



New insights into atmospherically relevant reaction systems using direct analysis in real time-mass spectrometry (DART-MS)

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# 1 Abstract

- 2 The application of direct analysis in real time mass spectrometry (DART-MS), which is finding
- 3 increasing use in atmospheric chemistry, to two different laboratory model systems for airborne
- 4 particles is investigated: (1) submicron  $C_3$ - $C_7$  dicarboxylic acid (diacid) particles reacted with
- 5 gas phase trimethylamine (TMA) or butylamine (BA); (2) secondary organic aerosol (SOA)
- 6 particles from the ozonolysis of  $\alpha$ -cedrene. The diacid particles exhibit a clear odd-even pattern
- 7 in their chemical reactivity toward TMA and BA, with the odd-carbon diacid particles being
- 8 substantially more reactive than even ones. The ratio of base to acids in reacted particles,
- 9 determined using known acid-base mixtures, was compared to that measured by high resolution
- 10 time-of-flight aerosol mass spectrometry (HR-ToF-AMS), which vaporizes the whole particle.
- 11 Results show that DART-MS probes mainly surface layers, consistent with other studies on
- 12 different systems. For  $\alpha$ -cedrene SOA particles, it is shown that varying the temperature of the
- 13 particle stream as it enters the DART-MS ionization region can distinguish between specific
- 14 components with the same molecular mass but different vapor pressures. These results
- 15 demonstrate the utility of DART-MS for (1) examining reactivity of heterogeneous model
- 16 systems for atmospheric particles and (2) probing components of SOA particles based on
- 17 volatility.
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#### 22 1. Introduction

- Organic aerosol (OA) particles are responsible for ~ 20-90% of atmospheric submicron 23 particulate matter, with a substantial fraction being secondary organic aerosol (SOA) particles 24 25 formed via oxidation of volatile organic compounds (VOCs) (Zhang et al., 2007; Jimenez et al., 26 2009; Hallquist et al., 2009; Ng et al., 2010; Finlayson-Pitts and Pitts, 2000). As a result, the chemistry and physics of OA particles have been of great interest to the atmospheric science 27 community over decades. Despite significant progress, many physicochemical processes of OA 28 29 particles such as formation, growth, aging, and water uptake remain to be quantitatively understood which is essential for a better understanding of their impacts on air quality, human 30 health, visibility and climate (Kroll and Seinfeld, 2008; Hallquist et al., 2009; Laskin et al., 2015; 31 Ziemann and Atkinson, 2012; Noziere et al., 2015; Glasius and Goldstein, 2016; George et al., 32 33 2015; Moise et al., 2015; Farmer et al., 2015). However, atmospheric OA particles consist of hundreds to thousands of organic compounds with a wide range of functionality, solubility, 34 35 polarity, and volatility, and hence pose many challenges and difficulties for characterization of their molecular composition (Hallquist et al., 2009; Noziere et al., 2015; Glasius and Goldstein, 36 2016). Therefore, there is a critical need for implementation of analytical instrumentation which 37 38 can be applied to elucidating the composition of OA particles. 39 Recent advances in the development and application of mass spectrometry (MS) techniques for the analysis of OA particles have been documented in a number of reviews (Noziere et al., 2015; 40 Laskin et al., 2012; Laskin et al., 2013; Nizkorodov et al., 2011; Pratt and Prather, 2012a, b). 41 Online particle MS techniques that use relatively high energy vaporization and ionization 42 43 processes, e.g., flash vaporization of particles followed by electron ionization (EI) (DeCarlo et al., 2006; Tobias et al., 2000; Smith et al., 2004) or laser ablation and ionization (Gard et al., 1997; 44 Zelenyuk and Imre, 2005; Murphy and Thomson, 1995), have advantages of high time resolution 45 and real-time quantitative information on composition (DeCarlo et al., 2006; Zhang et al., 2007; 46 47 Jimenez et al., 2009; Ng et al., 2010; Murphy and Thomson, 1995; Tobias et al., 2000; Zelenyuk and Imre, 2005; Gard et al., 1997; Pratt and Prather, 2012a, b). However, these techniques 48 49 typically cause extensive fragmentation of molecules, providing elemental information but limited molecular information on individual organic components. 50
- 51 In contrast, a number of soft-ionization techniques such as electrospray ionization (ESI),





52	chemical ionization, and photoionization have been deployed to probe the molecular composition
53	of atmospheric OA particles (Laskin et al., 2012; Laskin et al., 2013; Nizkorodov et al., 2011;
54	Pratt and Prather, 2012a, b). Variants of ESI such as extractive electrospray ionization mass
55	spectrometry (EESI-MS) (Chen et al., 2006), have recently been applied to the real-time
56	measurement of the molecular composition of OA particles (Doezema et al., 2012; Gallimore
57	and Kalberer, 2013; Horan et al., 2012). In this technique, analyte ionization occurs when the
58	charged solvent spray intersects the sample stream in front of the MS inlet. However, the
59	mechanism for the interaction between charged solvent droplets and samples is not yet well
60	understood (Law et al., 2010; Gallimore and Kalberer, 2013; Jackson et al., 2008; Chen et al.,
61	2006; Chingin et al., 2008; Wang et al., 2012; Chen et al., 2007). In addition, the use of charged
62	solvent sprays may lead to in-source ion clustering of analytes, which is prone to occur in ESI-
63	MS (Gao et al., 2010; Muller et al., 2009b). Chemical ionization mass spectrometry (CIMS) has
64	the advantages of high sensitivity and selectivity, high time resolution, and has been applied to
65	online detection of a variety of inorganic and organic gases (Huey, 2007; Noziere et al., 2015).
66	Recently, CIMS employing thermal desorption techniques has been used to measure the
67	molecular composition of OA particles collected onto a substrate (Smith et al., 2004; Winkler et
68	al., 2012; Bzdek et al., 2014; Yatavelli et al., 2012; Lopez-Hilfiker et al., 2014; Aljawhary et al.,
69	2013). As the CIMS technique with a specific reagent ion is highly selective toward certain
70	classes of organic compounds, a comprehensive analysis of the molecular composition of OA
71	particles may require the use of multiple reagent ions. In addition, CIMS is also possibly subject
72	to artifacts from gas phase ion-clustering (Aljawhary et al., 2013).
73	Direct analysis in real-time mass spectrometry (DART-MS) is an atmospheric pressure soft
74	ionization technique allowing for real-time in situ characterization of the molecular composition
75	of gaseous, liquid, and solid samples with a wide range of polarities (Cody et al., 2005; Gross,
76	2014). The samples are directly introduced into the ionization region between the DART ion
77	source and the MS inlet, where a heated helium gas flow containing metastable helium atoms
78	(He*) generated by a corona discharge is used to thermally volatilize and ionize the sample.
79	Under ambient laboratory conditions, ionization of the analyte occurs primarily through a series
80	of reactions with secondary species such as protonated water clusters, molecular oxygen ions
81	$(O_2^+)$ , and superoxide anions $(O_2^-)$ , generated by the reactions between He <sup>*</sup> species and

atmospheric water and oxygen molecules. The result is the production of mainly  $[M+H]^+$ ,  $M^+$ ,





- and  $[M-H]^+$  ions in the positive ion mode, and  $[M-H]^-$  and  $M^-$  ions in the negative ion mode
- 84 (Cody et al., 2005; Nah et al., 2013; Gross, 2014).
- 85 DART-MS has been widely applied to explosive detection, forensic analysis, food analysis, and
- clinical and pharmaceutical studies (see the review by Gross (Gross, 2014) and references therein)
- as well as to the analysis of OA particles (Chan et al., 2013; Nah et al., 2013; Chan et al., 2014;
- 88 Davies and Wilson, 2015; Zhou et al., 2015; Schilling Fahnestock et al., 2015; Zhao et al., 2016).
- 89 For example, Wilson and coworkers demonstrated that DART-MS probes several nanometers of
- 90 the surface layer (Nah et al., 2013; Chan et al., 2013) and applied this technique to investigate
- 91 the bulk and interface regions of particles during reaction (Nah et al., 2013; Chan et al., 2013;
- 92 Chan et al., 2014; Davies and Wilson, 2015). Zhou et al. (Zhou et al., 2015) employed DART-
- MS to study the heterogeneous reactions of O<sub>3</sub> with polycyclic aromatic hydrocarbon films
- 94 coated on the tip of a glass melting point capillary tube. Schilling Fahnestock et al. (Schilling
- 95 Fahnestock et al., 2015) recently reported the first application of DART-MS for off-line analysis
- of the composition of SOA from photooxidation of  $C_{12}$  alkanes. In a limited comparison of
- 97 DART-MS to ESI-MS, Zhao et al. (Zhao et al., 2016) reported that spectra of particles from α-
- 98 cedrene ozonolysis were similar using the two techniques.
- 99 In this study, we explore the online application of DART-MS to particles from the reaction of
- 100 submicron dicarboxylic acid (diacid) particles with gas phase trimethylamine (TMA) or
- 101 butylamine (BA) and also report more detailed studies on SOA particles from ozonolysis of the
- 102 sesquiterpene  $\alpha$ -cedrene (C<sub>15</sub>H<sub>24</sub>). For comparison, measurements by high resolution time-of-
- 103 flight aerosol mass spectrometry (HR-ToF-AMS) were also carried out on selected amine-acid
- 104 reacted particles. Diacids are among the most abundant components of atmospheric particles,
- 105 with a dominant source from photochemical and aqueous phase oxidation processes (Kawamura
- and Bikkina, 2016; Ervens et al., 2011; Herrmann et al., 2015). Amines, which are ubiquitous in
- 107 air (Ge et al., 2011), play an important role in particle nucleation and growth (Zhang et al., 2012;
- 108 Kulmala et al., 2014; Dawson et al., 2012; Chen et al., 2016), formation of light-absorbing OA
- 109 particles (Laskin et al., 2015; De Haan et al., 2011; Powelson et al., 2014; Duporte et al., 2016),
- as well as aging of OA particles (Laskin et al., 2015; Muller et al., 2009a). Results from this
- 111 study provide additional support for the application of DART-MS to probe heterogeneous
- 112 atmospheric reactions, and to provide additional insights into the nature of organic constituents
- 113 in complex SOA particles.





#### 114 **2. Experimental**

#### 115 **2.1** Generation and reaction of diacid particles with gas phase amines

Figure 1 is a schematic diagram of the glass flow reactor (Zhao et al., 2015) used to investigate 116 reactions between gas phase amines (trimethylamine or butylamine) and particles of malonic 117 acid ( $C_3$ ), succinic acid ( $C_4$ ), glutaric acid ( $C_5$ ), adipic acid ( $C_6$ ), and pimelic acid ( $C_7$ ). Gas 118 phase trimethylamine (TMA) was generated by passing 1.0 L min<sup>-1</sup> of clean dry air (Praxair, ultra 119 zero air) through a U-shaped glass holder containing pure liquid TMA sealed inside a permeation 120 tube (VICI Metronics Inc). Generation of gas phase butylamine (BA) was achieved by injecting 121 an aqueous solution (1% v/v), prepared from pure liquid BA (Sigma-Aldrich, 99.5%) and 122 nanopure water (18.2 M $\Omega$  cm), into a flow of 0.5 L min<sup>-1</sup> of dry air using an automated syringe 123 pump (Pump Systems Inc., model NE-1000) at a rate of 2.4 µL hr<sup>-1</sup>. The concentration of TMA 124 in the air flow exiting the permeation tube was measured by collection onto a weak cation 125 exchange resin followed by extraction and analysis using ion chromatography as described 126 127 previously (Dawson et al., 2014). The initial concentration of TMA in the flow reactor was calculated to be 50 ppb based on the measured concentration from the permeation tube and the 128 dilution factor. The initial concentration of BA, calculated from the amount of the aqueous 129 solution injected and the total air flow in the reactor, was also 50 ppb. 130

For each experiment, the flow reactor was first conditioned overnight with either 1.0 L min<sup>-1</sup> 131 TMA or 0.5 L min<sup>-1</sup> BA in addition to clean, dry air so that the total flow was ~ 2 L min<sup>-1</sup>. When 132 the gas phase concentration of the amine became stable as indicated by DART-MS signals, a 133 small flow (0.2-0.5 L min<sup>-1</sup>) of air containing dry diacid particles was added to the flow reactor 134 upstream of the amine inlet. The flow of clean, dry air was adjusted to bring the total flow in the 135 reactor to 2.0 L min<sup>-1</sup> corresponding to a residence time of 44 s. Acid particles were generated by 136 atomizing aqueous solutions of the corresponding diacid (1 g  $L^{-1}$  in nanopure water) using an 137 atomizer (TSI, model 3076) and dried by passing through two diffusion dryers in series (TSI, 138 139 model 3062). The desiccant inside the dryers was replaced daily to minimize water associated with the particles. The relative humidity (RH) in the flow reactor was < 5% as measured by a 140 humidity probe (Vaisala, HMT234). All diacids were purchased from Sigma-Aldrich and have a 141 142 stated purity of > 99 %. The size distribution of the particles formed in the flow reactor was 143 measured using a scanning mobility particle sizer (SMPS, TSI) consisting of an electrostatic





classifier (model 3080), a long differential mobility analyzer (model 3081), and a condensation particle counter (model 3025A or 3776). Because the flow system required extensive conditioning with the amine prior to introducing the diacid particles, the size distributions represent particles after reaction with amines. Typical surface weighted size distributions are shown in Fig. S1, and the different weighted geometric mean diameters ( $\overline{D}_{g,x}$ , where x = number (N), surface (S), or volume (V)) and the total concentrations for all diacid particles are given in Table S1.

151 The amine-reacted particle stream (PS) exiting the flow reactor was either directly introduced

152 into the DART ionization region for online measurement of the total (gas phase + particle-bound)

- amines, or passed through a 10 cm monolith carbon denuder (Novacarb<sup>TM</sup>; Mast Carbon, Ltd.) to
- remove gases and measure only particle-bound amines and diacids. The denuder was maintained
- at room temperature ( $T_{PS} = 23$  °C). As discussed below, the fraction of particle-bound amines
- 156 was corrected for particle loss in the denuder, which was  $\sim 10$  % at room temperature (Fig. S1).

#### 157 **2.2 α-Cedrene SOA particles generation**

- 158 Ozonolysis of α-cedrene in the absence of seed particles or OH scavengers was used to generate
- 159 SOA particles under dry conditions in the glass flow reactor described previously (Zhao et al.,
- 160 2016). Gas phase  $\alpha$ -cedrene was generated by injecting the pure liquid (Sigma-Aldrich, > 98%)
- 161 into a flow (1.8 or 3.0 L min<sup>-1</sup>) of clean, dry air using an automated syringe pump. Ozone,
- 162 produced by passing a flow of 0.24 L min<sup>-1</sup> of  $O_2$  (Praxair, Ultra High Purity, 99.993%) through a
- 163 Pen-Ray mercury lamp (model 11SC-2) was added to the flow reactor downstream of the  $\alpha$ -
- 164 cedrene inlet. The total gas flow in the reactor was 2.0 or 3.2 L min<sup>-1</sup>, giving a residence time of
- 165 44 or 27 s, respectively. The initial  $\alpha$ -cedrene concentration, calculated from the amount of  $\alpha$ -
- 166 cedrene liquid injected into the reactor and the total gas flow, was 138 ppb. The initial  $O_3$
- 167 concentration, measured at the source using a UV-VIS spectrometer (Ocean Optics, HR4000),
- 168 was calculated to be 16 ppm in the reactor after dilution.
- 169 Size distributions of SOA particles formed in the flow reactor at the two residence times (44 or
- 170 27 s) were also measured using SMPS and give a typical surface weighted geometric mean
- 171 diameter  $(\overline{D}_{q,S})$  of 28 nm and 21 nm and  $\overline{D}_{q,N}$  of 24 and 16 nm, respectively. Once stable, the
- 172 chemical composition of these particles at both reaction times was measured online using DART-





- 173 MS. Before entering into the DART ionization region, 2.0 L min<sup>-1</sup> of particle stream (PS) exiting 174 the reactor was first passed through a 10 cm monolith carbon denuder to remove the gas phase 175 species and then heated to different temperatures (up to  $T_{PS} = 160 \,^{\circ}$ C) in a stainless steel tube 176 wrapped with a heating tape. The residence time of the particle stream in the heated tube was ~ 177 4 s. Although the use of the denuder caused a ~ 30% loss of SOA particles at room temperature, 178 it has no significant influence on the size distribution for which a typical example is shown in
- 179 Fig. S2.

### 180 **2.3 DART-MS measurements operating conditions**

181 The chemical composition of either amine-reacted diacid particles or  $\alpha$ -cedrene SOA particles

182 was measured online using a Xevo TQS triple quadrupole mass spectrometer (Waters) equipped

- 183 with a commercial DART ion source (IonSense, DART SVP with Vapur<sup>®</sup> Interface). The DART
- probe is placed at the entrance of the MS, with a distance of 5 mm and a relative angle of  $180^{\circ}$
- 185 (Fig. 1), and was operated under the following conditions: He reagent gas flow 3.1 L min<sup>-1</sup>; He
- 186 gas temperature 350  $^{\circ}$ C (which gives a measured temperature of ~ 260  $^{\circ}$ C in the ionization region
- 187 with or without particle stream flow (Fig. S3)); grid electrode voltage 350 V. Mass spectra were
- 188 collected in the range m/z 20-500 for the amine-diacid particle system and m/z 100-1000 for  $\alpha$ -
- 189 cedrene SOA particles. Each spectrum was acquired by averaging the signal over 2-4 min of
- 190 sampling time. Background spectra were also recorded by measuring a clean air stream under
- 191 conditions identical to those for online particle stream measurements and subtracted from
- 192 particle spectra.

#### 193 2.4 DART-MS analysis of amine-reacted diacid particles

194 For the amine-diacid particle system, both the gas phase and particle-bound amines were

195 detected as  $[M+H]^+$  ions in the positive ion mode, and the diacids as  $[M-H]^-$  in the negative ion

196 mode. Diacid-amine clusters were not observed in the mass spectra (Fig. S4). As described

197 earlier, the particle-bound and the total (gas phase + particle-bound) amines can be measured in

the presence and absence of a denuder, respectively. Thus, the fraction of amine taken up by the

199 particles  $(f_p)$  can be derived from Eq. (1),

$$f_{p} = \frac{amine \ ion \ signal \ measured \ with \ denuder \times C_{f}}{amine \ ion \ signal \ measured \ without \ denuder}$$
(1)





- where  $C_f$  is the correction factor for the particle loss in the denuder and has a value of 1.1 (SI
- section 1). The value of  $f_p$  can be an indicator of the reactivity of diacid particles toward amines.
- 202 Given the difference in surface area concentrations of different diacid particles (Table S1), the
- 203 measured  $f_p$  was normalized to an arbitrary reference surface area of  $1 \times 10^{-4}$  cm<sup>-3</sup> for direct
- 204 comparisons of the reactivity of different amine-diacid systems. Thus, the surface area
- 205 normalized particle-phase fraction of amine taken up by the diacid is given by:

Normalized 
$$F_p = \frac{f_p}{\frac{aerosol \ surface \ area \ concentration \ (cm^2 \ cm^{-3})}{reference \ surface \ area \ (cm^2 \ cm^{-3})}}$$
 (2)

The molar ratio  $(R_{B/A})$  of amine (base, B) to diacid (A) in amine-reacted diacid particles can also 206 provide important insights into the reactivity of the diacid particles toward amines. Values of 207  $R_{B/A}$  were derived first from four aqueous standard solutions with different amine concentrations 208 (0.5-10 mM) but constant diacid concentrations (10 mM) for each amine-diacid system. As 209 210 shown below, this covers the range measured for the reacted particles. A melting point capillary tube was dipped into the standard solution and immediately placed into the DART ionization 211 region for analysis. A linear relationship between the base-to-acid molar ratio  $(R_{B/A})$  of the 212 aqueous solutions and the corresponding DART-MS signal ratios for amine  $([M+H]^{+})$  to acid 213 214 ([M-H]<sup>-</sup>) was observed for each standard solution (Fig. S5). These relationships were then used to estimate the  $R_{B/A}$  value in amine-reacted diacid particles. 215

### 216 **2.5 DART-MS analysis of α-cedrene SOA particles**

 $\alpha$ -Cedrene SOA particles were analyzed in the negative ion mode, where the deprotonated [M-H]<sup>-</sup> ions dominate. In other studies, DART-MS was proposed to preferentially probe the surface layers of particles and the measured ion signal was sensitive to the volatility of the analytes (Nah et al., 2013; Chan et al., 2013). In the present studies, the gas phase species were removed by a denuder and the particle stream was then exposed to temperatures up to 160 °C prior to introduction into the DART ionization region in order to probe the bulk of the particles and low volatility components of SOA particles such as HMW products.

### 224 2.6 HR-TOF-AMS measurements

225 In some experiments, the chemical composition of TMA-reacted diacid particles was also





- analyzed online using an Aerodyne high resolution aerosol mass spectrometer (HR-ToF-AMS).
- 227 Analysis of HR-ToF-AMS high resolution mass spectra was carried out using SQUIRREL
- 228 V1.56D-1.57I and PIKA V1.15D-1.61I analysis software with IGOR Pro (Wavemetrics, Inc.).
- 229 Default values for the fragmentation tables were used except for corrections to the isotopic
- abundance of  ${}^{15}N^{14}N$  which is not resolved from CHO<sup>+</sup> at m/z 29 and was quantified for each
- experiment with the use of a particle filter (Canagaratna et al., 2015). Default relative ionization
- 232 efficiencies (RIE) values were used for all organics, while that for TMA was measured as
- discussed in the SI (section 5). TMA-reacted diacid particles with and without a denuder gave
- similar results and were averaged to generate mass spectra for each TMA-diacid system (Fig. S6).
- From these mass spectra, the ratio of  $C_x H_y N_1^+$  fragments to the sum of  $C_x H_y^+$  and  $C_x H_y O_z^+$
- 236 fragments, which is a measure of the ratio of amine to diacid, was determined for each TMA-
- 237 diacid system (Fig. S7). Because these particles are efficiently vaporized at the vaporizer
- temperature employed ( $T_{vap} = 600^{\circ}$ ), the amine to diacid ratios from HR-ToF-AMS
- 239 measurements reflect the overall composition of the particle ensemble.

#### 240 **3. Results and Discussion**

#### 241 **3.1 Reaction of diacid particles with gas phase amines**

#### 242 **3.1.1 DART-MS data**

- Figure 2 shows the surface area normalized fraction  $(F_p)$  of BA or TMA in the particle phase of
- amine-reacted C<sub>3</sub>-C<sub>7</sub> diacid particles as a function of carbon number. The odd-carbon diacids
- take up much more base than the even-carbon acids, with no particle-bound amines detected for
- the C<sub>4</sub> and C<sub>6</sub> acids. The measured  $F_p$  values for both amines decrease with increasing carbon
- number, with no particle bound TMA observed for pimelic acid  $(C_7)$ . An odd-even alternation in
- 248 physical properties such as melting point (Thalladi et al., 2000), vapor pressure (Bilde et al.,
- 249 2003; Bilde et al., 2015; Cappa et al., 2007; Bruns et al., 2012), and solubility (Zhang et al., 2013)
- is well known for diacids. While some studies have probed a possible odd-even alternation in
- their reactivity with HO<sub>2</sub> (Taketani et al., 2013), NO<sub>3</sub> (de Semainville et al., 2010), and N<sub>2</sub>O<sub>5</sub>
- 252 (Griffiths et al., 2009), as well as in their  $TiO_2$ -based photocatalytic degradation (Sun et al.,
- 253 2014), extensive investigations of differences in chemical reactivity between odd and even
- diacids with amines have not been carried out.





255 The alternating behaviors between odd and even diacids have generally been attributed to the differences in their crystal structures. For example, odd-carbon diacids have higher aqueous 256 solubility than even-carbon diacids because of the energetically unfavorable and looser crystal 257 258 packing for the former, which facilitates penetration of water molecules between the molecular planes to dissolve the crystal (Zhang et al., 2013). It is possible that small amines, like water 259 molecules, can also disrupt the crystal lattice of odd-carbon diacids more readily than that of the 260 even-carbon species, thus leading to the observed odd-even alternation in the chemical reactivity. 261 262 This may also explain why uptake of TMA is significantly smaller than BA (Fig. 2), where the bulky TMA structure may hinder the penetration and disruption of the acid crystal lattice. A 263 264 similar steric effect has also been reported by Liu et al. (Liu et al., 2012) to explain the trends in reactivity on citric acid and humic acid particles of methylamine, dimethylamine, and TMA, 265 which decreases with an increasing number of methyl groups. 266 Alternatively, the odd-even differences could be due to differences in surface composition and 267 structure. Ruehl and Wilson (Ruehl and Wilson, 2014) observed an odd-even alternation in the 268 269 hygroscopic growth of aqueous ammonium sulfate particles with a diacid shell. They attributed

this behavior to the differences in the surface orientation of odd and even diacids on aqueous

droplets, i.e., the "end to end" alignment with only one carboxyl group in contact with the

aqueous phase for odd-carbon diacids versus the "folded" arrangement with both carboxyl

273 groups in contact with the aqueous phase for the even-carbon acids. If a similar effect is present

in the solids, an odd-even alternation in the reactivity with amines could result due to differences
 in surface availability of the -COOH groups.

Based on previous work by Lavi et al. (Lavi et al., 2015) the diacid and their alkylaminium salts 276 277 vaporize well below 100 °C . Thus, in some experiments, the amine-reacted diacid particles were heated after exiting the 10-cm monolith denuder and prior to entering the DART-MS 278 279 ionization region to probe whether the amine was distributed throughout the bulk of the particle or segregated on the surface. As seen in Fig. 3, there is no obvious temperature dependence, 280 indicating that all of the amines in the particles are being sampled under all conditions. One 281 explanation is that the entire particle is being sampled. Alternatively, if the amine reactions are 282 restricted to a surface layer as is common for gas-solid interactions, then the surface layer being 283 probed at all T<sub>PS</sub> is sufficiently deep to detect the entire particle-bound base. We show in the 284





following that the latter is the likely explanation.

- 286 The molar ratio of amine to diacid  $(R_{B/A})$  in amine-reacted diacid particles was estimated by
- comparing the DART-MS signal intensity ratio of amine to diacid measured at  $T_{PS} = 23$  °C with
- that for known amine-diacid standard solutions (Fig. S5). As listed in Table 1, the  $R_{B/A}$  values
- follow a similar trend as  $F_p$  (Fig. 2) for TMA- and BA-reacted malonic acid (C<sub>3</sub>) and glutaric
- 290 acid ( $C_5$ ) particles.

However, the value of  $R_{B/A}$  for BA-reacted pimelic acid (C<sub>7</sub>) particles is larger than that for BA-

- reacted glutaric acid and malonic acid, inconsistent with the trend in  $F_p$ . A possible explanation
- is the relative saturation vapor pressures  $(P_{sat})$  (Bilde et al., 2015) of these diacids. It has been
- shown that the probe depth of online DART-MS is positively correlated with the volatility of
- straight chain even-diacid particles (Chan et al., 2013). Given that the volatility of  $C_7 (P_{sat} = 1.1)$
- $\times 10^{-10}$  atm) is substantially lower than that of both C<sub>3</sub> and C<sub>5</sub> which are ~1.7 × 10<sup>-9</sup> atm, the
- 297 probe depth for  $C_7$  particles is expected to be significantly smaller than the other two diacid

298 particles, i.e., about a factor of 8 if the probe depth-volatility relationship reported for the even-

- diacid particles is extrapolated to the odd-diacids (Fig. S8). Correcting for this, the  $R_{B/A}$  value
- 300 would be about a factor of 8 smaller, i.e., ~ 0.05, which would follow the trend for the  $F_p$  values
- for all three amine-reacted odd-diacid particles. Note that although the probe depth may be
- 302 smaller for  $C_7$ , the  $F_p$  data (Fig. 2) for the BA reaction suggest that it is still sufficient to detect all
- 303 of the particle-bound amine (Fig. 3).

### 304 3.1.2 Comparison with HR-ToF-AMS data

305 The  $R_{B/A}$  values for TMA-reacted C<sub>3</sub> and C<sub>5</sub> diacid particles were also measured using HR-ToF-

- AMS and are shown in Table 1 and Fig. S7. The  $R_{B/A}$  values for malonic acid and glutaric acid
- 307 particles measured by HR-ToF-AMS are smaller than the corresponding values determined by

308 DART-MS. The interaction between amines and carboxylic acids forms aminium carboxylate

- 309 salts (Liu et al., 2012; Angelino et al., 2001; Lavi et al., 2015; Gomez-Hernandez et al., 2016),
- 310 so that the gas-solid reaction is expected to form a surface layer of the salt. However, HR-ToF-
- 311 AMS measures the entire particle (i.e., both the surface reacted layer and the unreacted bulk).
- 312 The larger  $R_{B/A}$  values from DART-MS show that it is probing the reacted surface layer
- 313 containing the aminium salt, plus perhaps some fraction of the underlying diacid. This is





314 consistent with other studies where DART-MS was shown to probe mainly the surface layer

- 315 (Chan et al., 2013; Nah et al., 2013).
- 316 In addition to direct measurements by HR-ToF-AMS, the  $R_{B/A}$  values for the entire amine-reacted
- 317 diacid particles can also be estimated by combining DART-MS with SMPS data. The number of
- amine molecules in the particles per cm<sup>3</sup> air ( $N_{p-amine}$ , molecules cm<sup>-3</sup> air, Table S2) can be
- 319 derived from Eq. (3),

$$N_{p-a\min e} = F_p \times N_{total} \tag{3}$$

where  $F_p$  is as defined in Eq. (2) above and  $N_{total}$  is the amount of amines in the gas phase plus those bound to the particles (molecules cm<sup>-3</sup>) estimated from the DART-MS signal for the total amines and the DART-MS sensitivity to amines calibrated using gas phase amines with known concentrations generated as described in the experimental section. The number of diacid molecules in the particles per cm<sup>3</sup> air ( $N_{p-acid}$ ) can be estimated from Eq. (4),

$$N_{p-acid} = \frac{\left[(V_p \times \rho) - m_{p-a\min e}\right] \times N_A}{MW_{acid}}$$
(4)

- where  $V_p$  is the total volume concentration of amine-reacted diacid particles measured by SMPS (cm<sup>3</sup> particle volume per cm<sup>-3</sup> air);  $\rho$  is the density of amine-reacted diacid particles (g cm<sup>-3</sup>), which is assumed to be the same as the solid diacid samples (i.e., 1.619 for malonic acid, 1.429 for glutaric acid, and 1.329 for pimelic acid (Lide, 2004));  $m_{p-amine}$  is the mass concentration of particle phase amines (g cm<sup>-3</sup> air), which can be determined from Eq. (3);  $MW_{acid}$  is the molecular
- 330 weight of the corresponding diacid (g mol<sup>-1</sup>); and  $N_A$  is Avogadro's number.
- 331 The  $R_{B/A}$  values calculated from the ratio of  $N_{p-amine}$  to  $N_{p-acid}$  are presented in Table 1. They are
- 332 significantly smaller than those directly determined by DART-MS, further confirming that
- DART-MS mainly probes the surface layer of particles, and that the amines are segregated at thesurface.
- 335 However, the calculated values are also smaller than the values measured by HR-ToF-AMS.
- 336 This is likely because the densities of the pure diacids were used in the calculations. Salts
- formed by reaction of amines with diacids tend to have densities that are smaller by as much as
- ~30% (Lavi et al., 2015). Small decreases in particle density would decrease the calculated





particle mass concentrations and  $N_{p-acid}$  (Eq. (4)), and hence increase calculated  $R_{B/A}$  values.

- 340 Despite the difference in the absolute values of  $R_{B/A}$ , the trends in  $R_{B/A}$  values for TMA-reacted
- 341 malonic acid and glutaric acid particles derived by DART-MS, HR-ToF-AMS, and calculations
- 342 are consistent within the experimental uncertainty.

### 343 3.1.3 Estimation of probe depth for TMA-reacted odd diacid particles

- 344 When an amine reacts with a diacid, the resulting particle with radius R, is assumed to contain a
- diacid core  $(r_1)$ , and an aminium salt shell of thickness  $L_{shell} = (R r_1)$  as shown in Fig. 4. The
- total volume of the particle, assuming a spherical geometry, can be expressed as:

$$V_{total} = \frac{4}{3}\pi R^3 \tag{5}$$

 $V_{total}$  can be obtained directly from SMPS data (Table S1). Since the total particle is comprised of the acid core and aminium salt shell, the total volume can also be expressed as,

$$V_{total} = V_s + V_c \tag{6}$$

where  $V_c$  is the volume of the acid core and  $V_s$  is the volume of the aminium salt shell. The volume of the shell can be obtained from the experimental data as follows:

353 
$$V_s = \frac{m_s}{\rho_s} = \frac{n_s M W_s}{\rho_s} \tag{7}$$

In Eq. (7),  $m_s$  is the mass of the aminium salt,  $\rho_s$  is the density of the salt,  $n_s$  is the number of moles of salt per cm<sup>3</sup> air, and  $MW_s$  is the molecular weight of the aminium salt. Note that two values of V<sub>s</sub> can be calculated if aminium salt forms with stoichiometric molar amine:acid ratios of either 1:1 or 2:1. In addition, the densities of the aminium salts are reported to be less than that of the pure acid, as much as ~30% lower for the 2:1 salt (Lavi et al., 2015). For the calculations below, the density of the salt is taken to be either 15% smaller than the acid for a 1:1 base-to-acid salt or 30% smaller for the 2:1 salt.

361 Thus, one can solve for  $r_1$  as follows:

362 
$$\frac{R}{r_1} = \left(\frac{V_{total}}{V_{core}}\right)^{\frac{1}{3}} = \left(\frac{V_{total}}{V_{total} - V_S}\right)^{\frac{1}{3}}$$
(8)

Using the volume weighted geometric mean diameter (nm) (Table S1) in Eq. (8) to obtain R, the radius of the acid core,  $r_1$ , as well as the thickness of the salt layer,  $L_{shell}$  ( $L_{shell} = R - r_1$ ) can be





obtained. Table 2 summarizes the results for TMA-reacted malonic acid and glutaric acidparticles.

- 367 The probe depth  $(L_{DART})$  is assumed to be comprised of the aminium salt shell (shaded red area)
- and some fraction of the acid core (shaded green area) (Fig. 4). The thickness of the aminium
- salt layer determined previously  $(L_{shell})$  along with the ratio of  $R_{B/A}$  values for a given diacid
- derived by DART-MS and HR-ToF-AMS (Table 1) can be used to estimate the probe depth of
- the reacted particles in the following manner.
- As discussed earlier, the independence of  $F_p$  on particle stream temperature (T<sub>ps</sub>) (Fig. 3)
- 373 suggests that DART-MS probes all of the aminium salt shell plus likely some of the pure acid
- 374 core. On the other hand, HR-ToF-AMS (by measuring the entire particles) probes the total
- amount of the amine present in the particles and *all* of the pure acid core. Thus, the ratio of the
- 376  $R_{B/A}$  values from DART-MS to that of the HR-ToF-AMS can be expressed as:

377 
$$\frac{R_{B/A,DART}}{R_{B/A,AMS}} = \frac{\frac{moles B(DART)}{moles A(DART)}}{\frac{moles B(AMS)}{moles A(AMS)}} = \frac{moles A(AMS)}{moles A(DART)}$$
(9)

The total volume of a particle can be expressed as a function of the different areas labelled in Fig.4 as,

 $V_{total} = V_s + V_m + V_{uc} \tag{10}$ 

where,  $V_s$ ,  $V_m$  and  $V_{uc}$  are the volume of the salt shell (shaded red area), the volume of the middle layer (i.e. the volume of the acid core that is probed by DART-MS, shaded green area) and the volume of the core that is not probed by DART (yellow area) respectively ( $V_{uc}$  = unprobed core). While DART-MS is assumed to probe the salt layer and some fraction of the acid core, the HR-ToF-AMS will probe the entire bulk of the particle. As a result, Eq. (9) can be expressed as follows,

387 
$$\frac{R_{B/A,DART}}{R_{B/A,AMS}} = \frac{\frac{\rho_s V_s}{MW_s} + \frac{\rho_A V_m}{MW_A} + \frac{\rho_A V_{uc}}{MW_A}}{\frac{\rho_s V_s}{MW_s} + \frac{\rho_A V_m}{MW_A}}$$
(11)

388 where  $\rho_s$  and  $MW_s$  are the density and molecular weight for the aminium salt,  $\rho_A$  and  $MW_A$  are the





density and molecular weight of the diacid contained in the 'middle' layer and the acid core thatis not probed by DART-MS.

391 The ratio of the base-to-acid molar ratio from DART-MS to that of the HR-ToF-AMS is ~2

392 (Table 1). As such, Eq. (11) can be simplified to yield Eq. (12):

$$\frac{\rho_s V_s}{MW_s} + \frac{\rho_A V_m}{MW_A} = \frac{\rho_A V_{uc}}{MW_A}$$
(12)

The spherical volumes of each section of the particle can now be expressed in terms of their respective radii based on Fig. 4:

396 
$$\frac{\rho_s(R^3 - r_1^3)}{MW_s} + \frac{\rho_A(r_1^3 - r_2^3)}{MW_A} = \frac{\rho_A r_2^3}{MW_A}$$
(13)

The values of  $r_2$  corresponding to a stoichiometric molar amine:acid ratio of 1:1 or 2:1 can then be derived along with the derived probe depth for DART-MS,  $L_{DART} = (R - r_2)$ . As can be seen in Table 2, using the volume weighted geometric mean diameter for the TMA-reacted malonic acid of 290 nm (Table S1), the decrease in the DART-MS ratio of  $R_{B/A}$  from 0.28 to 0.14 for HR-ToF-AMS is consistent with a probe depth of ~ 32 nm, and is similar for glutaric acid, ~28 nm. It is worth noting that the values obtained for  $r_2$  and  $L_{DART}$  are essentially independent of the assumed stoichiometry and would yield the same value for any mixture of 1:1 and 2:1 salt.

#### 404 **3.2 Characterization of α-cedrene SOA particles**

405 In earlier studies (Zhao et al., 2016), limited DART-MS measurements were made for SOA

406 particles at  $T_{PS} = 160$  °C from the ozonolysis of  $\alpha$ -cedrene for purposes of confirming high

407 molecular weight (HMW) products identified in ESI mass spectra. More extensive

408 measurements were carried out here to investigate in more detail the application of DART-MS to

409 organic particles of complex composition. Figure 5 shows DART(-) (negative ion mode) mass

- 410 spectra of polydisperse  $\alpha$ -cedrene SOA particles measured as a function of T<sub>PS</sub> for distributions
- 411 with different  $\overline{D}_{a,S}$ , 21 nm and 28 nm. The ion signals observed in the mass spectra of SOA
- 412 particles at  $T_{PS} = 23$  °C (Figs. 5a and 5c) are dominated by low molecular weight (LMW)
- 413 products (m/z 200-350), with a small contribution from HMW products (m/z 420-580). This is
- not surprising given the very short particle residence time in the ionization region (estimated to
- 415 be of the order of milliseconds under our conditions), which limits the vaporization of low





416	volatility HMW products from SOA particles. However, the signal intensities of HMW products
417	as well as most of the LMW products increase substantially at $T_{PS} = 125 \ ^{o}C$ (Figs. 5b and 5d). It
418	is not known if the entire particle is vaporized at this temperature, although essentially complete
419	vaporization has been reported for larger SOA particles precursors (Kolesar et al., 2015). Many
420	of the LMW products in $\alpha$ -cedrene SOA particles observed in DART mass spectra were also
421	detected using GC-MS (Jaoui et al., 2004; Yao et al., 2014; Jaoui et al., 2013) and APCI-MS
422	(Reinnig et al., 2009) in other studies. The possible structures and formation mechanism of
423	many of these LMW products were investigated in previous studies (Jaoui et al., 2004; Reinnig
424	et al., 2009; Jaoui et al., 2013; Yao et al., 2014; Zhao et al., 2016) and those for HMW products
425	in our previous study (Zhao et al., 2016).
426	Potential artifacts in DART-MS with respect to in-source oxidation chemistry and gas phase ion
427	clustering of organic compounds that forms non-covalently bound HMW species were evaluated
428	by analyzing different organic standards and $\alpha$ -cedrene SOA particles in the negative ion mode
429	under varying controlled conditions. Details of the analysis and results can be found in Section 8
430	of the SI. The results show that measurements of diacid particles and $\alpha$ -cedrene SOA particles
431	with DART-MS do not suffer from in-source oxidation and gas phase clustering artifacts.
432	Differences in DART mass spectra of $\alpha$ -cedrene SOA particles at T <sub>PS</sub> = 23 °C or 125 °C in Fig. 5
433	are consistent with a dependence of product distribution on particle size as reported earlier based
434	on ESI-MS (Zhao et al., 2016). To better explore the size- and temperature-dependent product
435	distribution in $\alpha$ -cedrene SOA particles, the intensity ratio of HMW to LMW products as well as
436	the intensity fraction of the two prominent LMW products, i.e., $m/z$ 253 and $m/z$ 267, was
437	examined as a function of $T_{PS}$ and particle size. Figure 6a shows the signal intensity ratio of
438	HMW products (summed over $m/z$ 420-580) to that of LMW products (summed over $m/z$ 200-

- 439 350) for  $\alpha$ -cedrene SOA particles with a  $\overline{D}_{g,S}$  of 21 nm and 28 nm at different T<sub>PS</sub>. Smaller
- $440 \qquad \text{particles at each $T_{PS}$ show a greater contribution from HMW products to the total ion signal,}$
- 441 consistent with these products serving as important agents for initial particle formation (Zhao et
- 442 al., 2016).
- 443 In our previous study (Zhao et al., 2016), HR-ToF-AMS was used to characterize the bulk
- 444 composition of  $\alpha$ -cedrene ozonolysis particles generated in Teflon chambers. Under dry
- 445 conditions (<5%), chamber-generated particles had an O:C = 0.34, which was characteristic of





446 LMW products that were shown to contribute primarily to particle growth rather than to initial 447 particle formation. This is not necessarily surprising since the chamber-generated particles had undergone significantly more particle growth ( $\overline{D}_{g,N} \sim 70$  nm) than particles generated in the flow 448 reactor ( $\overline{D}_{q,N}$  < 30 nm), which are too small to transmit through the HR-ToF-AMS lens. While 449 bulk particle composition measurements by AMS were limited to chamber particles, their 450 comparison to DART-MS measurements show that LMW components make up the majority of 451 the particle mass at long reaction times. This highlights the value of DART-MS in accessing the 452 453 markedly different compositions at varied extent of particle growth. Figure 6b shows the intensity fraction of products with peaks at m/z 253 or m/z 267 to the total 454 455 LMW products (m/z 200-350) at different T<sub>PS</sub> for polydisperse  $\alpha$ -cedrene SOA particles with distributions having a  $\overline{D}_{q,S}$  centered at 21 nm and 28 nm, respectively. For both distributions, the 456 fraction of product m/z 253 increases with rising T<sub>PS</sub> whereas that of product m/z 267 decreases 457 with increasing  $T_{PS}$ . The distinct temperature dependence of these two peaks may indicate that 458 459 the product responsible for m/z 253 has a lower volatility than product m/z 267 (although a contribution from decomposition of HMW products at higher T<sub>PS</sub> cannot be ruled out). Smaller 460 461 particles tend to have a greater fraction of m/z 253 compared to larger particles but a lower 462 fraction from m/z 267. This suggests that the species responsible for m/z 253 play a more important role in the early stages of particle growth, consistent with its lower volatility. Previous 463 studies have proposed multiple isomeric structures, i.e.,  $\alpha$ -cedrinic acid and 10-hydroxy- $\alpha$ -464 norcedralic acid for product m/z 253 (Jaoui et al., 2004; Reinnig et al., 2009; Jaoui et al., 2013; 465 Yao et al., 2014; Zhao et al., 2016). Using the EVAPORATION model (Compernolle et al., 466 2011), the  $P_{sat}$  of  $\alpha$ -cedrinic acid and 10-hydroxy- $\alpha$ -norcedralic acid are estimated to be 2.4  $\times$ 467  $10^{-12}$  atm and  $5.1 \times 10^{-11}$  atm, respectively, and the  $P_{sat}$  of the structures proposed for m/z 267 is 468 estimated to be  $(0.39-3.1) \times 10^{-11}$  atm (Zhao et al., 2016). Therefore,  $\alpha$ -cedrinic acid, the  $P_{sat}$  of 469 which is lower than all possible isomeric structures of m/z 263, is likely the dominant structure 470 471 for the product m/z 253. This illustrates that DART-MS measurements may help resolve structural isomers of some products by providing information on their volatility. 472

# 473 **4. Conclusions**

DART-MS was successfully applied to the real-time study of the reaction of submicron diacid
particles with gas phase amines and to the chemical composition of nanometer-sized SOA





476 particles from ozonolysis of  $\alpha$ -cedrene. The reactivity of C<sub>3</sub>-C<sub>7</sub> diacid particles toward TMA and 477 BA exhibits a clear alternation between the odd and even carbon numbers. Calibrations using known amine-diacid mixtures enable the determination of the ratios of the base to acid in reacted 478 479 particles. The relative increase in these ratios for DART-MS compared to those derived by HR-ToF-MS was used to estimate the probe depth of DART-MS. It is shown that DART-MS probes 480 mainly the surface layer of the particles, in agreement with other studies on different systems. 481 Results for  $\alpha$ -cedrene SOA particles show that HMW products are a major component of the 482 483 smaller particles, consistent with these products playing an important role in initial particle 484 formation (Zhao et al., 2016). Vaporization of particles at different temperatures before introduction into the DART ionization region permits the characterization of isomeric structures 485 of SOA particles based on their volatility. All of these studies were carried out under dry 486 conditions. The presence of water vapor would be expected to influence some of the physical 487 and chemical processes involved in both systems. This remains to be investigated. 488 Some challenges remain in applying DART-MS, for example quantification of individual 489 490 compounds. While relative concentrations can be determined by utilizing an internal (Zhou et al., 491 2015; Schilling Fahnestock et al., 2015) or external standard (as shown for the amine-diacid system in our present study), this assumes that DART-MS has the same sensitivity for the 492 standards and the analytes. This might not hold for SOA particles that consist of a complex 493

494 mixture of organic compounds with a wide diversity of functionality and polarity. In addition,

495 internal standards need to be well-mixed with the sample, which can be difficult if the standard

496 and analyte recrystallize separately. Furthermore, the standard configuration for DART-MS at

497 present operates in an open environment so the amount of the analyte actually sampled by the

498 MS may not be well controlled. As with many other ambient ionization techniques, caution is

warranted with respect to possible oxidation by OH and other reactive species generated in thesource.

However, this study in combination with previous work (Nah et al., 2013; Chan et al., 2013;

502 Zhou et al., 2015; Schilling Fahnestock et al., 2015; Chan et al., 2014; Davies and Wilson, 2015;

503 Zhao et al., 2016) demonstrates that DART-MS is a very useful complement to ESI-MS and

other mass spectrometric techniques for the analysis of complex atmospherically relevant

505 systems. Combined with temperature studies, it can provide depth information on spatially





- 506 heterogeneous particles and potentially differentiate between isobaric compounds of different
- 507 volatility.

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**Table 1.**  $R_{B/A}$  values for amine-reacted malonic acid (C<sub>3</sub>), glutaric acid (C<sub>5</sub>), and pimelic acid (C<sub>7</sub>)

	<i>R<sub>B/A</sub></i> (DART-MS)	R <sub>B/A</sub> (AMS)	Calculated $R_{B/A}$ from $F_p$ and the particle size distributions <sup>c</sup>
TMA-C <sub>3</sub>	$0.28\pm0.07$	$0.14\pm0.01$	$0.07\pm0.02$
TMA-C <sub>5</sub>	$0.05\pm0.02$	$0.03\pm0.01$	$0.02\pm0.003$
TMA-C <sub>7</sub>	a	$0.01\pm0.001$	<u> </u>
BA-C <sub>3</sub>	$0.40\pm0.09$	b	$0.09\pm0.03$
BA-C <sub>5</sub>	$0.22\pm0.02$	b	$0.07\pm0.01$
BA-C <sub>7</sub>	$0.42\pm0.06$	b	$0.07\pm0.02$

799 particles derived by DART-MS, HR-ToF-AMS, and calculations.

<sup>a</sup>No particle-bound amines were detected by DART-MS. <sup>b</sup>Measurements by AMS were not performed. <sup>c</sup>See Eq. (3) and (4) in text. Lower limit due to uncertainty in particle density as

802 described in text.

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805	Table 2.	Thickness of the	aminium sal	lt shell and	DART	probe dept	th for trimethy	ylamine (	TMA)	-

	R (nm)	<b>r</b> <sub>1</sub> ( <b>nm</b> )		<b>r</b> <sub>2</sub> ( <b>nm</b> )		L <sub>shell</sub> (nm)		L <sub>DART</sub> (nm)	
		1:1	2:1	1:1	2:1	1:1	2:1	1:1	2:1
Malonic Acid	145	139	140	113	113	5.5	4.5	32	32
Glutaric Acid	135	133	133	106	106	1.7	1.4	28	28

806 reacted malonic acid and glutaric acid.

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Figure 1. Schematic diagram of the experimental apparatus used for the study of the reaction of diacid particles with gas phase amines. The inset shows the configuration of DART ion source interfaced to the MS.





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Figure 2. Surface area normalized  $(F_p)$  of butylamine (solid square) and trimethylamine (open

diamond) in amine-reacted C<sub>3</sub>-C<sub>7</sub> dicarboxylic acid particles measured at  $T_{PS} = 23$  °C. Error bars are ±1 $\sigma$ .

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Figure 3. Particle phase fraction,  $F_p$ , of (a) butylamine and (b) trimethylamine in amine-reacted C<sub>3</sub>-C<sub>7</sub> diacid particles measured at different particle stream heating temperatures (T<sub>PS</sub>). The dashed line represents the average of  $F_p$  values at different T<sub>PS</sub>. Error bars are ±1 $\sigma$ .







# Figure 4. Schematic of a typical amine-reacted diacid particle as probed by DART-MS.





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Figure 5. DART (-) mass spectra of polydisperse  $\alpha$ -cedrene SOA particles with surface weighted geometric mean diameters ( $\overline{D}_{g,S}$ ) of 21 nm (a, b) and 28 nm (c, d) at T<sub>PS</sub> = 23 and 125 °C. T<sub>PS</sub> denotes the particle stream temperature before introduction into the DART ionization region.







Figure 6. The DART-MS signal intensity ratio of (a) high molecular weight (HMW) products (m/z 420-580) to low molecular weight (LMW) products (m/z 200-350) and (b) products at m/z253 (left y-axis) and m/z 267 (right y-axis) to LMW products (m/z 200-350) for  $\alpha$ -cedrene SOA particles. Data represent particles with  $\overline{D}_{g,5}$  of 21 nm (solid circles) and 28 nm (open diamonds) at different particle stream temperatures ( $T_{PS}$ ). Error bars are  $\pm 1\sigma$ .

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