported (Barthelmie and Pryor, 1988; Makar *et al.*, 1998). Nitric acid in the atmosphere is produced from NO_x by gas-phase oxidation reactions in the atmosphere (Chang *et al.*, 1979; Spicer, 1982). For the dissociation equilibrium of nitrate in the gas phase, some experimental and theoretical studies have been conducted by considering atmospheric conditions (Stelson *et al.*, 1979; Larson and Taylor, 1983; Bai *et al.*, 1995). Olszyna *et al.* (1976) examined the particle generation of ammonium nitrate through a reaction between ammonia (84-1440 mtorr) and ozone (9-130 mtorr). It was shown that nitric acid first reacted with ammonia to give ammonium nitrate particles, and that the rate of particle generation increased by adding water vapor to the reaction system. Raes *et al.* (1990) studied ammonium nitrate particle generation and growth by photo irradiating a reaction gas mixture containing NO_2 (50 ppmv) and NH_3 (20-100 ppmv) with a flow-type reactor. It was demonstrated that the classical Becker-Döing theory describes the particle generation process under the conditions in which excess ammonia was present.

The results of box-model calculation for SPM (Suspended Particulate Matters) concentration are in good agreement with those of the monitoring study when the effect of humidity is included (Winkler, 1973; Mizuno and Kaneyasu, 1994). However, experimental studies on the effects of humidity have not been conducted under conditions of low concentration reaction gases close to atmospheric level. One reason may be the difficulty in minimizing the loss of gases and particles due to their adsorption onto the wall surface of the reactors. This paper reports ammonium nitrate particle generation using a flow-type reactor with silane treatment, which makes it possible to keep the concentration of reaction gases at sub-ppm level. This system can be applied to a nitrate particle-supplying method for atmospheric chemistry experiments.

METHODS

The schematic illustration of the experimental apparatus is shown in Fig. 1. A flow-type reactor consists of three Pyrex glass tubes (11 cm in diameter, 40 cm in height) and Teflon connectors. The volume of the reactor is about 11×10^{-3} m^3. To prevent the adsorption of the reactive species onto the wall surface, the glass surface of the reactor was deactivated as follows: the inner wall was 1) soaked in an aqueous sulfuric acid solution (25%) and dried, 2) treated with a solution of $(CH_3)_2SiCl_2$ (Shin-etsu Kagaku Co.) (5%) in benzene for 10 minutes and dried, and 3) rinsed with anhydrous methanol and dried.
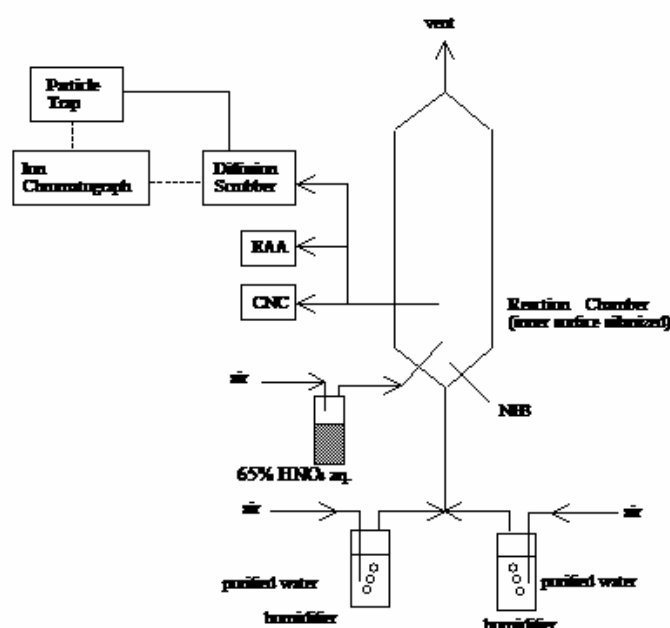

Fig. 1. Schematic diagram of experimental apparatus for aerosol formation.

Two nozzles (Pyrex glass: the surface was also deactivated) for introducing reaction gases are installed near the bottom of the reactor. Purified air (7×10^{-3} m^3/min) is fed from the bottom of the reactor to dilute and mix reaction gases. Part of the purified air supplied with an STEC Model SGPU-21 air purifier is passed through a portion of the deionized water to control the humidity of the reaction gas. To ensure that the reaction gases were completely mixed, ethylene and air were introduced into the reactor through the nozzles, and the gas mixture was sampled from the sampling ports. The sample gas was analyzed by a gas chromatograph with an FID (Flame Ionization Detector) detector. The ethylene was uniformly and accurately diluted with air to the intended concentrations at the top of the nozzles. The outlet of the reactor opens at a hood, so the pressure in the flow-reactor was kept at atmospheric pressure. All experiments were carried out at room temperature (25°C).

A standard gas mixture of ammonia-N_2 in a cylinder (Takachiho Kagaku Co.) was used for this experiment. Concentrated nitric acid is an azeotropic mixture at about 36 mol% (66 wt%), in which the concentration of nitric acid in the gas phase is equal to that of liquid phase. A solution of 65% aqueous nitric acid (20 mL, reagent grade, Wako Chemical Co.) was placed in a glass cylinder chilled at $5.0 \pm 0.05°C$. Purified air (1.55-7.75 mL/min) was passed over the nitric acid solution to obtain gaseous nitric acid. This method can supply gaseous nitric acid stably over several weeks. The concentration of nitric acid was checked as follows: nitric acid was reduced to NO_x by passing it through a gold tube converter with carbon monoxide as a reductant (reduction efficiency: more than 99.5%), and the NO_x generated was monitored by a ThermoElectron Model 42S chemiluminescence NO_x analyzer. The concentration of gaseous nitric acid and ammonia in the reaction gases ranged from 100-600 ppb, and the humidity was controlled from 0-95% relative humidity (RH).

The number concentration of generated particles was counted with a TSI Model 3022 condensation nucleus counter (CNC), which can detect particles as small as 0.01 μm in diameter. The size distribution of particles was measured from 0.018 to 0.1 μm in diameter with an electrical aerosol analyzer (EAA, Nihon Kanomax Model 3030).

A diffusion scrubber (Yokogawa Analytical Systems), which collects gaseous species selectively based on the difference in diffusion coefficient between molecules and particles, was used to remove gaseous HNO_3 and NH_3 from the sample gas (Kobara *et al.*, 1997). Particulate matter was collected with two midget impingers connected after the scrubber, then ions in the particles were analyzed with an ion chromatograph (Yokogawa Analytical Systems, IC 7000D). An efficiency of particle collection was > 99% since two impingers were connected in tandem, and the material balance was confirmed (Kobara *et al.*, 1997). An adhesion of particles on the inner wall of the scrubber will be described in *Results and Discussion*.

RESULTS AND DISCUSSION

Deactivation treatment to prevent adsorption

There are many polar hydroxyl groups on the surface of the glass, and the adsorption of reactive species, such as O_3, NO, NO_2, etc., by surface hydroxyl groups has been reported (Supina *et al.*, 1966). Nitric acid and ammonia may be strongly adsorbed, and the loss cannot be neglected in this experiment where the concentration of the gases is very low. When the surface of the glass was washed with sulfuric acid and treated with $(CH_3)_2SiCl_2$ and then rinsed with anhydrous methanol, the surface OH groups of the glass were converted to $-O-Si(CH_3)_2(OCH_3)$ (Ottenstein, 1968).

When gaseous nitric acid or ammonia was introduced into the flow reactor from the bottom after this treatment, the concentrations of the gases were the same at each sampling point. It is confirmed

that the adsorption of nitric acid and ammonia onto the inner wall of the reactor is entirely prevented with this treatment.

Measured particle number and size distribution

No particles ($\leq$ 1 /cm^3) were detected when nitric acid, ammonia or water at different concentrations were introduced separately into the reactor. Gaseous nitric acid or ammonia did not produce particles even under humid conditions. When nitric acid and ammonia coexisted, remarkable particle generation was observed. The concentration of generated particles increased by increasing the concentration of nitric acid or ammonia. Particle concentration was constant, independent of the sampling points. These results indicate that aerosol generation reached a state of equilibrium at the first sampling point due to the very high reaction rate.
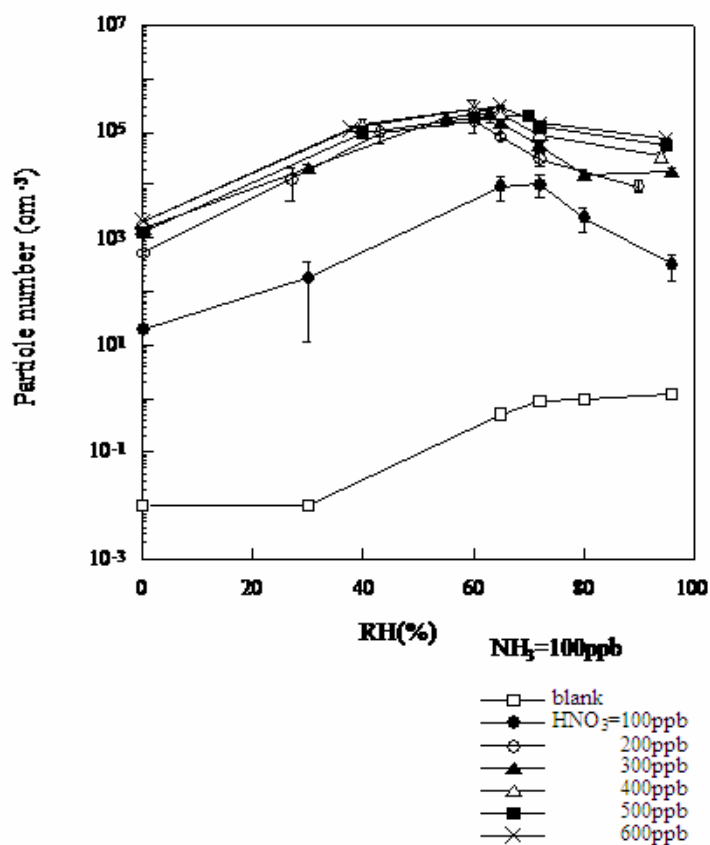

Fig. 2. Particle number concentration generated from gaseous nitric acid and ammonia. [NH$_3$] = 100 ppb, [HNO$_3$] = 100-600 ppb, 25°C.

When the RH was changed from 0 to 90% in constant concentrations of nitric acid and ammonia, the maximum number concentration of generated particles appeared at about an RH of 60%, as shown in Fig. 2. The maximum number concentration was also observed at the same humidity,

regardless of the concentration of nitric acid and ammonia. The deliquescence relative humidity (DRH) of ammonium nitrate has an RH of 62% at 25°C (Hidy, 1984), and the peak in the particle number observed in this measurement is in agreement with the DRH.

To clarify the effect of humidity on particle generation and growth, the size distribution of the generated particles was measured at an RH of 40% and 70%. When the concentrations of gaseous nitric acid and ammonia were both 100 ppb, the size distribution could not be measured because the particle concentration was too low. Therefore, conditions in which $[HNO_3]$ = 200 ppb and $[NH_3]$ = 100 ppb were selected as the second-lowest concentration of the reaction gas. Fig. 3 shows the results of the size distribution measurement. At an RH of 40%, more than 75% of the generated particles were smaller than 0.056 µm in diameter, and the particle concentration decreased with the increase in particle size as shown in Fig. 3(a). These results show that particles may grow only to a comparatively small size when solid particles are present. This agrees with the interpretation that particle growth does not occur under conditions below the DRH (Zufall *et al.*, 1998). On the other hand, the size distribution of particles generated at an RH of 70% showed a peak in the diameter range of 0.056 to 0.1 µm (Fig. 3(b)).
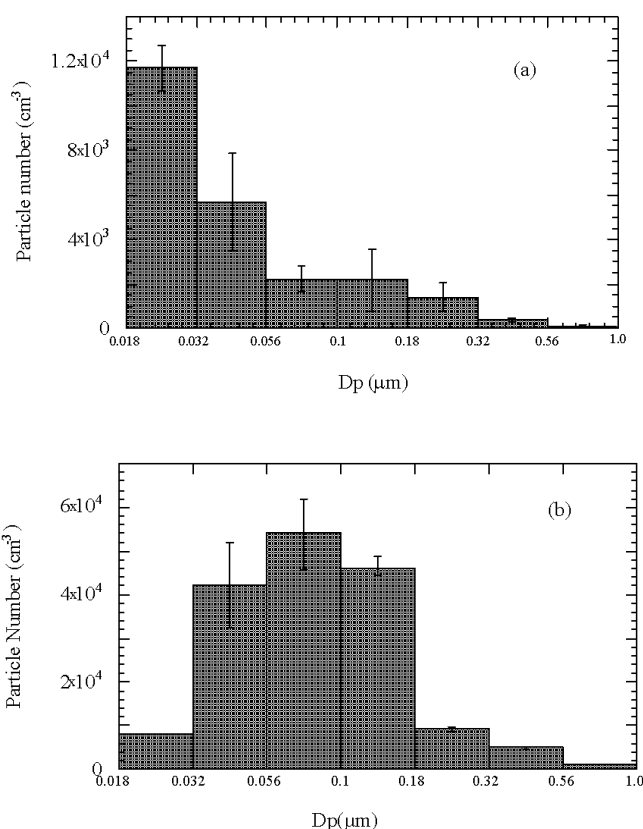

Fig. 3. Particle size distribution generated from gaseous nitric acid and ammonia. $[NH_3]$ = 100 ppb, $[HNO_3]$ = 200 ppb, 25 °C (a) RH 40%, (b) RH 70%

As shown in Fig. 2, particle number concentration decreases with RH over 60%, while it decreases with RH up to 60%. This particle generation reaction is a nitric acid-ammonia-water ternary system of aerosol formation. NH_4NO_3 particles involving water crystallization are produced under the condition in which the NH_4NO_3 particle exists as a solid. RH increase in the reaction system equals the increase in water molecules, which act as an adhesive between the nitric acid and ammonia. This results in increased embryo-generation frequencies. Particle number concentration at RH < 60% in Fig. 2 shows the increase of particles large enough to be detected by CNC. However, instead of embryo generation occurring under high RH conditions in which NH_4NO_3 is in liquid droplet form, particles apparently become larger through particle coagulation, while the number of particles decreases.

The ammonium nitrate concentration in the particles was measured by using a diffusion scrubber. The particles were removed selectively because of the difference in the diffusion coefficients between gaseous species and particulate matter. Particles that passed through the diffusion scrubber were absorbed by the water in the impingers. NH_4^+ and NO_3^- concentrations were analyzed by ion chromatography, and the amount of nitric acid and ammonia in the particle phase was determined. Total volume concentrations at RH 40% and 70%, V_{40} and V_{70}, were calculated by the size distributions. For liquid droplets at RH 70%, NH_4NO_3 concentration in particles was determined by particle volume and ion concentration, followed by the calculation of the number of water molecules in liquid droplets. Moles H_2O/Moles NH_4NO_3 were determined by the constituent in the liquid droplets. The NH_4NO_3 concentration in the liquid droplets generated at an RH of 70% was 14.3 mol/L.

The molecule ratio in the particles and the total volume ratio of wet to dry particle, V_{70} and V_{40}, are listed in Table 1. The size distributions were measured ranging in diameter from 0.018-1.0 μm by EAA. Particle number concentrations were measured for particles larger than 0.01 μm in diameter; therefore, no size information was obtained for particles 0.01-0.018 μm in diameter. However, the number concentration of particles from 0.01 to 0.18 μm was less than about 8×10^4 cm^{-3} according to a comparison of particle number and size distribution data (Fig. 2 and Fig. 3(a)). The contribution of particles smaller than 0.018 μm should be smaller at 70% RH (Fig. 2 and Fig. 3(b)). The volume of particles between 0.01 and 0.018 μm was less than 1% of the total volume of particles. Therefore, for the calculation of V_{40} and V_{70}, the contribution of particles smaller than 0.018 mm was judged to be negligible.

Materials adhered onto the scrubber's inner wall were 0.45 nmol of nitric acid and 0.52 nmol of ammonia when 1×10^{-2} m^3 of the sample gas was passed through the scrubber. These amounts corresponded to 10.8% and 12.1% of nucleated nitric acid and ammonia at RH 70%, respectively. At RH 40%, the amount of adhered nitric acid and ammonia was 4.4% and 4.8% of nucleated substances with 1×10^{-2} m^3 of the sample gas. The amount of ammonium nitrate in the particles

was determined by considering these amounts of adhered species during the transfer from the gas to particulate phase.

As described before, ammonium nitrate is a deliquescent salt. The ratio Moles H_2O/Moles NH_4NO_3 was determined to be about 3.3, and the mass ratio of liquid droplet to dry particle M/Mo was about 1.7 at an RH of 70% using thermodynamic model prediction and hydration-dehydration experiments (Clegg *et al.*, 1998; Lightstone *et al.*, 2000). If HNO_3 and NH_3 first form crystalline particles followed by H_2O uptake under humid conditions, the ratio of Moles H_2O/Moles NH_4NO_3 should be 3.3, the same as the ratio in the hydration of the crystals shown in Table 1. However, the ratio of Moles H_2O/Moles NH_4NO_3 of the particles was 3.9 in this experiment, and particles contained more water than expected from the hydration-dehydration loop (deliquescence). The water content in the droplets and the volume ratio of liquid droplet to dry particle are also greater than predicted by the deliquescence-efflorescence loop. This means that the initial step of particle generation is not the formation of crystalline particles. H_2O molecules are incorporated into the particles when HNO_3 and NH_3 aggregate through collision with each other. It is considered that particle generation at a high RH is promoted by the capturing of water and coagulation, which results in large Moles H_2O/Moles NH_4NO_3 and M/Mo values in the particles. To explain the difference in particle generation processes at different levels of humidity, nucleation rates can be estimated using the conditions in this experiment.

Table 1 Moles H_2O/Moles NH_4NO_3 and total volume ratio of wet particles to dry particles (V_{70}/V_{40}) of particles generated in this experiment, with Moles H_2O/Moles NH_4NO_3 and mass ratio of solution droplet to dry particle (M/Mo) of NH_4NO_3 salt in hydration/dehydration cycle.

	This experiment	NH_4NO_3 salt in hydration/dehydration cycle
Moles H_2O/Moles NH_4NO_3	3.9	3.3
V_{70}/V_{40}	6.0	
M/Mo		1.7

Relation to the nucleation model

In gas-phase homogeneous nucleation, the nucleation rate is generally represented as

$$J = A \cdot \exp(-\Delta G^*/kT) \tag{1}$$

$$G^* = 16\pi\gamma^3 v^2/3(RT\ln S)^2 \tag{2}$$

where A is the exponential prefactor that represents the collision frequency for a molecule to transition to the solid or liquid phase, ΔG^* is the barrier height at nucleation, k is Boltzmann's

constant, T is the Kelvin temperature, γ is the surface tension, ν is the molar volume of the particles and S is the saturation ratio.

In the system, including chemical reactions, reaction enthalpies are involved in the free energy (Kiang, 1975):

$$G' = \Delta G^* \pm \Delta H \tag{3}$$

Therefore, J is transformed into:

$$
\begin{aligned}
J &= A \cdot \exp\{-(\Delta G^* \pm \Delta H)/kT\} \\
&= A \cdot \exp(-\Delta G^*/kT) \cdot \exp\{-(\pm \Delta H)/kT\} \\
&= A' \cdot \exp(-\Delta G^*/kT)
\end{aligned}
\tag{4}
$$

where $A' = A \cdot \exp(\pm \Delta H/kT)^{-1}$

The value of $-\Delta G^*/kT$ can be calculated by using parameters of solid NH_4NO_3 (Rehbinder, 1926; Stelson *et al.*, 1982a; Raes *et al.*, 1990; Weast *et al.*, 1990a) at an RH less than the DRH, and aqueous NH_4NO_3 (Stelson *et al.*, 1982b; Söhnel and Novotny, 1985; Weast *et al.*, 1990b) at an RH greater than the DRH. In this experiment, the generated particle number concentration is 5×10^4 cm^{-3} under an RH of 40%, $[HNO_3]$ = 200ppb and $[NH_3]$ = 100ppb. Therefore, exponential prefactor A' including the thermodynamic parameter with the chemical reaction is estimated to be $A' \approx 8.85 \times 10^{22}$. A' at an RH of 70% under the same HNO_3 and NH_3 concentration is $\approx 3.27 \times 10^{32}$. The difference between these two reaction conditions is only the water vapor content (RH 40% / RH 70%), but the A' value at an RH of 70% is larger than that at a 40% RH; up to about 10 orders of magnitude. This A' difference shows that the collision frequencies of molecules increase exponentially with increasing water molecule concentrations in the nitric acid-ammonia-water ternary system. It is ascertained that the high probability of H_2O collision with HNO_3 and NH_3 leads to the formation of water-rich droplets. Total particle volume ratio of RH 70% to 40% is V_{70}/V_{40} = 6.0, while particle number concentrations are comparable. Particle nuclei generate more at RH 70% than at 40% because of high molecular collision frequencies. Particle volume becomes larger by particle nuclei coagulation, as well as gas molecule condensation on the surface of particles.

CONCLUSION

A flow-type reactor was used to experiment with particle generation from gaseous nitric acid and ammonia. With the inactivation of the reactor surface, loss of gaseous species and particulate matter by adsorption hardly occurred, so observation of particle generation from a low

concentration of gaseous nitric acid and ammonia could be conducted. The particle generation of ammonium nitrate was greatly affected by relative humidity, and the size distribution was quite different below and above the DRH of ammonium nitrate. The method in this report is a simple and convenient way to supply NH_4NO_3 particles; e.g., useful for aerosol experiments and standard examinations. Water content in liquid droplets was greater than the value of the equilibrium growth curve of ammonium nitrate salt with water deposits. The degree of swelling of the particles was also higher than indicated from the hydration-dehydration loop. The collision frequency of gaseous species was estimated, and it was clarified that it increased 10 orders of magnitude as the relative humidity increased from 40 to 70%. NH_4NO_3 particle generation under conditions of high humidity was promoted more than thermodynamic equilibrium due to the uptake of water when HNO_3 and NH_3 aggregated. This effect of humidity on the particle formation process should be considered, for example, when an atmospheric model is developed.

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