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The Chemistry of Drying an Aqueous Solution of Salts

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The fate of salts in drying aqueous solution was investigated. In the drying of acidic solutions, weak acid ions and chloride ions combine with protons and evaporate, depending on the proton concentration. In the drying of alkaline solutions, weak acid ions evaporate or remain as salts depending on the ratio of the concentrations of excess nonvolatile cations (the difference between concentrations of nonvolatile cation and nonvolatile anion) to volatile anions defined as ΔCA. Under neutral and alkaline conditions, the fate of nitrite depends not only on ΔCA but also on the drying speed. Nitrite is converted to N_2, which is formed by reacting nitrite with ammonium (denitrification), NO and NO_2, HONO and salts. In urban areas, nitrite and ammonium can appear in high concentrations in dew. HONO in the atmosphere affects the ozone concentration, but dew formation decreases the concentration of HONO. If chemical denitrification occurs, nitrogen species will decrease in the environment, and as a result, the ozone concentration could decrease. Ozone levels show an ozone depression when dew formed, and a Box model simulation showed an ozone depression by decreasing HONO levels.

Introduction

Water exists everywhere on the earth, and it helps cleanse the environment. Rain droplets absorb gaseous substances and aerosols during their formation and precipitation. There have been various studies on the ability of rain to scavenge substances in the atmosphere, but there have been few studies on the fate of solutes in rain or cloud droplets that are drying. Do solutes in water evaporate or deposit after drying? The fate of the solutes depends on the conditions of drying. For example, ammonium acetate is a solid that dissolves easily in water. When an aqueous solution of ammonium acetate was dried quickly by contact with a 100 °C hot plate, solid ammonium acetate was deposited, as show in Figure 1. On the other hand, when it was dried slowly at room temperature, no solid was formed and it evaporated, as shown in Figure 1.

It is reported that rain falls from clouds after an average of 9 to 10 condensation/evaporation cycles.[1] Rain, fog, and dew dry on the ground and on places such as leaves. If substances in the aqueous phase are concentrated by drying, they may react to form other substances, which may cause damage to the environment. Therefore, it is important to understand the fate of substances in drying aqueous solutions in order to evaluate their effects on the environment.

Nitrous acid (HONO) in the atmosphere plays an important role in the environment. HONO is photolyzed to produce OH radicals that affect the ozone concentration.[2] Because HONO easily dissolves in water, its concentration in the atmosphere decreases at night due to the formation of water droplets such as dew.[3] However, the behavior of nitrite (NO_2^- and HNO_2) in dew or water droplets has not been fully investigated. Nitrite in dew is highly concentrated by drying within a few hours after sunrise. The concentrated nitrite evaporates into the atmosphere, remains as a salt, reacts with other substances in the dew or undergoes another process such as thermal decomposition. In dew, there are also ammonium ions at very high concentrations. Concentrated ammonium nitrite is well-known to decompose to produce N_2, and the reaction is used for laboratory N_2 generation.[4−9]

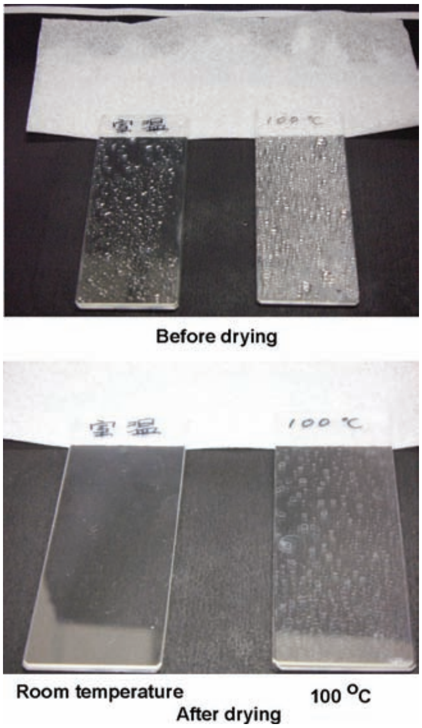

Figure 1. Photographs before and after drying CH_3COONH_4. The ammonium acetate solution was dried in 1 day at room temperature and within 1 min at 100 °C.

$$NH_4NO_2(aq) \rightarrow N_2(g) + 2H_2O \qquad (i)$$

Abel proposed a third-order rate law for reaction i[8]

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$$d[N_2]/dt = k[NH_4^+][HNO_2][NO_2^-] \tag{1}$$

On the other hand, Dusenburry and Powell proposed a second-order rate law.[5] Ewing and Bauer demonstrated that when the secondary salt effect and the effect of nitrous acid decomposition are both neglected, it is not possible to distinguish the rate law by Abel and that by Dusenburry and Powell.[6] If the ion strength of the solution or activity is considered, the rate calculated by the rate law of Dusenburry and Powell approaches the same value calculated by the Abel rate law. Generally, reaction i can be considered to be a third-order reaction.

At low pH, nitrous acid decomposes to NO and HNO_3 (reaction ii). However, the production of NO_2 by reaction iii was not observed in the decomposition of ammonium nitrite.[9] Ewing reported N_2O production by the decomposition of ammonium nitrite (reaction iv), and N_2O/N_2 was 2% and 20% at pH 4.29 and pH 5.03, respectively.[6]

$$3HNO_2 \rightarrow 2NO + HNO_3 + H_2O \tag{ii}$$

$$2HNO_2 \rightarrow NO + NO_2 + H_2O \tag{iii}$$

$$4HNO_2 \rightarrow N_2O + 2HNO_3 + H_2O \tag{iv}$$

At low pH, nitrous acid is oxidized by dissolved oxygen to produce nitrate.

$$2HNO_2 + O_2 \rightarrow 2H^+ + 2NO_3^- \tag{v}$$

This reaction obeys second order for nitrous acid and first order for oxygen.[10,11] The reactant is HNO_2 but not NO_2^-. Therefore, the reaction rate is fast in acidic solution but very slow at neutral and high pH.

We found that the fate of nitrite in dew depends on the concentration and drying speed. The drying speed is affected by meteorological conditions such as the temperature, humidity, and size of the droplets. Small droplets dehydrate faster than larger ones because water molecules evaporate from the surface of droplets and a surface-to-volume ratio of small droplets is larger than that of large droplets. While in the dew, if nitrite reacts with ammonium ions to produce N_2 but does not escape into the atmosphere due to drying, the HONO concentration in the atmosphere decreases, and it is speculated that the ozone concentration will also decrease. Here we report on the general fate of salts in drying dew and also test the effects of dew formation on the ozone concentration in the atmosphere.

Experimental Section

All reagents, obtained from Wako Pure Chemicals, Inc., were reagent grade and used without further purification. Pure water was prepared by Milli-Q Labo using distilled water. The resistivity of the pure water was higher than 18.2 MΩ cm. The pH was measured with a Horiba Co., Ltd., M-13 pH meter with a 6069-10C glass electrode and calibrated at pH 7 with phosphate buffer and pH 4 with phthalate buffer.

An aliquot of salt solution was put into a glass beaker, or on a PTFE plate (Figure 2a) or a PTFE watch dish (Figure 2b). These were placed in a small polypropylene chamber (typically 12.5(w) × 8.5(d) × 5.0(h) cm^3) and dried with an Ar gas flow of 50 cm^3 min^{-1}, as shown in Figure 2c. After the sample was completely dehydrated, the remaining salts in the beaker or on the dish were dissolved in known amounts of pure water to measure the ion concentrations.

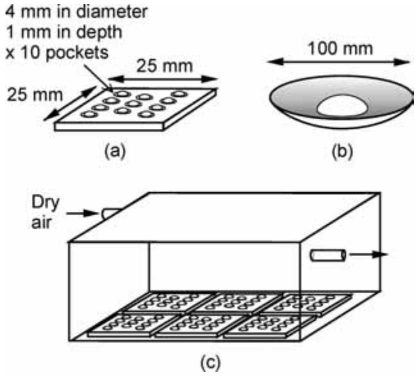

Figure 2. Experimental setups for drying solutions: (a) PTFE plate, 25 mm × 25 mm × 2 mm, the diameter and depth of holes were 4 and 1 mm, respectively. Ten holes were prepared. (b) A PTFE watch dish, 100 mm diameter. (c) The drying experiment box had dimensions of 12 cm × 9 cm × 4.5 cm or 42 cm × 33 cm × 25 cm. Commercial synthesized air or Ar was used to dry the solution.

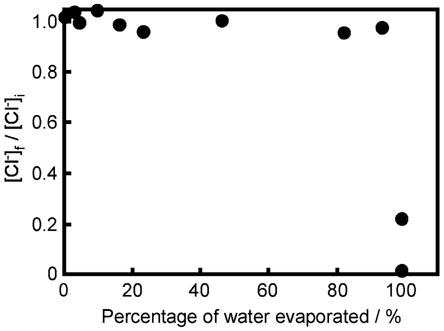

Figure 3. Evaporation loss of chloride by drying: initial volume of the sample, 1.1 cm^3; drying at 15 ± 5 °C; $[NaCl]_i = 5$ mmol dm^{-3}; $[H_2SO_4]_i = 5$ mmol dm^{-3} (pH 2.0).

Ion concentrations were measured with a Dionex ion chromatography system, ICS-1500, or a Yokogawa Analytical Systems Co., Ltd., IC-7000 ion-chromatographic analyzer with the following columns: inorganic anions; Dionex AS-12A column with 9 mM Na_2CO_3 eluent, cations; Yokogawa Analytical Systems, ICD-C25 column with 24 mM boric acid−5 mM L-(+)-tartaric acid−1 mM 2,6-pyridine dicarboxylic acid mixture eluent, and organic acids; Yokogawa Analytical Systems, CHA-E11 column with 1 mM H_2SO_4 eluent. Gaseous HONO and NH_3 were analyzed by a continuous concentrator[12,13] or by an annular denuder system. NO and NO_2 concentrations were analyzed by the Kimoto Electric Co. NA-623 automatic nitrogen oxides analyzer. In order to confirm drying, water vapor was monitored by a Pfeiffer Vacuum Co. Omnistar GSD300 O1 mass spectrometer. N_2 ($m/z = 28$), HONO ($m/z = 30$),[14] N_2O ($m/z = 44$ or CO_2), Ar ($m/z = 40$), and NO_2 ($m/z = 30$ and 46)[14] were also measured by a Pfeiffer Vacuum Co. Omnistar GSD300 O1 mass spectrometer.

Results and Discussion

Evaporation Loss of Chloride Ion. A 100 μmol dm^{-3} aqueous NaCl solution, adjusted to pH 4.5 with H_2SO_4 (with equimolar protons), was dried in a glass beaker at room temperature. All of the chloride ions disappeared from the salts. Figure 3 shows the results of drying a 5 mmol dm^{-3} aqueous NaCl solution, adjusted to pH 2 (higher proton concentration than chloride concentration) with H_2SO_4 at room temperature.

After complete drying, almost no chloride ions remained as salt deposits and were detected in the gas phase. In this case, the solution contained sodium ions, chloride ions, sulfate ions, and protons. When the solution was dried, these ions must combine with counterions to potentially form NaCl, Na_2SO_4, HCl, and H_2SO_4. The solubility of Na_2SO_4 is lower than that of NaCl. HCl is volatile, but H_2SO_4 is not volatile. As a result, HCl escapes to the gas phase and Na_2SO_4 remains as a salt. Under neutral or alkaline conditions, all of the chloride remained as salt. A similar result was also observed with HNO_3 instead of H_2SO_4. Most of Cl^- ions disappeared and almost all nitrate remained as a salt. This result indicates that when acid solutions containing Na^+, Cl^-, and SO_4^{2-} or NO_3^- are dried to form aerosols in the environment, Cl^- is lost in a way that depends on the amounts of sulfate or nitrate.

When the $NaNO_3-H_2SO_4$ mixture at pH 2 was dried, 96% of the nitrate evaporated and Na_2SO_4 remained. Therefore, in drying solutions including strong acid ions under acidic condition, chloride ions evaporate first, and then nitrate ions evaporate depending on amounts of proton, but sulfate ions do not evaporate. Under acidic condition, weak acid ions of which undissociated forms are gaseous or volatile at room temperature also evaporate.

Evaporation Loss of Weak Acid. As mentioned above, pH is a very important factor that determines the fate of solutes by drying. The pH dependence of ratios of the amounts of nitrite in salt after drying to those in the initial solution was investigated under neutral and alkaline conditions. Hereafter, the ratio of the amounts of a compound in salt after drying to those in the initial solution is defined as the "residual ratio". We investigated the residual ratios of nitrite in three series, which were as follows: (1) $NaNO_2-Na_2SO_4-(NH_4)_2SO_4$ mixture; Na_2SO_4 and $(NH_4)_2SO_4$ concentrations were altered, but the SO_4^{2-} concentration was constant (the $[Na^+]/[NH_4^+]$ ratio was changed); (2) $NaNO_2-Na_2SO_4-NaOH$ mixture; Na_2SO_4 and NaOH concentrations were altered, but the Na^+ concentration was constant; (3) $NaNO_2-(NH_4)_2SO_4-NH_4OH$ mixture; $(NH_4)_2SO_4$ and NH_4OH concentrations were altered, but the NH_4^+ concentration was constant. The results are shown in Figure 4a. It was found that the pH is not a dominant factor determining fate of nitrite in drying solutions. The acid dissociation constant of nitrous acid is $10^{-3.25}$ at 25 °C.[15] Therefore, it is expected that nitrite can only evaporate under acidic conditions. As shown in Figure 4a, nitrite was evaporated at pH higher than 5.6, and even at pH 9.7, almost all the nitrite evaporated. However, in some cases, the nitrite did not evaporate not only at pH 10 but also at pH 5.6. This result indicates that pH is not the dominant factor that explains the fate of nitrite at neutral and high pH. As shown in Figure 4b, the residual ratios of the same data in Figure 4a can be explained by concentration ratios of $([Na^+]_i-2[SO_4^{2-}]_i)/[\text{nitrite}]_i$, which is expressed as ΔCA. Here, the subscript i denotes initial conditions, and concentrations are expressed as mol dm^{-3}. In Figure 4b, a value of zero for ΔCA means that all Na^+ ions combine with SO_4^{2-} after drying and that no free Na^+ remains to combine with NO_2^-. The nitrite must combine with protons or ammonium ions. Therefore, nitrite ions can evaporate into the gas phase, probably as HONO. At $\Delta CA < 0$, more SO_4^{2-} exists than Na^+ in solution, and no free Na^+ remains after producing Na_2SO_4. Therefore, all the nitrite disappeared from the salt formed by drying. A ΔCA value of 1 means that Na^+ combines with all of the SO_4^{2-} and that the same amount of Na^+ as nitrite remains in the sample. Therefore, $NaNO_2$ is produced, and all the nitrite remains as a salt. At $\Delta CA > 1$, more sodium ions exist than nitrite after all the sulfate ions combine with sodium ions, and therefore, all nitrite ions exists as a salt. Nitrite evaporates depending on ΔCA values between 0 and 1. The line for ideal behavior was drawn in Figure 4b.

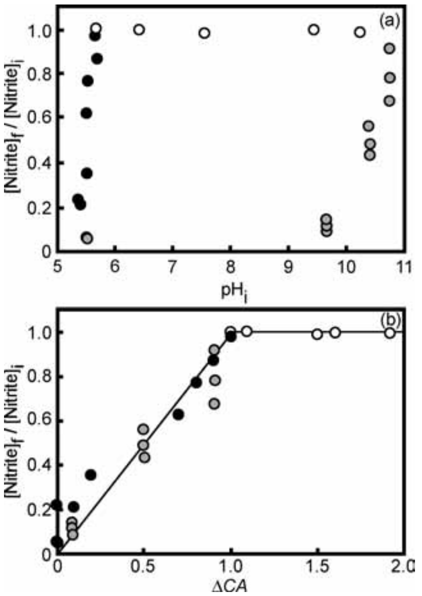

Figure 4. Dependence of pH (a) and ΔCA (b) on the ratio of nitrite remaining after drying to the initial nitrite concentration. Vertical axis: measured ratio of nitrite concentration remaining as a salt to the initial ion concentration. Horizontal axis: (a) pH and (b) calculated ratio of the concentrations of excess nonvolatile cations to volatile anions. In this case $\Delta CA = ([Na^+]_i-2[SO_4^{2-}]_i)/[\text{nitrite}]_i$ in molar concentration units. The initial nitrite concentration was 5 mmol dm^{-3}. Black circles: $NaNO_2-Na_2SO_4$ (0.025−2.5 mmol dm^{-3})$-(NH_4)_2SO_4$ (0.025−2.5 mmol dm^{-3}) system. White circles: $NaNO_2-Na_2SO_4$ (0.025−2.5 mmol dm^{-3})−NaOH (0.050−5.0 mmol dm^{-3}) system. Gray circles: $NaNO_2-(NH_4)_2SO_4$ (0.025−2.5 mmol dm^{-3})$-NH_4OH$ (0.050−5.0 mmol dm^{-3}) system. The total equivalent ion concentrations were the same in all cases. The subscripts i and f denote initial and final conditions, respectively. Solid line: ideal behavior line expected from the hypothesis (see text). Volume of the sample: 0.1 cm^3. Temperature: 20 ± 5 °C.

The same results were obtained for acetate and formate, which are shown in Figure 5 along with the nitrite results. The lines for ideal behavior were also drawn in Figure 5. As shown in parts a and b of Figure 5, the residual ratios of nitrite and acetate reached zero. Only the residual ratios of formate did not reach zero, even at $\Delta CA < 0$, and showed slightly higher ratios than the ideal ones, as shown in Figure 5c. These results can be summarized as follows. The ratio of $([Na^+]_i-2[SO_4^{2-}]_i)/[\text{weak acid anion}]_i$, which indicates the concentration ratio of excess nonvolatile cations to volatile anions, is expressed as ΔCA. The excess nonvolatile cations indicate the difference between the concentrations of nonvolatile cations and nonvolatile anions. Therefore, ΔCA is redefined as

$$\Delta CA = \frac{\sum[\text{excess nonvolatile cation}]}{\sum[\text{volatile anion}]} = \frac{\sum[\text{nonvolatile cation}]-\sum[\text{nonvolatile anion}]}{\sum[\text{volatile anion}]} \qquad (2)$$

Under neutral and alkaline conditions, the nonvolatile cations include Na^+, K^+, Ca^{2+}, and Mg^{2+}, and the nonvolatile anions include SO_4^{2-}, NO_3^-, and Cl^-. Here, the concentrations of

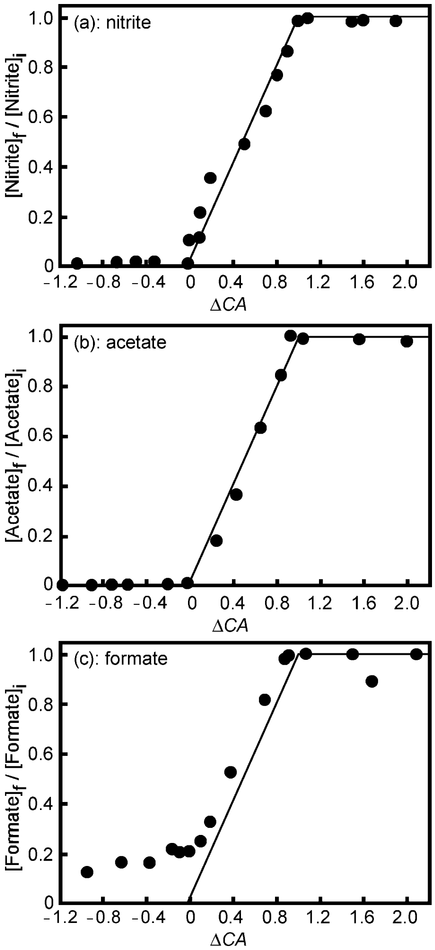

Figure 5. Dependence of ΔCA on the ratios of nitrite, acetate, and formate remaining after drying to the initial concentrations. Vertical: measured ratio of ion concentrations remaining as a salt to the initial ion concentrations. Horizontal: calculated ratio of the concentration of excess nonvolatile cations to volatile anions. ΔCA = ($[Na^+]_i-2[SO_4^{2-}]_i$)/[weak acid anion]$_i$ in molar concentration units. Solid line: ideal behavior line expected from the hypothesis (see text). The subscripts i and f denote initial and final conditions, respectively. Volume of the sample: 0.1 cm^3. Temperature: 20 ± 5 °C. (a) nitrite, (b) acetate, (c) formate. Concentrations of the weak acids were 10 mmol dm^{-3}.

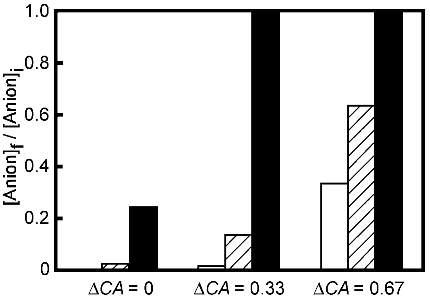

Figure 6. Evaporation loss of weak acids mixed solution: white line, acetate; hatched line, nitrite; black line, formate. ΔCA = 0: $[CH_3COONa]_i$ = 10 mmol dm^{-3}, $[NaNO_2]_i$ = 10 mmol dm^{-3}, $[HCOONa]_i$ = 10 mmol dm^{-3}, $[(NH_4)_2SO_4]_i$ = 15 mmol dm^{-3}. ΔCA = 0.33: $[CH_3COONa]_i$ = 10 mmol dm^{-3}, $[NaNO_2]_i$ = 10 mmol dm^{-3}, $[HCOONa]_i$ = 10 mmol dm^{-3}, $[(NH_4)_2SO_4]_i$ = 10 mmol dm^{-3}. ΔCA = 0.67: $[CH_3COONa]_i$ = 10 mmol dm^{-3}, $[NaNO_2]_i$ = 10 mmol dm^{-3}, $[HCOONa]_i$ = 10 mmol dm^{-3}, $[(NH_4)_2SO_4]_i$ = 5 mmol dm^{-3}. Volume of the sample: 0.1 cm^3. Temperature: 20 ± 5 °C.

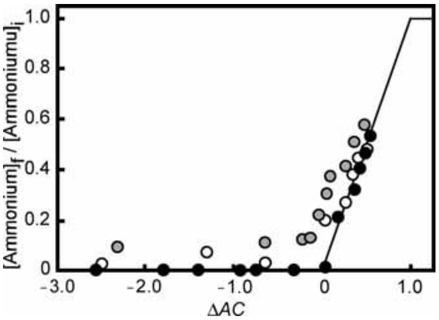

Figure 7. Dependence of ΔAC on the ratios of ammonium remaining after drying to the initial concentrations. ΔAC = ($2[SO_4^{2-}]_i-[Na^+]_i$)/[ammonium]$_i$ in molar concentration units. Solid line: ideal behavior line expected from the hypothesis (see text). The subscripts i and f denote initial and final conditions, respectively. White circle: nitrite system, $[NaNO_2]_i$ = 10 mmol dm^{-3}, $[(NH_4)_2SO_4]_i$ = 0−10 mmol dm^{-3}, $[NaOH]_i$ = 0−20 mmol dm^{-3}. Gray circle: formate system, $[HCOONa]_i$ = 10 mmol dm^{-3}, $[(NH_4)_2SO_4]_i$ = 0−10 mmol dm^{-3}, $[NaOH]_i$ = 0−20 mmol dm^{-3}. Black circle: acetate system, $[CH_3COONa]_i$ = 10 mmol dm^{-3}, $[(NH_4)_2SO_4]_i$ = 0−10 mmol dm^{-3}, $[NaOH]_i$ = 0−20 mmol dm^{-3}. Volume of the sample: 0.1 cm^3. Temperature: 20 ± 5 °C.

bivalent ions must be doubled for stoichiometric reasons. The chloride and nitrite ions are volatile in acidic solutions but nonvolatile in neutral and alkaline solutions. The volatile cation is NH_4^+, and volatile anions include NO_2^-, $HCOO^-$, and CH_3COO^-. The reason why ammonium salts of weak acids evaporate as gaseous NH_3 and gaseous weak acid is discussed later, but the phenomenon is the same as Figure 1.

The evaporative loss from a mixed solution of nitrite, acetate, and formate is shown in Figure 6. Each concentration of nitrite, acetate, and formate was 10 mmol dm^{-3}. When ΔCA = 0, based on the ideas presented, all the volatile anions should evaporate. It was found that all of acetate, most of nitrite, and 75% of formate evaporated. When ΔCA = 0.333, the model predict that two-thirds of the volatile anions should evaporate. It was found that almost all of acetate and most of nitrite evaporated, but no formate evaporated. About two-thirds of the weak acids evaporated. When ΔCA = 0.667, one-third of the anions should evaporate. It was observed that approximately two-thirds of acetate, approximately one-third of nitrite, and no formate evaporated. In total, about one-third of the weak acids evaporated. The total evaporation amounts showed good agreement with those expected from the results of Figure 5. However, acetate most readily evaporated among the three weak acids and then nitrite. If a solution includes these three weak acids, this result indicates that acetate will evaporate first, followed by nitrite, and finally formate.

Evaporation Loss of Ammonia. If ΔCA is redefined as the ratio of the concentration of excess nonvolatile anions to ammonium, expressed as ΔAC, then the same results could be obtained for ammonium. The excess nonvolatile anions indicate the difference between the concentrations of nonvolatile anions and nonvolatile cations. The result is shown in Figure 7. In the case of acetate and nitrite salts of ammonium, the results showed good agreement with the expected ratios. However, in the case of ammonium formate, the ratios were slightly high. The residual ratios of formate vs ΔCA showed the same trend. The ammonium and formate remain as ammonium formate salt. Table 1 shows the acid dissociation constants, Henry's law constants, and boiling points of nitrous, acetic, formic acids, and ammonia. In order to evaporate, the anions must combine with protons, and ammonium ions must release protons. Therefore, the acid dissociation constants, K_a, are an important factor, and acids with a small dissociation constant are expected to evaporate easily, since the acids with small K_a are present to a larger extent in their undissociated form. The vapor pressures or Henry's law constants are also an important factor of the

TABLE 1: Henry's Law Constants and Acid Dissociation Constants of Nitrous Acid, Formic Acid, and Acetic Acid

	nitrous acid	formic acid	acetic acid	ammonia
acid dissociation constants[a]/mol dm^{-3} (ref 15)	5.62×10^{-4}	1.78×10^{-4}	1.75×10^{-5}	5.62×10^{-10}
Henry's law constants[a]/mol dm^{-3} atm^{-1}	4.9×10^{1} [16]	5.2×10^{3} [17]	5.2×10^{3} [17]	5.8×10^{1} [16]
boiling point at 1 atm/K (ref 15)		374	391.05	239.82

[a] 298 K.

vaporization. Compounds having large vapor pressures or small Henry's law constants evaporate easily. Among the three weak acids, acetic acid has the smallest dissociation constant and evaporates most readily, as shown in Figure 6. Nitrous acid has the largest dissociation constant but evaporates more easily than formic acid. As shown in Table 1, nitrous acid has the smallest Henry's law constant, and acetic and formic acids have the same values. From the Henry's law constants, it is expected that nitrous acid will evaporate most quickly, but acetic acid evaporated faster than nitrous acid. These acids probably evaporate due to interactions with the ammonium ion. Following the data displayed in Figure 7, ammonium ions are also deposited as a salt in the case of formate. This means that formic acid does not stick to the glass, but ammonium formate forms instead. The solubility of salts also relates to the evaporation.

$$NH_4^+(aq) + A^-(aq) \rightleftharpoons NH_4A(s) \tag{vi}$$

Here, A indicates each acid. The mole ratios (salt/H_2O) of saturated aqueous solution of NH_4NO_2, $HCOONH_4$, and CH_3COONH_4 are 0.352 (0 °C),[15] 0.291 (0 °C),[18] and 0.346 (4 °C),[18] respectively. The solubility of ammonium formate is the smallest among three salts. Therefore, it is speculated that formate ion combined with ammonium ion and produced salts before all formate evaporated. The solubility of ammonium nitrite is the largest. When aqueous solution is drying, anions must combine with proton or ammonium ions. The acid dissociation constants, K_a are related to combine with proton, and K_a of nitrous acid is larger than that of acetic acid. Therefore, it is considered that acetate evaporated most easily. From these considerations, it can be concluded that, first, the evaporation of salts is determined by acid dissociation constants of acids, second, Henry's law constants or vapor pressures of undissociated acid and base are related to the vaporization, and, third, solubility of salts prevent to evaporation depending on the solubility values. The complete understanding will be performed by introducing thermodynamic stabilities of salts, ions, and gases.

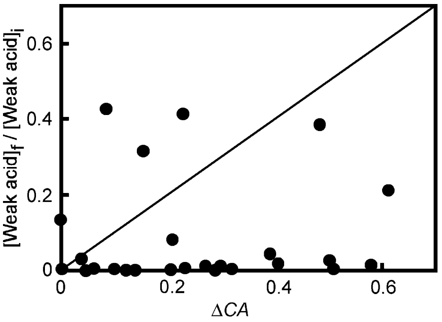

Figure 8. Evaporation loss of weak acids in the natural sample ΔCA = ([Na$^+$]$_i$ + [K$^+$]$_i$ + 2[Ca^{2+}]$_i$ + 2[Mg^{2+}]$_i$) − ([Cl$^-$]$_i$ + [NO$_3^-$]$_i$ + 2[SO$_4^{2-}$]$_i$))/([nitrite]$_i$ + [formate]$_i$ + [acetate]$_i$) in molar concentration ratio. Solid line: ideal behavior line expected from the hypothesis (see text). The subscripts i and f denote initial and final condition, respectively. Volume of the sample: 0.1 cm^3. Temperature: 20 ± 5 °C.

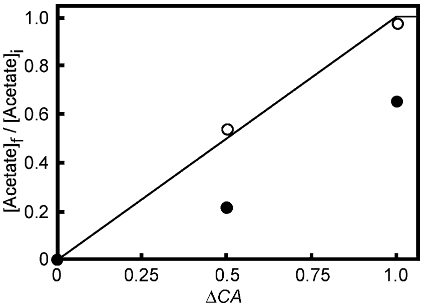

Figure 9. Effect of CO_2 on the fate of nitrite. ΔCA = ([Na$^+$]$_i$−2[SO$_4^{2-}$]$_i$)/[CH$_3$COO$^-$]$_i$. [(CH$_3$COO)$_2$Ca]$_i$ = 20 mmol dm^{-3}, [(NH$_4$)$_2$SO$_4$)]$_i$ = 7.5−12.5 mmol dm^{-3}, [Na$_2$SO$_4$]$_i$ = 0−2.5 mmol dm^{-3}, [Ca(OH)$_2$]$_i$ = 7.5−10 mmol dm^{-3}, ([Na$^+$] + [Ca^{2+}] = 40 mmol dm^{-3}). Solid line: ideal behavior line expected from the hypothesis (see text). The subscripts i and f denote initial and final conditions, respectively. Black circle: Under air (with CO_2). White circle: Under Ar (without CO_2). Volume of the sample: 0.1 cm^3. Temperature: 20 ± 5 °C.

Evaporation of Weak Acids in Natural Aqueous Sample. It is found that ΔCA can predict the fate of weak acids in natural samples. Dew samples obtained outdoors and indoors (dew was formed by artificially cooling down the surface of the sampler) in the Autumn of 2000 and 2002−2003 were used. The results are shown in Figure 8. The pH values of dew samples, shown in Figure 8, ranged from 5.53 to 7.40. Most of the results showed lower residual ratio values than the predict ones. We then investigated the effect of each inorganic ion on the residual ratios by drying artificial droplets. Each salt of NO_3^-, SO_4^{2-}, Cl^-, Na^+, K^+, Ca^{2+}, and Mg^{2+} was added to weak acid−SO_4^{2-}−Na^+−NH_4^+ mixture solution, and the residual ratios by drying each sample solution were investigated. For example, when the effect of calcium ion was investigated, $Ca(CH_3COO)_2$−$Ca(OH)_2$−Na_2SO_4−$(NH_4)_2SO_4$ mixture was prepared. As a result, we found that the addition of calcium and /or magnesium caused lower residual ratios than hypothetical values shown in Figure 9. When the aqueous solution was concentrated, calcium and magnesium ions are also concentrated. These ions combined easily with carbonate and precipitated. As a result, ΔCA was expected to decrease. The drying experiments were performed under CO_2-free conditions, and the results are shown in Figure 9. The residual ratios completely recovered. The concentrations of calcium and magnesium in the sample were subtracted from the ΔCA calculations. The ΔCA thus calculated is defined as the "effective ΔCA". All the effective ΔCA values were lower than zero. This means that the effective ΔCA values of the horizontal axis in Figure 8 are negative. If all of the calcium and magnesium combine with carbonate ions to deposit, all vertical values in Figure 8 must be zero. However, the vertical values of some data points in Figure 8 were not zero, and therefore, in the natural sample, not all of the calcium and magnesium ions combined with carbonate ions. In Figure 8, some points are higher than the theoretically predicted line. The reason is not clear, but weak acids may form complexes as ligands or salts with low solubility.

Fate of Nitrite. Acetate and formate in solution escaped into the gas phase as acetic acid and formic acid, respectively. These

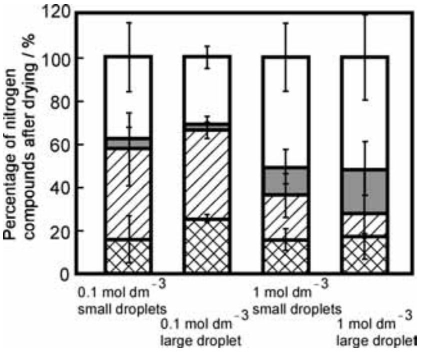

Figure 10. The fate of nitrite in artificial droplets after drying: cross hatched area, nitrite in the residue; hatched area, gaseous HONO, solid black area, NO + NO_2; white area, N_2. A mixed solution of sodium nitrite and ammonium sulfate was dried. Small droplets: 0.025 cm^3 × 40 droplets. Large droplet: 1 cm^3 × 1 droplet. The error bar shows 1 standard deviation of the three samples. Temperature: 20 ± 5 °C.

compounds were detected in the gas phase. However, not all of the nitrite was detected in the gas phase. The fate of nitrite in drying solution was investigated in more detail.

The concentration of nitrite is sometimes several hundred μmol dm^{-3} in natural dew.[19–22] The nitrite is concentrated from several mmol dm^{-3} to several mol dm^{-3} by drying. Therefore, 0.10 and 1.0 mol dm^{-3} of nitrite salt solutions were used as the initial conditions in the study of the fate of nitrite by drying. Ammonium nitrite is unstable[4] and is not available commercially. A mixture solution of sodium nitrite and ammonium sulfate was used instead of ammonium nitrite for the experiments. In the preliminary experiments, the product reproducibility was very poor when drying was carried out in a glass beaker. The droplets in the beaker separated into different sizes in each experiment. Different droplet sizes experience different drying speeds. We speculated that the drying speed affected the results. Teflon concave vessels, as shown in parts a and b of Figure 2, were used to keep one droplet in each concave hole. In order to change the drying speed, large and small droplets were prepared. There was one large droplet that was 1 cm^3 in volume, and all of the small droplets were 0.025 or 0.010 cm^3.

Figure 10 shows typical experimental results for the ratios of the fate of nitrite after drying the ammonium nitrite solutions. Residual nitrite and HONO, NO, NO_2, and N_2 were produced after drying. The amounts of N_2 shown in Figure 10 were calculated by subtracting the amounts of HONO and NO_x in the gas phase and residual nitrite from the initial amounts of nitrite (the reason for calculating the values of N_2 will be discussed below). In the case of the 0.1 mol dm^{-3} solution, gaseous HONO was the main product. It is considered that the gaseous HONO is produced by the evaporation of HONO. In the case of the 1 mol dm^{-3} solution, N_2 production was the main product. In all cases, N_2 was produced. It is considered that N_2 is produced from the decomposition of ammonium nitrite. The formation of ammonium nitrite can be expected because the solubility of sodium sulfate (21.94 g in 100 g of solution, that is, a mole fraction of 0.034)[15] is much lower than the solubility of sodium nitrite (45.9 g, 0.18)[15] and ammonium sulfate (43.3 g, 0.094),[15] and nitrite must combine with ammonium to produce solid ammonium nitrite. Ammonium nitrite is known to be unstable, and concentrated ammonium nitrite in an aqueous solution is more rapidly decomposed into N_2 and H_2O than solid ammonium nitrite (reaction i).[4] We confirmed that solid ammonium nitrite is more stable than concentrated aqueous solutions of ammonium nitrite. When an aqueous solution of a mixture of ammonium sulfate and sodium nitrite was dried very slowly at room temperature, only sodium sulfate was obtained in the salt. Solid ammonium nitrite was deposited when it was dried very rapidly at higher temperature around 120 °C. This indicates that, in Figure 10, ammonium nitrite decomposed to produce N_2 in the concentrated aqueous solution until the droplets were completely dry.

Comparing NO_2 and NO in the experiments in Figure 10, NO_2 concentrations were much higher than NO concentrations in all cases. In the NO_x measurements, the sample air was passed through a Na_2CO_3 denuder to remove HONO, and therefore, the NO_2 values do not include HONO. The carrier gas was Ar, and no oxygen was included. A blank drying test for droplets of pure water was performed, and only a trace amount of nitrogen was released when the sample dried completely. Therefore, O_2 in the pure water was also removed in the Ar flow. NO_x can be produced from eqs ii or iii.

$$3HNO_2 \rightarrow 2NO + HNO_3 + H_2O \tag{ii}$$

$$2HNO_2 \rightarrow NO + NO_2 + H_2O \tag{iii}$$

In both cases, NO must be converted to NO_2. The nitrate formation was not observed, and therefore, reaction iii could proceed. The conversion of NO to NO_2 is probably via the following reaction.

$$3NO \rightarrow N_2O + NO_2 \tag{vii}$$

N_2O was detected but could not be determined by the mass spectrometer because of the higher detection limit than the concentration of N_2O released. More research could be required to understand the productions of NO_2. In Figure 10, the effects of droplet size on the nitrite are not clearly shown because the concentrations were very high.

The fate of nitrite in drying solution at neutral and high pH that includes ammonium is expected as follows

$$NH_4NO_2(aq) \rightarrow HONO(g) + NH_3(g) \tag{viii}$$

$$2HNO_2(aq) \rightarrow NO(g) + NO_2(g) + H_2O \tag{ix}$$

$$NH_4NO_2(aq) \rightarrow N_2(g) + 2H_2O \tag{i}$$

$$NH_4NO_2(aq) \rightarrow NH_4NO_2(s) \tag{x}$$

Reaction viii is expected to obey the first-order kinetics for the nitrite or ammonium concentration. Reaction viii is reversible, but in the case of drying, the reverse reaction is negligible since the concentration of solutes in the solution increases more and more. Reaction ix is reported to be second order in the nitrite concentration.[23] Reaction i, which is a denitrification process, is reported to have third-order kinetics, due to it being first order in ammonium ion, nitrite ion, and nitrous acid concentrations, respectively (eq 1).[6–9] As the solution dehydrates, the concentrations of dissolved species increase. For example, we consider the case in which the concentrations of the compounds increases by a factor of 10, as the volume of the droplets decreases to 1/10 of the original volume. The concentrations of all of the components increase 10 times. The rate of reaction viii increases

10 times compared to the initial one at the same temperature. The rate of reaction ix increases 100 times, and the rate of reaction i increases 1000 times. If the drying speed is slow, the sample maintains a low concentration for a long time, and as a result, the most nitrite is lost by reaction viii. On the other hand, if the drying speed is fast, the concentration of nitrite increases immediately, and the production of N_2 according to reaction i proceeds before most nitrites are lost by reaction viii. The drying speed depends on the surface-to-volume ratio. When the size of the droplet is small, the drying speed is fast, and as a result, small droplets of 0.1 mol dm^{-3} produced more N_2 than the large droplet. In most of the experiments we performed, the N_2 productions in small droplets were higher than those in the large droplets. Note that if the drying speed is much faster, reaction x will be dominant, as mentioned above.

In the drying experiment on large droplets, when dry air was used as the carrier gas, brown bubbles likely consisting of N_2 and NO_x were formed in the droplet. The bubbles were broken after a certain size, concomitant with the loss of some liquid, and mass balance of all the ions could not be obtained. Therefore, Ar was used as a carrier gas. When Ar was used as a carrier gas, the N_2 produced by reaction i was dissolved in the droplet and escaped into the carrier gas flow without forming bubbles. The use of Ar did not significantly alter the fate of the salts when compared to the use of dry air in the case of small droplets.

Under our experimental condition, the determination of N_2 was very difficult because, in order to dry the sample, dry air flow was required. The nitrogen released was diluted by the air flow. The quantitation limit ($S/N = 10$) of N_2 for the mass spectrometer was 21 ppmv. The maximum concentration of N_2 released from a 1 mol dm^{-3} sample was about 100 ppmv, and N_2 released only from a 1 mol dm^{-3} sample could be determined (Figure S1 in Supporting Information). The concentrations of nitrite in the residue, NO + NO_2, HONO, and N_2 determined were 194.3, 260.8, 254.6, and 271 μmol, respectively. In total, 980 μmol was obtained compared to the initial concentration of 1000 μmol. N_2O produced by reaction iv amounted to less than 1% of N_2. The exact amount could not be determined. N_2O may have been produced, but the amount could have been very low compared to other compounds shown in Figure 10, and therefore, N_2O contributions are ignored in Figure 10. The oxidation of nitrite to nitrate is negligibly slow[10] in the pH range of the experiments in Figure 10, and in fact, nitrate was not detected by ion chromatography. The contributions of other compounds were negligibly small, and therefore, only HONO, NO, NO_2, and N_2 were discussed in the present study. Furthermore, in the experiment with 0.1 mol dm^{-3}, the N_2 concentration could not be determined because the concentrations of N_2 released were lower than the detection limit. Therefore, the calculated values of N_2 were used in the present study.

Figure 11 shows the cumulative concentration of HONO released from the dehydrating sample with time. In the case of 1 mol dm^{-3} samples, the concentrations were very high supporting reaction i, and the amounts of HONO released from reaction viii were small. In the case of small droplets of 0.1 mol dm^{-3}, the time needed for the sample to reach a high concentration was short, and therefore, reaction i proceeded before large amounts of HONO were released via reaction viii. As a result, the amounts of HONO released were very small, and nitrogen production was dominant. When the large droplet of 0.1 mmol dm^{-3} was dried, there was enough time for HONO to evaporate according to reaction viii. As a result, more HONO was released before all of the water had evaporated. The dominant process for nitrite depends on the concentrations of reactants and the drying speed as well.

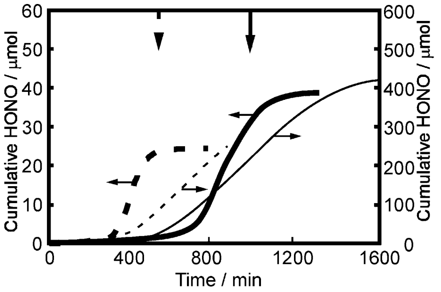

Figure 11. Cumulative concentration of HONO released by drying with time. The experimental conditions were the same as those in Figure 10. Bold broken line: small droplets of 0.1 mol dm^{-3}, bold solid line: large droplet of 0.1 mol dm^{-3}, narrow broken line: small droplets of 1 mol dm^{-3}, narrow solid line: large droplet of 1 mol dm^{-3}. The arrows of broken and solid lines are the time when the small droplets and large droplets, respectively, were dry. The dryness was confirmed by the signal intensities of $m/e = 18$ of the mass spectrometer. The vertical scales for the 0.1 and 1.0 mol dm^{-3} samples are indicated in the left and right axes, respectively.

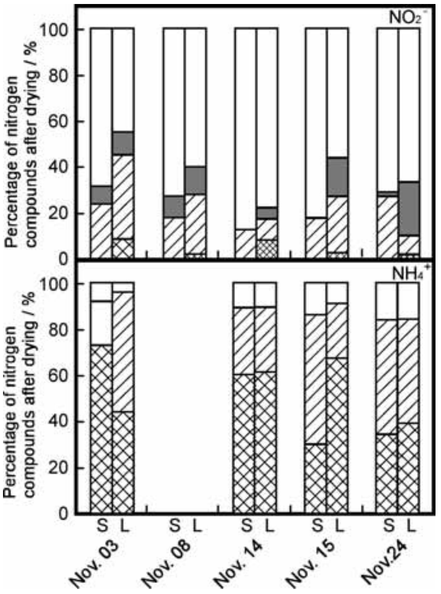

Figure 12. The fate of nitrite in the natural dew droplets after drying. Droplets were artificially produced by drying: cross hatched lines, nitrite in the residue; hatched lines, gaseous HONO, gray areas, NO + NO_2; white areas, N_2. S indicates the 100 small droplets (0.010 cm^3), and L indicates the large droplet (1 cm^3). Temperature: 17 ± 5 °C. The dew samples were collected on November 3, 8, 14, 15, and 24, in 2007. The vertical axis indicates the percentage of fate of nitrite, that is, percent ratio of equivalent of nitrogen compounds produced to the initial nitrite (upper graph) or the initial ammonium (lower graph). The concentrations of nitrite and ammonia were as follows: Nov 3, [nitrite] = 43.2 μmol dm^{-3} and [NH_4^+] = 196.4 μmol dm^{-3}; Nov 8, [nitrite] = 41.6 μmol dm^{-3} and [NH_4^+] = 287.5 μmol dm^{-3}; Nov 14, [nitrite] = 48.5 μmol dm^{-3} and [NH_4^+] = 258.2 μmol dm^{-3}; Nov 15, [nitrite] = 59.1 μmol dm^{-3} and [NH_4^+] = 247.8 μmol dm^{-3}; Nov 24, [nitrite] = 113.1 μmol dm^{-3} and [NH_4^+] = 411.1 μmol dm^{-3}. The other concentrations in the dew, gaseous HONO, and the residual salts are shown in Table S1 (Supporting Information).

Figure 12 shows the ratios of the fate of nitrite after drying natural dew collected on the roof of the Osaka Prefecture University in Sakai, Japan. There were 100 small droplets of 0.01 cm^3 and 1 large, 1 cm^3 droplet. In Figure 12, S denotes small droplets and L denotes the large droplet. The dominant product was N_2. The N_2 concentrations presented are calculated

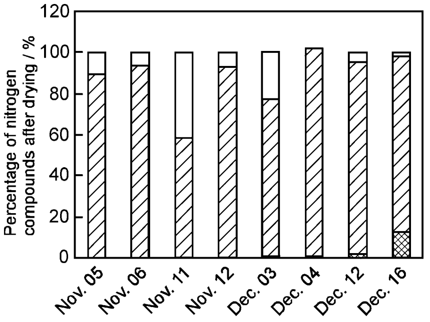

Figure 13. The fate of nitrite in the natural dew droplets after drying. The natural dew was dried without any treatment. cross hatched lines, nitrite in the residue; hatched lines, gaseous HONO; black area, NO + NO_2; white area, N_2. The two Teflon plates were used to collect dew samples. The dew formed on one plate was collected, and the ion concentrations were determined. The dew on the other plate was moved to the laboratory without any treatment, and then dew was dried with pure, dry air. The dew samples were collected on the campus of Osaka Prefecture University in November and December 2008. Concentrations of nitrite and ammonium and the volume of the dew samples were as follows: Nov 5, [nitrite] = 20.6 μmol dm^{-3}, [NH_4^+] = 164.6 μmol dm^{-3}, dew volume = 8.5 cm^3; Nov 6, [nitrite] = 41.5 μmol dm^{-3}, [NH_4^+] = 138.9 μmol dm^{-3}, dew volume = 14.2 cm^3; Nov 11, [nitrite] = 45.8 μmol dm^{-3}, [NH_4^+] = 207.2 μmol dm^{-3}, dew volume = 4.7 cm^3; Nov 12, [nitrite] = 33.5 μmol dm^{-3}, [NH_4^+] = 184.3 μmol dm^{-3}, dew volume = 9.1 cm^3; Dec 3, [nitrite] = 38.3 μmol dm^{-3}, [NH_4^+] = 64.9 μmol dm^{-3}, dew volume = 18.6 cm^3; Dec 4: [nitrite] = 38.6 μmol dm^{-3}, [NH_4^+] = 108.5 μmol dm^{-3}, dew volume = 13.9 cm^3; Dec 12, [nitrite] = 44.5 μmol dm^{-3}, [NH_4^+] = 135.6 μmol dm^{-3}, dew volume = 17.6 cm^3, Dec. 16: [nitrite] = 46.1 μmol dm^{-3}, [NH_4^+] = 84.6 μmol dm^{-3}, dew volume = 13.3 cm^3. The other concentrations in the dew, gaseous HONO and the residual salts, are shown in Table S2 (Supporting Information).

values. The mass spectrometer detected an increase in the N_2 signal ($m/z = 28$) in the same time period of drying as in the results in Figure 10; however, the nitrogen concentrations measured were much higher than the total mass balance. This is due to the fact that N_2 concentrations were much lower than the detection limit. Furthermore, the nitrate production by oxidation of nitrite with dissolved oxygen can be neglected because the reaction rate was very slow at neutral and alkaline pHs.[10] In most cases, the pH of dew was higher than 5, and thus the oxidation of nitrite to nitrate is negligible. Therefore, it is assumed that the greatest fraction of the difference in the concentration of initial nitrite and the concentrations of residual nitrite, NO_x, and HONO is N_2. The amounts of N_2 in the results of the small droplets in Figure 12 were larger than those in the large droplet. These results were similar to those in Figure 10. Initial ammonium concentrations were very high compared to nitrite. It was not clear how to attribute differences in the production of N_2, but the N_2 concentration in the small droplets was slightly higher than that in the large droplet. In considering the fate of solutes in natural dew, there are more unknown factors such as the composition of the dew and production of deposition that obscure full understanding. Furthermore, the sizes of real dew droplets also vary widely and depend on meteorological conditions, characteristics of the surface on which the dew is formed,[24] etc. Natural dew was then allowed to form on a Teflon sheet at the Osaka Prefecture University in Sakai, Japan, in 2008, and the sheet was transferred in the laboratory without collecting the dew. The dew was dried under a dry air flow. Figure 13 shows the ratios of the fate of nitrite after drying. The sizes of droplets were much smaller than 0.01 cm^3, and the total volumes of dew samples were much larger than 1 cm^3. As shown in Figure 13, the dominant product was HONO. This was probably due to the larger total volume of the dew droplets or higher relative humidity, which caused a longer drying time (ca. 24 h) than the results in Figures 10 and 12 (ca. 9 h for small droplets and ca. 17 h for large droplets). In most cases, N_2 was produced. Further studies are required in order to estimate the amount of N_2 produced. The fact that N_2 is produced by drying dew is very important. If dew forms and absorbs HONO in the atmosphere, the total amount of nitrogen oxides in the environment decreases due to the chemical denitrification reaction by drying.

Effect of Drying Dew on Ozone Concentration. HONO is a main source of OH radicals in the morning, and OH radicals influence the ozone concentration.[2] Therefore, if the HONO concentration in the atmosphere decreases in the morning, the ozone concentration is expected to decrease. Dew formation and disappearance may remove and decompose HONO or nitrite. It is expected that dew formation affects the ozone concentration. Figure 14 shows an increase in the ozone concentrations in the morning, which were measured at the Kanaoka Air Pollution Monitoring Station in Sakai-City, Japan,[25] with and without formation of dew. The Kanaoka Air Pollution Monitoring Station is located about 3 km from the dew sampling point. The minimum concentration of ozone from 6 to 11 a.m. on each day is set to zero. Deciding on which days the dew formed was based on our sampling data. Deciding on which days the dew did not form was determined as follows: (I) exclude the dew sampling days, (II) exclude the rainy and cloudy days from the rainfall and the solar radiation data,[25] and (III) exclude days in which the time profile of the ozone data was atypical, such as negligible variation in the ozone concentration. As shown in parts a−g of Figure 14, in most cases, the ozone concentrations increased slower when the dew formed than on days when the dew did not form, despite the fact that the days when dew was formed had generally weaker wind and finer weather. The ozone concentration is influenced by the many other factors such as solar radiation, wind speed, and NO_x and hydrocarbon concentrations. Therefore, in order to confirm the relevance of the results of Figure 14a−g, increases in the ozone concentration were calculated by a CBM-IV box model simulation[26] under the following three conditions: (I) the dew forms at night and absorbs all HONO in the atmosphere, and then all nitrite in the dew is decomposed by reaction i; (II) no dew forms at night, and HONO produced at night remains in the morning; and (III) the dew forms at night and absorbs all HONO in the atmosphere, and then all nitrite in the dew is released into the atmosphere as HONO within 2 h after sunrise. All other conditions were assumed to be the same in the three cases. In this model, the HONO concentration released from the exhaust gas of vehicles is assumed to be 2.3% of NO_2.[27] The result is shown in Figure 14h. Clearly, the ozone concentration increases slower when the dew forms than that when the dew does not form. Furthermore, it is found from the calculation that about 20% of ozone concentration in case I is reduced compared to case II at 11 a.m. In the real environment, the meteorological conditions vary along with the dew formation. The most important difference could be the altitude of the inversion layer. Dew forms when there is no wind and clouds, and the altitude of the inversion layer is low. With no wind and clouds, photochemical activity is very high and the concentration of pollutants is increased. However, during the formation of dew, the ozone concentration decreases in the calculation. Furthermore, if the NO concentration increases when the dew forms, ozone is decreased by titration with NO and slower increase in the ozone concentration is expected. However, in the calculation,

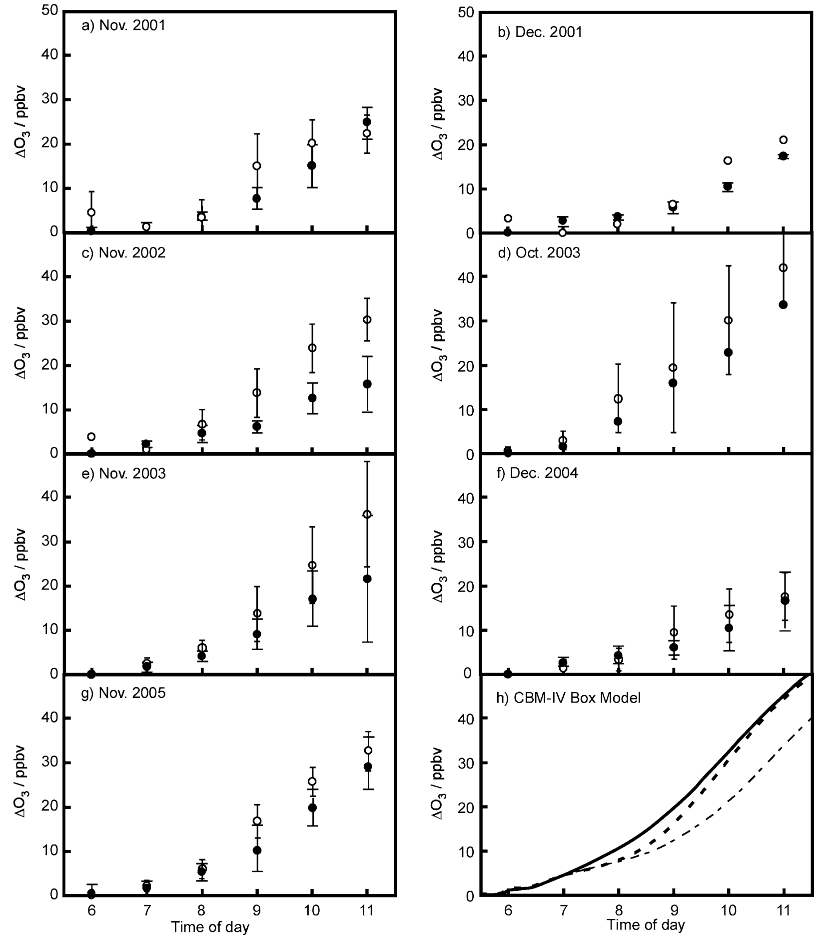

Figure 14. The increase in the ozone concentration in the morning on days with and without dew formation at the Kanaoka Monitoring Station:[25] black circles and horizontal wide error bars (1 σ), ozone concentration when dew formed; white circles and horizontal narrow error bars (1σ), ozone concentration when dew did not form; (a) Nov 2001, 10 data (dew events) and 4 data (no dew events); (b) Dec 2001, 6 data (dew) and 3 data (no dew); (c) Nov 2002, 5 data (dew) and 5 data (no dew); (d) Oct 2003, 3 data (dew) and 4 data (no dew); (e) Nov 2003, 6 data (dew) and 4 data (no dew); (f) Dec 2004, 9 data (dew) and 4 data (no dew); (g) Nov 2005, 13 data (dew) and 4 data (no dew); (h) calculation results from the CBM-IV box model.[26] The concentrations of HONO emitted from vehicles and other sources is assumed to be 2.3% of the NO_2 concentration emitted:[27] dash dot lines, all HONO was absorbed in the dew and decomposed to produce N_2; solid line, no dew formed; dashed line, all HONO was absorbed in the dew and emitted into the atmosphere from the dew within 2 h from sunrise. All the other conditions in the calculations were the same. The all ozone data used in the Figure are shown in Table S3 (Supporting Information).

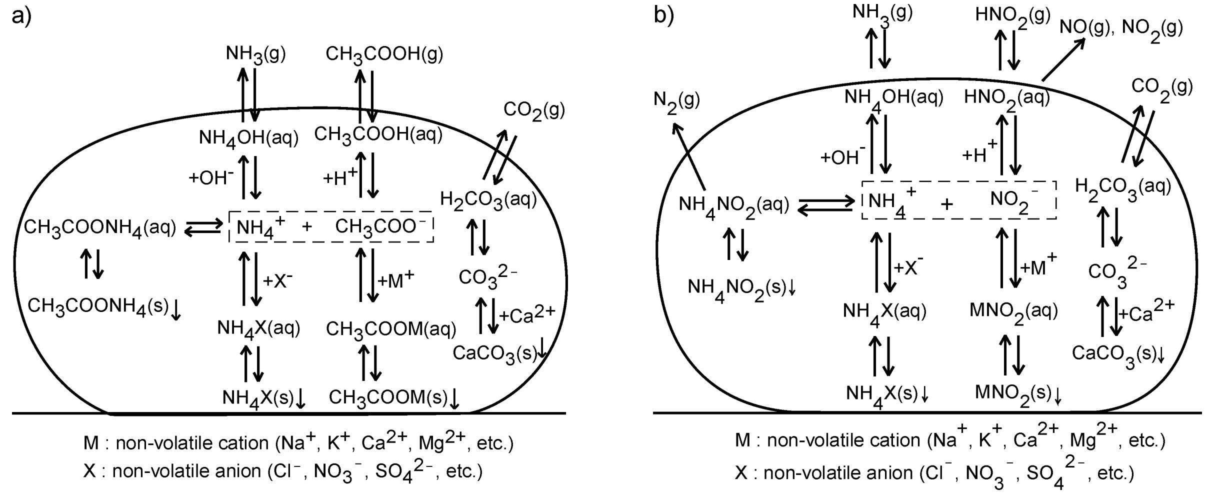

Figure 15. Schematic images of the fate of drying salt solutions: (a) The case of acetate as one example of a general salt. (b) The case of nitrite, s, aq, and g indicate solid, aqueous, and gaseous, respectively.

it is assumed that the NO concentrations are the same regardless of dew formation. If we assume that a low inversion layer occurs when dew is formed, the calculation predicts a much lower ozone concentration. The results in Figure 14h did not include differences in the altitude of the inversion layer and showed only the effect of HONO, that is, the dew formation. In the natural environment, it is reported that the HONO concentration at night actually decreases due to dissolution into the dew.[3] We also observed a decrease in the HONO concentration at night, from ca. 3 ppbv at midnight to less than 1 ppbv just before sunrise in Sakai City, Japan. However, even if dew forms, the ozone concentration is unchanged when all nitrite in the dew evaporates as HONO, as shown in Figure 14h. In the real environment, not all the nitrite in the dew evaporates as HONO or transforms to N_2. Because the ratio of N_2 produced from the reaction of nitrite with ammonium depends on various conditions, further studies are required to clarify the effect of dew formation on ozone concentration. It is concluded that the dew could decrease the ozone concentration.

The global warming in recent years will cause aridification of the environment.[28] Dew formation in Sakai City, Japan, was found to decrease. While the formation of dew has not been continuously monitored, it is reported that frost events have also decreased.[28] A decrease in dew formation due to aridification could raise the ozone concentration. Further detailed experiments and observations, especially those involved in the formation and disappearance of dew, are required.

Conclusions

The fate of salts in drying aqueous solution can be summarized as follows.

1. In acidic solutions, the total concentration of anions, except OH^-, is higher than that of the cations, except H^+, and excess anions combine with protons and evaporate if they are volatile. In alkaline solutions, the total concentration of cations, except H^+, is higher than that of anions, except OH^-, and excess cations, such as ammonium, combine with OH^- and evaporate if they are volatile.

2. Under neutral and alkaline conditions, volatile anions remain as a salt depending on the ΔCA value.

$$\Delta CA = \frac{\sum[\text{nonvolatile cation}]_i - \sum[\text{nonvolatile anion}]_i}{\sum[\text{volatile anion}]_i}$$

Here, the nonvolatile cations include Na^+, K^+, Ca^{2+}, and Mg^{2+}, and the nonvolatile anions include SO_4^{2-}, NO_3^-, and Cl^-. The volatile anions include NO_2^-, $HCOO^-$, and CH_3COO^-. The unit of concentrations of ions is mol dm^{-3}, and those of bivalent ions must be doubled.

3. The ammonium ion remains as a salt, depending on the ΔAC value, where

$$\Delta AC = \frac{\sum[\text{nonvolatile anion}]_i - \sum[\text{nonvolatile cation}]_i}{\sum[\text{volatile cation}]_i}$$

4. In the case of nitrite under neutral and alkaline conditions, its fate will depend not only on ΔCA but also on the drying speed. Whether nitrite remains as a salt or not depends on ΔCA. The fate of nitrite is N_2 production by reacting with ammonium, NO, and NO_2 production, evaporation as HONO or formation of salt depending on the drying speed. The temperature could also affect these relative reaction rates.

5. In the case of other reactive species, it is expected that several reactions occur depending on concentration effects and reaction rates.

6. When drying speed is extremely fast, almost all the volatile ions will remain as salts.

Finally, schematic images of the fate of salt in drying solutions are summarized in Figure 15a) for general salt (ammonium acetate is used as a representative of the general salt) and Figure 15b) for ammonium nitrite.

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Supporting Information Available: Figure showing mass signal change and tables showing ion concentrations of natural dew samples and residual salts after drying and ozone concentrations on days with dew and no dew. This material is available free of charge via the Internet at http://pubs.acs.org.

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