

1 **Chemical Characterization of Gas- and Particle-Phase**
2 **Products from the Ozonolysis of α -Pinene in the**
3 **Presence of Dimethylamine**

4 *Geoffroy Duporté,[†] Matthieu Riva,[‡] Jevgeni Parshintsev,[†] Enna Heikkinen,[†] Luís M. F. Barreira,[†]*
5 *Nanna Myllys,[‡] Liine Heikkinen,[‡] Kari Hartonen,[†] Markku Kulmala,[‡] Mikael Ehn,[‡] and Marja-*
6 *Liisa Riekkola^{*†}*

7 [†] Laboratory of Analytical Chemistry, Department of Chemistry, P.O. Box 55, 00014 University of
8 Helsinki, Finland

9 [‡] Division of Atmospheric Sciences, Department of Physics, P.O. Box 64, 00014 University of
10 Helsinki, Finland

11

12 ABSTRACT

13 Amines are recognized as key compounds in new particle formation (NPF) and secondary organic
14 aerosol (SOA) formation. In addition, ozonolysis of α -pinene contributes substantially to the
15 formation of biogenic SOAs in the atmosphere. In the present study, ozonolysis of α -pinene in
16 presence of dimethylamine (DMA) was investigated in a flow tube reactor. Effects of amines on SOA
17 formation and chemical composition were examined. Enhancement of NPF and SOA formation was
18 observed in presence of DMA. Chemical characterization of gas- and particle-phase products by high-
19 resolution mass spectrometric techniques revealed the formation of nitrogen containing compounds.
20 Reactions between ozonolysis reaction products of α -pinene, such as pinonaldehyde or pinonic acid,
21 and DMA were observed. Possible reaction pathways are suggested for the formation of the reaction
22 products. Some of the compounds identified in the laboratory study were also observed in aerosol
23 samples (PM_{10}) collected at the SMEAR II station (Hyytiälä, Finland) suggesting that DMA might
24 affect the ozonolysis of α -pinene in ambient conditions.

25 INTRODUCTION

26 Atmospheric particles are known to have a significant influence on global climate
27 change, regional air quality and human health.¹⁻³ They can be directly emitted by anthropogenic or
28 natural sources (primary aerosols), such as wood burning and fossil fuel combustion. However, a
29 significant fraction of atmospheric aerosol is organic in nature and often dominated by secondary
30 organic aerosols (SOAs) formed from the oxidation of volatile organic compounds (VOCs).⁴⁻⁵
31 Although SOAs contribute to a major mass fraction of ambient fine particle matter (PM_{2.5}), current
32 models continue to under-predict the SOA mass observed during field measurements. In addition,
33 uncertainties remain in the chemical processes governing the SOA formation and aging.
34 Understanding the potential species driving SOA formation and aging is therefore critical for the
35 prediction of aerosol impact on climate change and human health.

36 Amines, ubiquitous in the atmosphere, are emitted into the atmosphere by a large variety
37 of anthropogenic and natural sources. Globally, animal husbandry, combustion processes and
38 industry are the main anthropogenic sources while oceans, vegetation and soils represent the main
39 natural sources.⁶ Ge *et al.*⁶ have identified more than 150 atmospheric amines emitted from either
40 anthropogenic or natural sources in the atmosphere. Low-molecular weight aliphatic amines, such as
41 methylamine (MA), dimethylamine (DMA), trimethylamine (TMA) or ethylamine (EA), are the most
42 abundant amines in the atmosphere. For instance, Kieloaho *et al.*⁷ have reported that the combined
43 concentration of the major alkylamines (EA and DMA) in the boreal forest in southern Finland is
44 around 150 pptv. DMA has been also detected as a major alkyl amine species in particles and cloud
45 water in semi-arid and coastal regions.⁸

46 Amines are highly reactive species and they are expected to play a key role in new
47 particle formation (NPF) and SOA formation.^{6,9-12} For instance, they are more likely to enhance NPF
48 than ammonia (NH₃).^{9,13-14} Therefore, understanding the transformation and fate of amines and/or

49 NH₃ is currently one of the main challenges in the field of atmospheric chemistry. Other laboratory
50 studies have demonstrated that amines considerably enhance nucleation of the sulfuric acid-water
51 system.^{10, 15-16} Indeed, Almeida *et al.*,⁹ showed that a few ppt of DMA enhance the aerosols formation
52 rates of sulfuric acid by several orders of magnitudes. Evidence for the participation of amines in gas
53 and/or multiphase chemistry has also been demonstrated.^{10, 17-19} Recent studies have suggested that
54 carbonyl compounds such as glyoxal,²⁰ methylglyoxal,²¹ glycoaldehyde,²⁰ acetaldehyde²⁰ or
55 pinonaldehyde²² are able to react in aerosol phase or bulk aqueous solution with small amines. The
56 resulting nitrogen (N)-containing compounds could then participate in SOA growth due to their low
57 vapor pressures. In addition, Stropoli and Elrod²³ have reported potential multiphase reactions
58 between amines and epoxides, which could further contribute to SOA formation. A previous
59 experimental study has shown that the saturation vapor pressures of alkylammonium carboxylates are
60 lower than those of their organic acid precursors, likely explaining that alkylamine neutralization by
61 carboxylic acid enhances SOA formation.²⁴ In addition, a recent study has also shown that alkylamine
62 neutralization of carboxylic acids also enhanced the particle hygroscopicity and the cloud
63 condensation nuclei (CCN) activity.²⁵ It is worth nothing that, Mäkela *et al.*¹⁷ have observed that
64 DMA concentrations were 30 times higher in aerosol samples collected during NPF events than those
65 in non-event samples in the boreal forest at Hyytiälä Forestry Field Station in Finland. Likewise,
66 Smith *et al.*,¹⁸ have reported that aliphatic amines contributed to 23 % of the positive ions detected
67 during NPF events at the same boreal forest site, and to 47 % at an urban site in Tecamac, Mexico.
68 Finally, Tao *et al.*¹² have revealed that the heterogeneous uptake of amines is dominated by the acid-
69 base reaction mechanism, which may contribute to particle growth in NPF events.

70 In this context, the aim of this work was to improve our understanding of amine
71 chemistry in the atmosphere and to assess their contribution to NPF and SOA growth. Since
72 ozonolysis of α -pinene contributes substantially to the formation of biogenic SOAs in the atmosphere,
73 its reaction was investigated in the presence of DMA in a flow tube reactor to evaluate the effect of

74 amines on SOA formation and chemical composition. Gas-phase products were characterized using
75 an Aerodyne high-resolution time-of-flight chemical ionization mass spectrometer (HR-ToF-CIMS)
76 equipped with iodide reagent ion chemistry. Aerosol size distribution was measured with a
77 differential mobility particle sizer (DMPS). In addition, gas- and particle-phase samples collected
78 from flow tube experiments were analyzed by ultra-high-performance liquid chromatography coupled
79 to electrospray ionization orbitrap mass spectrometry (UHPLC-HRMS). To confirm the relevance of
80 the laboratory findings to the ambient atmosphere, aerosol samples (PM₁) were collected from the
81 SMEAR II boreal forest site at Hyytiälä, Finland, during May–June 2016 and analyzed by the same
82 off-line analytical methodologies. Quantum chemistry calculations were also used for the clarification
83 of enamine formation from pinonaldehyde and dimethylamine.

84 EXPERIMENTAL SECTION

85 **Flow Tube Reactor Experiments.** The ozonolysis of α -pinene in the presence or absence of DMA
86 was carried out in a borosilicate glass flow tube reactor (205 cm long, 4.7 cm i.d.). The experimental
87 set-up is presented in Figure S1 while the initial experimental conditions are detailed in Table 1. The
88 flow tube is operated using purified dry air at atmospheric pressure and room temperature ($T = 293$
89 ± 3 K) under laminar flow conditions.²⁶⁻²⁷ The total gas flow was adjusted to 4.5 L/min resulting in a
90 residence time of 53 s in the flow tube reactor. The purified air was generated by an air purification
91 system (AADCO, 737 Series) that runs on compressed air and reduces concentrations of O₃/NO_x and
92 non-methane hydrocarbons to less than 1 ppb and 5 ppb, respectively. In experiments E1-E3, 100-
93 120 ppb (Table 1) of O₃ was generated by an ozone generator (Dasibi 1008-PC) and injected into the
94 flow tube. When the ozone concentration, determined by an ozone analyzer (Thermo Scientific model
95 49), was stable, ~ 5 ppm of α -pinene was introduced into the flow tube through a mobile injector
96 (Figure S1). The concentration of α -pinene was estimated from the vapor pressure²⁸ and the measured
97 gas flows. Finally, ~ 500 ppb of DMA was introduced in the flow tube (Experiments E1'-E3') to
98 investigate the impact of amines on the ozonolysis of α -pinene. DMA (Sigma-Aldrich, 40 wt. % in

99 H₂O) and α -pinene (Sigma-Aldrich, 98 %) were generated by flushing nitrogen (N₂) through the
100 liquid compounds in glass bubblers. The DMA concentration was determined by GC-MS after solid
101 phase micro extraction (SPME) using a SPME Arrow (Carbon WR, CTC Analytik).²⁹ Details on
102 DMA calibration can be found elsewhere.²⁹ Aerosol size distributions were continuously measured
103 using a differential mobility particle sizer (DMPS) in order to monitor aerosol number, surface area,
104 and volume concentration. The different flows were controlled using mass flow controllers (MKS).
105 All experiments were performed without an OH radical scavenger. Once aerosol volume
106 concentration stabilized as well as the gas-phase oxidation products, aerosols were collected on filters
107 (47 mm PTFE filters) and gaseous products on solid phase extraction (SPE) cartridges
108 (divinylbenzene), for 1 hour at a flow rate of 1 L/min. SPE sampling was used to identify semi-
109 volatile organic compounds in gas phase, complementary to on-line analysis by HR-ToF-CIMS.
110 Filters and SPE cartridges were stored in dark in a freezer at – 18°C until extraction. It is worth noting,
111 that clear memory effect was observed after switching off the injection of DMA, as it took long time
112 to restore the initial O₃ concentration. Hence, to ensure reproducibility, the flow tube was cleaned
113 between each experiments with high purity methanol (Sigma-Aldrich, HPLC grade) and flushed with
114 clean air overnight. Methanol extracts were kept after the reactions E2' and E3' in order to study the
115 chemical composition of the products adsorbed on the walls of the flow tube.

116 **Chemical Characterization of Gas- and Particle-Phase Constituents.** Real-time measurements of
117 gas-phase oxidation products were performed with an Aerodyne high-resolution time-of-flight
118 chemical ionization mass spectrometer (HR-ToF-CIMS), equipped with iodide (I⁻) reagent ion
119 chemistry. Analyses were restricted to ions containing an iodide adduct, which guarantees detection
120 of the parent organic compound without substantial fragmentation. Iodide-HR-ToF-CIMS has been
121 described previously and demonstrated high sensitivity towards multifunctional oxygenated organic
122 compounds in the gas and particle phases.³⁰⁻³² Characterization of N-containing compounds from the
123 flow tube reactor experiments was performed using a Thermo Ultimate 3000 UHPLC coupled with

124 an Orbitrap Fusion TMS (Tribrid mass spectrometer) operated in positive mode. Detailed
125 characterization of analytical procedure has previously been described.²² Before extraction, an
126 internal standard aliquot (caffeine, Sigma Aldrich, *ReagentPlus*®), controlled by gravimetry, was
127 added to the samples. Filter samples were extracted in 7.5 mL of acetonitrile (HPLC grade, Sigma
128 Aldrich) during 30 min of sonication at room temperature. Caffeine was used as an internal standard
129 for semi-quantification of N-containing reaction products, due to the lack of commercially available
130 authentic standards. Then, extracts were filtered through 0.45 μm PTFE syringe filters (Merck
131 Millipore Ltd.) to remove insoluble particles. The SPE samples were extracted by slowly passing 7.5
132 mL of acetonitrile through the cartridges by vacuum. Finally, the extracts were dried under a gentle
133 stream of nitrogen at 30 °C and reconstituted with 100 μL of a 50/50 (v/v) mixture of acetonitrile and
134 water (milli-Q water). Ten μL were injected onto the UPLC column (Phenomenex Luna Omega Polar
135 C₁₈ column, 100 \times 2.1 mm, 1.6 μm) at a flow rate of 0.6 mL/min. The eluent composition was (A)
136 0.1 % formic acid in Milli-Q grade water and (B) 0.1 % formic acid (HPLC grade, Sigma Aldrich) in
137 acetonitrile. The mobile phase gradient was initially 95:5 (v/v, A/B), increased to 100 % B along 15
138 min and returned to 95:5 (v/v, A/B) in 1 min and then kept for 4 min to equilibrate the column.

139 **Ambient Samples.** Boreal forest samples were collected from May 3 to June 26, 2016 at the Station
140 for Measuring Forest Ecosystem-Atmosphere Relations (SMEAR II) at Hyytiälä, in southern Finland
141 (61°50.845' N, 24°17.686' E, 179 m above sea level).³³ The largest nearby city is Tampere, situated
142 60 km southwest from SMEAR II with around 200 000 inhabitants. The most dominant species
143 emitted by the forest, mainly constituted by Scots pine and Norway spruces, are α -pinene and Δ^3 -
144 carene.³⁴ Ambient aerosols were collected using a high volume sampler equipped with PM₁ inlet at a
145 flow rate of 30 m³/h (Digital DA-80) on quartz fiber filter (Sigma-Aldrich, Whatman®) with a
146 diameter of 150 mm. Prior to sampling, quartz fiber filters were calcined at 450 °C for 6 hours to
147 remove any possible organic contamination. Sampling was performed over a period of 12 hours (day
148 sample, from 7 am to 7 pm and night sample, from 7 pm to 7 am). Filters were wrapped in aluminum

149 foil and placed in antistatic bags, which were stored at $-18\text{ }^{\circ}\text{C}$ until extraction. In total 107 samples
150 were collected. Filters from the field study were punched (31.25 cm^2) and extracted using the protocol
151 described above. Selected ion monitoring (SIM) method was applied by choosing the reaction product
152 ions identified in the laboratory experiments. Tandem mass spectra (MS^2) analyses were also
153 performed to compare the MS^2 fragmentation patterns of the product ions detected from ambient and
154 laboratory samples. Field and laboratory blanks were extracted and analyzed following the same
155 procedures to determine any potential contamination during the sampling, transportation, storage
156 and/or analysis. The extraction efficiency for all the samples was $94 \pm 16\%$.

157 RESULTS AND DISCUSSION

158 **Enhancement of NPF in the Presence of DMA.** Aerosol size distributions of SOAs formed from
159 the ozonolysis of α -pinene were continuously measured using a DMPS. As shown in Table 1, the
160 number of particles in the experiments E1-E3 ranged from 9500 to 26000 particles per cm^{-3} . After
161 the injection of DMA (experiment E1'-E3'), all experiments revealed a subsequent increase of the
162 number of particles (70 000-80 000 particles per cm^3). This clearly indicates a strong influence of
163 DMA on SOA formation from the ozonolysis of α -pinene. Such results are in agreement with
164 observations from other laboratory studies, underlying the enhancement of NPF due to the presence
165 of amines.^{9, 15, 35-37} A recent theoretical study has revealed that the interaction between amines and
166 dicarboxylic acids likely exerts a synergetic effect on NPF due to the formation of aminium
167 carboxylate ion pairs.³⁸ As presented in Figure 1, the average median diameter of the SOAs formed
168 from the ozonolysis of α -pinene was $20 \pm 2\text{ nm}$, while being $27 \pm 2\text{ nm}$ in the presence of DMA. The
169 increase of 7 nm could be attributed to the potential reactions between organic compounds, such as
170 aldehydes, ketones or carboxylic acids with DMA.¹¹ These reactions could lead to the formation of
171 semi- and low- volatile organic compounds, which might further participate in the SOA formation.
172 Therefore, to better understand the mechanisms governing the enhancement of NPF and the SOA

173 growth in the presence of DMA, chemical characterization of both gas- and particle-phase reaction
174 products was performed.

175 **Chemical Characterization of Gaseous Reaction Products.** Gaseous reaction products were
176 characterized by HR-ToF-CIMS. The ions selected were detected as iodide clusters ($M + 126.9050$
177 Da). The mass spectra of gaseous compounds identified by HR-ToF-CIMS from the ozonolysis of α -
178 pinene and the α -pinene- O_3 -DMA reaction are presented in Figure S2. As can be seen, spectra differ
179 significantly between both set of experiments. The subtracted mass spectrum from the experiments
180 is shown in Figure 2, demonstrating the clear effect of DMA on the ozonolysis of α -pinene. The
181 positive values correspond to the formation of reaction products after the injection of DMA and the
182 negative values to the depletion of products due to the presence of DMA. As shown in Figure 2, a
183 subsequent decrease of the signal of ions attributed to pinonic (m/z 311, $C_{10}H_{16}O_3I^-$), pinic (m/z 313
184 $C_9H_{14}O_4I^-$) and hydroxy-pinonic acids (m/z 327, $C_{10}H_{16}O_4I^-$) were observed after the injection of
185 DMA into the flow tube. This change can also be seen in Figure 3 especially for pinonic acid
186 ($C_{10}H_{16}O_3I^-$) whose signal dropped by a factor of ~ 2.5 . In addition, depletion of highly oxidized
187 molecules (m/z 340–500 Da) previously identified in laboratory or field studies,³⁹⁻⁴¹ was also
188 observed after the injection of DMA as shown in Figure 2.

189 A surprising increase of the signals of oxygenated compounds was also observed after
190 the injection of DMA (Figures 2, 3 and S3). Figure S3 presents a mass defect plot of reaction products
191 identified by HR-ToF-CIMS. A mass defect plot provides an effective visualization of high-resolution
192 mass spectral data of a complex mixture in a two-dimensional way. More details about this approach
193 can be found elsewhere.⁴²⁻⁴³ As displayed in Figure S3, a large amount of gas-phase oxygenated
194 products are formed after the injection of DMA. For example, the signal of the ion at m/z 297,
195 attributed to nor-pinonic acid ($C_9H_{14}O_3I^-$), was 5 times higher in the presence of DMA. The
196 experiments were carried out under steady-state conditions; meaning that a constant flow of reactants,
197 oxidants and particles were continuously added to the chamber. Therefore, additional formation of

198 nor-pinonic acid from OH-initiated oxidation of pinonaldehyde would require additional formation
199 of OH radicals in the system. The ozonolysis of unsaturated products arising from aldehyde-
200 dimethylamine reaction may lead to OH radicals which could result in the formation of nor-pinonic
201 acid. It is worth noting that the products formed from the reactions of oxygenated species with DMA
202 exhibit a smaller carbon skeleton than the precursors, suggesting that amine chemistry induces the
203 formation of smaller oxygenated products with a larger O/C ratio. As previously reported,
204 pinonaldehyde is one of the major reaction product from the oxidation of α -pinene.⁴⁴ We have
205 recently reported the subsequent reaction of pinonaldehyde with DMA and identified the formation
206 of N-containing compounds in both gas and particulate phases. The main gaseous products observed
207 was an enamine (m/z 196.1696 detected in positive mode - $C_{12}H_{22}NO^+$).²² The presence of such
208 compounds was observed also in this work suggesting that aldehydes can react with DMA and lead
209 to a large variety of oxygenated and/or N-containing species. It is important to note that due to the
210 poor sensitivity of iodide ionization towards aldehydes and/or low oxidized compounds (e.g.
211 $C_{12}H_{21}NO$),³⁰ the direct observation of reactions between aldehydes and DMA was not possible here.
212 All together 45 N-containing compounds were observed in the gas phase from the α -pinene- O_3 -DMA
213 reactions (e.g. $C_6H_9NO_3$ and $C_3H_7NO_2$, Figure 3) by HR-ToF-CIMS (Table S1). As discussed below,
214 the oxidation of enamine or imine arising from the reactions of carbonyl and/or carboxylic acids with
215 DMA,^{11, 45} might explain the large amount of the small oxygenated and N-containing compounds
216 observed in the gas-phase.

217 Previous studies have reported the reactions of amines with carboxylic acids and/or
218 carbonyl compounds in either bulk solution,²⁰⁻²¹ or aerosol phase,⁴⁶ and identified the formation of
219 N-containing species. In order to investigate whether enamine formation takes place in gas or aerosol
220 phase, we calculated the Gibbs free energies along to the reaction coordinate using the combination
221 of density functional theory and coupled cluster methods. Detailed description of the calculations is
222 given in Supplementary Material (Figure S4-S7, Table S2). The reaction is suggested to begin with

223 the formation of carbinolamine followed by subsequent dehydration leading to enamine. Calculations
224 resulted in so high activation energy of carbinolamine formation that the bimolecular addition
225 reaction in the atmospheric conditions is unlikely. Based on the computed Gibbs free energies the
226 dehydration of carbinolamine is the rate-limiting step, and even the reaction is thermodynamically
227 favourable under atmospheric conditions, the direct formation of enamine through an addition-
228 elimination mechanism is kinetically restricted. In contrast, we investigated the stabilization effect of
229 a single water molecule, and found that the activation energies are reduced by more than 10 kcal/mol
230 for both addition and elimination steps. Therefore, we suggest that the reaction occurs on the
231 molecular cluster surface. Later, enamine, formed in the aerosol phase, can evaporate to the gas phase.
232 Also, facilitation of heterogeneous reactions by aerosol water has been shown elsewhere⁴⁷.

233 **Ozone reduction from α -pinene-O₃-DMA Reaction.** As shown in Table 1, the ozone concentration
234 dropped significantly after the addition of DMA. On average, the ozonolysis of α -pinene decreased
235 the ozone concentration from 110 ppb to 42 ppb, while the presence of DMA decreased it down to 8
236 ppb. The large reduction of ozone observed in these experiments cannot be solely explained by the
237 reaction of DMA with O₃ or OH according to the rate constants ($1.67 \pm 0.20 \times 10^{-18}$ and $6.27 \pm 0.63 \times$
238 10^{-11} cm³/molecule/s, respectively).⁴⁸⁻⁴⁹ Further decrease is expected due to the products formed from
239 the reaction of oxygenated species with DMA that could undergo further oxidation processes with
240 ozone. Indeed, carbonyl groups, such as aldehydes, can react with DMA to form enamine
241 compounds.¹¹ For instance, we have previously reported that DMA can react on the aldehyde function
242 of pinonaldehyde and lead to carbinolamines, which then dehydrate to generate enamine compounds.
243 In addition, formation of imines from the reaction between amines and carbonyl compounds have
244 been observed.⁵⁰ Hence, ozone can react with the double bond of the enamine and/or imines species
245 (Figure S8), leading to a primary ozonide, which decomposes to produce a Criegee biradical
246 intermediate and a carbonyl compound. Formation of carboxylic acids can also be explained by
247 Criegee biradical rearrangement.⁵¹ As an example ozonolysis of C₁₂H₂₁NO is expected to lead to the

248 formation of nor-pinonaldehyde ($C_9H_{14}O_2$), nor-pinonic ($C_9H_{14}O_3$) and carbamic acids ($C_3H_7O_2N$).
249 A tentative reaction pathway is proposed in Figure S8, which is supported by the subsequent
250 formation of nor-pinonic and carbamic acids after the injection of DMA (Figure 3). Other
251 N-containing compounds, such as imines or nitroamines, may also contribute to the ozone
252 consumption. Ge *et al.*⁵² have identified $CH_3N=CH_2$, $(CH_3)_2NCHO$, CH_3NO_2 , $CH_3N(OH)CHO$ and
253 CH_3NHOH as major products from the ozonolysis of alkylamines. Hence, ozonolysis of these
254 N-containing species might explain the large concentration of oxygenated compounds in the gas
255 phase. The formation of the N-containing compounds and the increase of concentration of
256 oxygenated compounds in the gas phase can explain the enhancement of NPF and SOA growth from
257 the ozonolysis of α -pinene in the presence of DMA. It should be noted, however, that oligomerization
258 through accretion reactions would lead to the formation of unsaturated compounds in particle phase,
259 which could also participate in the ozone reduction. These observations suggest that amines may play
260 an important role in the gas and heterogeneous chemistry of oxygenated species governing the SOA
261 formation and aging.

262 **Chemical Characterization of Particulate Reaction Products.** Table 2 presents the most abundant
263 N-containing compounds identified from the filter or the flow tube wall extract samples. These
264 compounds were not observed without DMA in either the α -pinene ozonolysis or in the laboratory
265 blank samples. Differences between theoretical and measured masses obtained by HRMS are small
266 and within commonly acceptable errors (i.e., ± 5 ppm). As indicated in Table 2, the major
267 N-containing compounds detected in particle phases are $C_{11}H_{19}O_2N$, $C_{10}H_{17}O_3N$, $C_{12}H_{21}O_2N$,
268 $C_{12}H_{19}O_3N$ and $C_{13}H_{17}O_4N_3$. Smaller N-containing compounds from 176 to 230 Da were also
269 identified in the gas phase, by either HR-ToF-CIMS or by analysis of samples collected on SPE
270 cartridges, demonstrating the partitioning of these compounds between gas and particle phases. High-
271 molecular weight N-containing compounds (MW > 300 Da) were also identified. The accurate mass
272 measurements of the corresponding $[M + H]^+$ ions indicate the formation of C_{15} - C_{30} carbon

273 compounds, presence of such compounds supports accretion reactions occurring in particle phase.
274 Reaction between oxygenated dimers and DMA, assumed from the HR-ToF-CIMS results (Figure 2,
275 depletion of highly oxidized molecules m/z 340–500 Da) is also another hypothesis. It is worth
276 nothing that molecules with 3 and 5 nitrogen atoms were also identified in the particle phase. They
277 might take part in the formation of imidazole type compounds, previously observed from the reaction
278 of glyoxal or methylglyoxal with amines in particle phase, suggesting that heterogeneous reactions
279 should also be considered here.^{21, 50}

280 Interestingly, as shown in Table 2, eleven N-containing compounds exhibit an identical
281 fragment ion at m/z 72.044 ($C_3H_6ON^+$) in their MS^2 spectra as revealed in Figure S9. Ion at m/z 72 is
282 characteristic to a tertiary amide, which is likely produced from the reaction between a carboxylic
283 acid and DMA. This observation suggests that carboxylic acid-amine reaction is an important reaction
284 pathway leading to specific products as discussed above. Bastanti and Pankow⁵³ have concluded that
285 for all the acids studied (acetic, malic, maleic and pinic acids), amide formation was
286 thermodynamically favored, supporting the hypothesis presented in this work. As for organosulfates,
287 fragment ions at m/z 80 ($SO_3^{\bullet-}$), 96 (HSO_3^-) and 97 (HSO_4^-) are characteristic for their detection in
288 negative ion mode,⁵⁴ and ion m/z 72 might be a beneficial product ion for the identification of
289 compounds arising from carboxylic acid-secondary amine reaction in positive ion mode.

290 A potential mechanism for the formation of products with a fragment ion at m/z 72 is tentatively
291 proposed in Figure S10. As an example, pinonic acid can react with DMA to form $C_{12}H_{21}NO_2$ (m/z
292 212.164). Signal of pinonic acid decreased after the DMA addition, while product at m/z 212.164
293 increased. In contrast, nor-pinonic acid, which is tentatively proposed to be formed from the
294 ozonolysis of $C_{12}H_{21}NO$ (a pinonaldehyde/DMA reaction product), might further react with DMA
295 and lead to the product ion at m/z 198.149 ($C_{11}H_{19}NO_2$). The MS^2 spectra for the $C_{11}H_{19}NO_2$ is given
296 in Figure S11, and the identified fragments support the presence of an amide functional group in the
297 structure. Hence, organic acids formed from the ozonolysis of α -pinene, such as terebic, nor-pinonic,

298 terpenylic, nor-pinic, pinonic, oxopinonic and hydroxyl-pinonic acids (Figure S11), previously
299 observed in laboratory and field studies,⁵⁵⁻⁵⁸ can further react with DMA and lead to the formation of
300 N-containing reaction products, yielding a fragment ion at m/z 72 in their MS² spectra (Table 2).
301 These results are in agreement with the results of the study of Lavi et al.²⁴ in which they observed that
302 alkylammonium carboxylates can enhance SOA formation. Furthermore, as it has been shown by
303 Gomez-Hernandez et al.²⁵, alkylamine neutralization of carboxylic acids also enhances the particle
304 hygroscopicity.

305 **Reaction Products from α -pinene-O₃-DMA Reaction in Ambient Aerosol.** Figure 4 presents the
306 extracted ion chromatograms (EICs) of parent ions at m/z 198.149 and 212.164 from α -pinene + O₃
307 experiment (E3), α -pinene + O₃ + DMA experiment (E3'), blank filter and PM₁ samples collected at
308 Hyytiälä Forestry Field Station (23th of May, 2016). MS² fragmentation patterns of parent ion at m/z
309 198.149 and 212.164 from laboratory and field samples are shown in Figure S12.

310 Based on the excellent agreement between the retention times, the accurate masses and
311 the MS² fragmentation pattern, parent ions at m/z 198.149 (RT 4.57 min) and 212.164 (RT 5.07 min)
312 found in the boreal forest samples were attributed to N-containing compounds formed from the
313 oxidation of α -pinene in the presence of DMA. Three other reaction products were also identified in
314 PM₁ samples at the SMEAR II Station in Hyytiälä, using accurate masses. The other reaction products
315 identified in laboratory experiments samples were not observed in the boreal forest samples. Semi-
316 quantification was performed using caffeine as a surrogate standard, resulting in potential large
317 uncertainties for the estimated concentrations of these products, mainly due to different extraction
318 yields and ionization efficiency between caffeine and the analytes. However, such approach allows
319 us to provide information on variations and time-trends that cannot be obtained otherwise. The
320 average concentration of compounds observed at m/z 198.149 was 0.161 ng/m³ with a maximum
321 concentration of 0.990 ng/m³, while it was 0.035 ng/m³ for the parent ions at m/z 212.164 with a
322 maximum concentration of 0.161 ng/m³. A temporal profile of the concentration of both compounds

323 is proposed in Figure S13. The concentration of these two compounds are fairly correlated ($r^2 = 0.46$),
324 suggesting similar source of emission or formation, except from 15th of May 2016 to 20th of May
325 2016. Even if relatively low concentration of DMA has been reported for the clean boreal forest
326 atmosphere,⁷ the identification of these two compounds in ambient samples suggests that DMA may
327 have an effect on the ozonolysis of α -pinene disproportional to its concentration. However, additional
328 field measurements should be performed in order to estimate the contribution of these compounds to
329 aerosol particles. Because amines are ubiquitous in the atmosphere,⁶ similar reactions in ambient
330 conditions could be important for the formation and growth of SOAs in the atmosphere. Finally, more
331 laboratory studies are needed to elucidate the formation pathways and quantify the impact of amine
332 reactions on the SOA formation.

333 ASSOCIATED CONTENT

334 **Supporting Information.**

335 Figure S1 presents the scheme of the experimental set-up used in this work. Figure S2 shows the
336 representative high-resolution mass spectra obtained by HR-ToF-CIMS from the laboratory
337 experiments. Figure S3 presents the mass defect plot of reaction products identified by HR-ToF-
338 CIMS from the ozonolysis of α -pinene in presence and absence of DMA. Figures S4-S7 describe the
339 results from quantum chemistry calculations. Figure S8 displays the proposed mechanism for the
340 formation of $C_9H_{14}O_2$, $C_9H_{14}O_3$ and $C_3H_7O_2N$ from the ozonolysis of enamine arising from the
341 pinonaldehyde-DMA reaction. Figure S9 presents the MS^2 fragmentation patterns of selected product
342 ions, leading to the formation of a fragment ion at m/z 72.044. Figure S10 gives a proposed
343 mechanism for tertiary amide reaction products obtained from organic acids-DMA reactions. Figure
344 S11 presents the MS^2 fragmentation pathway of the product ion at m/z 198.149. Figure S12 shows
345 the MS^2 fragmentation pattern of product ions at m/z 198.149 and 212.164 from laboratory and field
346 samples. Figure S13 presents the concentration in $ng.m^{-3}$ of reaction products identified in Hyytiälä,

347 Finland. Table S1 lists the N-containing compounds detected by HR-ToF-CIMS from the ozonolysis
348 of α -pinene in the presence of DMA. Table S2 presents the Gibbs free energies relative to the reactants
349 at 298.15K. This material is available free of charge via the Internet at <http://pubs.acs.org>.

350 AUTHOR INFORMATION

351 Corresponding Author

352 *Marja-Liisa Riekkola. Tel: +358 405058848. E-mail address: marja-liisa.riekkola@helsinki.fi

353 Notes

354 The authors declare no competing financial interest.

355

356 ACKNOWLEDGMENT

357 The financial support of the Academy of Finland Center of Excellence program (project no 272041),
358 European Research Council (COALA, grant 638703 and MOCAPAF, grant 57360) is gratefully
359 acknowledged. The CSC-IT Center for Science in Espoo (Finland) is also thank for computational
360 resources. Technical staff at the SMEAR II Station are thanked for the valuable help. SPME Arrows
361 were kindly provided by CTC Analytik (Switzerland).

362 REFERENCE

- 363 1. Pope III, C. A.; Dockery, D. W. Health effects of fine particulate air pollution: lines that connect. *J. Air Waste*
364 *Manage. Assoc.* **2006**, *56* (6), 709–742.
- 365 2. IPCC, Climate Change 2013: The Physical Science Basis: Working Group I Contribution to the Fifth
366 Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press: 2013.
- 367 3. Kanakidou, M.; Seinfeld, J.; Pandis, S.; Barnes, I.; Dentener, F.; Facchini, M.; Dingenen, R. V.; Ervens, B.;
368 Nenes, A.; Nielsen, C. Organic aerosol and global climate modelling: a review. *Atmos. Chem. Phys.* **2005**, *5*
369 (4), 1053–1123.
- 370 4. Hallquist, M.; Wenger, J.; Baltensperger, U.; Rudich, Y.; Simpson, D.; Claeys, M.; Dommen, J.; Donahue, N.;
371 George, C.; Goldstein, A. H.; Hamilton, J. F.; Herrmann, H.; Hoffmann, T.; Iinuma, Y.; Jang, M.; Jenkin, M. E.;

- 372 Jimenez, J. L.; Kiendler-Scharr, A.; Maenhaut, W.; McFiggans, G.; Mentel, Th. F.; Monod, A.; Prévôt, A. S. H.;
373 Seinfeld, J. H.; Surratt, J. D.; Szmigielski, R.; Wildt, J. The formation, properties and impact of secondary
374 organic aerosol: current and emerging issues. *Atmos. Chem. Phys.* **2009**, *9* (14), 5155–5236.
- 375 5. Ziemann, P. J.; Atkinson, R. Kinetics, products, and mechanisms of secondary organic aerosol formation.
376 *Chem. Soc. Rev.* **2012**, *41* (19), 6582–6605.
- 377 6. Ge, X.; Wexler, A. S.; Clegg, S. L. Atmospheric amines—Part I. A review. *Atmos. Environ.* **2011**, *45* (3),
378 524–546.
- 379 7. Kieloaho, A.-J.; Hellén, H.; Hakola, H.; Manninen, H. E.; Nieminen, T.; Kulmala, M.; Pihlatie, M. Gas-phase
380 alkylamines in a boreal Scots pine forest air. *Atmos. Environ.* **2013**, *80*, 369–377.
- 381 8. Youn, J.-S.; Crosbie, E.; Maudlin, L.; Wang, Z.; Sorooshian, A., Dimethylamine as a major alkyl amine species
382 in particles and cloud water: Observations in semi-arid and coastal regions. *Atmos. Environ.* **2015**, *122*,
383 250–258.
- 384 9. Almeida, J.; Schobesberger, S.; Kuerten, A.; Ortega, I. K.; Kupiainen-Maatta, O.; Praplan, A. P.; Adamov, A.;
385 Amorim, A.; Bianchi, F.; Breitenlechner, M.; David, A.; Dommen, J.; Donahue, N. M.; Downard, A.; Dunne, E.;
386 Duplissy, J.; Ehrhart, S.; Flagan, R. C.; Franchin, A.; Guida, R.; Hakala, J.; Hansel, A.; Heinritzi, M.; Henschel, H.;
387 Jokinen, T.; Junninen, H.; Kajos, M.; Kangasluoma, J.; Keskinen, H.; Kupc, A.; Kurten, T.; Kvashin, A. N.;
388 Laaksonen, A.; Lehtipalo, K.; Leiminger, M.; Leppä, J.; Loukonen, V.; Makhmutov, V.; Mathot, S.; McGrath, M.
389 J.; Nieminen, T.; Olenius, T.; Onnela, A.; Petaja, T.; Riccobono, F.; Riipinen, I.; Rissanen, M.; Rondo, L.;
390 Ruuskanen, T.; Santos, F. D.; Sarnela, N.; Schallhart, S.; Schnitzhofer, R.; Seinfeld, J. H.; Simon, M.; Sipila, M.;
391 Stozhkov, Y.; Stratmann, F.; Tome, A.; Troestl, J.; Tsagkogeorgas, G.; Vaattovaara, P.; Viisanen, Y.; Virtanen,
392 A.; Vrtala, A.; Wagner, P. E.; Weingartner, E.; Wex, H.; Williamson, C.; Wimmer, D.; Ye, P.; Yli-Juuti, T.; Carslaw,
393 K. S.; Kulmala, M.; Curtius, J.; Baltensperger, U.; Worsnop, D. R.; Vehkamäki, H.; Kirkby, J. Molecular
394 understanding of sulphuric acid-amine particle nucleation in the atmosphere. *Nature* **2013**, *502* (7471),
395 359–363.
- 396 10. Yu, H.; McGraw, R.; Lee, S. H. Effects of amines on formation of sub-3 nm particles and their subsequent
397 growth. *Geophys. Res. Lett.* **2012**, *39* (2), L02807.
- 398 11. Qiu, C.; Zhang, R., Multiphase chemistry of atmospheric amines. *Phys. Chem. Chem. Phys.* **2013**, *15* (16),
399 5738–5752.
- 400 12. Tao, Y.; Ye, X.; Jiang, S.; Yang, X.; Chen, J.; Xie, Y.; Wang, R. Effects of amines on particle growth observed
401 in new particle formation events. *Journal of Geophysical Research: Atmospheres* **2016**, *121* (1), 324–335.
- 402 13. Glasoe, W.; Volz, K.; Panta, B.; Freshour, N.; Bachman, R.; Hanson, D.; McMurry, P.; Jen, C. Sulfuric acid
403 nucleation: An experimental study of the effect of seven bases. *Journal of Geophysical Research:
404 Atmospheres* **2015**, *120* (5), 1933–1950.
- 405 14. Kurtén, T.; Loukonen, V.; Vehkamäki, H.; Kulmala, M. Amines are likely to enhance neutral and ion-
406 induced sulfuric acid-water nucleation in the atmosphere more effectively than ammonia. *Atmos. Chem.
407 Phys.* **2008**, *8* (14), 4095–4103.
- 408 15. Erupe, M.; Viggiano, A.; Lee, S.-H. The effect of trimethylamine on atmospheric nucleation involving
409 H₂SO₄. *Atmos. Chem. Phys.* **2011**, *11* (10), 4767–4775.
- 410 16. Kurten, A.; Jokinen, T.; Simon, M.; Sipila, M.; Sarnela, N.; Junninen, H.; Adamov, A.; Joao Almeida, A.;
411 Amorim, A.; Bianchi, F.; Breitenlechner, M.; Dommen, J.; Donahue, N. M.; Duplissy, J.; Ehrhart, S.; Flagan, R.
412 C.; Franchin, A.; Hakala, J.; Hansel, A.; Heinritzi, M.; Hutterli, M.; Kangasluoma, J.; Kirkby, J.; Laaksonen, A.;

- 413 Lehtipalo, K.; Leiminger, M.; Makhmutov, V.; Mathot, S.; Onnela, A.; Petaja, T.; Praplan, A. P.; Riccobono, F.;
414 Rissanen, M. P.; Rondo, L.; Schobesberger, S.; Seinfeld, J. H.; Steiner, G.; Tome, A.; Trostl, J.; Winkler, P. M.;
415 Williamson, C.; Wimmer, D.; Ye, P.; Baltensperger, U.; Carslaw, K. S.; Kulmala, M.; Worsnop, D. R.; Curtius, J.
416 Neutral molecular cluster formation of sulfuric acid–dimethylamine observed in real time under atmospheric
417 conditions. *Proc. Natl. Acad. Sci. USA* **2014**, *111* (42), 15019–15024.
- 418 17. Mäkelä, J.; Yli-Koivisto, S.; Hiltunen, V.; Seidl, W.; Swietlicki, E.; Teinilä, K.; Sillanpää, M.; Koponen, I.;
419 Paatero, J.; Rosman, K. Chemical composition of aerosol during particle formation events in boreal forest.
420 *Tellus B* **2001**, *53* (4), 380–393.
- 421 18. Smith, J. N.; Barsanti, K. C.; Friedli, H. R.; Ehn, M.; Kulmala, M.; Collins, D. R.; Scheckman, J. H.; Williams,
422 B. J.; McMurry, P. H., Observations of aminium salts in atmospheric nanoparticles and possible climatic
423 implications. *Proc. Natl. Acad. Sci. USA* **2010**, *107* (15), 6634–6639.
- 424 19. Zhao, J.; Smith, J.; Eisele, F.; Chen, M.; Kuang, C.; McMurry, P. Observation of neutral sulfuric acid-amine
425 containing clusters in laboratory and ambient measurements. *Atmos. Chem. Phys.* **2011**, *11* (21),
426 10823–10836.
- 427 20. Galloway, M. M.; Powelson, M. H.; Sedehi, N.; Wood, S. E.; Millage, K. D.; Kononenko, J. A.; Rynaski, A. D.;
428 De Haan, D. O. Secondary organic aerosol formation during evaporation of droplets containing atmospheric
429 aldehydes, amines, and ammonium sulfate. *Environ. Sci. Technol.* **2014**, *48* (24), 14417–14425.
- 430 21. De Haan, D. O.; Hawkins, L. N.; Kononenko, J. A.; Turley, J. J.; Corrigan, A. L.; Tolbert, M. A.; Jimenez, J. L.
431 Formation of nitrogen-containing oligomers by methylglyoxal and amines in simulated evaporating cloud
432 droplets. *Environ. Sci. Technol.* **2010**, *45* (3), 984–991.
- 433 22. Duporté, G.; Parshintsev, J.; Barreira, L. s. M.; Hartonen, K.; Kulmala, M.; Riekkola, M.-L. Nitrogen-
434 Containing Low Volatile Compounds from Pinonaldehyde-Dimethylamine Reaction in the Atmosphere: A
435 Laboratory and Field Study. *Environ. Sci. Technol.* **2016**, *50* (9), 4693–4700.
- 436 23. Stropoli, S. J.; Elrod, M. J. Assessing the Potential for the Reactions of Epoxides with Amines on Secondary
437 Organic Aerosol Particles. *J. Phys. Chem. A* **2015**, *119* (40), 10181–10189.
- 438 24. Lavi, A.; Segre, E.; Gomez-Hernandez, M.; Zhang, R.; Rudich, Y. Volatility of atmospherically relevant
439 alkylaminium carboxylate. *J. Phys. Chem. A* **2015**, *119* (19), 4336–4346.
- 440 25. Gomez-Hernandez, M.; McKeown, M.; Secrest, J.; Marrero-Ortiz, W.; Lavi, A.; Rudich, Y.; Collins, D. R.;
441 Zhang, R. Hygroscopic characteristics of alkylaminium carboxylate aerosols. *Environ. Sci. Technol.* **2016**, *50* (5),
442 2292–2300.
- 443 26. Rissanen, M. P.; Kurtén, T.; Sipilä, M.; Thornton, J. A.; Kangasluoma, J.; Sarnela, N.; Junninen, H.;
444 Jørgensen, S.; Schallhart, S.; Kajos, M. K.; Taipale, R.; Springer, M.; Mentel, T. G.; Petäjä, T.; Worsnop, D. R.;
445 Kjaergaard, H. G.; Ehn, M. The formation of highly oxidized multifunctional products in the ozonolysis of
446 cyclohexene. *J. Am. Chem. Soc.* **2014**, *136* (44), 15596–15606.
- 447 27. Rissanen, M. P.; Kurtén, T.; Sipilä, M.; Thornton, J. A.; Kausiala, O.; Garmash, O.; Kjaergaard, H. G.; Petäjä,
448 T.; Worsnop, D. R.; Ehn, M. Effects of chemical complexity on the autoxidation mechanisms of endocyclic
449 alkene ozonolysis products: From methylcyclohexenes toward understanding α -pinene. *J. Phys. Chem. A*
450 **2015**, *119* (19), 4633–4650.
- 451 28. Hawkins, J. E.; Armstrong, G. T. Physical and Thermodynamic Properties of Terpenes. 1 III. The Vapor
452 Pressures of α -Pinene and β -Pinene. *J. Am. Chem. Soc.* **1954**, *76* (14), 3756–3758.

- 453 29. Helin, A.; Rönkkö, T.; Parshintsev, J.; Hartonen, K.; Schilling, B.; Läubli, T.; Riekkola, M.-L. Solid phase
454 microextraction Arrow for the sampling of volatile amines in wastewater and atmosphere. *J. Chromatogr. A*
455 **2015**, 1426, 56–63.
- 456 30. Lee, B. H.; Lopez-Hilfiker, F. D.; Mohr, C.; Kurtén, T.; Worsnop, D. R.; Thornton, J. A. An iodide-adduct
457 high-resolution time-of-flight chemical-ionization mass spectrometer: Application to atmospheric inorganic
458 and organic compounds. *Environ. Sci. Technol.* **2014**, 48 (11), 6309–6317.
- 459 31. Lopez-Hilfiker, F. D.; Lee, B. H.; D'Ambro, E. L.; Thornton, J. A. Constraining the sensitivity of iodide adduct
460 chemical ionization mass spectrometry to multifunctional organic molecules using the collision limit and
461 thermodynamic stability of iodide ion adducts. *Atmos. Meas. Tech.* **2016**, 9 (4), 1505–1512.
- 462 32. Lopez-Hilfiker, F.; Mohr, C.; D'Ambro, E. L.; Lutz, A.; Riedel, T. P.; Gaston, C. J.; Iyer, S.; Zhang, Z.; Gold, A.;
463 Surratt, J. D.; Lee, B. H.; Kurten, T.; Hu, W. W.; Jimenez, J.; Hallquist, M.; Thornton, J. A. Molecular
464 Composition and Volatility of Organic Aerosol in the Southeastern US: Implications for IEPOX Derived SOA.
465 *Environ. Sci. Technol.* **2016**, 50 (5), 2200–2209.
- 466 33. Hari, P.; Kulmala, M. Station for measuring ecosystem-atmosphere relations. *Boreal Environ. Res.* **2005**,
467 10 (5), 315–322.
- 468 34. Rinne, J.; Hakola, H.; Laurila, T.; Rannik, Ü. Canopy scale monoterpene emissions of *Pinus sylvestris*
469 dominated forests. *Atmos. Environ.* **2000**, 34 (7), 1099–1107.
- 470 35. Berndt, T.; Sipilä, M.; Stratmann, F.; Petäjä, T.; Vanhanen, J.; Mikkilä, J.; Patokoski, J.; Taipale, R.; Mauldin
471 III, R. L.; Kulmala, M. Enhancement of atmospheric H₂SO₄/H₂O nucleation: organic oxidation products versus
472 amines. *Atmos. Chem. Phys.* **2014**, 14 (2), 751–764.
- 473 36. Berndt, T.; Stratmann, F.; Sipilä, M.; Vanhanen, J.; Petäjä, T.; Mikkilä, J.; Grüner, A.; Spindler, G.; Mauldin
474 III, L.; Curtius, J.; Kulmala, M.; Heintzenberg, J. Laboratory study on new particle formation from the reaction
475 OH + SO₂: influence of experimental conditions, H₂O vapour, NH₃ and the amine tert-butylamine on the
476 overall process. *Atmos. Chem. Phys.* **2010**, 10 (15), 7101–7116.
- 477 37. Zollner, J.; Glasoe, W.; Panta, B.; Carlson, K.; McMurry, P.; Hanson, D. Sulfuric acid nucleation: power
478 dependencies, variation with relative humidity, and effect of bases. *Atmos. Chem. Phys.* **2012**, 12 (10),
479 4399–4411.
- 480 38. Xu, W.; Zhang, R. A theoretical study of hydrated molecular clusters of amines and dicarboxylic acids. *J.*
481 *Chem. Phys.* **2013**, 139 (6), 064312.
- 482 39. Ehn, M.; Thornton, J. A.; Kleist, E.; Sipilä, M.; Junninen, H.; Pullinen, I.; Springer, M.; Rubach, F.; Tillmann,
483 R.; Lee, B.; Lopez-Hilfiker, F.; Andres, S.; Acir, I.-H.; Rissanen, M.; Jokinen, T.; Schobesberger, S.; Kangasluoma,
484 J.; Kontkanen, J.; Nieminen, T.; Kurten, T.; Nielsen, L. B.; Jorgensen, S.; Kjaergaard, H. G.; Canagaratna, M.;
485 Maso, M. D.; Berndt, T.; Petaja, T.; Wahner, A.; Kerminen, V.-M.; Kulmala, M.; Worsnop, D. R.; Wildt, J.;
486 Mentel, T. F. A large source of low-volatility secondary organic aerosol. *Nature* **2014**, 506 (7489), 476–479.
- 487 40. Mutzel, A.; Poulain, L.; Berndt, T.; Iinuma, Y.; Rodigast, M.; Böge, O.; Richters, S.; Spindler, G.; Sipilä, M.;
488 Jokinen, T.; Kulmala, M.; Herrmann, H. Highly oxidized multifunctional organic compounds observed in
489 tropospheric particles: A field and laboratory study. *Environ. Sci. Technol.* **2015**, 49 (13), 7754–7761.
- 490 41. Tu, P.; Hall IV, W. A.; Johnston, M. V. Characterization of Highly Oxidized Molecules in Fresh and Aged
491 Biogenic Secondary Organic Aerosol. *Anal. Chem.* **2016**, 88 (8), 4495–4501.

- 492 42. Kendrick, E. A Mass Scale Based on CH₂= 14.0000 for High Resolution Mass Spectrometry of Organic
493 Compounds. *Anal. Chem.* **1963**, 35 (13), 2146–2154.
- 494 43. Walser, M. L.; Desyaterik, Y.; Laskin, J.; Laskin, A.; Nizkorodov, S. A. High-resolution mass spectrometric
495 analysis of secondary organic aerosol produced by ozonation of limonene. *Phys. Chem. Chem. Phys.* **2008**, 10
496 (7), 1009–1022.
- 497 44. Jang, M.; Kamens, R. M. Newly characterized products and composition of secondary aerosols from the
498 reaction of α -pinene with ozone. *Atmos. Environ.* **1999**, 33 (3), 459–474.
- 499 45. Gomez, S.; Peters, J. A.; Maschmeyer, T. The reductive amination of aldehydes and ketones and the
500 hydrogenation of nitriles: mechanistic aspects and selectivity control. *Adv. Synth. Catal.* **2002**, 344 (10),
501 1037–1058.
- 502 46. Zahardis, J.; Geddes, S.; Petrucci, G. The ozonolysis of primary aliphatic amines in fine particles. *Atmos.*
503 *Chem. Phys.* **2008**, 8 (5), 1181–1194.
- 504 47. Sareen, N.; Waxman, E. M.; Turpin, B. J.; Volkamer, R.; Carlton A. G. Potential of aerosol liquid water to
505 facilitate organic aerosol formation: assessing knowledge gaps about precursors and partitioning. *Environ.*
506 *Sci. Technol.* **2017**, 51 (6), 3327–3335.
- 507 48. Onel, L.; Thonger, L.; Blitz, M.; Seakins, P.; Bunkan, A.; Solimannejad, M.; Nielsen, C. Gas-Phase Reactions
508 of OH with Methyl Amines in the Presence or Absence of Molecular Oxygen. An Experimental and Theoretical
509 Study. *J. Phys. Chem. A* **2013**, 117 (41), 10736–10745.
- 510 49. Tuazon, E. C.; Atkinson, R.; Aschmann, S. M.; Arey, J. Kinetics and products of the gas-phase reactions of
511 O₃ with amines and related compounds. *Res. Chem. Intermed.* **1994**, 20 (3-5), 303–320.
- 512 50. De Haan, D. O.; Tolbert, M. A.; Jimenez, J. L. Atmospheric condensed-phase reactions of glyoxal with
513 methylamine. *Geophys. Res. Lett.* **2009**, 36 (11), L11819.
- 514 51. Jenkin, M. E.; Shallcross, D. E.; Harvey, J. N. Development and application of a possible mechanism for the
515 generation of cis-pinic acid from the ozonolysis of α - and β -pinene. *Atmos. Environ.* **2000**, 34 (18), 2837–2850.
- 516 52. Ge, Y.; Liu, Y.; Chu, B.; He, H.; Chen, T.; Wang, S.; Wei, W.; Cheng, S. Ozonolysis of Trimethylamine
517 Exchanged with Typical Ammonium Salts in the Particle Phase. *Environ. Sci. Technol.* **2016**, 50 (20),
518 11076–11084.
- 519 53. Barsanti, K. C.; Pankow, J. F. Thermodynamics of the formation of atmospheric organic particulate matter
520 by accretion reactions—Part 3: Carboxylic and dicarboxylic acids. *Atmos. Environ.* **2006**, 40 (34), 6676–6686.
- 521 54. Surratt, J. D.; Gómez-González, Y.; Chan, A. W.; Vermeylen, R.; Shahgholi, M.; Kleindienst, T. E.; Edney, E.
522 O.; Offenberg, J. H.; Lewandowski, M.; Jaoui, M.; Maenhaut, W.; Claeys, M.; Flagan, R. C.; Seinfeld, J. H.,
523 Organosulfate formation in biogenic secondary organic aerosol. *J. Phys. Chem. A* **2008**, 112 (36), 8345–8378.
- 524 55. Anttila, P.; Rissanen, T.; Shimmo, M.; Kallio, M.; Hyötyläinen, T.; Kulmala, M.; Riekkola, M.-L. Organic
525 compounds in atmospheric aerosols from a Finnish coniferous forest. *Boreal Environ. Res.* **2005**, 10 (5),
526 371–384.
- 527 56. Jaoui, M.; Kamens, R. M. Mass balance of gaseous and particulate products analysis from α -pinene/NO
528 x/air in the presence of natural sunlight. *J. Geophys. Res. Atmos.* **2001**, 106 (D12), 12541–12558.

529 57. Kristensen, K.; Enggrob, K. L.; King, S. M.; Worton, D.; Platt, S.; Mortensen, R.; Rosenoern, T.; Surratt, J.;
530 Bilde, M.; Goldstein, A.; Glasius, M., Formation and occurrence of dimer esters of pinene oxidation products
531 in atmospheric aerosols. *Atmos. Chem. Phys.* **2013**, *13* (7), 3763–3776.

532 58. Kristensen, K.; Cui, T.; Zhang, H.; Gold, A.; Glasius, M.; Surratt, J. D. Dimers in α -pinene secondary organic
533 aerosol: effect of hydroxyl radical, ozone, relative humidity and aerosol acidity. *Atmos. Chem. Phys.* **2014**, *14*
534 (8), 4201–4218.

535

536

537

538 **Table 1.** Summary of the Experimental Conditions

Experiments	Initial [α -pinene] (ppm)	Initial [O ₃] (ppb)	Initial [DMA] (ppb)	Residence time (s)	Final [O ₃] (ppb)	Number of particles ⁻³ (#.cm ⁻³)
E1	5.0	104.4	-	53	38.5	25800 ± 4500
E1'	5.0	104.4	500	53	8.8	76300 ± 3100
E2	5.0	113.0	-	53	42.9	9500 ± 2000
E2'	5.0	113.0	500	53	7.5	71300 ± 3200
E3	5.0	116.4	-	53	43.5	15500 ± 2500
E3'	5.0	116.4	500	53	8.2	71700 ± 1500
E4	7.0	130.0	700	56	3.1	93300 ± 2500

539

540

541 **Table 2.** N-containing compounds detected in filter and flow tube wall samples by UHPLC-HRMS in positive
 542 mode from α -pinene-O₃-DMA experiment. Δm is the difference in ppm between theoretical masses and
 543 experimental masses of the ions.

[M+H] ⁺ detected ions (m/z)	molecular formula	Δm (ppm)	% of the total N-containing compounds identified in particulate phase ^a	Tertiary amide functionality MS ² fragment C ₃ H ₆ ON ⁺ (m/z 72.0444)	Detected in gas phase		Detected in PM ₁ ambient samples
					HR- CI- APi- TOF	SPE cartridge UHPLC- HRMS	
176.09171	C ₇ H ₁₃ O ₄ N	- 0.26	< 1 ^b	X	X		
186.11244	C ₉ H ₁₅ O ₃ N	0.01	< 1 ^b	X	X		
196.13366	C ₁₁ H ₁₇ O ₂ N	- 0.04	< 1 ^b	X		X	X ^f
196.16959	C ₁₂ H ₂₁ ON	- 0.01	< 1 ^b			X	X ^{f,g}
198.14880	C ₁₁ H ₁₉ O ₂ N	- 0.26	7 ± 3 ^b	X	X	X	X ^e
200.12796	C ₁₀ H ₁₇ O ₃ N	- 0.79	6 ± 3 ^b	X	X	X	X ^f
208.10800	C ₁₀ H ₁₃ O ₂ N ₃	-0.24	2 ± 3 ^c				
210.14890	C ₁₂ H ₁₉ O ₂ N	- 0.21	< 1 ^b	X	X	X	
212.16443	C ₁₂ H ₂₁ O ₂ N	- 0.36	35 ± 2 ^b	X	X	X	X ^e
214.14368	C ₁₁ H ₁₉ O ₃ N	- 0.38	< 1 ^b	X	X		
216.12294	C ₁₀ H ₁₇ O ₄ N	- 0.45	< 1 ^b		X		
226.14366	C ₁₂ H ₁₉ O ₃ N	- 0.65	26 ± 15 ^b	X	X	X	
228.15930	C ₁₂ H ₂₁ O ₃ N	- 0.38	3 ± 1 ^b	X	X	X	
230.13858	C ₁₁ H ₁₉ O ₄ N	- 0.38	< 1 ^b	X	X		
241.19099	C ₁₃ H ₂₄ O ₂ N ₂	- 0.23	- ^d				
244.15422	C ₁₂ H ₂₁ O ₄ N	- 0.46	< 1 ^b				
266.11325	C ₁₂ H ₁₅ O ₄ N ₃	1.07	< 1 ^c				
280.12920	C ₁₃ H ₁₇ O ₄ N ₃	- 0.42	15 ± 14 ^c				
300.15506	C ₁₃ H ₂₁ O ₅ N ₃	1.13	< 1 ^c				
308.16010	C ₁₅ H ₂₁ O ₄ N ₃	1.20	< 1 ^b				
334.22200	C ₁₆ H ₃₁ O ₆ N	- 0.54	- ^d				
342.22729	C ₁₈ H ₃₁ O ₅ N	- 0.54	< 1 ^b				
358.25861	C ₁₉ H ₃₅ O ₅ N	- 0.62	- ^d				
364.16119	C ₁₆ H ₂₁ O ₅ N ₅	0.98	< 1 ^b				
364.26923	C ₁₈ H ₃₇ O ₆ N	- 0.54	- ^d				
376.19638	C ₁₇ H ₂₉ O ₈ N	- 0.48	- ^d				
384.17606	C ₁₇ H ₂₅ O ₇ N ₃	1.22	< 1 ^c				
388.19678	C ₁₈ H ₂₉ O ₈ N	- 0.62	- ^d				
390.28491	C ₂₀ H ₃₉ O ₆ N	- 0.34	- ^d				
394.31610	C ₂₀ H ₄₃ O ₆ N	- 0.61	- ^d				
401.13489	C ₂₀ H ₂₀ O ₇ N ₂	-1.01	< 1 ^b				
411.17007	C ₂₆ H ₂₂ O ₃ N ₂	0.61	< 1 ^b				
442.21826	C ₂₀ H ₃₁ O ₈ N ₃	0.3	< 1 ^b				
444.33182	C ₂₄ H ₄₅ O ₆ N	- 0.11	- ^d				
488.35812	C ₂₆ H ₄₅ O ₆ N	0.15	- ^d				
504.20868	C ₂₃ H ₂₉ O ₈ N ₅	0.42	< 1 ^c				
532.38452	C ₂₈ H ₅₃ O ₈ N	- 0.09	- ^d				
576.41060	C ₃₀ H ₅₇ O ₉ N	- 0.01	- ^d				

544 ^aPeak area (ion_i)/ΣPeak area (ions)

545 ^bdetected in aerosol samples and in the flow tube wall samples

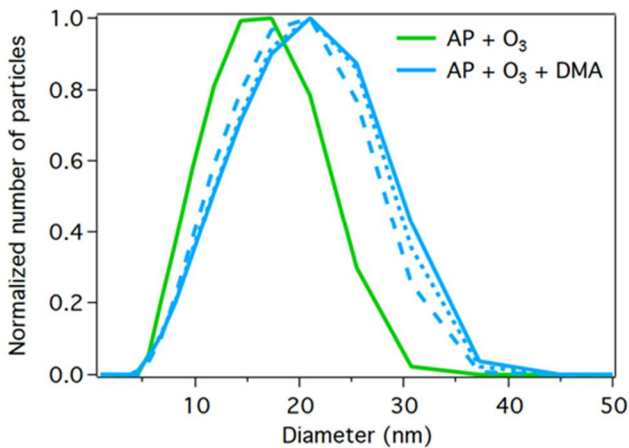
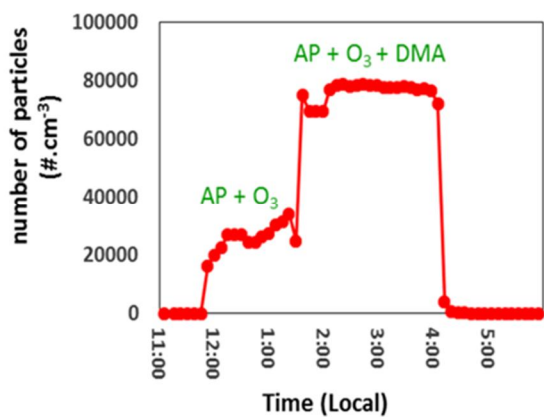
546 ^conly detected in aerosol samples

547 ^donly detected in the flow tube wall samples

548 ^econfirmed by retention times, accurate masses and MS-MS fragmentation patterns

549 ^fconfirmed by accurate masses

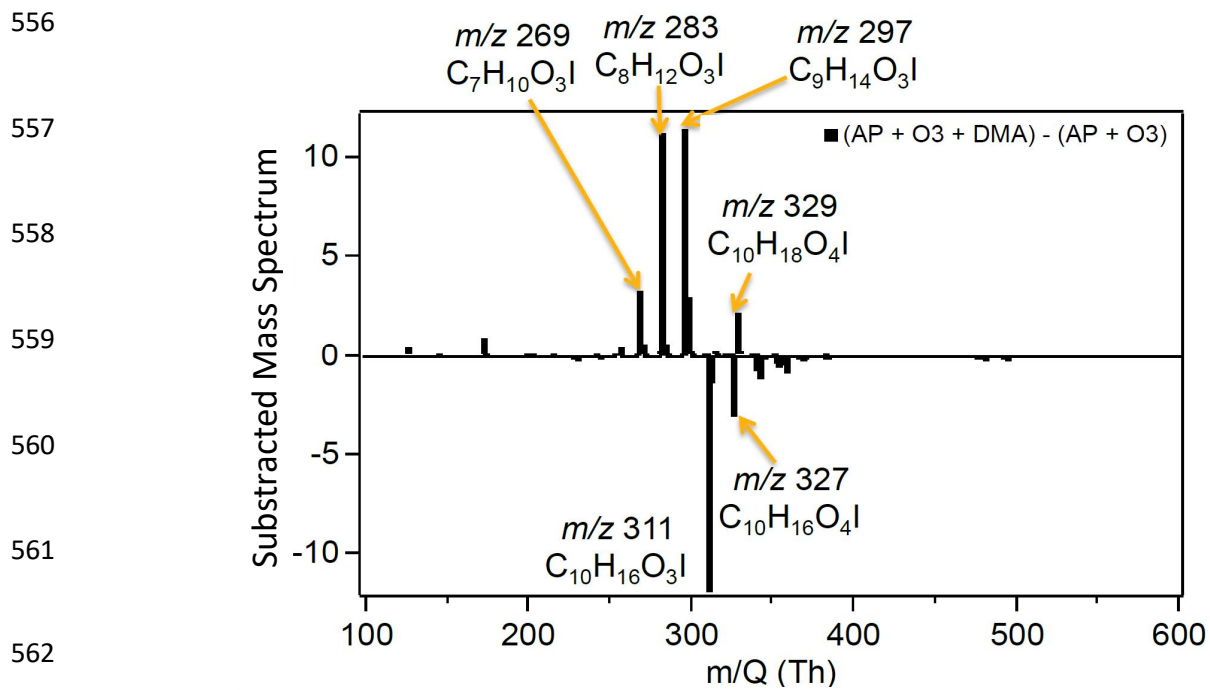
550 ^gpreviously observed in ambient samples²²



551

552 **Figure 1.** Particle number concentration (left) and particle size distribution (right) from α -pinene-O₃
 553 experiment (E1) and α -pinene-O₃-DMA experiment (E1'). The blue curves represent 3 different times of the
 554 particle size distribution from α -pinene-O₃-DMA experiment.

555



563 **Figure 2.** Difference in Mass Spectra from α -pinene- O_3 -DMA (experiment E2') and α -pinene- O_3
 564 experiments (experiment E2). Positive signals correspond to new products formed in the presence of DMA
 565 and negative signals are compounds lost when DMA is introduced.

566

567

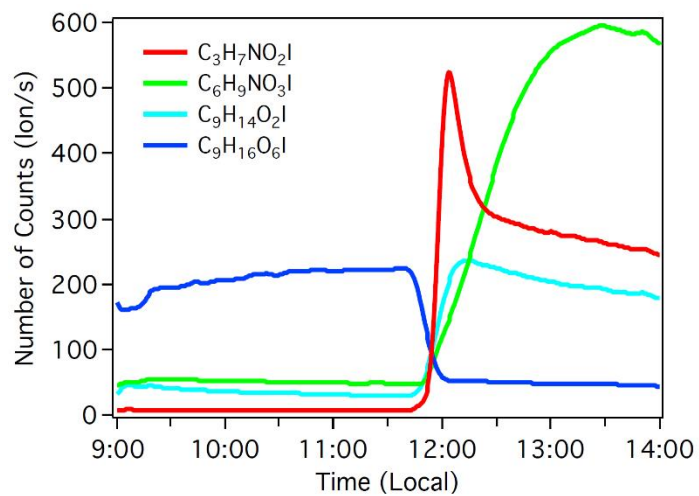
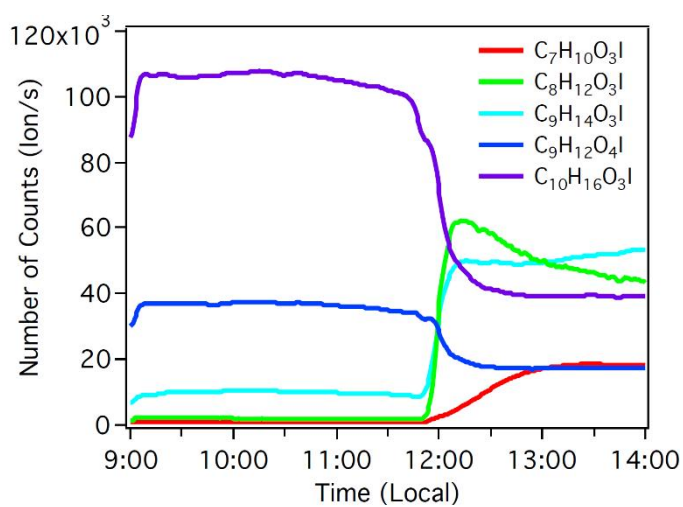
568

569

570

571

572



573

574

575

576

Figure 3. Temporal profiles of selected ion HR-ToF-CIMS (Experiments E2 and E2'), DMA was injected at 11:45. $C_9H_{14}O_4I$ ion is attributed to nor-pinonic acid signal, $C_{10}H_{16}O_3I$ to pinonic acid signal, and $C_9H_{14}O_2I$ to nor-pinonaldehyde signal.

577

578

579

580

581

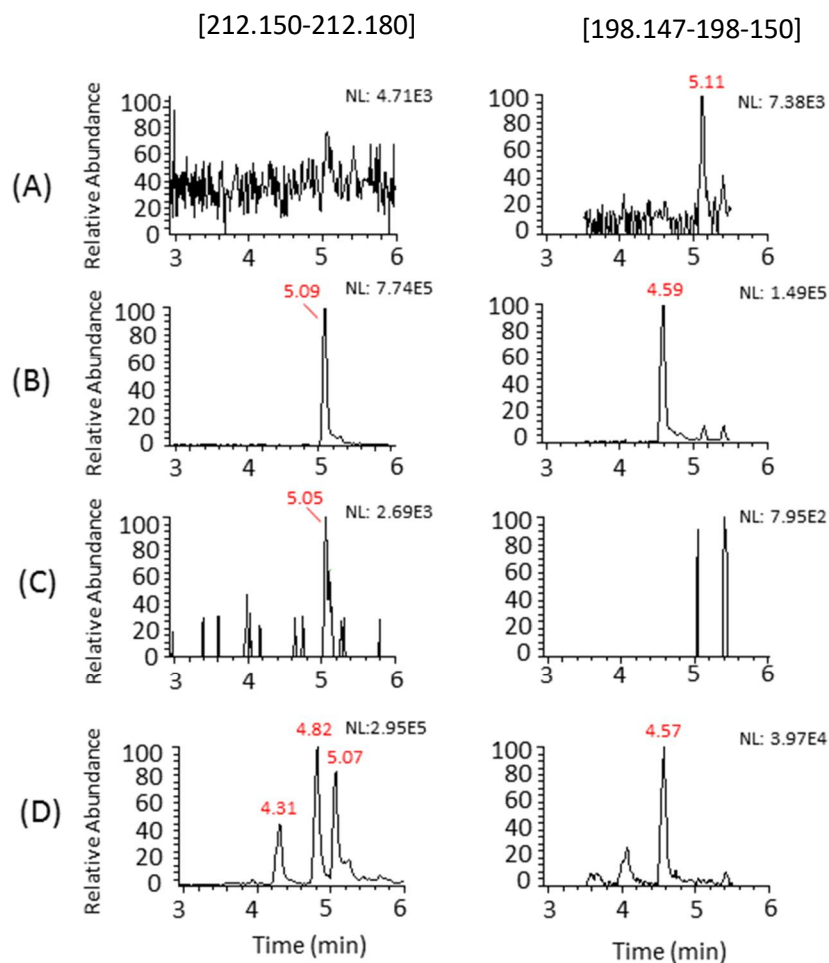
582

583

584

585

586



587 **Figure 4.** Extracted ion chromatograms of m/z 198.1489 \pm 0.0015 and 212.1644 \pm 0.0015 from (A) α -pinene
588 + O₃ experiment, (B) α -pinene + O₃ + DMA experiment, (C) blank filter sample, and (D) PM₁ sample collected
589 in Hyytiälä (23th of May, 2016).

590

591

592

593

594

595

596

597

598

599

600

601

602

603 TOC ABSTRACT

604

605

