2019

Molecular insights into organic particulate formation

Manoj Kumar
University of Nebraska - Lincoln

Emily Burrell
BYU

Jason C. Hansen
BYU

Joseph S. Francisco
University of Nebraska - Lincoln, francisc@purdue.edu

Follow this and additional works at: https://digitalcommons.unl.edu/chemfacpub

Part of the Analytical Chemistry Commons, Medicinal-Pharmaceutical Chemistry Commons, and the Other Chemistry Commons

Kumar, Manoj; Burrell, Emily; Hansen, Jason C.; and Francisco, Joseph S., "Molecular insights into organic particulate formation" (2019). Faculty Publications -- Chemistry Department. 169.
https://digitalcommons.unl.edu/chemfacpub/169

This Article is brought to you for free and open access by the Published Research - Department of Chemistry at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Faculty Publications -- Chemistry Department by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.
Molecular insights into organic particulate formation

Manoj Kumar¹, Emily Burrell², Jaron C. Hansen² & Joseph S. Francisco¹

Carboxylic acids have been detected in particles collected in various regions of the world. Here, we use experiments and Born-Oppenheimer molecular dynamics simulations to better understand the mechanism of particle formation from gas phase mixtures of formic acid (HCOOH), (CH₃)₃N, and water vapor. A flow reaction cell coupled to two scanning mobility particle sizers has been used to measure particle size, absolute number of particles and kinetics of particle formation. Experimental results show that the addition of (CH₃)₃N to a mixture of HCOOH and water vapor results in a dramatic increase in particle formation. Simulation results indicate that the ion-pair formation on the water surface involves direct proton transfer between HCOOH and (CH₃)₃N. The HCOO⁻-(CH₃)₃NH⁺ ion-pair remains at the air-water interface due to hydrogen bonding and the interfacial hydration shell. This experiment-theory study shows the formation of aerosol particles from the organic acid-amine interactions, which may aid in understanding the role of organics in haze and cloud droplet formation and nanoparticle growth.

¹Department of Chemistry, University of Nebraska-Lincoln, Lincoln, NE 68588, USA. ²Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602, USA. Correspondence and requests for materials should be addressed to J.S.F. (email: francisc@purdue.edu)
Atmospheric aerosols affect air quality, human health, and the global climate\textsuperscript{1–3}. Aerosols act as cloud condensation nuclei (CCN) and ice nuclei, and impact frequency of occurrence, and lifetime of clouds\textsuperscript{4–7}. Despite their broad impact, the exact formation pathways for the atmospheric particles remain largely unknown\textsuperscript{8}. Sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) is recognized as perhaps the most important nucleating species in the atmosphere\textsuperscript{8–11}. However, binary homogeneous nucleation of H\textsubscript{2}SO\textsubscript{4} and water (H\textsubscript{2}O) is insufficient to explain the nucleation events under actual atmospheric conditions\textsuperscript{12, 13}, suggesting that other species may also participate in nucleation events\textsuperscript{13–15}.

Amines and carboxylic acids are an important class of compounds that have recently been found to contribute to the particle formation under certain conditions\textsuperscript{8, 16}. It is noted that molecules with high vapor pressures, which includes certain carboxylic acids, would be unlikely to contribute to new particle formation. However, recent field studies from a variety of locations around the world have found evidence of carboxylic acids contributing to new particle formation. For example, the mass spectra of nanoparticles obtained during new particle formation events in Hyytiala, Finland is suggestive of the presence of alkylaminium and carboxylate ions in the particles\textsuperscript{17}.

Organic species are also predicted to play an important role in the particle growth in Tecamac, Mexico\textsuperscript{13}. Zhang et al. observed a marked increase in the particle concentration when benzoic, p-toluic, m-toluic, or cis-pinonic acid vapor was added to the H\textsubscript{2}SO\textsubscript{4}–H\textsubscript{2}O vapor system\textsuperscript{18, 19}. Additional measurements in Shanghai, China observed increased rates of particle formation containing markers for the sulfuric acid dimer, H\textsubscript{2}SO\textsubscript{4}–dimethylamine (DMA) clusters and H\textsubscript{2}SO\textsubscript{4}–DMA–H\textsubscript{2}O nucleation\textsuperscript{20}. The role of oxalic acid in particle formation from vapor phase methanesulfonic acid, methylamine, and H\textsubscript{2}O has been recently examined experimentally\textsuperscript{21}. The addition of water to the mixture of oxalic acid and methylamine enhanced the rate of particle formation by an order of magnitude. Although the amine concentrations are 1–3 orders of magnitude lower than that of NH\textsubscript{3} in the atmosphere\textsuperscript{22}, amines are experimentally found to be more effective than NH\textsubscript{3} in enhancing particle formation\textsuperscript{11, 23–26}. For example, the CLOUD chamber experiments at CERN have demonstrated the superior particle formation efficacy of DMA compared to NH\textsubscript{3}\textsuperscript{11}. The vapor pressure of monocarboxylic acids is higher, by a factor of 10\textsuperscript{2} to 10\textsuperscript{4} than that of the corresponding dicarboxylic acids\textsuperscript{27}, suggesting that the latter is likely to play a bigger role in the new particle formation. Despite that, monocarboxylic acids have been detected in aerosol particles collected in various regions of the world\textsuperscript{28–34}. Supplementary Table 1 summarizes the concentration of HCOOH and CH\textsubscript{3}COOH measured in air samples collected in a variety of environments. In the urban environment of New Mexico City, HCOOH and CH\textsubscript{3}COOH were predominantly detected in the particulate phase\textsuperscript{35}. On average, 53% of HCOOH and 67% of CH\textsubscript{3}COOH were present in particulate matter. The presence of particulate organic salts was also raised as a possible explanation for the relatively high aerosol hygroscopicity and CCN concentrations observed in the Amazon basin\textsuperscript{36}.

Despite being ubiquitous in diverse environments, the mechanism of organic particulate formation is yet to be fully established. Specifically, identifying key organic species and the underlying chemical mechanisms responsible for the nucleation and growth of atmospheric particles remains a significant challenge. Our current understanding about the role of organics in initial atmospheric nucleation events is based on quantum chemical calculations\textsuperscript{8, 37–42}, which are typically limited to few atom clusters. This hampers the generalization of gas-phase results to the water surfaces, such as fog, snow, clouds and water microdroplets, which are present in the troposphere and are believed to impact the chemistries occurring there\textsuperscript{33–39}.

We have performed experiments and BOMD simulations to explore the particle formation from HCOOH, TMA ((CH\textsubscript{3})\textsubscript{3}N), and water. The BOMD simulations and performed experiments provide a further understanding as to the mechanism behind high vapor pressure molecules contributing to new particle formation. The results of this experiment-theory study also help in understanding the role of organics in both haze and cloud droplet formation, and to nanoparticle growth in urban, rural and remote regions.

**Results**

**Experimental results of particle formation enhanced by trimethylamine.** Experiments were conducted by flowing gas mixtures of formic acid, water vapor, and TMA in a flow reaction cell. The instrumental set-up is shown in Supplementary Fig. 1. Three sets of conditions were analyzed for each precursor, which resulted in 27 conditions (Supplementary Table 2), each analyzed at 6 different reaction times (8, 16, 24, 32, 40, and 48 s). The analysis of the 8 minimal and maximal concentrations are discussed in the following figures. However, it should be noted that the additional 19 conditions agree with the minimal and maximal results. The size distribution and total number of particles at each reaction time under each reaction condition was measured. Figure 1a compares particle formation and particle size distributions as a result of flowing a mixture of formic acid (140 ppm) and water vapor (630 ppm) in the absence and presence of 200 ppb TMA. The total number of particles and particle size distribution is plotted for both 8 and 48 s reaction times. Figure 1b offers a closer look at particle concentrations vs particle diameters ranging from 300–500 nm. Figure 1c shows particle concentrations vs diameter from 0–100 nm. No particles are observed while flowing only N\textsubscript{2}, 630 ppm H\textsubscript{2}O, 140 ppm formic acid or 200 ppb TMA. Particles did form as a result of flowing a mixture of formic acid (140 ppm) and water vapor (630 ppm); however, with the addition 200 ppb of TMA to the mixture, there is a dramatic increase in the formation of smaller particles at both reactions. The mixture of formic acid (140 ppm) and water vapor (630 ppm) without any TMA, generated a maximum of 3.3 ± 0.3 × 10\textsuperscript{6} particles cm\textsuperscript{-3} at a diameter of 1.29 nm and a total number of particles of 7.2 ± 0.3 × 10\textsuperscript{6} particles ranging in diameter from 1.09–498 nm. 99.4 % of the particles were <40 nm in diameter and 0.6% of particles were >40 nm. Inclusion of 200 ppb TMA to this formic acid/water vapor mixture resulted in an increase in the total number of particles to 7.1 ± 0.05 × 10\textsuperscript{7} particles between 1.09 and 498 nm in diameter with a maximum of 3.4 ± 0.3 × 10\textsuperscript{6} particles cm\textsuperscript{-3} generated at a diameter of 1.09 nm at 8 s of reaction time. The percentage of particles formed at 8 s with a diameter of <40 nm decreased to 98.7 % while the percentage of particles with a diameter of >40 nm rose to 1.3%. With an increase of reaction time to 48 s, the total number of particles rose to 4.1 ± 0.11 × 10\textsuperscript{8} particles with a maximum concentration of 7.3 ± 0.9 × 10\textsuperscript{6} particles cm\textsuperscript{-3} generated at a diameter of 1.54 nm. The percentage of particles formed <40 nm in diameter dropped to 98.6 % while the percentage of particles >40 nm rose to 1.4%. By comparison, the formic acid/water vapor mixture containing 200 ppb TMA shows an increased formation of both smaller diameter particles, <40 nm, and larger diameter particles (>300 nm), compared to the formic acid/water vapor mixture without TMA. The difference in the number of total particles and formation of particles (>300 nm) increases with longer reaction times for mixtures that include TMA.

Table 1 lists the conditions probed for each trial and the measured rate of particle formation. Figure 2 compares particle formation enhanced by trimethylamine.
of formic acid (140 ppm), water vapor (630 ppm) and TMA (200 ppb) in the reaction cell shown in red compared to increased TMA concentration (400 ppb) shown in black. The rate of particle formation under these conditions is measured to be $1.0 \pm 0.2 \times 10^6$ particles cm$^{-3}$ s$^{-1}$. The rate of particle formation under higher concentrations could not be determined due to the aggregation of smaller sized particles leading to an increased concentration of larger particles, which skewed the calculations needed to determine the rate of particle formation. Figure 2a compares trials A and C (shown in black) with lower formic acid concentrations and an increase concentration of TMA from 200 ppb to 400 ppb, which shows a definite increase in the smaller particles at the shorter reaction times. Increasing the TMA concentration by a factor of 2 results in a 6.6% increase in the number of particles formed with diameters <20 nm at 8 s. A shift in the size distribution of smaller particles (<20 nm) and an increase in the number of particles >40 nm is also observed. In Fig. 2b, trials B (red) and D (black) are shown. The formic acid (140 ppm) and higher water vapor (1550 ppm) concentrations were kept constant but the concentration of TMA was double in trial D compared to B. The total number of particles grown in trial D at 8 s was 36% larger compared to that in B. In addition, evaluation of the particle size distribution shows 3.9% of the total particles in B are >20 nm in diameter but upon doubling of the concentration of TMA the total number of particles >20 nm in trial D increased to 4.2%. Figure 2c, which shows trials E (red) and G (black), the formic acid (540 ppm) and water concentrations (630 ppm) were kept constant but the TMA concentration was double in trial G compared to E. The total number of particles in trial G at 8 s was 17% smaller compared to that in E. In addition, evaluation of the particle size distribution shows that 3.1% of the total particles in E are >20 nm in diameter but upon increasing the concentration of TMA, the total number of particles >20 nm in trial D increased to 3.3%. In Fig. 2d, which shows trials F (red) and H (black), the formic acid (540 ppm) and water concentrations (630 ppm) were kept constant but the TMA concentration was double in trial H compared to F. The total number of particles grown in trial H at 8 s was 4.8% larger compared to that in H. In addition, evaluation of the particle size distribution shows that 4.1% of the total particles in F are >20 nm in diameter but upon increasing the concentration of TMA, the total number of particles >20 nm in trial H increased to 4.5%. Comparison of Fig. 2a–d (Supplementary Table 4) indicate an increase in the concentration of TMA increases the rate of particle formation and perturbs the particle size distribution a table of the values is found in supplemental materials. However, due to the high concentrations of formic acid and TMA in these trials, nucleation was not the only mechanism contributing to particle formation as is discussed later.

The effect of TMA on the kinetics of particle formation was next measured by changing the TMA concentrations and comparing the changed rates of particle formation. To overcome a secondary mechanism via aggregation and to determine the rate of particle formation via nucleation, the formic acid and TMA concentrations were decreased minimizing aggregation in the flow cell. A gas mixture of 60 ppm formic acid and 630 ppm water vapor with varying concentrations of TMA was studied in the reaction cell. The concentration of TMA was varied in the reaction mixture between 12 and 20 ppb and the total number of particles >2.5 nm in diameter was measured at reaction times ranging between 8 and 48 s. These experiments allowed for measurement of the reaction rate coefficient, $k_{>2.5\text{ nm}}$, for new particle formation. The rate of particle formation was determined by finding the linear slope

**Table 3**

| Particle diameter (nm) | Particle concentration (particles cm$^{-3}$) |
|------------------------|---------------------------------------------|
| 100                    | 1e + 7                                      |
| 200                    | 2e + 6                                      |
| 300                    | 3e + 6                                      |
| 400                    | 4e + 6                                      |
| 500                    | 5e + 6                                      |

**Fig. 1** Particle formation. Particle formation initiated by the addition of 140 ppm formic acid, 630 ppm water vapor, 200 ppb trimethylamine (TMA) at different reaction times (green-no TMA, red-8 s and blue-48 s). a Overall comparison of particle concentration vs particle diameter (0.8-500 nm). b Comparison of larger diameter particle concentration vs particle diameter (300-500 nm) at different times (blue- 48 s, red- 8 s, green-no TMA). c Comparison of smaller diameter particle concentration vs particle diameter (0.8-100 nm). Numerical values are given in Supplementary Table 3.

formation as a function of initial formic acid, water vapor, and TMA concentrations. Additional comparisons of Table 1 conditions are found in the supplemental data. See Supplementary Fig. 2 and Supplementary Note 1. Figure 2a shows that the particle formation occurs even at the lowest concentration conditions are found in the supplemental data. See Supplementary Table 4.
between the reaction times (8–48 s) and the total number of particles. Figure 3 shows a comparison of \( k_{>2.5\text{ nm}} \) for three different formic acid, water vapor, TMA mixtures. A linear relationship between total number of particles formed >2.5 nm in diameter and increasing concentration of TMA is observed. The rate of particle formation is observed to increase with the TMA concentration. The only anomaly observed in these series of experiments occurred when 200–400 ppb of TMA was introduced into the reaction cell. Under these conditions, the total number of particles formed, and shift in the particle size distribution did not follow the linear trend (Fig. 4), but instead, a decrease in rate of particle formation was measured. This rate decrease can be associated to the inability to measure particles with a diameter >500 nm using the SMPS’s used in this project. Figure 4a compares formation of particles >300 nm in diameter as a function of the reaction time under conditions of flowing 140 ppm formic acid, 630 ppm water vapor and 200 ppb TMA. At 8 s, the shortest reaction time probed, particle concentration peaks at \( 1.9 \pm 0.4 \times 10^4 \) particles cm\(^{-3} \) at 332 nm in diameter. As the reaction time increases to 24 s, the maximum concentration increases to \( 4.7 \pm 0.1 \times 10^4 \) particles cm\(^{-3} \) at a particle diameter of 332 nm. A long, shallow tail is observed in the observed particle diameters for both reaction times, 8 and 24 s. As the reaction time increases to 32 s the previously observed maximum in particle concentration observed in reaction times 8 and 24 s disappears, and a strong, broad distribution of particles >375 nm forms. At 48 s reaction time, a large peak in concentration is measured at 375 nm and a second broad tail is observed rising from 440 nm in diameter. Fine particles are classified into three distinct ranges: the
ultramine particle range (<10 nm), the transient nuclei range (10–100 nm) and the accumulation range (100 nm–1.2 µm). Figure 4b separately particle diameters for each reaction time into these three models versus particle concentration. At the earliest reaction time, there is a high particle concentration for the ultramine particle range and a constant particle concentration for the accumulation range with an increase in reaction time. However, at the next shortest reaction time, there is an unexpected decrease in particle concentration in the ultramine particle range followed by a slow increase in the ultramine particle concentration with an increase in reaction time. In contrast, there is still an increase in the total number of particles in the accumulation range. The sudden decrease and subsequent increase in smaller diameter particles (<10 nm) along with the continuous increase in larger diameter particles indicates a two-fold nature of particle growth occurring in the reaction cell via nucleation and aggregation. To better comprehend the influence of TMA and H2O on the two-fold mechanism of particle growth, Fig. 5 compares the change in particle diameter distribution versus either a change in TMA or H2O concentration. Figure 5a analyzes particle concentration versus particle diameter distribution with 140 ppm formic acid, 630 ppm water vapor, 200 ppb TMA. Figure 5b shows a change in particle distribution with an increase in TMA. While Fig. 5c shows the change in particle distribution with an increase in H2O. The concentrations of H2O and TMA were respectively increased from 630 ppm to 1550 ppm, and 200 ppb to 400 ppb. Figure 5b indicates that with increased TMA concentrations particles with a diameter between 2.5 and 10 nm decreased and increased the number of particles with diameters between 100 and 500 nm six-fold at 8 s. Compared with Fig. 5c, there is a decrease in the number of particles with in diameter range diameters between 2.5 and 10 nm and three-fold increase in particles with diameters between 100 and 500 nm at 8 s. Increased reaction times show the expected decrease in the overall particle concentration followed by an increase in the larger sized particles. The overall decrease is attributed to the inability to measure particles larger than 500 nm in diameter. The aggregation of smaller sized particles leading to the formation of particles with diameters 100–500 nm may be enhanced by the dipole moment caused by the TMA complexing with formic acid which in turn forms a hydrophobic/hydrophilic interaction as stated in the computational section. A similar enhancement may occur with increased H2O concentration, however to a lesser extent due to the smaller dipole moment. Ultramine particles are formed as formic acid/water/TMA clusters grow with increasing reaction time in the cell. As the concentration of these particles increases the probability that these particles will collide with one another and aggregate to form a larger diameter particle increases. Aggregation of particles in the ultramine and accumulation size range results in a decrease in the total number of these particles but an increase in the formation of particles >100 nm in diameter. We see both particle growth as water adheres to the nucleating site but also observe aggregation as small particles collide into one another to produce larger diameter particles.

Simulation evidence of the formic acid–TMA interaction at air–water interface. The BOMD simulations provide useful information into the time scale, molecular mechanism of the
ion-pair formation as well as the dynamic behavior of the ion-pair formed on the aqueous surface. The BOMD simulations were performed on a water droplet of 191 H$_2$O molecules probing the nature of the interaction between HCOOH and (CH$_3$)$_3$N. The details of the simulation procedure are provided in the Methods section. The initial configuration of the HCOOH–(CH$_3$)$_3$N complex adsorbed on the water droplet surface are given in the Supplementary Fig. 3. We initiated BOMD simulations from hydrogen-bonded and non-hydrogen-bonded complexes of HCOOH with (CH$_3$)$_3$N. Surprisingly, only the hydrogen-bonded configurations resulted in the ion-pair formation on the water surface, implying that the formation of hydrogen-bonded HCOOH–(CH$_3$)$_3$N complex in the gas-phase constitutes a crucial step in the particle formation on the water surface. In a recent experimental study$^{48}$, Eugene et al. also observed interfacial proton transfer from simpler carboxylic acids. Though the role of gas-to-particle partitioning in the particle formation has been speculated before$^5$, our simulations provide a mechanistic rationale why the gas-to-particle conversion is actually required for the particle formation.

The HCOOH–(CH$_3$)$_3$N interaction follows a typical trajectory of acid-base chemistry and involves a proton transfer between HCOOH and (CH$_3$)$_3$N without the direct involvement of surface water molecules. This results in the formation of HCOO$^-$–(CH$_3$)$_3$NH$^+$ ion-pair on a picosecond (ps) time scale (Fig. 6). As just described, Eugene et al. have recently also observed interfacial proton transfer from simpler carboxylic acids that can play an important role in aerosol formation$^{48}$. The role of water droplet here is to stabilize the ion-pair particle by forming a hydration shell around it. These findings are also consistent with field measurements predicting the presence of ammonium salts in aged organic carbon particles in certain regions of California$^{31,32}$. The reactive uptake of NH$_3$ onto slightly soluble organic acid particle is also found to enhance the CCN activity and the formation rates of these particles$^{33}$. For the reaction between HCOOH and (CH$_3$)$_3$N, the transition state like complex is formed at 5.18 ps (Fig. 6a and Supplementary Movie 1). In this complex, the hydroxyl proton of HCOOH is partially dissociated and transferred towards (CH$_3$)$_3$N, i.e., the O1–H1 bond is 1.33 Å long whereas the H1–N1 bond is 1.29 Å long. This complex is converted into the HCOO$^-$–(CH$_3$)$_3$NH$^+$ ion pair at 5.23 ps. The O1–H1 bond is now lengthened to 1.70 Å, indicative of a hydrogen bonding interaction whereas the H1–N1 bond has become a true covalent bond (H1–N = 1.06 Å).

**Dynamic behavior of HCOO$^-$–(CH$_3$)$_3$NH$^+$ ion-pair at the air–water interface.** To gain deeper insights into the dynamic behavior of the HCOO$^-$–(CH$_3$)$_3$NH$^+$ ion-pair, we next analyzed its locus on the water droplet. Supplementary Fig. 4 shows the distance between the center of mass of the ion-pair and that of the water droplet as a function of the simulation time. The HCOO$^-$–(CH$_3$)$_3$NH$^+$ ion-pair is situated at 10–13 Å distance from the center of the water droplet, implying that it preferentially resides at the air-water interface. There are two main interactions responsible for the interfacial locus of the HCOO$^-$–(CH$_3$)$_3$NH$^+$ ion-pair: (i) intraparticle hydrogen bonding (O1–H1–N1), and (ii) interfacial hydration shell. The intraparticle hydrogen bond in HCOO$^-$–(CH$_3$)$_3$NH$^+$ ion-pair is quite strong as is evidenced from the combined distribution functions shown in Fig. 6c, d, respectively. The calculated average number of hydrogen bonds formed by the HCOO$^-$–(CH$_3$)$_3$NH$^+$ ion-pair with interfacial water molecules provides useful insight into its interfacial hydration shell. Our model specified a hydrogen bond between a formate oxygen and H$_2$O, if the O1/02-H-O or O-H1–N1 distance was <2.5 Å and the O1/O2-H-O or O-H1–N1 hydrogen bond angle was >150°. The COO$^-$–group forms 1.9 hydrogen bonds whereas the amminium proton does not form any hydrogen bond with H$_2$O molecules. The hydrophobicity of trimethyl group in the HCOO$^-$–(CH$_3$)$_3$NH$^+$ ion-pair prevents any
interaction between the aminium proton and interfacial water molecules. To deeply understand the solvation structure of HCOO\(^{-}\cdot\text{(CH}_3\text{)}_3\text{NH}^+\) ion-pair at the air-water interface, we next identified key \([m,n]\) configurations and calculated their probabilities (Fig. 7). Here \(m\) and \(n\) are the number of interfacial \(\text{H}_2\text{O}\) molecules bound to the HCOO\(^-\) and \((\text{CH}_3\text{)}_3\text{NH}^+\), respectively. The configurations, in which only the HCOO\(^-\) group of HCOO\(^-\cdot\text{(CH}_3\text{)}_3\text{NH}^+\) ion-pair binds to one, two and three interfacial \(\text{H}_2\text{O}\) molecules, are the most probable ones and account for 31\%, 38\%, and 26\% of the total configurations, respectively (Fig. 7). Since there remains significant uncertainty about the exact composition of the particle in air\(^8\)\(^{,}\)\(^{37-42}\), our results may play a crucial role in revealing a fundamental yet vital piece of information on the particle formation on the water surfaces.

**Atmospheric implications.** The growth of atmospheric nanoparticles was initially proposed to occur via direct condensation of organic acids\(^{54}\). However, the high saturation pressure of organic acids over nanoparticles\(^{55}\) negates the possibility of such a mechanism. On contrary, thermal desorption chemical ionization mass spectrometry (TDClMS) analysis of the particles formed in Tecamaco, Mexico shows the presence of carboxylic and hydroxycarboxylic organic acids\(^{13}\), suggesting that organics play a key role in the nanoparticle growth.

Our experimental and theoretical results may help in resolving the discrepancy in the role of organic acids in nanoparticle growth. The current BOMD simulations suggest a new gas-to-particle partitioning mechanism for the formation of organic particles that involves two steps: (i) formation of hydrogen-bonded complexes of organic acids with amines in the gas-phase, and their adsorption on the aqueous surface, and (ii) subsequent proton transfer between hydrogen-bonded entities. The mechanistic beauty of this new mechanism lies in the fact that it does not require direct condensation of organic acids, but rather involves hydrogen bonding between organic acids and amines. The organic-amine salts formed in this mechanism will have reduced volatility, as has been pointed out in a recent study\(^{56}\). This new mechanism is supported by combined laboratory investigation and field measurements using TDClMS and ultrafine hygroscopicity tandem differential mobility analyzer (TDMA) confirming that carboxylate-alkylaminium salts contribute to the
particle growth in atmosphere\textsuperscript{47}. Additional support for this mechanism comes from the study of Dinar et al. showing that the reactive uptake of NH\textsubscript{3} can enhance the CCN activity and hygroscopic growth of organic acid particles\textsuperscript{53}. Our BOMD simulations suggest that the carboxylate-aminium ion-pair remained stable on the water surface over the simulated time scale of 20 ps. This is again consistent with high thermal stability of alkylaminium carboxylate salts from the organic acid-amine reaction\textsuperscript{57}.

Discussion

Our experiments show the nanoparticle formation under conditions that are typically outside what is expected if you use classical nucleation theory to describe particle formation. That is to say, we see nanoparticle growth under conditions of <100\% RH. Under the classical nucleation model, it is suggested that 100\% RH is necessary for particle formation and growth to occur. We speculate that by adding trace amounts of amines and/or formic acid, we may "seed" a cloud to increase the rate of particle formation. Our experimental results are consistent with what is observed around the world in terms of measuring carboxylic acids in particles as shown in the Sao Paulo, Brazil and Tecama, Mexico studies. The conclusions from our work could be used to better understand the role of other monocarboxylic acids such as CH\textsubscript{3}COOH, and dicarboxylic acids such as oxalic acid and malonic acid in the particle formation under diverse environmental conditions, including semirural sites in the northeastern United States\textsuperscript{58}, urban environments\textsuperscript{59–61}, and remote locations\textsuperscript{62,63}.

Though considered unlikely due to their high vapor pressures atmospheric gaseous- and particle-phase, carboxylic acids have been measured in the urban environment of Sao Paulo, Brazil\textsuperscript{64}. Carboxylic acids accounted for a fraction of 7\% of the total organic carbon in the particle phase, with formate and oxalate being two of the most abundant carboxylates. Though the major source of these carboxylates is suggested to be traffic emissions, the comprehensive insights into their emission source are still lacking. Our results suggest that the acid-base chemistries between organic acids and organic nitrogens could be an overlooked source of organic particulate in urban air. The organic nitrogens could be transported from the rural agricultural sites to the urban regions where they react with organic acids and result in the particulate formation. These new findings may help in improving the accuracy of existing atmospheric models.

Methods

Experimental details. A flow cell set-up was used to experimentally verify the formation of particles initiated by formic acid, water vapor, and TMA. Supplementary Fig. 1 shows the experimental setup, a 180 cm long Pyrex flow cell (5.1 cm i.d.) was connected to two aluminum boxes (26.5 cm × 26.5 cm × 26.5 cm) that allowed for UV light to pass through the flow cell for detection of formic acid and TMA. Formic acid, water vapor, and N\textsubscript{2} were separately introduced at the top of the cell. The TMA was introduced at varying points in the flow cell by a Teflon coated shower ring. Particle size distribution with particle diameter sizes ranging from 1.09 nm to 493.95 nm were analyzed using two Grimm Aerosol Technik scanning mobility particle sizer (SMPS, model: 5.710) each consisting of a differential mobility analyzer (DMA) Electrostatic Classifier (Vienna/Reidsh type, model 55–u; 55–100) and a faraday cup electrometer (TCE, model 5705).

Prior to each experiment, the flow cell was cleaned out with ozone, N\textsubscript{2} (2 SLM) and O\textsubscript{3} (100 sccm) for 1 h between experiments and overnight. This allowed for the complete removal of any formic acid or TMA that had been introduced in previous experiments. The flow cell was kept at a constant temperature (22 ± 1 °C) and pressure (650 ± 5 Torr). In all experiments, formic acid and water vapor were introduced separately into the flow cell by bubbling N\textsubscript{2} (100–300 sccm) through 88\% proof formic acid and purified water. Additional N\textsubscript{2} was introduced into the flow cell for a total flow rate of 3.125 SLM. As previously mentioned TMA (25–125 sccm) was introduced at varying points in the flow cell by a Teflon coated shower ring. The shower ring (i.d. 4.5 cm) with pin holes was attached to a stainless-steel rod which allowed for movement up and down the flow cell. This method of introducing TMA allows for reaction times varying from 8 to 48 s. A range of concentrations for formic acid and TMA were varied by varying the flow of gases and subsequently using UV absorption spectroscopy to determine formic acid and TMA concentrations. Using Beer’s Law and previously published cross sections from 220.16 to 250.9 nm the concentrations of TMA were determined to be 200 and 400 ppb. Using previously published formic acid cross sections from 210.88 to 230.86 nm the formic acid concentrations were determined to be 140 and 540 ppb. A water vapor calibration curve was determined by introducing known concentrations of water vapor via a syringe pump (KD Scientific KDS-100 Syringe Pump) at known flow rates. Water was introduced into a stainless-steel tee packed with glass wool heated to 150 °C. N\textsubscript{2} (3.1 SLM) passed through the glass wool into the flow cell and the absorption from the water concentration was determined by dissolving an IR diode over 1380 to 1384 nm and the area under the desired peak was integrated for the known concentration of water vapor. Water vapor concentrations were used as 630 and 1550 ppm.

Computational details. Born–Oppenheimer molecular dynamics (BOMD) simulations were performed based on a density functional theory (DFT) method implemented in the CP2K\textsuperscript{64} code. In the BOMD simulation, the droplet system contained 191 water molecules, one HCOOH molecule and one N(CH\textsubscript{3})\textsubscript{3} molecule. We have explored a total number of 10 different trajectories, in which five of them started from non-hydrogen-bonded configurations of HCOOH and N(CH\textsubscript{3})\textsubscript{3} whereas the other five started from hydrogen-bonded configurations. The dimension of the simulation box is x = 35 Å, y = 35 Å, z = 35 Å, which is large enough to neglect interactions between adjacent periodic images of the water droplet. Prior to the BOMD simulation, the system was fully relaxed using a DFT method, in which the exchange and correlation interaction is treated with the Becke-Lee-Yang-Parr (BLYP) functionals\textsuperscript{65,66}. The Grimme’s dispersion correction method is applied to account for the weak dispersion interaction\textsuperscript{67,68}. A double-\(\zeta\) Gaussian basis set combined with an auxiliary basis set and the Goedecker-Teter-Hutter (GTH) norm-conserved pseudopotentials were adopted to treat the valence electrons and the core electrons, respectively\textsuperscript{69,70}. An energy cutoff of 280 Rydberg was set for the plane-wave basis set and 40 Rydberg for the Gaussian basis set. The BOMD simulations were carried out in the constant volume and temperature (NVT) ensemble, with the Nose-Hoover chain method for controlling the temperature (300 K) of the system. The integration step was set as 1 fs, which had been proven to achieve sufficient energy conservation for the water system.

Data availability

The authors declare that all data supporting the findings of this study are available within the paper or are available from the authors upon request.

Received: 24 October 2018 Accepted: 19 June 2019
Published online: 26 July 2019

References

1. Intergovernmental Panel on Climate Change. Climate Change 2007: The Physical Science Basis (eds Solomon, S. et al.) (Cambridge Univ. Press, Cambridge, UK, 2007).
2. Pillar-Little, E. A. & Guzman, M. I. An overview of dynamic heterogeneous oxidations in the troposphere. Environments 5, 104 (2018).
3. Liu, Z., Yim, S. H. L., Wang, C. & Lau, N. C. The impact of the aerosol direct radiative forcing on deep convection and air quality in the Pearl river delta region. Geophys. Res. Lett. 45, 4410 (2018).
4. Fan, J. W., Zhang, R. Y., Li, G. H. & Tao, W. K. Effects of aerosols and relative humidity on Cumulus clouds. J. Geophys. Res. 112, D14204 (2007).
5. Zhang, R. Y., Li, G. H., Fan, J. W., Wu, D. I. & Molina, M. L. Intensification of Pacific storm track linked to Asian pollution. Proc. Natl Acad. Sci. USA 104, 5295–5299 (2007).
6. Fan, J. W., Zhang, R. Y., Tao, W. K. & Mohr, K. I. Effects of aerosol optical properties on deep convective clouds and radiative forcing. J. Geophys. Res. 113, D08209 (2008).
7. Zhang, R. Getting to the critical nucleus of aerosol formation. Science 328, 1366–1367 (2010).
8. Zhang, R., Khalizov, A., Wang, L., Hu, M. & Xu, W. Nucleation and growth of nanoparticles in the atmosphere. Chem. Rev. 112, 1957–2011 (2012).
9. Spilia, M. et al. M. The role of sulfuric acid in atmospheric nucleation. Science 327, 1243–1246 (2010).
10. Chen, M. et al. Acid-base chemical reaction model for nucleation rates in the polluted atmospheric boundary layer. Proc. Natl Acad. Sci. USA 109, 18713–18718 (2012).
11. Almeida, J. et al. Molecular understanding of sulphuric acid–amine particle nucleation in the atmosphere. Nature 502, 359–363 (2013).
12. Kirby, J. et al. Role of sulphuric acid, ammonia and galactic cosmic rays in atmospheric aerosol nucleation. Nature 476, 429–433 (2011).
13. Smith, J. N. et al. Chemical composition of atmospheric nanoparticles formed from nucleation in Tecamac, Mexico: evidence for an important role for organic species in nanoparticle growth. Geophys. Res. Lett. 35, L04808 (2008).

14. Kuang, C. et al. An improved criterion for new particle formation in diverse atmospheric environments. Atmos. Chem. Phys. 10, 8469–8480 (2010).

15. Kulmala, M. & Kerminen, V.-M. On the growth of atmospheric nanoparticles. Atmos. Res. 90, 132–150 (2008).

16. Barlow, C., Caut, P. H., Smith, J. N. The potential contribution of organic salts to new particle growth. Atmos. Chem. Phys. 9, 2949–2957 (2009).

17. Smith, J. N. et al. Observations of aminium salts in atmospheric nanoparticles and possible climatic implications. Proc. Natl Acad. Sci. USA 107, 6634–6639 (2010).

18. Zhang, R. Y. et al. Atmospheric new particle formation enhanced by organic acids. Science 304, 1487–1490 (2004).

19. Zhang, R. et al. Formation of nanoparticles of blue haze enhanced by anthropogenic pollution. Proc. Natl Acad. Sci. USA 106, 17650–17654 (2009).

20. Yao, L. et al. Atmospheric new particle formation from sulfuric acid and amines in a Chinese megacity. Science 361, 278–281 (2018).

21. Arquero, K. D., Gerber, R. B. & Finlayson-Pitts, B. J. The role of oxalic acid in new particle formation from methanesulfonic acid, methylamine, and water. Environ. Sci. Technol. 51, 2124–2130 (2017).

22. Ge, X., Wexler, A. S. & Clegg, S. L. Atmospheric amines – Part I. A review. Atmos. Environ. 45, 524–546 (2011).

23. Kurtén, T., Loudon, V., Vehkamäki, H. & Kulmala, M. Amines are likely to enhance neutral and ion-induced sulfuric acid/dimethylamine nucleation in the atmosphere more effectively than ammonia. Atmos. Chem. Phys. 8, 4095–4103 (2008).

24. Berndt, T. et al. Laboratory study on new particle formation from the reaction OH+SO2: influence of experimental conditions H2O vapour, NH3, and the amine tert-butylamine on the overall process. Atmos. Chem. Phys. 10, 1499–1511 (2010).

25. Yu, H., McGraw, R. & Lee, S.-H. Effects of amines on formation of sub-3 nm particles and their subsequent growth. Geophys. Res. Lett. 39, 1 (2012).

26. Glasoe, W. A. et al. Sulfuric acid nucleation: an experimental study of the effect of seven bases. J. Geophys. Res. 120, 1933–1950 (2015).

27. Makar, P. A. The estimation of organic gas vapor pressure. Atmos. Environ. 35, 961–974 (2001).

28. Andreake, M. O., Talbot, R. W. & Li, S. M. Atmospheric measurements of pyruvic and formic acid. J. Geophys. Res. 92, 6635–6641 (1987).

29. Andreake, M. O., Talbot, R. W., Andreake, T. W. & Harris, R. C. Formic and acetic acid over the central Amazon region, Brazil: 1. dry season. J. Geophys. Res. 93, 1616 (1988).

30. Talbot, R. W. et al. Distribution and geochemistry of aerosols in the tropical north Atlantic troposphere: relationships to Saharan dust. J. Geophys. Res. 91, 5173–5182 (1986).

31. Talbot, R. W., Beecher, K. M., Harris, R. C. & Cofer III, W. R. Atmospheric geochemistry of formic and acetic acids at a mid-latitude temperate site. J. Geophys. Res. 97, 16525–16532 (1992).

32. Li, S. M. & Winchester, J. W. Geochemistry of organic and inorganic ions of the late winter Arctic aerosol. Atmos. Chem. Phys. 23, 2401–2416 (1999).

33. Kawamura, K., Steinberg, S. & Kaplan, I. R. Homologous series of C1-C10 dicarboxylic acids, ketoacids and dicarbonyls in Artic aerosols: one year of observations. Atmos. Chem. Phys. 30, 1709–1722 (1996).

34. Mokoma, S. L. et al. Major ions in PM2.5 and PM10 released from buses: the use of diesel/biodiesel fuels under real conditions. Fuel 115, 109–117 (2014).

35. VadeVondele, J. et al. QUICKSTEP: Fast and accurate density functional calculations using a mixed Gaussian and plane wave approach. Comput. Phys. Commun. 167, 103–128 (2015).

36. Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. Phys. Rev. A 38, 5281–5286 (1988).

37. Lee, C., Yang, W. & Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B 38, 785–791 (1988).

38. Grimmer, A. Accurate description of van der Waals complexes by density functional theory including empirical corrections. J. Comput. Chem. 25, 1463–1473 (2004).

39. Grimsrud, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. J. Comput. Chem. 27, 1787–1799 (2006).

40. Weckhuysen, B., Goedeker, S., Teus, M. & Hutter, J. Separable dual-space Gaussian pseudopotentials. Phys. Rev. B 54, 1703 (1996).

41. Harteigen, C., Goedeker, S. & Hutter, J. Relativistic separable dual-space Gaussian pseudopotentials from H to Rn. Phys. Rev. B 58, 3641 (1998).

Acknowledgements

M. Kumar and J.S. Francisco acknowledge the computational support from the University of Nebraska Holland Computing Center.

Author contributions

M.K. and J.S.F. conceived the idea. E.B. and J.H. performed the experiments. M.K. and J.S.F. performed simulations. E.B. and J.H. analyzed experimental results. M.K. and J.S.F.
analyzed simulation results. E.B., J.H., M.K., and J.S.F. wrote the manuscript. All authors read and approved the manuscript.

**Additional information**

Supplementary information accompanies this paper at https://doi.org/10.1038/s42004-019-0183-7.

**Competing interests:** The authors declare no competing interests.

**Reprints and permission** information is available online at http://npg.nature.com/reprintsandpermissions/

**Publisher’s note:** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

---

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2019