Effect of Inorganic Salts on the Volatility of Organic Acids

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Supporting Information

ABSTRACT: Particulate phase reactions between organic and inorganic compounds may significantly alter aerosol chemical properties, for example, by suppressing particle volatility. Here, chemical processing upon drying of aerosols comprised of organic (acetic, oxalic, succinic, or citric) acid/monovalent inorganic salt mixtures was assessed by measuring the evaporation of the organic acid molecules from the mixture using a novel approach combining a chemical ionization mass spectrometer coupled with a heated flow tube inlet (TPD-CIMS) with kinetic model calculations. For reference, the volatility, i.e. saturation vapor pressure and vaporization enthalpy, of the pure succinic and oxalic acids was also determined and found to be in agreement with previous literature. Comparison between the kinetic model and experimental data suggests significant particle phase processing forming low-volatility material such as organic salts. The results were similar for both ammonium sulfate and sodium chloride mixtures, and relatively more processing was observed with low initial aerosol organic molar fractions. The magnitude of low-volatility organic material formation at an atmospherically relevant pH range indicates that the observed phenomenon is not only significant in laboratory conditions but is also of direct atmospheric relevance.

INTRODUCTION

The chemical and physical properties of atmospheric aerosol particles affect their ability to serve as cloud condensation nuclei (CCN), thus influencing cloud properties and lifetime and Earth’s radiative balance. Organic compounds explain a large fraction of aerosol mass in various environments. There are thousands of different organic compounds in the atmosphere, either directly emitted from anthropogenic and biogenic sources or formed via various pathways in the gas or particulate phase. Organics are shown to contribute to the growth of nanoparticles (<100 nm in diameter), even the smallest ones. The condensing organic species must have very low volatilities in order to overcome the Kelvin effect and stay in the particulate phase. Concerning this, there is evidence of effectively nonvolatile organic material in atmospheric nanoparticles. The formation of nonvolatile organics can occur either in the gas phase by oxidation of initially volatile species or in the particulate phase e.g. via organic salt formation or oligomerization. Particulate-phase chemical reactions in mixtures of organic acids with amines, and with monovalent and divalent inorganic salts, have been reported to lead to formation of low-volatility organic material.

While aerosol processing within organic acid/divalent inorganic salt mixtures has been shown to significantly alter aerosol properties such as hygroscopicity and volatility, in recent studies notable organic salt formation has been observed also in mixtures of weak organic acids with monovalent salts NaCl and NaNO₃. The observed phenomenon is linked to chloride/nitrate depletion from the aerosol surface due to evaporation of HCl/HNO₃ upon drying and is considered to be important for small, submicron sized, particles. Laskin et al. demonstrated that gas-particle partitioning of HCl and possible aerosol processing in the mixed aerosol is not restricted only to dry particles but can also occur in wet conditions with atmospherically relevant concentrations of NaCl. Results by Zardini et al. support this conclusion. They found that the evaporation behavior of aqueous succinic acid/NaCl aerosol could not be predicted correctly assuming no interaction between these compounds. Recently also the volatility of deliquesced succinic acid/ammonium sulfate (denoted here as AS) aerosol has been investigated and, as in the work of Zardini et al., a notable discrepancy between the observed and modeled aerosol evaporation was found. The observations indicate lowering of the activity coefficient of succinic acid in the aerosol by AS addition or point to yet-unknown aerosol processing, e.g. formation of low-volatility organic salts, organosulfates or -nitrates, that enhances succinic acid partitioning.

While data on the saturation vapor pressures of the least volatile atmospheric organics at ambient temperatures are scarce due to experimental limitations, the volatility of
dicarboxylic acids has been investigated widely with several techniques. These techniques provide information on aerosol volatility by probing changes in size/volume of aerosol particle population in gas-phase composition via mass spectrometry using thermal desorption or Knudsen cell based methods. The variation in saturation vapor pressures ($p_{sat}$) and vaporization enthalpies ($\Delta H_{vap}$) of organic acids reported in the previous studies is large—$p_{sat}$ varies over 2 orders of magnitude, while differences in $\Delta H_{vap}$ can be up to 50 kJ mol$^{-1}$. 

In this work we present a novel method for quantifying the volatility of aerosol organics and demonstrate its application for dicarboxylic acids. This method, for the first time, combines data from a TPD-CIMS (temperature-programmed desorption chemical ionization mass spectrometer) with the kinetic model of Rippinen et al. describing aerosol evaporation in a heated flow tube. Unlike the previously used thermal desorption methods, with our setup, the aerosol is vaporized at atmospheric pressure and the changes in aerosol gas-phase composition are monitored online. The presented setup has been used in other studies to investigate general evaporation behavior of aerosol mixtures, e.g. for indirect observations of effectively nonvolatile oxalates in aerosol particles. However, no quantitative information on the saturation vapor pressures of the aerosol constituents based on this technique has been previously reported.

With the presented approach, we also investigated the formation of low-volatility organics in mixtures of the organic acids with NaCl or AS upon drying. The experiments were performed using succinic acid and oxalic acid, which are among the most abundant dicarboxylic acids in the atmospheric aerosol, as well as tri- and monocarboxylic acids (citric acid and acetic acid). Our technique allows us, for the first time, to quantify the amount of low-volatility organic material formed in these aerosol mixtures, and its dependence on the mixture properties and atmospheric conditions. Our main goals are to (1) introduce a novel method for estimating the vapor pressures of pure component organic acids, (2) investigate the effect of inorganic salts on the volatility of the organic acid, (3) quantify the magnitude of the formation of low-volatility organics in the studied mixtures, and (4) assess the atmospheric relevance of our observations.

# MEASUREMENTS

**Aerosol Generation.** Submicron aerosol particles were generated using an atomizer (TSI 3076). Aqueous solutions were prepared by mixing the organic acid—oxalic acid (OA, Fisher Scientific), succinic acid (SA, Acros Organics), citric acid (CA, Sigma-Aldrich), or acetic acid (AA, Sigma-Aldrich)—with sodium chloride (NaCl, Fisher Scientific) or ammonium sulfate (AS, Sigma-Aldrich) in deionized water (Millipore). All the used organic acids and inorganic salts were high in purity ($\geq99\%$). Solutions with organic molar fraction in the total solute ($F_{org}$) of 0.2–0.5 were tested (Table 1). All the studied organic acids were mixed with NaCl. SA and OA were also mixed with AS.

The concentrations of the atomized solutions were adjusted to match the sensitivity of the instrument—less concentrated solutions were used for succinic acid and oxalic acid due to high sensitivity of the CIMS to these compounds (see Tables S1–S4). After the particle generation, the aerosol was dried using a diffusion dryer filled with silica gel beads. With a combination of a dryer and dry dilution stream of N$_2$, RH was kept below 12% during an experiment to ensure the crystalization of the particles and minimize the potential condensed-phase residual water effects on particle evaporation. After drying, prior to introducing the aerosol to the TPD-CIMS, the dry particle size distribution was determined with a TSI SMPS (scanning mobility particle sizer). The lower cutoff size of the SMPS was 17 nm and time resolution 2 min.

**TPD-CIMS.** TPD-CIMS, a combination of a continuous heated flow tube and a chemical ionization mass spectrometer, probes changes in aerosol gas-phase composition upon heating. Since effectively nonvolatile aerosol compounds (evaporating above 180 °C) cannot be detected with our setup, when it comes to aerosol mixtures of organic acid and inorganic salt, only evaporation of the organic acid is detected. Technical details of the setup used in this study can be found in previous publications.

Volatilized aerosol material was ionized via clustering with negative parent ion ($I^-$, m/z 127.0 ± 0.2) and the mass to charge ratios of the ion clusters were detected with a quadrupole mass spectrometer (Extrel CMS). Peaks related to the studied organic acid in the CIMS spectra were determined by comparing background spectra to aerosol spectra. Due to small amounts of contamination in the tubing or in the CIMS itself, a low background signal of the traced mobility particle sizer. The background signal was determined before every experiment and removed from the traced signal prior to further data analysis.

Chemical ionization enables the detection of relatively large organic molecules as a whole—typically as a cluster of the parent ion—and thus, no detailed information on the fragmentation patterns of molecules is necessarily needed. Many large organic molecules withstand volatilization at moderate temperatures ($\leq150$ °C) and ionization and thus are detected without fragmentation via TPD-CIMS. However, in this study citric acid was not detected as one but in several fragmented peaks instead (see the Supporting Information, SI). Also, decomposition of oxalic acid occurred (see SI).

The heating temperature was increased stepwise from room temperature to around 100 °C (mean inlet temperature of the flow tube) depending on the volatility of the traced compounds. A maximum of seven different temperatures were used. At each temperature, the monitored gas-phase signal of interest was allowed to stabilize before moving on to

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<th>Table 1. Organic Acid/Inorganic Salt Mixtures$^a$</th>
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$^a$Organic molar fraction in the total solute ($F_{org}$) consisting of an organic acid and an inorganic salt (sodium chloride (NaCl) or ammonium sulfate (AS)) as well as the number of individual experiments performed in each group.
the next heating temperature. In all cases the traced signal responded quickly, within 1 min, to the changes in heating temperature, and the stabilization of the signal took around 30–90 min.

The residence time in the heating tube was around 0.7 s, which is a typical residence time used in aerosol volatility measurements in both laboratory and in the field. However, as Riipinen et al. showed, aerosol might not reach thermodynamic equilibrium in a flow tube if too short residence times are used. Indeed, a kinetic calculation suggests that in this study full evaporation of pure organic acid aerosol could be reached, even at room temperature, with long enough residence times (around 17 s for SA and 40 s for OA). In order to obtain relevant information on the volatility of aerosol constituents, we therefore apply the kinetic model of Riipinen et al., which accounts for the nonequilibrium conditions inside a flow tube. Prior to this study, the volatility of aerosol constituents has been analyzed using TPD-CIMS data alone with an assumption of gas-particle phase equilibrium in the flow tube (Clausius–Clapeyron relation). This approach gives a low-end estimate of ΔH_vap if the assumption does not hold up.

### Modeling

**Kinetic Evaporation Model.** Aerosol evaporation monitored through changes in aerosol gas-phase composition with the TPD-CIMS can be further investigated by applying the kinetic evaporation model developed by Riipinen et al. The model provides time-dependent information on multicomponent aerosol evaporation inside a heated flow tube (length, L), therefore, accounting for the effect of residence time on the evaporation process. Aerosol, initially at T_0 (here room temperature), is brought to a higher temperature, T. Aerosol is allowed to evaporate at T for residence time t. Time-dependent evaporation of the aerosol is obtained by solving mass transfer equations of a monodisperse aerosol population with the total mass concentration corresponding to the experimental conditions. Changes in both particulate and gas phase mass concentrations are determined. Other dynamical processes, such as coagulation and nucleation, are not accounted for.

Mass flux I_i of an aerosol constituent i from the particle can be written as

$$I_i = \beta_{ni}(Kn, \alpha_m) \frac{2\pi d_i p M_i D_i}{RT} \ln \left( \frac{1 - \frac{p^i}{P}}{1 - \frac{p}{P}} \right)$$

where β_{ni}(Kn, α_m) is mass transfer correction factor and a function of the Knudsen number Kn and mass accommodation coefficient α_m. d_i is particle diameter, p is ambient pressure, M_i and D_i are molar mass and diffusion coefficient of aerosol compound i, R is the gas constant, p^i and p are partial pressures of compound i at the particle surface and far from the particle, respectively. Partial pressure (assumed to be equilibrium vapor pressure, p_{eqi}) of compound i at the particle surface can be expressed as

$$p^i(T) = p_{eqi}(T) = X_i p_{sat} \exp \left( \frac{4 M_i \sigma}{RT(1 - \beta_{eff} P)} \right)$$

where X_i is the molar fraction of compound i in the aerosol (here F_{eq} for dry aerosol), γ is the activity coefficient of compound i, p_{sat} is the saturation vapor pressure of pure compound i over flat surface, and the exponential term is the Kelvin effect, where σ and ρ are particle surface tension and density that are calculated as mole and mass fraction weighted averages of aerosol constituents, respectively.

Partial pressure of compound i far from the particle can be written as

$$p(T) = \frac{c_i RT}{M_i}$$

where c_i is the gas phase concentration of compound i. To initialize the differential equation solver, initial particle mass (/mass concentration) and initial mass concentration of i in the gas phase are needed. Total particle mass concentration was determined from the SMPS data. Gas phase concentrations of the evaporating compounds were assumed to be zero in the beginning. Model input parameters—chemical properties of the studied organics (OA and SA) and information on their particle size distributions—are given in Table 2.

### Evaporation of Organic Acids from Pure and Mixture Aerosols.** Quantitative information on the volatility of the studied organic acids was obtained by combining TPD-CIMS data with the kinetic evaporation model. For pure organic acids,

| Table 2. Properties of Pure Oxalic Acid and Succinic Acid Aerosol As Input Parameters for the Evaporation Model |
|---|---|---|---|
| | unit | oxalic acid | succinic acid |
| molar mass, M | g mol⁻¹ | 90.03 | 118.09 |
| density, ρ | kg m⁻³ | 1900 | 1566 |
| surface tension, σ | N m⁻¹ | 0.15 | 0.125 |
| diffusion coefficient, D | 10⁻⁶ m² s⁻¹ | 7.5 | 10⁻⁶ |
| parameter for the calculation of T-dependence of D, μ | | 1.75 | 1.75 |
| saturation vapor pressure, p_{sat} | Pa | 10⁻⁴ | 16.7–26 |
| enthalpy of vaporization, ΔH_vap | kJ mol⁻¹ | 76 | 62 |
| mass accommodation coefficient, α_m | | 1 | 1 |
| activity coefficient, γ | | 1 | 1 |
| particle volumetric diameter, d_p | nm | 86–117 | 38–47 |
| particle total mass, m_{tot} | μg m⁻³ | 3–17 | 0.02–0.10 |

*The surface tension of oxalic acid was estimated from other dicarboxylic acid data in the work of Bilde et al. (rounded average of all the data given). Bilde et al. and Poling et al. Vapor pressures and vaporization enthalpies were obtained from the evaporation model by minimizing the difference between measured and modeled evaporation of organic acid. Given are the averages of all experiments (four experiments for OA and five for SA). In parentheses the average of maximum and minimum values is given. Minimum and maximum p_{sat} and ΔH_vap were determined by testing their sensitivity for organic properties (σ, D) and aerosol mass (m_{tot}) as well as the measured CIMS signal. Properties of the aerosol size distribution were obtained from the SMPS. Given are the range of median geometric mean diameters and mean mass concentrations of all the experiments. In the analysis a diameter–mass pair specific for an individual experiment was used.*
an evaporation curve similar to the one observed was reproduced with the model. This was done by searching the optimal \( p_{\text{sat}} \) and \( \Delta H_{\text{vap}} \) pair that minimizes the difference between the measured and modeled normalized aerosol evaporation data (Figure S1).

A two-component model approach was used to estimate the amount of effectively nonvolatile organic material formed in organic acid/inorganic mixtures upon drying. The aerosol was assumed to compose of two types of material—semivolatile and nonvolatile. The semivolatile aerosol fraction was given the properties of the organic acid (SA/OA) and the nonvolatile fraction—including both inorganic salt and effectively nonvolatile organic material—was given the properties of the corresponding inorganic salt, for simplicity. This assumption regarding the properties of the nonvolatile aerosol fraction does not significantly affect the results (see SI). The evaporation model searched for the optimal combination of the initial molar fraction of the semivolatile component (/nonvolatile component) and its enthalpy of vaporization to reproduce, with the modeled pure component organic acid evaporation data, the observed relative difference between the CIMS signals (mixture vs pure) (Figure 1). The obtained initial semivolatile organic molar fraction of dry particle (\( F_{\text{org,model}} \)) was compared to the known solute organic fraction in the aqueous aerosol (\( F_{\text{org}} \)). Lower \( F_{\text{org,model}} \) compared to \( F_{\text{org}} \) indicates organic salt formation or other aerosol processing converting organic acid to effectively nonvolatile organic matter. Here it was assumed that—if no aerosol processing occurs—\( F_{\text{org}} \) is the same before and after drying (residence time of around 5 s between atomizer and vaporization flow tube). This assumption is only reasonable for low-volatility organic species. Succinic acid and oxalic acid were deemed low-volatility enough especially since low \( F_{\text{org}} \) values were used (cf. Raoult’s law) (see the SI). The fraction of nonvolatile organic material of the initial organic molar fraction (NVF, “non-volatile fraction”) was thus estimated as

\[
\text{NVF} = \frac{F_{\text{NVorg}}}{F_{\text{org}}}
\]

where \( F_{\text{NVorg}} = F_{\text{org}} - F_{\text{org,model}} \) is the molar fraction of the nonvolatile organic material in the dry aerosol.

When analyzing the mixtures, pure organic acid data obtained with the same CIMS settings as the aerosol mixture data were applied (see Tables S3–S4). This was done to ensure that the correspondence between the CIMS signal and the modeled evaporated mass was the same between experiments. When investigating normalized aerosol evaporation, i.e. the volatility of pure organic acids, this was not an issue. Uncertainty analysis was performed by testing the sensitivity of the optimized parameters to changes in the model input parameters. The following model parameters were varied: aerosol mass (±standard deviation), surface tension (±0.1 N m\(^{-1}\)), and diffusion coefficient (±10%). The uncertainty in the CIMS signal was also included. Not only the noise in the raw CIMS signal, but also some additional perturbation was added to the signal at all \( T \) to take into account the potential for subjective error in the data analysis, as well as possible effects of excess water in the aerosol and further aerosol evaporation after the heated inlet (see the SI). By testing different combinations of the parameters included in the uncertainty analysis, the maximum and minimum \( p_{\text{sat}} \) and \( \Delta H_{\text{vap}} \) (one component modeling) and \( F_{\text{org,model}} \) (two component modeling) were obtained.

## RESULTS AND DISCUSSION

### Evaporation of Pure Organic Acids

Qualitative differences in the volatilities of the studied organic acids were investigated by analyzing the TPD-CIMS data (see Figure SS). Acetic acid aerosol was found to be completely volatilized already at room temperature since the traced signal of acetic acid (\( 1^-\text{C}_2\text{H}_4\text{O}_2 \)) increased notably from background at room temperature and did not show any significant changes when heating was added. This observation is in agreement with high \( p_{\text{sat}} \) values of acetic acid (roughly 10\(^3\) Pa).\(^{38}\) On the contrary, pure citric acid aerosol was observed to be of very low volatility—notable aerosol evaporation only occurred above temperatures of around 60 °C. High evaporation temperatures of pure citric acid aerosol have also been reported by Tritscher et al.\(^{40}\) Pure oxalic acid and succinic acid aerosols were partly in the gas phase already at room temperature, and complete particle evaporation was reached around 55 °C for OA and around 75 °C for SA with a residence time of 0.7 s.

Since acetic acid was observed to be completely in the gas phase already at room temperature, its \( p_{\text{sat}} \) and \( \Delta H_{\text{vap}} \) could not be reliably determined with the optimization method. In addition, the \( p_{\text{sat}} \) and \( \Delta H_{\text{vap}} \) of citric acid were uncertain since citric acid was detected in the CIMS as several molecule fragments and significant thermal degradation was observed (Figure SS). However, a rough estimate was obtained for citric

![Figure 1. Method for determining \( F_{\text{org,model}} \) and \( \Delta H_{\text{vap}} \) of an organic acid in an inorganic salt mixture—example case (OA/NaCl, \( F_{\text{org}} = 0.2 \) in the atomized solution). (a) Optimal \( F_{\text{org,model}} \) and \( \Delta H_{\text{vap}} \) pair found by minimizing the difference between the ratios (mixture vs pure) of (b) observed CIMS signals and (c) modeled evaporated masses. Red refers to TPD-CIMS measurements and black to the model. Solid lines illustrate the evaporation of oxalic acid from pure aerosol and dashed lines its evaporation from oxalic acid/NaCl mixture (in b and c). The pure oxalic acid data set used in the illustration has been used in previous studies.\(^{17,18}\)
acid vapor pressure ($p_{\text{sat}}$ at 298 K < $10^{-6}$ Pa, best estimate $\sim 10^{-9}$ Pa), which is comparable to values found in the literature.45

Saturation vapor pressures of OA and SA obtained from the measurement-model analysis were in the range of values reported in previous studies (Figure 2a).23,26−30,32,45,47,48 However, there was a lot of variability in the $\Delta H_{\text{vap}}$ values between individual experiments and more often low bias compared to literature values was observed (Figure 2b). Mean values of $p_{\text{sat}}$ and $\Delta H_{\text{vap}}$ were 4.0 × 10$^{-4}$ Pa and 62 kJ mol$^{-1}$ for SA and 1.6 × 10$^{-3}$ Pa and 76 kJ mol$^{-1}$ for OA. On average oxalic acid volatility was similar to what has been reported before—values are close to those obtained by Soonsin et al.32 for solid oxalic acid particles. Concerning succinic acid volatility only the higher estimates of $\Delta H_{\text{vap}}$ gave a good agreement with the literature data (84−89 kJ mol$^{-1}$ and 0.9−1.5 × 10$^{-3}$ Pa), especially with the work of Saleh et al.26 and Booth et al.29

While the uncertainties in the experiments affect the determination of both $p_{\text{sat}}$ (at 298 K) and $\Delta H_{\text{vap}}$, the effect is much stronger on $\Delta H_{\text{vap}}$. There are several possible reasons that could lead to the underestimation of $\Delta H_{\text{vap}}$ (and overestimation of $p_{\text{sat}}$) in our approach (see the SI). Further evaporation of particles after the heated inlet but prior to entering the CIMS (around 10 cm distance) may change the observed evaporation behavior especially at room temperature. In addition, excess water in the aerosol may affect the detected evaporation behavior—although this is not expected based on the reported crystallization RHs of oxalic and succinic acids.36

**Evaporation of Organic Acids from Mixtures—Qualitative Analysis.** Organic evaporation from mixed organic acid/inorganic salt aerosols with low initial organic molar fractions ($F_{\text{org}} = 0.5$ and below) was investigated. Qualitative analysis of the TPD-CIMS data showed that compared to pure acetic acid aerosol the addition of NaCl to the aerosol ($F_{\text{org}} = 0.5$) did not change acetic acid evaporation behavior (see Figure S5). This result is in line with what Laskin et al.12 reported—no organic salt formation was observed in mixed acetic acid/NaCl aerosol upon drying. Evaporation of highly volatile acetic acid from the mixed particles is preferred.
over the formation and evaporation of HCl, and the solute remaining after drying is mostly sodium chloride.

Mixed citric acid/NaCl particles were found to be even less volatile than pure citric acid aerosol—significant evaporation occurred only above 100 °C (Figure S5). These results support the observations by Laskin et al.12 indicating significant citrate formation when the mixed aerosol particles were dried.

No change in the onset temperature of organic acid evaporation from oxalic acid and succinic acid salt mixtures was observed (see Figure 1b, as an example). However, the volatility was clearly lower for the mixtures as compared to pure oxalic acid and succinic acid—evaporation of these organic acids from mixtures continued beyond the temperatures where pure organic aerosol reached complete volatilization.

The observed evaporation of oxalic acid from mixed oxalic acid/NaCl was compared with that of pure sodium oxalate, presented in Drozd et al.17 Onset temperature for the evaporation of oxalic acid from the oxalate particles was around 100 °C. Thus, the volatility of oxalic acid in the salt mixtures was intermediate between that of pure oxalic acid and pure sodium oxalate. This conclusion is reasonable as complete chloride depletion is not expected when organics more volatile than citric acid are mixed with NaCl (1:1 molar ratio).12 However, with the TPD-CIMS data alone it cannot be assessed how much of the suppressed evaporation of OA and SA from mixtures is explained by Raoult’s effect. More information on the magnitude of the formation of effectively nonvolatile organic material was obtained by applying the evaporation model.

Magnitude of Low-Volatility Organic Material Formation. In Figure 3a $F_{\text{org,model}}$ is compared against $F_{\text{org}}$ of the atomized solution. The fact that data points did not align on the 1:1 line but $F_{\text{org,model}}$ was more often lower compared to $F_{\text{org}}$ is indicative of partial conversion of organic acid to less volatile organic matter. The difference between $F_{\text{org,model}}$ and $F_{\text{org}}$ increased with decreasing $F_{\text{org}}$. This is consistent with the results reported by Zardini et al.13 and Yli-Juuti et al.14. OA data differed from the 1:1 line notably only with low initial organic molar fractions ($F_{\text{org}} = 0.2$) whereas SA data differed already with $F_{\text{org}} = 0.5$. The similarity of our results to those reported for wet particles along with previous studies on morphologies of dried mixed organic acid/inorganic salt particles$^4,2,45$ give confidence that morphology effects, in particular the formation of inorganic salt coating, are not the primary reason behind the decrease in the volatility of the organic acids, but this effect is indeed due to particulate phase processing. However, the assumption of a spherical morphology naturally adds some uncertainty in the exact $F_{\text{org,model}}$ values—thus highlighting the need for further studies on size- and temperature-dependent morphologies of realistic aerosol particles$^50$ and the impact of nonsphericity on particle evaporation.

In Figure 3b the fraction of the initial organic acid molar fraction converted to effectively nonvolatile aerosol material (NVF) is presented. Succinic acid evaporation was reduced slightly more (<20%) in AS mixtures than in NaCl mixtures. The percentage of organic acid that reacts to form low-volatility organics (organic conversion) varied on average 42–95% for SA mixtures and ~0–77% for OA mixtures.

The optimal $\Delta H_{\text{vap}}$ values paired with $F_{\text{org,model}}$ were on average 20–57 kJ mol$^{-1}$ for SA mixtures and 16–81 kJ mol$^{-1}$ for OA mixtures (Figure S6). $\Delta H_{\text{vap}}$ of oxalic acid—in oxalic acid/NaCl mixtures ($F_{\text{org}} = 0.4$) where no significant aerosol processing was observed—was close to $\Delta H_{\text{vap}}$ of pure oxalic acid. For the rest of the data, $\Delta H_{\text{vap}}$ was clearly lower for organics in mixtures than in pure aerosol. These results indicate that enhanced partitioning of organic acid in the mixtures leads to low $\Delta H_{\text{vap}}$ values. Lowered vaporization enthalpies over mixtures, and for very low-volatility species, have been observed also before with the same instrumental setup and with other measurement techniques.18,33,34,51,52 The reason behind the unphysically low $\Delta H_{\text{vap}}$ values is not fully understood, but it is linked to interactions between aerosol constituents, as also suggested in this study. Measurements on the evaporation of the least volatile aerosol compounds are difficult since only minimal changes in the monitored parameter, e.g. CIMS signal, as a function of temperature are observed, and $\Delta H_{\text{vap}}$ close to zero is obtained.17,52 Since $\Delta H_{\text{vap}}$ is the energy related to evaporation process, for compounds that do not significantly evaporate in the temperature range used, the $\Delta H_{\text{vap}}$ value obtained should not be taken as its thermodynamic counterpart. In the literature, the term “effective vaporization enthalpy” ($\Delta H_{\text{vap,eff}}$) has been used to encompass the gentler evaporation curve observed for aerosol mixtures.52
Based on the consistent results between this study and the study by Laskin et al., organic salt formation due to evaporation of HCl can be considered as the main candidate for low-volatility material formation within mixtures of organic acids and NaCl. It has been observed that reactions in aqueous organic aerosols in the presence of ammonium sulfate can lead to organonitrate or sulfate formation that is further enhanced when water is removed from the aerosol. Even though these compounds can have a significant effect on aerosol properties, the total amount formed is likely to be small and, thus, may not be detectable with aerosol mass spectrometry. Concerning our experiments and relatively fast drying process, the formation of organonitrates or sulfates is not expected, or at least, it cannot explain all the observed low-volatility organic material. Even without acid removal from the aerosol, organic salt formation, as observed within organic acid/divalent inorganic salt mixtures (e.g., oxalic acid/CaSO₄), is a plausible explanation for the low-volatility organic material also in submicron organic acid/AS aerosol.

Effect of Aerosol Acidity on Formation of Low-Volatility Organics. In order to investigate the effect of aerosol acidity on the formation of effectively nonvolatile organic matter, the pH values of the atomized solutions (i.e., aqueous aerosols) were determined (pH meter by Thermo Scientific). In Figure 4a, the NVF is illustrated as a function of the aerosol pH. The results from the qualitative analysis of citric acid/NaCl and acetic acid/NaCl mixtures (NVF ~ 0% and pH = 3.1 for AA/NaCl and NVF ~100% and pH = 2.4 for CA/NaCl) were included. When all the available data was considered, no clear pH dependence of low-volatility material formation was found. However, within data sets of oxalic acid and succinic acid, the observed organic conversion increased as aerosol pH increased. In general, succinic acid mixtures had higher pH (on average 4.5) than oxalic acid solutions and succinic acid, the observed organic conversion increased as aerosol pH increased. In general, succinic acid mixtures had higher pH (on average 4.5) than oxalic acid solutions and succinic acid, the observed organic conversion increased as aerosol pH increased. In general, succinic acid mixtures had higher pH (on average 4.5) than oxalic acid solutions and succinic acid, the observed organic conversion increased as aerosol pH increased.

Atmospheric Relevance. The formation of low-volatility organics strongly depends on the volatility of the organic acid used in the mixture (Figure 4b). However, aerosol pH should also be considered, since the aerosol processing can be hindered at low pH, as observed within the SA and OA data sets. In this study, aerosol pH was in the range of 2–5 (prior to drying), which is similar to the average pH range found in atmospheric aerosols. The relation between aerosol pH and organic conversion suggests that, while in acidic urban environments aerosol processing in organic acid/AS mixtures may be low, at e.g. marine sites, organic salt formation can be even more than reported here. While NaCl is an important contributor to aerosol chemical composition near the sea, the contribution of AS to aerosol mass is significant almost everywhere else. Thus, it is likely that the observed aerosol processing, especially within organic acid/AS mixtures, at least partly explains anthropogenic enhancement of the formation of secondary organic aerosol (SOA) from biogenic precursors, which has been reported in previous research work. In the review by Hoyle et al. on the anthropogenic enhancement of organic aerosol burden, condensed phase acid-catalyst reactions, leading to formation of e.g. organosulfates, were highlighted, but the importance of organic salt formation or other aerosol processing under less acidic conditions was not discussed. Within aerosols containing ammonium sulfate, the acidity is reduced compared to sulfate aerosol, and therefore other aerosol processing than acid-catalyzed reactions is likely to become important.

Depending on the properties of organic and inorganic aerosol constituents as well as on aerosol acidity, different types of particle-phase chemistry will occur. All of these reactions can lead to enhanced partitioning of atmospheric organics and have a notable effect on aerosol mass loadings. Furthermore, other aerosol properties, such as hygroscopicity, can change as a result of aerosol processing. For some organic salts (e.g., ammonium oxalate and sodium succinate), the formed anhydrous state upon drying is not thermodynamically the most stable form—bulk studies have shown that these organic salts are rather mono- or multihydrates even at low RHs. Ling and Chan et al. found metastable forms of organic acid within mixtures of organic acid and ammonium sulfate upon crystallization. Our results support their suggestion of metastable organic salt formation upon the dissociation of the organic acid. Further work is needed, however, to determine the phase state that bears the most relevance for atmospheric aerosols.

It is important to assess which aerosol reactions enhance SOA formation and, thus, affect SOA properties the most. Currently, anthropogenic enhancement of SOA is taken into account in atmospheric models simply by adding an extra SOA yield of 100 Tg a⁻¹ that is correlated with CO emissions—also highlighting this significant but yet poorly understood source of SOA.

ASSOCIATED CONTENT

Supporting Information
Information about the atomized solutions and the properties of the generated particle size distributions, molecule fragmentation in TPD-CIMS, analysis on the volatility of pure organic acids with uncertainty estimation, discussion of possible reasons affecting the low bias observed in the vaporization enthalpies of pure organic acids, discussion about the properties assumed for the effectively nonvolatile aerosol material, estimation on organic acid evaporation from the mixtures upon drying, chloride depletion from aqueous organic acid/NaCl aerosol via E-AIM modeling, observed organic acid evaporation from pure component aerosol and from mixture, and vaporization enthalpies of organic acids in organic acid/inorganic salt mixtures. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes
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