PCCP

PAPER



Cite this: DOI: 10.1039/c7cp05252a

Received 3rd August 2017, Accepted 14th September 2017

DOI: 10.1039/c7cp05252a

rsc.li/pccp

Introduction

The formation of secondary organic aerosol (SOA) in the atmosphere arises from the oxidation of gas phase species emitted from biogenic and anthropogenic sources.^{1–9} These oxidation products are lower in volatility than their precursors, facilitating condensation onto existing particles as a mechanism of growth^{7,10–12} as well as generating new particles.^{10,13–15} These particles can affect climate^{15–19} by growing to sizes (~100 nm) where they scatter incoming solar radiation,^{16,20–22} and act as cloud condensation nuclei.^{23–28} Ultrafine and fine particles whose diameters are smaller than 2.5 µm have also been shown to adversely affect health,^{29–31} often leading to serious respiratory illnesses^{15,17,29,30,32–38} and increased mortality.^{33,39–41} Thus, the need to understand how these particles form and grow is crucial in order to inform public policy and mitigate their atmospheric and biological impacts.

Atmospheric models tend to under-predict ambient organic particle concentrations.^{42–45} This discrepancy may stem from

Department of Chemistry, University of California, Irvine, CA 92697, USA. E-mail: bjfinlay@uci.edu; Fax: +1 (949) 824-2420; Tel: +1 (949) 824-7670

Knudsen cell studies of the uptake of gaseous ammonia and amines onto C3–C7 solid dicarboxylic acids

Michelle C. Fairhurst, 🔟 Michael J. Ezell ២ and Barbara J. Finlayson-Pitts ២ *

While atmospheric particles affect health, visibility and climate, the details governing their formation and growth are poorly understood on a molecular level. A simple model system for understanding the interactions between the gas and particle phases is the reaction of bases with acids, both of which are common constituents of atmospheric particles. In the present study, uptake coefficients for the reactions of gas phase ammonia, methylamine, ethylamine, dimethylamine and trimethylamine with a series of solid dicarboxylic acids (diacids) were measured at 296 \pm 1 K using a Knudsen cell interfaced to a quadrupole mass spectrometer. The uptake coefficients (γ) for a given amine follow an odd-even trend in carbon number of the diacid, and are larger for the odd carbon diacids. Values range from γ = 0.4 for ethylamine on malonic acid (C3) to less than $\sim 10^{-6}$ for ammonia and all amines on adjpic (C6) and pimelic (C7) acids. Basicity or structure of the amines/ammonia alone do not explain the effect of the base on uptake. The crystal structures of the diacids also play a key role, which is especially evident for malonic acid (C3). Evaporation of aqueous mixtures of amines/ammonia with odd carbon diacids show the formation of ionic liquids (ILs) or in some cases, metastable ILs that revert back to a stable solid salt upon complete evaporation of water. The trends with amine and diacid structure provide insight into the mechanisms of uptake and molecular interactions that control it, including the formation of ionic liquid layers in some cases. The diversity in the kinetics and mechanisms involved in this relatively simple model system illustrate the challenges in accurately representing such processes in atmospheric models.

> the inability to account for the complex heterogeneous chemistry occurring in the atmosphere.^{42–45} For example, it is known that the phase of particles governs the partitioning mechanism of gas phase molecules into the condensed phase.^{1,2,46–48} It had been assumed that SOA particles are liquid-like, and thus grow *via* a thermodynamic quasi-equilibrium with gas phase species.^{4,14,49–54} However, recent work has shown that SOA particles can adopt a more viscous or tar-like phase,^{55–67} in which case gas phase species condense by a kinetic, diffusion-limited process.^{1,2,48} In this context, laboratory studies on model systems can help elucidate mechanisms behind typical atmospheric observations and potentially reduce the discrepancies between modeled and measured atmospheric particle concentrations.

> Extensive studies of the reaction of amines and/or ammonia (NH₃) with inorganic acids such as sulfuric and nitric acid,^{10,68–79} and recent studies with methanesulfonic acid^{80–86} have been conducted to assess their importance in new particle formation and growth. Amines and ammonia are ubiquitous in the atmosphere, with concentrations of ammonia generally surpassing those of amines.^{87–93} Ammonia has been shown to affect properties of SOA, including yield,^{94,95} composition,^{94,96–100}



View Article Online

optical properties^{94,101–103} and evaporation kinetics.⁹⁶ However, ammonia has been shown to be less effective at forming particles with sulfuric acid^{68,71,78,79,104–106} and methanesulfonic acid^{80,81} compared to amines.

Dicarboxylic acids (diacids) are another important class of atmospherically relevant acids found in particles from different regions around the world.^{107–114} Furthermore, ammonium and aminium ions often coexist with dicarboxylic acid anions in atmospheric particles.^{115–117} Thus, a molecular level understanding of amine–diacid reactions would be helpful in accurately predicting particle formation and growth in the atmosphere. It is also of significant intrinsic chemical interest because of the dependence of the physical properties and chemical reactivity of diacids on carbon chain length and structure.^{118–123}

Reactive uptake of amines on some organic acids has been studied. Uptake coefficients, defined as the fraction of collisions leading to reaction, ranged from $(6-7) \times 10^{-3}$ to $(5-13) \times 10^{-6}$ for citric and humic acids, respectively.¹²⁴ The larger uptake coefficients for amines on citric acid were correlated with the higher acidity of citric acid compared to humic acid,¹²⁴ and steric effects were evident. In our previous study of the reactions of gaseous *n*-butylamine (BA) with a series of solid diacids, the uptake coefficients exhibited an odd–even carbon dependence.¹²⁵ Increased uptake on the odd carbon diacids was interpreted in terms of formation of ionic liquid (IL) layers on the surface of the diacid crystals to create a multi-phase system in which continued uptake and reaction can occur.

Here we report studies of the interactions of gas phase ammonia and a series of amines (methylamine, ethylamine, dimethylamine and trimethylamine) with solid C3 to C7 diacids (HOOC–(CH₂)_{*n*}–COOH, n = 1-5). The dependence of the uptake coefficient on the structures of both the diacid and base are investigated to obtain a molecular level understanding of the factors controlling the kinetics and mechanisms of these reactions.

Experimental

Knudsen cell experiments

Measurements of the uptake of amines and ammonia on solid diacids were performed using a Knudsen cell coupled to an electron impact ionization (70 eV) quadrupole mass spectrometer (QMS, Extrel) described in detail previously.¹²⁵⁻¹³⁰ The Knudsen cell was interfaced to the QMS using orifices with diameters of either 1.40 or 6.28 mm. Experiments were performed at ambient temperature (296 \pm 1 K). To ensure free-molecular regime kinetics,131-133 pressures within the Knudsen cell were kept ≤ 0.3 mTorr and monitored using a Pirani pressure gauge (Edwards, APG100-XLC) with an active gauge controller (Edwards). Malonic acid (C3), succinic acid (C4), glutaric acid (C5), adipic acid (C6), and pimelic acid (C7) (Fig. 1) were used, all having a stated purity of \geq 99% (Sigma-Aldrich). As described in detail previously,¹²⁵ samples of diacid crystals were first sieved between two sieve sizes and then placed in a sample holder coated with halocarbon wax (Halocarbon Products Corporation, Series 1500) and arranged so that the majority of crystals were non-contiguous



Fig. 1 Structures of gas phase ammonia and amines and solid diacids used in uptake experiments.

and covered an area less than that of the sample holder. Diacid samples were kept covered by a moveable lid mounted on a vacuum feedthrough and opened under vacuum for 20 minutes to remove loosely bound water. The lid was then closed until introduction of the gaseous base.

Gas phase methylamine (MA; Sigma-Aldrich, \geq 98%), ethylamine (EA; Sigma-Aldrich, 97%), dimethylamine (DMA; Sigma-Aldrich, \geq 99%), trimethylamine (TMA; Sigma-Aldrich, \geq 99%) and ammonia (Matheson, 99.99%) (Fig. 1) were used without further purification. For concentrations $(3-6) \times 10^{12}$ molecules cm⁻³, the gas phase amine or ammonia was stored without dilution in an evacuated 5 L bulb. For lower concentrations, $(3-5) \times 10^{11}$ molecules cm⁻³, the base was diluted with helium (Praxair, 99.999%). With the moveable lid closed, the amine or ammonia was introduced into the Knudsen cell via a vacuum manifold using a stainless steel needle valve and allowed to condition the cell until a steady signal was achieved. The following mass fragments were monitored: for MA and EA m/z 30 (H₂C=NH₂⁺); DMA m/z 44 (H₂C=NH(CH₃)⁺); TMA m/z58 (H₂C=N(CH₃)₂⁺). The background intensity of m/z 17, which corresponds to the most intense fragment of ammonia (NH_3^+) , was significant without added ammonia due to background water. Therefore, the ion at m/z 16 (NH_2^+) for ammonia was used instead. There was still a contribution from background water at this mass, but it was about an order of magnitude smaller than that at m/z 17.

Uptake coefficients were calculated using eqn (1):^{1,131}

$$\gamma = \left(\frac{I_0}{I_r} - 1\right) \left(\frac{A_{\text{orifice}}}{A_{\text{surf}}}\right) \tag{1}$$

In eqn (1), I_0 is the background-corrected amine/ammonia QMS signal intensity during the steady-state flow of amine/ammonia into the Knudsen cell with the diacid sample covered and unavailable for reaction, and I_r is the background-corrected signal intensity observed with the diacid sample uncovered and thus available for reaction. A_{orifice} is the area of the orifice (cm²)

separating the QMS from the Knudsen cell, and A_{surf} is the reactive surface area of the diacid (cm²) sample. A_{orifice} was determined from the orifice diameters measured by calipers.

The surface area of the diacid (A_{surf}) in an experiment was calculated as the product of the number of diacid crystals and the average surface area of a single crystal.¹²⁵ Three separate measurements of the total mass of 50 or more sieved crystals (Sartorius scale model 1702, ± 0.0001 g) were used to determine the average mass of one crystal. The total number of sieved crystals in a given Knudsen cell experiment was calculated from the mass of sample used and the averaged mass per crystal. The edges of 20 randomly chosen sieved crystals were also measured separately using calipers to get an average edge length of a single crystal. Assuming the crystals are cubic with five sides available for reaction, the average reactive surface area of a single crystal was calculated and using the number of crystals, the total reactive surface area was obtained.

To calculate the uncertainty in the uptake coefficient in each experiment, a propagation of errors from signal intensity, orifice area and surface area was used to account for random errors. However, the uncertainty in the surface area of the diacids is the largest contributor to the uncertainty in the uptake coefficients,¹²⁵ which includes both random and systematic errors. The 2σ statistical uncertainty in the surface area is in the range of 30–60% (Tables 1–5). However, given the assumptions regarding the crystal shapes, number of sides available for reaction and that one average particle size is representative, we estimate the overall uncertainty is a factor of two for a given experiment. The statistical uncertainty associated with the

average value of the uptake coefficient from replicate experiments was significantly smaller than this in some cases. The values of the uptake coefficients reported in Tables 1–3 are the averages of replicate experiments $\pm 2\sigma$, reflecting only the reproducibility from one experiment to another.

Formation of ammonium or aminium salts and viscosity measurements

Mixtures of *n*-butylamine (BA) with odd carbon diacids¹²⁵ and amines with monocarboxylic acids¹³⁴ have been previously shown to form ionic liquids. To explore the propensity to form ionic liquids in the current study, aqueous solutions of MA (Sigma-Aldrich, 40 wt% in H₂O), EA (Sigma-Aldrich, 66.0-72.0 wt% in H₂O), DMA (Sigma-Aldrich, 40 wt% in H₂O), TMA (Sigma-Aldrich, 45 wt% in H₂O) and ammonium hydroxide (Fisher Scientific, 29 wt%) were used to make 2:1 and 1:1 molar ratio solutions with each solid diacid mixed in Milli-Q[™] water (18.2 M Ω cm). Solutions were evaporated using a roto-vap (Wheaton, SPIN-VAP) at T = 80-90 °C and the resulting products were stored under either nitrogen (Praxair, 99.999%) or ultra-zero air (Praxair, 19.5–23.5% oxygen, <2 ppm water, <0.1 ppm total hydrocarbons, <0.5 ppm carbon monoxide, <0.5 ppm carbon dioxide, balance nitrogen). If the resulting product was a liquid, the viscosity (μ) was measured with a falling sphere viscometer using eqn (2):135

$$\mu = \frac{2gr^2(\rho_{\rm s} - \rho_{\rm f})}{9V} \tag{2}$$

In eqn (2), g is the gravitational constant (9.8 m s⁻²), r is the radius of a metal sphere (2.18 \times 10⁻³ m) of known density

Table 1Uptake coefficients (γ) for ammonia and amines on malonic acid (C3)					
Gas phase species	Surface area $\pm 2\sigma^a$ (cm ²)	$[\text{Gas}]_0 \pm 2\sigma^b (\text{units of } 10^{12} \text{ cm}^{-3})$	$\gamma_0{}^d\pm 2\sigma^e$	$\gamma_{0,\mathrm{ss}}{}^f\pm2\sigma^e$	$\gamma_{ m ss}{}^g\pm 2\sigma^e$
NH ₃	9.2 ± 4.6	0.44 ± 0.04 (3)	_	_	$(2.1 \pm 1.2) imes 10^{-3}$
	9.4 ± 4.7	4.0 ± 0.4 (3)	—	—	$(8.8 \pm 2.8) \times 10^{-3 h}$
MA	1.7 ± 0.7	0.42 ± 0.07 (4)	0.58 ± 0.21	0.20 ± 0.03	_
	4.3 ± 1.8	0.42 ± 0.09 (4)	0.26 ± 0.04	0.25 ± 0.04	_
	1.6 ± 0.8	$4.5 \pm 0.4 (4)$	0.48 ± 0.10	0.11 ± 0.01	_
	4.1 ± 2.0	4.4 ± 1.4 (3)	0.24 ± 0.10	0.11 ± 0.02	—
EA	1.8 ± 0.7	0.44 ± 0.10 (5)	0.85 ± 0.26	0.39 ± 0.16	_
	4.0 ± 2.0	0.42 ± 0.13 (3)	0.44 ± 0.18		0.38 ± 0.10^{h}
	1.8 ± 0.8	$4.7 \pm 0.4 (4)$	0.99 ± 0.08	0.32 ± 0.09	_
	4.2 ± 1.5	4.5 ± 1.3 (6)	0.55 ± 0.45	0.35 ± 0.05	_
DMA	1.8 ± 0.9	0.42 ± 0.07 (3)	0.75 ± 0.19	0.30 ± 0.03	_
	4.2 ± 2.1	0.40 ± 0.08 (3)	0.43 ± 0.27	0.28 ± 0.05	_
	1.8 ± 0.8	4.2 ± 0.5 (4)	0.78 ± 0.17	0.21 ± 0.04	_
	4.3 ± 2.2	4.5 ± 0.4 (3)	0.48 ± 0.05	0.28 ± 0.04	_
TMA	1.7 ± 0.9	0.37 ± 0.04 (3)	_	_	0.14 ± 0.04
	4.0 ± 2.0	$0.38^{c}(3)$	_	_	0.13 ± 0.03
	1.7 ± 0.7	3.0 ± 0.6 (4)	_	_	0.13 ± 0.09
	4.1 ± 2.0	2.8 ± 0.4 (3)	—	—	0.15 ± 0.02

^{*a*} Standard deviations represent 2σ for the distribution of crystal sizes in each sample. Orifice areas for all experiments were 0.31 cm², except for those with NH₃ which were 0.015 cm². ^{*b*} Standard deviations represent 2σ for the variation in amine concentration. Number of experiments given in parentheses. ^{*c*} Amine concentration for all samples was the same. ^{*d*} Average of the rapid, initial uptake for the first trial for all samples. ^{*e*} Errors are reported as two sample standard deviations of the average of replicate experiments. However, as described in the text, the overall uncertainty is estimated to be about a factor of two. ^{*f*} Uptake coefficients are extrapolated as described in the text for the first trial for all samples. ^{*g*} Uptake is constant with time as indicated in Fig. 3b. Averages are of repeated trials. ^{*h*} Uptake coefficients were steady-state for each trial, however they decreased with each increasing trial, and thus represent an average of the first trial for all samples.

Table 2 Uptake coefficients (γ) for ammonia and amines on succinic acid (C4)

Gas phase species	${f Surface}\ { m area}\pm 2\sigma^a\ ({ m cm}^2)$	$[\mathrm{Gas}]_0\pm 2\sigma^b \ (\mathrm{units~of}\ 10^{12}~\mathrm{cm}^{-3})$	${\gamma_{ m ss}}^d\pm 2\sigma^e$
NH ₃	$\begin{array}{c} 18.9\pm5.7\\ 19.4\pm5.8 \end{array}$	$\begin{array}{c} 0.42^c (3) \\ 3.8 \pm 0.4 (3) \end{array}$	$\begin{array}{l} \leq 2 \times 10^{-6} \\ \leq 9 \times 10^{-6} \end{array}$
MA	$\begin{array}{c} 19.6\pm5.9\\ 19.8\pm6.0 \end{array}$	$\begin{array}{c} 0.41 \pm 0.1 \ (2) \\ 4.2 \pm 1.1 \ (3) \end{array}$	$egin{aligned} (6.4 \pm 1.9) imes 10^{-5} \ (4.0 \pm 0.4) imes 10^{-5} \end{aligned}$
EA	$\begin{array}{c} 18.6\pm5.6\\ 18.9\pm5.7\end{array}$	$\begin{array}{c} 0.37 \pm 0.04 \; (3) \\ 3.8 \pm 1.0 \; (3) \end{array}$	$egin{array}{l} (6.7 \pm 2.8) imes 10^{-5} \ (6.5 \pm 0.7) imes 10^{-5} \end{array}$
DMA	$\begin{array}{c} 19.1 \pm 5.7 \\ 19.5 \pm 5.9 \end{array}$	$\begin{array}{c} 0.43 \pm 0.07 \ (3) \\ 4.5 \pm 0.4 \ (3) \end{array}$	$egin{array}{l} (1.0 \pm 0.6) imes 10^{-4} \ (0.45 \pm 0.02) imes 10^{-4} \end{array}$
TMA	$\begin{array}{c} 19.4\pm5.8\\ 20.1\pm7.4\end{array}$	$\begin{array}{c} 0.38 \pm 0.04 \; (3) \\ 4.6^c (2) \end{array}$	$\begin{array}{l} \leq 2 \times 10^{-5} \\ \leq 1 \times 10^{-5} \end{array}$

^{*a*} Standard deviations represent 2σ for the distribution of crystal sizes in each sample. Orifice areas were 0.015 cm² for all experiments. ^{*b*} Standard deviations represent 2σ for the variation in amine concentration. Number of experiments given in parentheses. ^{*c*} Amine concentration for all samples was constant. ^{*d*} Uptake coefficients decreased with increasing numbers of trials; these values represent the average of the first trial for all samples. ^{*e*} Errors are reported as two sample standard deviations of the average of replicate experiments. However, as described in the text, the overall uncertainty is estimated to be about a factor of two.

 $(\rho_{\rm s}, 7.96 \times 10^3 \text{ kg m}^{-3}), \rho_{\rm f}$ is the density of the liquid (kg m⁻³), and *V* is the velocity of the metal sphere in the liquid (m s⁻¹). The density of the liquid was measured from the mass of a known liquid volume. Velocity was measured by recording the metal sphere falling through the liquid in slow motion and measuring the distance travelled over a given time.

Results and discussion

Fig. 2 shows typical data for the uptake of amines and ammonia on malonic (C3), succinic (C4) and glutaric (C5) acids at amine concentrations of $(3-5) \times 10^{11}$ molecules cm⁻³. No uptake was observed on a clean, halocarbon wax coated sample holder. Data for adipic (C6) and pimelic (C7) acids consistently yielded very small decreases in intensities when the lid was open so that values for γ were the same order of magnitude as the error, 2σ , and thus were treated as upper limits for the uptake coefficient. The same is true of TMA uptake on succinic acid (C4). Tables 1–5 summarize the experimental conditions for all base–acid combinations studied here.

The initial uptake behavior on malonic acid (C3) differed from that on the larger diacids. Thus, the uptake of MA, EA and DMA on malonic acid (C3) showed an initial, very rapid, shortlived uptake that was not seen for the other four diacids (Fig. 2). This was followed by a slower, declining uptake similar to that observed for the other diacids. In order to quantify both the initial large uptake and that observed at longer times, the data for malonic acid (C3) were analyzed as illustrated schematically in Fig. 3. Initial uptake coefficients, defined as γ_0 , reflect the spike in the uptake at the shortest reaction times; note these may be lower limits as the time resolution of the measurements may not have been sufficiently high to capture the true minimum in I_r . To obtain the steady-state values of the uptake coefficients for malonic acid (C3), the linear portion of the signals that followed the spike were extrapolated back to the time at which the initial spike occurred, t_{spike} (Fig. 3a), using a linear regression. These values are reported as $\gamma_{0,ss}$. For the rest of the diacids where no initial spike was observed, the steady-state uptake coefficient is defined as γ_{ss} (Fig. 3b).

	1.	5		
Gas phase species	Surface area $\pm 2\sigma^a$ (cm ²)	$[Gas]_0 \pm 2\sigma^b$ (units of 10 ¹² cm ⁻³)	${\gamma_0}^c\pm 2\sigma^d$	${\gamma_{ m ss}}^e\pm 2\sigma^d$
NH ₃	14.2 ± 6.6	0.46 ± 0.04 (3)	_	\leq 3 $ imes$ 10 ⁻⁵
	13.9 ± 6.4	$3.9 \pm 0.01(3)$	—	\leq 2 $ imes$ 10 $^{-5}$
MA	1.8 ± 0.7	0.45 ± 0.1 (4)	_	0.066 ± 0.025
	4.5 ± 1.8	0.45 ± 0.05 (4)	_	0.046 ± 0.012
	1.9 ± 0.8	$4.1 \pm 1.1 (4)$	0.083 ± 0.025	
	4.4 ± 2.0	5.1 ± 0.8 (3)	0.085 ± 0.012	_
EA	1.8 ± 0.8	0.42 ± 0.07 (3)	_	0.056 ± 0.030
	4.4 ± 2.0	0.50 ± 0.10 (3)	_	0.056 ± 0.022
	1.9 ± 0.9	4.0 ± 1.0 (4)	0.12 ± 0.03	_
	4.6 ± 2.1	3.9 ± 0.7 (3)	0.10 ± 0.02	—
DMA	1.9 ± 0.9	0.45 ± 0.04 (3)	_	0.038 ± 0.022
	4.5 ± 2.1	0.47 ± 0.04 (3)		0.027 ± 0.006
	1.8 ± 0.8	4.3 ± 0.8 (3)	0.10 ± 0.01	
	4.3 ± 2.0	4.3 ± 0.4 (3)	0.073 ± 0.006	_
TMA	16.6 ± 7.8	0.33 ± 0.09 (3)	_	$(4.2 \pm 1.1) imes 10^{-5 f}$
	16.1 ± 7.5	$5.1 \pm 1.0 (3)$	_	$(6.2 \pm 3.1) \times 10^{-5f}$

Table 3 Uptake coefficients (γ) for ammonia and amines on glutaric acid (C5)

^{*a*} Standard deviations represent 2σ for the distribution of crystal sizes in each sample. Orifice areas for all experiments were 0.31 cm², except for those with NH₃ and TMA which were 0.015 cm². ^{*b*} Standard deviations represent 2σ for the variation in amine concentration for those runs. Number of experiments are given in parentheses. ^{*c*} Uptake coefficients decreased with time, these values represent the average of the initial uptake region for the first trial for all samples. ^{*d*} Errors are reported as two sample standard deviations of the average of replicate experiments. However, as described in the text, the overall uncertainty is estimated to be about a factor of two. ^{*e*} Uptake is represent the average of the first trial for all samples.

Table 4 Upper limits for the uptake coefficients (γ) for ammonia and amines on adipic acid (C6)

Gas phase species	Surface area $\pm 2\sigma^a$ (cm ²)	$[\mathrm{Gas}]_0\pm 2\sigma^b$ (units of 10 ¹² cm ⁻³)	γ_{ss}
NH ₃	$\begin{array}{c} 29.2 \pm 18.6 \\ 27.5 \pm 17.5 \end{array}$	$\begin{array}{c} 0.48 \pm 0.07 \ (3) \\ 4.0 \pm 0.4 \ (3) \end{array}$	$\begin{array}{c} \leq 6 \times 10^{-6} \\ \leq 3 \times 10^{-6} \end{array}$
MA	$\begin{array}{c} 31.3 \pm 19.9 \\ 28.7 \pm 18.2 \end{array}$	$0.40 \pm 0.1 \ (3) \\ 4.2 \pm 0.6 \ (3)$	${\leq}5 imes10^{-6}\ {\leq}4 imes10^{-6}$
EA	$\begin{array}{c} 28.6 \pm 18.1 \\ 28.2 \pm 17.9 \end{array}$	$\begin{array}{c} 0.39 \pm 0.07 \ (3) \\ 4.2 \pm 1.3 \ (3) \end{array}$	${\leq}1 imes10^{-5}\ {\leq}7 imes10^{-6}$
DMA	$\begin{array}{c} 28.0 \pm 17.8 \\ 27.3 \pm 17.3 \end{array}$	$\begin{array}{c} 0.34 \pm 0.04 \; (3) \\ 4.3 \pm 0.4 \; (3) \end{array}$	${\leq}5 imes10^{-6}\ {\leq}5 imes10^{-6}$
TMA	$\begin{array}{c} 30.3 \pm 19.3 \\ 30.2 \pm 16.6 \end{array}$	$\begin{array}{c} 0.40 \pm 0.08 \ (3) \\ 3.8 \pm 1.6 \ (4) \end{array}$	$\begin{array}{l} \leq 3 \times 10^{-6} \\ \leq 5 \times 10^{-6} \end{array}$

^{*a*} Standard deviations represent 2σ for the distribution of crystal sizes in each sample. Orifice areas were 0.015 cm² for all experiments. ^{*b*} Standard deviations represent 2σ for the variation in amine concentration for those runs. Number of experiments given in parentheses.

Table 5 Upper limits for uptake coefficients (γ) for ammonia or amines on pimelic acid (C7)

Gas phase species	Surface area $\pm 2\sigma^a$ (cm ²)	$[\mathrm{Gas}]_0\pm 2\sigma^b$ (units of 10 ¹² cm ⁻³)	$\gamma_{\rm ss}$
NH ₃	$\begin{array}{c} 9.2 \pm 5.0 \\ 9.1 \pm 6.1 \end{array}$	$\begin{array}{c} 0.43 \pm 0.07 \ (3) \\ 4.1 \pm 0.5 \ (2) \end{array}$	$\leq 4 imes 10^{-5} \ \leq 8 imes 10^{-6}$
MA	$\begin{array}{c} 9.0 \pm 4.9 \\ 9.3 \pm 5.1 \end{array}$	$\begin{array}{c} 0.41 \pm 0.08 \ (3) \\ 3.7 \pm 0.4 \ (3) \end{array}$	$\begin{array}{l} \leq 2 \times 10^{-5} \\ \leq 2 \times 10^{-5} \end{array}$
EA	$\begin{array}{c} 9.1 \pm 4.9 \\ 9.2 \pm 5.0 \end{array}$	$\begin{array}{c} 0.42 \pm 0.13 \ (3) \\ 4.4 \pm 0.8 \ (3) \end{array}$	${\leq}2 imes10^{-5}\ {\leq}2 imes10^{-5}$
DMA	$\begin{array}{c} 9.1 \pm 5.0 \\ 9.2 \pm 5.0 \end{array}$	$\begin{array}{c} 0.46 \pm 0.07 \ (3) \\ 4.5 \pm 0.4 \ (3) \end{array}$	${\leq}2 imes10^{-5}\ {\leq}9 imes10^{-6}$
TMA	$\begin{array}{c} 9.1 \pm 6.0 \\ 9.2 \pm 5.0 \end{array}$	$\begin{array}{c} 0.44 \pm 0.05 \ (2) \ 4.6 \pm 1.0 \ (3) \end{array}$	${\leq}1 imes10^{-5}\ {\leq}1 imes10^{-5}$

^{*a*} Standard deviations represent 2σ for the distribution of crystal sizes in each sample. Orifice areas were 0.015 cm² for all experiments. ^{*b*} Standard deviations represent 2σ for the variation in amine concentration for those runs. Number of experiments are given in parentheses.

Tables 1–5 summarize the measured uptake coefficients for each experimental condition for all base–acid combinations. Note that the uncertainties reported are determined by propagation of errors, and do not include possible systematic errors. As discussed above, the largest potential systematic error is in the available surface area which we estimate to be as much as a factor of two. Thus, uptake coefficients are considered significantly distinctive if they differ by more than a factor of two.

The values of the steady-state uptake coefficients for malonic (C3), succinic (C4) and glutaric (C5) acids that show measurable uptake is independent of the mass of the diacid used, *i.e.*, of the total surface area, as expected (Tables 1–3). This is not the case for the initial uptake coefficients, γ_0 , for malonic acid (C3), where the values were smaller for the larger diacid mass (Table 1). Possible reasons for this are discussed below. Uptake

coefficients for the most part are relatively insensitive to the amine concentration. The exception is glutaric acid (C5), where there is a trend to higher uptake coefficients at higher gas phase base concentration (Table 3).

Fig. 4 summarizes the uptake coefficients as a function of carbon number for ammonia and each amine. As observed in the earlier studies of BA with diacids, all of the amines studied here exhibit an odd-even carbon trend in the uptake coefficients. with the values decreasing with increasing chain length. Fig. 4 also shows that uptake coefficients for even carbon diacids are orders of magnitude smaller than those for odd carbon diacids. This behavior likely reflects the differences in the crystal structure of the even carbon diacids compared to the odd carbon compounds.¹²¹ Solid C2-C10 diacids self-assemble end-to-end via hydrogen bonds to form infinite chains. In C4-C10 diacids, adjacent elongated chains aggregate due to hydrophobic interactions between methylene chains to form monoclinic crystal structures. However, there is a difference in inter-chain packing between the even and odd carbon diacids in their crystal structure. Even carbon diacids \geq C6 stack in an offset packing arrangement along the methylene chains. On the other hand, odd carbon diacids \geq C5 have their -COOH groups out of plane with the methylene chains, leading to torsional strain on the carbon chains and higher energy conformations. This torsional strain also results in more space between chains. The combination of lower lattice stability and larger inter-chain spacing has been proposed to facilitate the penetration of water in between lattice chains, and thus contribute to a higher aqueous solubility for the odd carbon diacids.122 A similar phenomenon is expected to allow the gas phase amines to exhibit greater penetration in the odd carbon diacids. In DART-MS (direct analysis in real time mass spectrometry) studies of amine-reacted diacid particles using a flow reactor, the odd-even alternation was observed in the fraction of amine taken up into the diacid particles.136 The amount of amine in the diacid particles also decreased with each increasing carbon number.

Malonic acid (C3) is unique in its crystal structure, in that it is the only triclinic structure of the diacids investigated here,^{121,137} has the least crystal symmetry¹³⁷ and the weakest hydrophobic interactions compared to the other diacids since there is only a single methylene group interacting between adjacent chains. The orientation of the -COOH groups is different from the rest of the diacid series, in that one acidic group lies roughly in plane with the carbon chain, while the other is rotated about 90°. This orientation is in contrast to the other odd carbon diacids where there are two regions of symmetry: one along the carbon chain and one within the two -COOH groups.137 These characteristics suggest that of all the diacids in this study, malonic acid (C3) has the loosest crystal packing, potentially the highest number of crystal defects, and at least one acidic group that might be more readily available for reaction. All these factors may increase its reactivity compared to the larger diacids.

In general, when an ammonia or amine molecule reacts with the diacid surface, the first step involves formation of a monoammonium or aminium carboxylate salt (molar ratio 1:1). This is expected to disrupt the crystal surface, making it more porous.



Fig. 2 Uptake of ammonia (NH₃) and amines at concentrations of $(3-5) \times 10^{11}$ molecules cm⁻³ on malonic acid (C3), succinic acid (C4) and glutaric acid (C5). The succinic acid surface area was ~20 cm². For all of the malonic acid runs except NH₃, $A_{surf} \sim 2 \text{ cm}^2$; for NH₃, $A_{surf} \sim 9 \text{ cm}^2$. For glutaric acid, $A_{surf} \sim 2 \text{ cm}^2$ for MA, EA and DMA, 14 cm² for NH₃ and 16 cm² for TMA. Note the expanded scales used to show the succinic acid (C4) data. No uptake was observed on adipic (C6) or pimelic (C7) acids. For all primary and secondary amines on malonic (C3) and glutaric (C5) acids, sensitivity on the lock-in amplifier was 100 mV. For all amines (except for EA) and ammonia on succinic acid (C4) and TMA on glutaric acid (C5) sensitivity on the lock-in amplifier was 10 mV. For EA on succinic acid (C4), the sensitivity was 10 mV.



Fig. 3 Schematic of uptake coefficients derived for (a) amines on malonic acid (C3), and (b) derivation of steady-state uptake coefficients for all other diacids.

This could effectively lead to reaction of many underlying layers of the diacid, not just the surface monolayer. As this occurs, the 1:1

salt can be converted to the dicarboxylate salt (molar ratio 2:1). If these top salt product layers are themselves solid, then surface passivation would be expected to set in as slow diffusion in the solid would limit the depth of penetration and reaction of the amine. This would manifest itself as a decrease in uptake coefficient over timescales that would depend on the magnitude of γ .

The reactions of the even carbon diacids fall into this solid product category. For example, as seen in the data for succinic acid (C4) in Fig. 2, the uptake of MA, EA and DMA is small and all show evidence of surface passivation over the course of the experiments (*i.e.* initial uptake of the amine onto the diacid surface that decreases slightly within a single measurement and decreases for each subsequent exposure to the amine). Surface saturation times for MA, EA and DMA on succinic acid (C4) were calculated as described in detail previously.¹²⁵ Briefly, the number of diacid molecules in a single unit cell can be calculated using the unit cell dimensions of the diacid. The initial number density of surface sites, S_0 , can then be derived using the weighting factor, or the fraction of the surface area that is made up of acidic groups. The first order rate constant (k') for the amine reaction on the surface is derived using kinetic molecular theory, the reactive surface area and S_0 . Assuming that the decay in surface sites follows first order kinetics, the decay in reactive sites can be expressed as $S_t = S_0 e^{-k't}$. Thus, the reciprocal of k' will give the 1/e lifetime of the reactive sites. The observation of surface saturation in Fig. 2 for succinic acid (C4) is consistent with a calculated 1/e surface saturation time of ~5 min, using $\gamma_{ss} = 6.4 \times 10^{-5}$ for MA as an example.

Paper



Fig. 4 Summary of uptake coefficients (γ_{ss}) ($\pm 2\sigma$) for amines and ammonia on C3–C7 solid diacids. Dashed lines are data at 10¹¹ molecules cm⁻³ and solid lines are data at 10¹² molecules cm⁻³. Uptake coefficients for MA, EA and DMA on malonic acid (C3) are extrapolated uptake coefficients ($\gamma_{0,ss}$) as reported in Table 1. Values for glutaric acid (C5) at 10¹² cm⁻³ are γ_0 as reported in Table 3. Arrows and parentheses indicate an upper limit.

No uptake of NH_3 was observed on succinic acid (C4). While a small change was observed in the TMA signal upon opening the lid (Fig. 2), I_r was within experimental error of I_0 and as discussed above, only an upper limit for the uptake coefficient was therefore derived.

The very small uptake of TMA is likely due to steric factors, where the highly branched amine structure minimizes penetration into the tightly packed first layers of the crystal lattice of the even carbon diacid. The lack of measurable uptake of $\rm NH_3$ may reflect its lower basicity compared to the amines, 138,139 which also is responsible for it having the lowest uptake coefficients compared to the amines across the diacid series. Lastly, there was no measurable uptake of $\rm NH_3$ nor any uptake of the amines on adipic acid (C6) (Table 4). This is attributed to the stronger hydrophobic forces between the longer methylene chains of adipic acid (C6), which makes penetration of the amines into the crystal and disruption of the structure energetically less favorable.

In the previous studies of the reactions with BA on the odd carbon diacids, uptake of the amine continued at reaction times much longer than expected for the reaction of the gas with the surface layer of the diacids.¹²⁵ This was shown to be due to the formation of an ionic liquid (IL) layer that then provided a liquid film into which the gas phase amine and underlying diacid dissolved and reacted continuously.¹²⁵ Thus, the system became a multiphase gas–liquid–solid reaction, which did not lead to surface passivation as is usually the case with gas–solid reactions. Formation of ILs for the C3, C5 and C7 diacid reactions was confirmed by mixing aqueous solutions of the acid and base, and evaporating off the water to determine if a solid or liquid salt remained.¹²⁵

In the systems under study here, uptake also continued at much longer reaction times than expected for reaction of just the surface of the odd carbon diacids. Saturation times for malonic (C3) and glutaric (C5) acids were calculated using the same method as described above for succinic acid (C4). For example, for uptake of EA on malonic acid (C3) with $\gamma_{ss} = 0.4$, the expected time to react 1/e of the surface molecules at an amine concentration of 4 \times 10¹¹ cm⁻³ is of the order of 0.2 seconds, and for glutaric acid (C5) with $\gamma_{ss} = 0.06$, is ~ 0.5 seconds. The data in Fig. 2 clearly indicate that uptake continues to occur on much longer timescales. This continuous uptake suggests that more than a monolayer at the surface is available for reaction and that formation of ionic liquids may be occurring similar to the BA reaction.¹²⁵ In the case of malonic acid (C3) reacting with the amines, there is a trend to decreasing values of $\gamma_{0,ss}$ with time, which may reflect slower diffusion of the amine through an ever-thickening reacted layer and/or solubility limitations into the developing liquid layer.

Thus, a general scenario for the reaction of the odd carbon diacids is formation of a salt product that is a stable or metastable IL that forms on the surface during reaction. In this case, surface passivation does not shut off the reaction and suggests that these liquid layers on the surface are the cause for continuous uptake observed on odd carbon diacids. The lack of reaction of pimelic acid (C7) may be due to the stronger interactions between the longer methylene chains, making initial disruption of the crystal structure more difficult on the timescale of our experiments.

As shown in Table 3, uptake coefficients for MA, EA and DMA on glutaric acid (C5) showed a trend to higher values at

higher amine concentrations. This dependence may be due to the kinetic limitations on formation of the IL layer. At the higher amine concentration, the formation of the IL may occur more rapidly than at the smaller concentration, causing more rapid formation of the IL and hence higher initial uptake of the amine into it.

To probe which amine-diacid combinations form room temperature ionic liquids, aqueous mixtures were prepared and the excess water evaporated off as in earlier studies of the BA reaction.¹²⁵ A variety of behaviors were observed in the present study. In some cases, the remaining material was a liquid whose viscosity could be measured, and which remained liquid during storage under nitrogen or ultra-zero air for up to several months. These are considered to be stable, room temperature ionic liquids. In other cases, a liquid was formed for sufficient time to make viscosity measurements, but subsequently formed a slushy material. This suggests that the salt formed initially is a thermodynamically unstable liquid, dubbed here as a metastable ionic liquid (MSIL) which, under the appropriate conditions, converts to a stable higher viscosity salt. In other cases, a solid was formed immediately. The properties of the final solid as visually observed varied from a hard solid to a softer material.

Table 6 Measured viscosities (μ) and densities ($\rho_{\rm f}$) for 2:1 and 1:1 ammonia or amines-diacid mixtures

	2:1		1:1	
Salt	μ (Pa s) $\pm 2\sigma$	$ ho_{ m f}$ (units of 10^3 kg m ⁻³)	μ (Pa s) \pm 2 σ	$ ho_{ m f}$ (units of 10 ³ kg m ⁻³)
Maloni	ic (C3)+			
NH ₃	à	а	12.1 ± 3.8^b	1.4
MA	0.9 ± 0.4	1.2	а	а
EA	13.1 ± 1.2^{b}	1.1	10.1 ± 1.4	1.3
DMA	3.5 ± 0.8^b	1.2	а	а
TMA	а	а	а	а
Succini	ic (C4)+			
MA	à	а	а	а
EA	а	а	а	а
DMA	а	а	а	а
TMA	32.3 ± 2.8	1.2	26.3 ± 2.8	1.2
Glutari	c (C5)+			
MA	15 ± 4^b	1.2	а	а
EA	8.5 ± 1.6	1.1	а	а
DMA	а	а	а	а
TMA	6.1 ± 0.8	1.1	13.9 ± 2.4	1.1
Adipic	(C6)+			
MA	a	а	а	а
EA	а	а	а	а
DMA	а	а	а	а
TMA	а	а	а	а
Pimelio	c (C7)+			
MA	20.5 ± 2^b	1.1	а	а
EA	9.8 ± 1.6^b	1.1	18.0 ± 2.2^{b}	1.1
DMA	9.9 ± 1.4	1.1	10.1 ± 1.6	1.1
TMA	13.0 ± 3.4	1.1	9.4 ± 0.6	1.1

^{*a*} Viscosity measurements could not be made. ^{*b*} Liquid product is a MSIL that subsequently formed a higher viscosity slushy material over several hours.

Table 6 indicates which products formed a MSIL, and summarizes the results of the viscosity measurements.

Photographs of the hard solid, slushy material, or liquid salts formed from evaporation of amine/ammonia and diacid mixtures are shown in Fig. 5 (odd carbon diacids) and 6 (even carbon diacids). These photographs show that most of the 2:1 mixtures of the odd carbon diacids formed either an IL or MSIL, consistent with continued uptake of most of the amines onto malonic (C3) and glutaric (C5) acids. However, the TMAmalonic acid (C3) and the DMA-glutaric acid (C5) salts were exceptions. In these two cases, the evaporation of the aqueous mixtures formed a slushy material (Fig. 5) immediately after excess water was removed. Nonetheless, dissolution of both the underlying diacid and the gas phase amine might still be expected to occur in the soft product layer. This is supported by continuous uptake of gas phase TMA on malonic acid (C3), and DMA on glutaric acid (C5) (Fig. 2). Most amines on pimelic acid (C7) form a stable IL or MSIL (Fig. 5), however no measurable uptake is observed in the Knudsen cell experiments. Results from the aqueous mixtures of pimelic acid (C7) and Knudsen cell experiments suggest that penetration into the solid and disruption of the crystal structure to form an IL layer is not sufficiently fast on the timescales and small gas phase concentrations of the Knudsen cell experiments to form an IL or MSIL layer, and hence there is no measurable uptake. It should be noted that while the determination of whether various aqueous mixtures form ILs, MSILs or salts provides some insight into the Knudson cell results, there is not a direct correlation in all cases. This likely reflects very different reaction conditions and timescales for the Knudsen cell experiments compared to evaporation of aqueous mixtures.

The overall trends in uptake shown in Fig. 2 and 4 and summarized in Tables 1-5 indicate the following. First, the uptake coefficients for all amines on malonic acid (C3) are large $(\gamma > 0.1)$ and reflect the unique crystal structure of malonic acid (C3) discussed above. Of all the amines, EA and DMA have the largest uptake coefficients. Their larger values compared to MA may be due to their higher gas phase basicity,^{138,139} while steric factors come into play with TMA. Second, the higher uptake on odd carbon diacids seen earlier for BA¹²⁵ continues to hold for the series of amines studied here. Finally, the even carbon diacids have uptake coefficients that are orders of magnitude smaller than for the odd carbon compounds, and only succinic acid (C4) gave measurable uptake for MA, EA and DMA. Lower uptake onto even carbon diacids is consistent with their more stable crystal structure and the fact that they tend to form hard solid salts rather than ILs (Fig. 6). The exception is the TMA-succinic acid (C4) reaction for which there was no measurable uptake but the aqueous mixtures did form a viscous IL (Table 6). Steric factors are likely to play a role in the penetration of TMA into the crystal, limiting the extent of reaction and formation of a liquid layer at the concentrations and timescales of the Knudsen cell experiments.

Ammonia has a much smaller uptake coefficient on malonic acid (C3) compared to the amines, and shows no evidence of observable uptake on any of the other diacids. The reaction of

Paper



Fig. 5 Products formed from the evaporation of aqueous 2:1 or 1:1 mixtures of MA, EA, DMA, TMA or NH₃ with odd carbon diacids. Green stars indicate a MSIL that converted to a higher viscosity slushy material.

 NH_3 with malonic acid (C3) shows signs of surface saturation (Fig. 2), consistent with the formation of a hard solid from its 2:1 aqueous mixture (Fig. 5). This one reaction of malonic acid (C3) therefore falls into the same category of succinic acid (C4), *i.e.* a gas–solid reaction without formation of a quasi-liquid layer.

Unique to malonic acid (C3) is a large initial uptake for most amines when the lid is first opened (Fig. 2). This is indicative of the presence of highly reactive sites such as the steps and edges of a crystal.¹⁴⁰ Once those have reacted, the molecules in the more stable crystal structure dominate, resulting in a slower gas uptake. Such behavior was previously observed for example, in the reaction of gas phase HNO₃ with solid NaCl.^{126,129,141–143} In the case of malonic acid (C3), the more easily accessible acidic group may provide the highly reactive sites, in addition to any steps/edges present on the crystals. The large initial uptake was not present with TMA in the current study, or in studies with BA on malonic acid (C3).¹²⁵ It could be that MA, EA and DMA are small enough to access these highly reactive sites more readily than BA or TMA.

It is, however, unusual that this initial "uptake spike" occurs repeatedly when the lid is opened and closed a number of times on one sample. In the case of HNO3-NaCl, the spikes only occur at the first exposures since the highly reactive sites are removed by reaction.^{126,129,141} The repetition of the spikes within one experiment seen here for malonic acid (C3) (Fig. 2) suggests that if it is due to some highly reactive sites, they must be regenerated relatively rapidly. Since these reactions form ILs and/or MSILs as the reaction proceeds (Table 6), it is possible that once the lid is closed, the ionic liquid layer may coalesce into small regions, exposing new reactive sites so that when the lid is subsequently opened, another rapid, initial uptake of the amine occurs. A similar reorganization of the sodium nitrate surface layer resulting from the reaction of NaCl with gas phase nitric acid or NO₂ was observed; in that case, exposure to water vapor induced recrystallization to generate a fresh NaCl surface.^{143,144} Reactions of SO₂ with CaCO₃ in the presence of water vapor were also observed to form islands and microcrystallite layers of CaSO3 which subsequently exposed fresh CaCO₃ sites for further reaction.¹⁴⁵ The reactions of MA, EA and DMA with malonic acid (C3) reported here are, however, unique in that water vapor is not required for this hypothesized reorganization.



Fig. 6 Products formed from the evaporation of aqueous 2:1 or 1:1 mixtures of MA, EA, DMA or TMA with even carbon diacids.

Conclusions

Both the structure of the amine and that of the solid diacid play a role in the reactive uptake of amines on solid diacids. The smaller NH_3 molecule has the lowest gas phase basicity, which plays a significant role in determining the small values for the uptake coefficients. However, for TMA, basicity alone cannot explain the trend in reaction with the diacids. TMA has the highest gas phase basicity, but also has small uptake coefficients. The bulky structure of TMA likely hinders penetration into the diacid lattices. This minimizes disruption of the surface layers and the availability of the underlying layers for reaction.

The dominant variable that appears to affect these reactions is their propensity to form an IL or MSIL layer on the surface. The amines and odd carbon diacids in the present study do not always form ILs, in contrast to the reactions of BA with odd carbon diacids.¹²⁵ In the present studies, the formation of an IL under the conditions used in the Knudsen cell is determined by both the kinetics of disruption of the surface layer, and by the thermodynamic stability of the ILs.

These data suggest that the factors affecting gas-solid uptake are varied and numerous. Although solid diacid salts are not typically found in the atmosphere, it is possible that ionic liquids may be formed *via* reactions of amines with the acidic components of semisolid SOA. This illustrates the importance of having a molecular level understanding in order to translate the results of laboratory studies into atmospheric models and ultimately into control strategies.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors are grateful for the support of the National Science Foundation (Grant #AGS-1647386) and the Army Research Office (#W911NF-17-1-0105). We are deeply appreciative to Dr Sergey Nizkorodov for lending us an optics supply board to keep the mass spectrometer functioning.

References

1 B. J. Finlayson-Pitts and J. N. Pitts Jr., *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*, Academic Press, 2000.

- 2 J. H. Seinfeld and S. N. Pandis, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley & Sons, 1998.
- 3 P. J. Ziemann and R. Atkinson, *Chem. Soc. Rev.*, 2012, **41**, 6582–6605.
- 4 M. Hallquist, J. C. Wenger, U. Baltensperger, Y. Rudich, D. Simpson, M. Claeys, J. Dommen, N. M. Donahue, C. George, A. H. Goldstein, J. F. Hamilton, H. Herrmann, T. Hoffmann, Y. Iinuma, M. Jang, M. E. Jenkin, J. L. Jimenez, A. Kiendler-Scharr, W. Maenhaut, G. McFiggans, T. F. Mentel, A. Monod, A. S. H. Prevot, J. H. Seinfeld, J. D. Surratt, R. Szmigielski and J. Wildt, *Atmos. Chem. Phys.*, 2009, 9, 5155–5236.
- 5 N. M. Donahue, A. L. Robinson and S. N. Pandis, *Atmos. Environ.*, 2009, **43**, 94–106.
- 6 J. H. Seinfeld and J. F. Pankow, Annu. Rev. Phys. Chem., 2003, 54, 121-140.
- 7 J. H. Kroll and J. H. Seinfeld, Atmos. Environ., 2008, 42, 3593-3624.
- 8 E. von Schneidemesser, P. S. Monks, J. D. Allan, L. Bruhwiler, P. Forster, D. Fowler, A. Lauer, W. T. Morgan, P. Paasonen, M. Righi, K. Sindelarova and M. A. Sutton, *Chem. Rev.*, 2015, 115, 3856–3897.
- 9 B. Noziere, M. Kaberer, M. Claeys, J. Allan, B. D'Anna, S. Decesari, E. Finessi, M. Glasius, I. Grgic, J. F. Hamilton, T. Hoffmann, Y. Iinuma, M. Jaoui, A. Kahno, C. J. Kampf, I. Kourtchev, W. Maenhaut, N. Marsden, S. Saarikoski, J. Schnelle-Kreis, J. D. Surratt, S. Szidat, R. Szmigielski and A. Wisthaler, *Chem. Rev.*, 2015, **115**, 3919–3983.
- 10 R. Y. Zhang, A. Khalizov, L. Wang, M. Hu and W. Xu, *Chem. Rev.*, 2012, **112**, 1957–2011.
- 11 M. Kulmala and V. M. Kerminen, Atmos. Res., 2008, 90, 132-150.
- 12 I. Riipinen, T. Yli-Juuti, J. R. Pierce, T. Petaja, D. R. Worsnop, M. Kulmala and N. M. Donahue, *Nat. Geosci.*, 2012, 5, 453–458.
- M. Ehn, J. A. Thornton, E. Kleist, M. Sipila, H. Junninen, I. Pullinen, M. Springer, F. Rubach, R. Tillmann, B. Lee, F. Lopez-Hilfiker, S. Andres, I. H. Acir, M. Rissanen, T. Jokinen, S. Schobesberger, J. Kangasluoma, J. Kontkanen, T. Nieminen, T. Kurten, L. B. Nielsen, S. Jorgensen, H. G. Kjaergaard, M. Canagaratna, M. Dal Maso, T. Berndt, T. Petaja, A. Wahner, V. M. Kerminen, M. Kulmala, D. R. Worsnop, J. Wildt and T. F. Mentel, *Nature*, 2014, **506**, 476–479.
- 14 N. M. Donahue, I. K. Ortega, W. Chuang, I. Riipinen, F. Riccobono, S. Schobesberger, J. Dommen, U. Baltensperger, M. Kulmala, D. R. Worsnop and H. Vehkamaki, *Faraday Discuss.*, 2013, **165**, 91–104.
- 15 U. Poschl, Angew. Chem., Int. Ed., 2005, 44, 7520-7540.
- 16 T. Stocker, D. Qin, G. Plattner, M. Tignor, S. Allen, J. Boschung, A. Nauels, Y. Xia, B. Bex and B. Midgley, *IPCC*, 2013: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, 2013.
- 17 U. Poschl and M. Shiraiwa, Chem. Rev., 2015, 115, 4440-4475.
- 18 V. Ramanathan, P. J. Crutzen, J. T. Kiehl and D. Rosenfeld, *Science*, 2001, 294, 2119–2124.

- 19 P. R. Buseck and M. Posfai, Proc. Natl. Acad. Sci. U. S. A., 1999, 96, 3372–3379.
- 20 W. C. Hinds, Aerosol Technology: Properties, Behavior and Measurement of Airborne Particles, John Wiley & Sons Inc., New York, 1999.
- 21 N. Lang-Yona, Y. Rudich, T. F. Mentel, A. Bohne, A. Buchholz, A. Kiendler-Scharr, E. Kleist, C. Spindler, R. Tillmann and J. Wildt, *Atmos. Chem. Phys.*, 2010, 10, 7253–7265.
- 22 T. Moise, J. M. Flores and Y. Rudich, *Chem. Rev.*, 2015, **115**, 4400–4439.
- 23 D. K. Farmer, C. D. Cappa and S. M. Kreidenweis, *Chem. Rev.*, 2015, **115**, 4199–4217.
- 24 V. F. McNeill, N. Sareen and A. N. Schwier, Surface-Active Organics in Atmospheric Aerosols, in *Atmospheric and Aerosol Chemistry*, ed. V. F. McNeill and P. A. Ariya, Springer Berlin Heidelberg, Berlin, Heidelberg, 2014, pp. 201–259.
- 25 M. O. Andreae and D. Rosenfeld, *Earth-Sci. Rev.*, 2008, **89**, 13–41.
- 26 J. M. Sun and P. A. Ariya, Atmos. Environ., 2006, 40, 795-820.
- 27 B. Ervens, Chem. Rev., 2015, 115, 4157-4198.
- 28 H. Wex, M. D. Petters, C. M. Carrico, E. Hallbauer, A. Massling, G. R. McMeeking, L. Poulain, Z. Wu, S. M. Kreidenweis and F. Stratmann, *Atmos. Chem. Phys.*, 2009, 9, 3987–3997.
- 29 P. M. Mannucci, S. Harari, I. Martinelli and M. Franchini, *Intern. Emerg. Med.*, 2015, 10, 657–662.
- 30 M. R. Heal, P. Kumar and R. M. Harrison, *Chem. Soc. Rev.*, 2012, **41**, 6606–6630.
- 31 R. F. Phalen, Inhalation Studies: Foundations and Techniques, CRC Press, Boca Raton, FL, 1984.
- 32 C. A. Pope and D. W. Dockery, J. Air Waste Manage. Assoc., 2006, 56, 709–742.
- 33 D. W. Dockery, C. A. Pope, X. Xu, J. D. Spengler, J. H. Ware, M. E. Fay, B. G. J. Ferris and F. E. Speizer, *N. Engl. J. Med.*, 1993, **329**, 1753–1759.
- 34 P. K. Hopke, Atmos. Environ., 2008, 42, 3192-3194.
- 35 B. R. Gurjar, A. Jain, A. Sharma, A. Agarwal, P. Gupta, A. S. Nagpure and J. Lelieveld, *Atmos. Environ.*, 2010, 44, 4606–4613.
- 36 J. L. Mauderly and J. C. Chow, *Inhalation Toxicol.*, 2008, **20**, 257–288.
- 37 R. E. Wyzga and A. C. Rohr, J. Air Waste Manage. Assoc., 2015, 65, 523–543.
- 38 P. S. J. Lakey, T. Berkemeier, H. J. Tong, A. M. Arangio, K. Lucas, U. Poschl and M. Shiraiwa, *Sci. Rep.*, 2016, 6, 32916.
- 39 J. I. Halonen, T. Lanki, T. Yli-Tuomi, P. Tiittanen, M. Kulmala and J. Pekkanen, *Epidemiology*, 2009, 20, 143–153.
- 40 X. X. Tie, D. Wu and G. Brasseur, *Atmos. Environ.*, 2009, **43**, 2375–2377.
- 41 J. Lelieveld, J. S. Evans, M. Fnais, D. Giannadaki and A. Pozzer, *Nature*, 2015, **525**, 367–371.
- 42 K. Dzepina, R. M. Volkamer, S. Madronich, P. Tulet, I. M. Ulbrich, Q. Zhang, C. D. Cappa, P. J. Ziemann and J. L. Jimenez, *Atmos. Chem. Phys.*, 2009, 9, 5681–5709.

- 43 C. L. Heald, D. J. Jacob, R. J. Park, L. M. Russell, B. J. Huebert, J. H. Seinfeld, H. Liao and R. J. Weber, *Geophys. Res. Lett.*, 2005, 32, L18809.
- 44 R. Volkamer, J. L. Jimenez, F. San Martini, K. Dzepina, Q. Zhang, D. Salcedo, L. T. Molina, D. R. Worsnop and M. J. Molina, *Geophys. Res. Lett.*, 2006, 33, L17811.
- 45 A. Hodzic, J. L. Jimenez, S. Madronich, A. C. Aiken, B. Bessagnet, G. Curci, J. Fast, J. F. Lamarque, T. B. Onasch, G. Roux, J. J. Schauer, E. A. Stone and I. M. Ulbrich, *Atmos. Chem. Phys.*, 2009, **9**, 6949–6981.
- 46 T. Koop, J. Bookhold, M. Shiraiwa and U. Poschl, *Phys. Chem. Chem. Phys.*, 2011, **13**, 19238–19255.
- 47 M. Shiraiwa, M. Ammann, T. Koop and U. Poschl, Proc. Natl. Acad. Sci. U. S. A., 2011, 108, 11003–11008.
- 48 M. Shiraiwa and J. H. Seinfeld, *Geophys. Res. Lett.*, 2012, 39, L24801.
- 49 J. R. Odum, T. Hoffmann, F. Bowman, D. Collins, R. C. Flagan and J. H. Seinfeld, *Environ. Sci. Technol.*, 1996, **30**, 2580–2585.
- 50 N. M. Donahue, S. A. Epstein, S. N. Pandis and A. L. Robinson, *Atmos. Chem. Phys.*, 2011, **11**, 3303–3318.
- 51 N. M. Donahue, A. L. Robinson, C. O. Stanier and S. N. Pandis, *Environ. Sci. Technol.*, 2006, **40**, 2635–2643.
- 52 J. F. Pankow, Atmos. Environ., 1994, 28, 185-188.
- 53 J. F. Pankow, Atmos. Environ., 1994, 28, 189-193.
- 54 J. F. Pankow, Atmos. Environ., 2015, 122, 448-453.
- 55 C. Kidd, V. Perraud and B. J. Finlayson-Pitts, *Phys. Chem. Chem. Phys.*, 2014, **16**, 22706–22716.
- 56 C. Kidd, V. Perraud, L. M. Wingen and B. J. Finlayson-Pitts, *Proc. Natl. Acad. Sci. U. S. A.*, 2014, **111**, 7552–7557.
- 57 V. Perraud, E. A. Bruns, M. J. Ezell, S. N. Johnson, Y. Yu, M. L. Alexander, A. Zelenyuk, D. Imre, W. L. Chang, D. Dabdub, J. F. Pankow and B. J. Finlayson-Pitts, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, **109**, 2836–2841.
- 58 M. Shrivastava, A. Zelenyuk, D. Imre, R. Easter, J. Beranek, R. A. Zaveri and J. Fast, *J. Geophys. Res.: Atmos.*, 2013, **118**, 3328–3342.
- 59 T. D. Vaden, D. Imre, J. Beranek, M. Shrivastava and A. Zelenyuk, Proc. Natl. Acad. Sci. U. S. A., 2011, 108, 2190–2195.
- 60 A. Zelenyuk, D. Imre, J. Beranek, E. Abramson, J. Wilson and M. Shrivastava, *Environ. Sci. Technol.*, 2012, 46, 12459–12466.
- 61 E. Abramson, D. Imre, J. Beranek, J. Wilson and A. Zelenyuk, *Phys. Chem. Chem. Phys.*, 2013, **15**, 2983–2991.
- 62 C. D. Cappa and K. R. Wilson, *Atmos. Chem. Phys.*, 2011, 11, 1895–1911.
- 63 E. Saukko, H. Kuuluvainen and A. Virtanen, *Atmos. Meas. Tech.*, 2012, 5, 259–265.
- 64 A. Virtanen, J. Joutsensaari, T. Koop, J. Kannosto, P. Yli-Pirila, J. Leskinen, J. M. Makela, J. K. Holopainen, U. Poschl, M. Kulmala, D. R. Worsnop and A. Laaksonen, *Nature*, 2010, 467, 824–827.
- 65 L. Renbaum-Wolff, J. W. Grayson, A. P. Bateman, M. Kuwata, M. Sellier, B. J. Murray, J. E. Shilling, S. T. Martin and A. K. Bertram, *Proc. Natl. Acad. Sci. U. S. A.*, 2013, **110**, 8014–8019.
- 66 Y. J. Li, P. F. Liu, Z. H. Gong, Y. Wang, A. P. Bateman, C. Bergoend, A. K. Bertram and S. T. Martin, *Environ. Sci. Technol.*, 2015, **49**, 13264–13274.

- 67 R. E. O'Brien, A. Neu, S. A. Epstein, A. C. MacMillan, B. B. Wang, S. T. Kelly, S. A. Nizkorodov, A. Laskin, R. C. Moffet and M. K. Gilles, *Geophys. Res. Lett.*, 2014, **41**, 4347–4353.
- 68 C. N. Jen, P. H. McMurry and D. R. Hanson, J. Geophys. Res.: Atmos., 2014, **119**, 7502–7514.
- 69 L. Wang, V. Lal, A. F. Khalizov and R. Y. Zhang, *Environ. Sci. Technol.*, 2010, 44, 2461–2465.
- 70 T. Berndt, M. Sipila, F. Stratmann, T. Petaja, J. Vanhanen, J. Mikkila, J. Patokoski, R. Taipale, R. L. Mauldin and M. Kulmala, *Atmos. Chem. Phys.*, 2014, 14, 751–764.
- 71 T. Berndt, F. Stratmann, M. Sipila, J. Vanhanen, T. Petaja, J. Mikkila, A. Gruner, G. Spindler, R. L. Mauldin, J. Curtius, M. Kulmala and J. Heintzenberg, *Atmos. Chem. Phys.*, 2010, 10, 7101–7116.
- 72 J. Zhao, J. N. Smith, F. L. Eisele, M. Chen, C. Kuang and P. H. McMurry, *Atmos. Chem. Phys.*, 2011, **11**, 10823–10836.
- 73 E. Swartz, Q. Shi, P. Davidovits, J. T. Jayne, D. R. Worsnop and C. E. Kolb, *J. Phys. Chem. A*, 1999, **103**, 8824–8833.
- 74 S. Schobesberger, A. Franchin, F. Bianchi, L. Rondo, J. Duplissy, A. Kurten, I. K. Ortega, A. Metzger, R. Schnitzhofer, J. Almeida, A. Amorim, J. Dommen, E. M. Dunne, M. Ehn, S. Gagne, L. Ickes, H. Junninen, A. Hansel, V. M. Kerminen, J. Kirkby, A. Kupc, A. Laaksonen, K. Lehtipalo, S. Mathot, A. Onnela, T. Petaja, F. Riccobono, F. D. Santos, M. Sipila, A. Tome, G. Tsagkogeorgas, Y. Viisanen, P. E. Wagner, D. Wimmer, J. Curtius, N. M. Donahue, U. Baltensperger, M. Kulmala and D. R. Worsnop, *Atmos. Chem. Phys.*, 2015, 15, 55–78.
- 75 P. H. McMurry, H. Takano and G. R. Anderson, *Environ. Sci. Technol.*, 1983, 17, 347–352.
- 76 R. C. Robbins and R. D. Cadle, J. Phys. Chem., 1958, 62, 469-471.
- 77 J. J. Huntzicker, R. A. Cary and C. S. Ling, *Environ. Sci. Technol.*, 1980, 14, 819–824.
- 78 J. H. Zollner, W. A. Glasoe, B. Panta, K. K. Carlson,
 P. H. McMurry and D. R. Hanson, *Atmos. Chem. Phys.*, 2012, 12, 4399–4411.
- 79 M. E. Erupe, A. A. Viggiano and S. H. Lee, Atmos. Chem. Phys., 2011, 11, 4767–4775.
- 80 H. H. Chen and B. J. Finlayson-Pitts, *Environ. Sci. Technol.*, 2017, **51**, 243–252.
- 81 H. H. Chen, M. E. Varner, R. B. Gerber and B. J. Finlayson-Pitts, J. Phys. Chem. B, 2016, 120, 1526–1536.
- 82 H. H. Chen, M. J. Ezell, K. D. Arquero, M. E. Varner, M. L. Dawson, R. B. Gerber and B. J. Finlayson-Pitts, *Phys. Chem. Chem. Phys.*, 2015, 17, 13699–13709.
- 83 M. L. Dawson, M. E. Varner, V. Perraud, M. J. Ezell,
 R. B. Gerber and B. J. Finlayson-Pitts, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, **109**, 18719–18724.
- 84 B. R. Bzdek, D. P. Ridge and M. V. Johnston, J. Geophys. Res.: Atmos., 2011, 116, D03301.
- 85 K. D. Arquero, R. B. Gerber and B. J. Finlayson-Pitts, *Environ. Sci. Technol.*, 2017, **51**, 2124–2130.
- 86 J. Xu, B. J. Finlayson-Pitts and R. B. Gerber, J. Phys. Chem. A, 2017, 121, 2377–2385.
- 87 X. L. Ge, A. S. Wexler and S. L. Clegg, *Atmos. Environ.*, 2011, 45, 524–546.

Phys. Chem. Chem. Phys

- 88 M. L. Dawson, V. Perraud, A. Gomez, K. D. Arquero, M. J. Ezell and B. J. Finlayson-Pitts, *Atmos. Meas. Tech.*, 2014, 7, 2733–2744.
- 89 Y. You, V. P. Kanawade, J. A. de Gouw, A. B. Guenther, S. Madronich, M. R. Sierra-Hernandez, M. Lawler, J. N. Smith, S. Takahama, G. Ruggeri, A. Koss, K. Olson, K. Baumann, R. J. Weber, A. Nenes, H. Guo, E. S. Edgerton, L. Porcelli, W. H. Brune, A. H. Goldstein and S. H. Lee, *Atmos. Chem. Phys.*, 2014, 14, 12181–12194.
- 90 G. W. Schade and P. J. Crutzen, *J. Atmos. Chem.*, 1995, **22**, 319–346.
- 91 S. W. Gibb, R. F. C. Mantoura and P. S. Liss, *Global Biogeochem. Cycles*, 1999, 13, 161–177.
- 92 I. H. Chang, C. G. Lee and D. S. Lee, *Anal. Chem.*, 2003, 75, 6141–6146.
- 93 T. C. VandenBoer, A. Petroff, M. Z. Markovic and J. G. Murphy, *Atmos. Chem. Phys.*, 2011, **11**, 4319–4332.
- 94 Z. B. Babar, J.-H. Park and H.-J. Lim, Atmos. Environ., 2017, 164, 71–84.
- 95 K. Na, C. Song, C. Switzer and D. R. Cocker, *Environ. Sci. Technol.*, 2007, 41, 6096–6102.
- 96 D. M. Bell, D. Imre, S. T. Martin and A. Zelenyuk, *Phys. Chem. Chem. Phys.*, 2017, **19**, 6497–6507.
- 97 B. W. Chu, X. Zhang, Y. C. Liu, H. He, Y. Sun, J. K. Jiang, J. H. Li and J. M. Hao, *Atmos. Chem. Phys.*, 2016, 16, 14219–14230.
- 98 Y. Liu, J. Liggio, R. Staebler and S. M. Li, Atmos. Chem. Phys., 2015, 15, 13569–13584.
- 99 M. Kuwata and S. T. Martin, Proc. Natl. Acad. Sci. U. S. A., 2012, 109, 17354–17359.
- 100 K. M. Updyke, T. B. Nguyen and S. A. Nizkorodov, Atmos. Environ., 2012, 63, 22–31.
- 101 H. J. Lee, P. K. Aiona, A. Laskin, J. Laskin and S. A. Nizkorodov, *Environ. Sci. Technol.*, 2014, 48, 10217–10226.
- 102 M. L. Hinks, M. V. Brady, H. Lignell, M. J. Song, J. W. Grayson, A. K. Bertram, P. Lin, A. Laskin, J. Laskin and S. A. Nizkorodov, *Phys. Chem. Chem. Phys.*, 2016, **18**, 8785–8793.
- 103 D. L. Bones, D. K. Henricksen, S. A. Mang, M. Gonsior, A. P. Bateman, T. B. Nguyen, W. J. Cooper and S. A. Nizkorodov, *J. Geophys. Res.: Atmos.*, 2010, **115**, D05203.
- 104 T. Kurten, V. Loukonen, H. Vehkamaki and M. Kulmala, *Atmos. Chem. Phys.*, 2008, **8**, 4095–4103.
- 105 J. Almeida, S. Schobesberger, A. Kurten, I. K. Ortega, O. Kupiainen-Maatta, A. P. Praplan, A. Adamov, A. Amorim, F. Bianchi, M. Breitenlechner, A. David, J. Dommen, N. M. Donahue, A. Downard, E. Dunne, J. Duplissy, S. Ehrhart, R. C. Flagan, A. Franchin, R. Guida, J. Hakala, A. Hansel, M. Heinritzi, H. Henschel, T. Jokinen, H. Junninen, M. Kajos, J. Kangasluoma, H. Keskinen, A. Kupc, T. Kurten, A. N. Kvashin, A. Laaksonen, K. Lehtipalo, M. Leiminger, J. Leppa, V. Loukonen, V. Makhmutov, S. Mathot, M. J. McGrath, T. Nieminen, T. Olenius, A. Onnela, T. Petaja, F. Riccobono, I. Riipinen, M. Rissanen, L. Rondo, T. Ruuskanen, F. D. Santos, N. Sarnela, S. Schallhart, R. Schnitzhofer, J. H. Seinfeld, M. Simon, M. Sipila, Y. Stozhkov, F. Stratmann, A. Tome, J. Trostl,

G. Tsagkogeorgas, P. Vaattovaara, Y. Viisanen, A. Virtanen, A. Vrtala, P. E. Wagner, E. Weingartner, H. Wex, C. Williamson, D. Wimmer, P. L. Ye, T. Yli-Juuti, K. S. Carslaw, M. Kulmala, J. Curtius, U. Baltensperger, D. R. Worsnop, H. Vehkamaki and J. Kirkby, *Nature*, 2013, **502**, 359–363.

- 106 W. A. Glasoe, K. Volz, B. Panta, N. Freshour, R. Bachman,
 D. R. Hanson, P. H. McMurry and C. Jen, *J. Geophys. Res.: Atmos.*, 2015, **120**, 1933–1950.
- 107 K. Kawamura and K. Ikushima, *Environ. Sci. Technol.*, 1993, 27, 2227–2235.
- 108 K. Kawamura, Y. Imai and L. A. Barrie, *Atmos. Environ.*, 2005, **39**, 599–614.
- 109 M. P. Fraser, G. R. Cass and B. R. T. Simoneit, *Environ. Sci. Technol.*, 2003, **37**, 446–453.
- 110 Z. W. Yue and M. P. Fraser, Atmos. Environ., 2004, 38, 3253-3261.
- 111 A. Limbeck, Y. Kraxner and H. Puxbaum, J. Aerosol Sci., 2005, 36, 991–1005.
- 112 A. Limbeck, H. Puxbaum, L. Otter and M. C. Scholes, Atmos. Environ., 2001, 35, 1853–1862.
- 113 H. Satsumabayashi, H. Kurita, Y. Yokouchi and H. Ueda, Atmos. Environ., Part A, 1990, 24, 1443–1450.
- 114 S. Saarikoski, S. Carbone, S. Decesari, L. Giulianelli, F. Angelini, M. Canagaratna, N. L. Ng, A. Trimborn, M. C. Facchini, S. Fuzzi, R. Hillamo and D. Worsnop, *Atmos. Chem. Phys.*, 2012, **12**, 8401–8421.
- 115 J. N. Smith, K. C. Barsanti, H. R. Friedli, M. Ehn, M. Kulmala, D. R. Collins, J. H. Scheckman, B. J. Williams and P. H. McMurry, *Proc. Natl. Acad. Sci. U. S. A.*, 2010, **107**, 6634–6639.
- 116 P. Schlag, F. Rubach, T. Mentel, D. Reimer, F. Canonaco, J. Henzing, M. Moerman, R. Otjes, A. Prévôt and F. Rohrer, *Faraday Discuss.*, 2017, 200, 331–351.
- 117 J. M. Makela, S. Yli-Koivisto, V. Hiltunen, W. Seidl, E. Swietlicki, K. Teinila, M. Sillanpaa, I. K. Koponen, J. Paatero, K. Rosman and K. Hameri, *Tellus B*, 2001, 53, 380–393.
- 118 C. D. Cappa, E. R. Lovejoy and A. R. Ravishankara, *J. Phys. Chem. A*, 2007, **111**, 3099–3109.
- M. Bilde, K. Barsanti, M. Booth, C. D. Cappa, N. M. Donahue, E. U. Emanuelsson, G. McFiggans, U. K. Krieger, C. Marcolli, D. Tropping, P. Ziemann, M. Barley, S. Clegg, B. Dennis-Smither, M. Hallquist, A. M. Hallquist, A. Khlystov, M. Kulmala, D. Mogensen, C. J. Percival, F. Pope, J. P. Reid, M. A. V. R. da Silva, T. Rosenoern, K. Salo, V. P. Soonsin, T. Yli-Juuti, N. L. Prisle, J. Pagels, J. Rarey, A. A. Zardini and I. Riipinen, *Chem. Rev.*, 2015, 115, 4115–4156.
- 120 M. Bilde, B. Svenningsson, J. Monster and T. Rosenorn, *Environ. Sci. Technol.*, 2003, **37**, 1371–1378.
- 121 V. R. Thalladi, M. Nusse and R. Boese, *J. Am. Chem. Soc.*, 2000, **122**, 9227–9236.
- 122 H. Zhang, C. Xie, Z. K. Liu, J. B. Gong, Y. Bao, M. J. Zhang,
 H. X. Hao, B. H. Hou and Q. X. Yin, *Ind. Eng. Chem. Res.*,
 2013, 52, 18458–18465.
- 123 H. Zhang, Q. X. Yin, Z. K. Liu, J. B. Gong, Y. Bao, M. J. Zhang, H. X. Hao, B. H. Hou and C. Xie, *J. Chem. Thermodyn.*, 2014, 77, 91–97.

- 124 Y. C. Liu, Q. X. Ma and H. He, *Environ. Sci. Technol.*, 2012, 46, 11112–11118.
- 125 M. C. Fairhurst, M. J. Ezell, C. Kidd, P. S. J. Lakey, M. Shiraiwa and B. J. Finlayson-Pitts, *Phys. Chem. Chem. Phys.*, 2017, **19**, 4827–4839.
- 126 P. Beichert and B. J. Finlayson-Pitts, *J. Phys. Chem.*, 1996, **100**, 15218–15228.
- 127 M. E. Gebel, B. J. Finlayson-Pitts and J. A. Ganske, *Geophys. Res. Lett.*, 2000, 27, 887–890.
- M. E. Gebel and B. J. Finlayson-Pitts, *J. Phys. Chem. A*, 2001, 105, 5178–5187.
- 129 R. C. Hoffman, M. A. Kaleuati and B. J. Finlayson-Pitts, J. Phys. Chem. A, 2003, 107, 7818–7826.
- 130 R. C. Hoffman, M. E. Gebel, B. S. Fox and B. J. Finlayson-Pitts, *Phys. Chem. Chem. Phys.*, 2003, **5**, 1780–1789.
- 131 F. Caloz, F. F. Fenter, K. D. Tabor and M. J. Rossi, *Rev. Sci. Instrum.*, 1997, 68, 3172–3179.
- 132 D. M. Golden, G. N. Spokes and S. W. Benson, Angew. Chem., Int. Ed. Engl., 1973, 12, 534–546.
- 133 W. Winterbottom and J. Hirth, J. Chem. Phys., 1962, 37, 784–793.
- 134 A. Lavi, E. Segre, M. Gomez-Hernandez, R. Y. Zhang and Y. Rudich, *J. Phys. Chem. A*, 2015, **119**, 4336–4346.

- 135 J. B. Franzini, E. J. Finnemore and R. L. Daugherty, *Fluid Mechanics with Engineering Applications*, McGraw-Hill, New York, 9th edn, 1997.
- 136 Y. Zhao, M. C. Fairhurst, L. M. Wingen, V. Perraud, M. J. Ezell and B. J. Finlayson-Pitts, *Atmos. Meas. Tech.*, 2017, **10**, 1373–1386.
- 137 J. A. Goedkoop and C. H. Macgillavry, Acta Crystallogr., 1957, 10, 125–127.
- 138 G. N. Merrill and G. D. Fletcher, THEOCHEM, 2008, 849, 84-97.
- 139 J. I. Brauman, J. M. Riveros and L. K. Blair, *J. Am. Chem. Soc.*, 1971, **93**, 3914–3916.
- 140 C. Qiu, L. Wang, V. Lal, A. F. Khalizov and R. Y. Zhang, *Environ. Sci. Technol.*, 2011, **45**, 4748-4755.
- 141 J. A. Davies and R. A. Cox, *J. Phys. Chem. A*, 1998, **102**, 7631-7642.
- 142 F. F. Fenter, F. Caloz and M. J. Rossi, J. Phys. Chem., 1994, 98, 9801–9810.
- 143 H. C. Allen, J. M. Laux, R. Vogt, B. J. Finlayson-Pitts and J. C. Hemminger, *J. Phys. Chem.*, 1996, **100**, 6371–6375.
- 144 R. Vogt and B. J. Finlayson-Pitts, *J. Phys. Chem.*, 1994, **98**, 3747–3755.
- 145 H. A. Al-Hosney, S. Carlos-Cuellar, J. Baltrusaitis and V. H. Grassian, *Phys. Chem. Chem. Phys.*, 2005, 7, 3587–3595.