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Environ. Sci. Technol., **Just Accepted Manuscript** • DOI: 10.1021/acs.est.9b03265 • Publication Date (Web): 25 Sep 2019

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Molecular Composition and Volatility of Nucleated Particles from α -Pinene Oxidation between -50 °C and $+25$ °C

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Abstract

We use a real-time temperature-programmed desorption chemical-ionization mass spectrometer (FIGAERO-CIMS) to measure particle-phase composition and volatility of nucleated particles, studying pure α -pinene oxidation over a wide temperature range (-50 °C to +25 °C) in the CLOUD chamber at CERN. Highly-oxygenated organic molecules are much more abundant in particles formed at higher temperatures, shifting the compounds towards higher O:C and lower intrinsic (300 K) volatility. We find that pure biogenic nucleation and growth depends only weakly on temperature. This is because the positive temperature dependence of degree of oxidation (and polarity) and the negative temperature dependence of volatility counteract each other. Unlike prior work that relied on estimated volatility, we directly measure volatility via calibrated temperature programmed desorption. Our particle-phase measurements are consistent with gas-phase results and indicate that during new-particle formation from α -pinene oxidation, gas-phase chemistry directly determines the properties of materials in the condensed phase. We now have consistency between measured gas-phase product concentrations, product volatility, measured and modeled growth rates, and the particle composition over most temperatures found in the troposphere.

Introduction

Atmospheric new-particle formation contributes up to half of the global cloud condensation nuclei (CCN) number concentration.¹⁻³ Important processes include formation of molecular clusters, stabilization where the rate of growth greatly exceeds any evaporation, and finally growth to CCN size (50-100 nm diameter) with sufficient speed to avoid coagulation loss.⁴⁻⁶ However, the sensitivities of the CCN budget to the mechanisms and rates of new-particle formation and growth are highly uncertain. Accurate representation and parameterization of new-particle formation for different environmental conditions in models remains a critical challenge in predicting climate forcing from aerosol indirect effects.^{1,7-9}

Biogenic volatile organic compounds (VOC) dominate total VOC concentrations across the globe, especially in clean or moderately-polluted environments.^{10,11} Monoterpenes comprise a major fraction of biogenic VOCs, and low-volatility organic compounds from monoterpene oxidation play an essential role in new-particle formation.^{12,13} However, until quite recently the chemical mechanism governing formation of organic vapors that nucleate or drive condensational growth of extremely small particles (smaller than 10 nm diameter) has been unclear. Peroxy radical (RO₂) auto-oxidation and subsequent fast association (“dimerization”) of peroxy radicals in the gas phase has emerged as a major formation pathway of highly-oxygenated organic molecules (HOMs)¹⁴⁻¹⁸ with (extremely) low vapor pressures that participate in nucleation¹² and initial particle growth.¹⁹

However, several questions remain unanswered. First, there is a long-standing question whether particle growth via organic condensation is rate limited by gas-phase production of low-volatility products or by reactive uptake of more volatile products followed by condensed-phase chemistry forming low-volatility products in the particle phase (glyoxal being a canonical example).²⁰⁻²² Second, the temperature dependence of condensable product formation (and thus secondary organic aerosol yields) remains uncertain and could depend strongly on whether condensation is rate

36 limited by gas-phase oxidation or condensed-phase chemistry.

37 Quantum chemical calculations confirm that the unimolecular H-atom transfers within monoterpene-derived per-
38 oxy radicals have an activation energy on the order of 20 kcal mol⁻¹.^{23,24} At warmer temperatures, auto-oxidation
39 may outpace bimolecular termination reactions and generate products with high oxygen content and thus lower vapor
40 pressures. At lower temperatures, due to the high energy barriers, auto-oxidation is expected to significantly slow
41 down compared to the barrierless termination reactions; this will suppress the yield of highly oxygenated organic
42 compounds. In addition to influencing auto-oxidation and the formation of HOMs, lowering temperature also re-
43 duces saturation vapor pressures, increases saturation ratios for the same production rates, and thus provides more
44 condensable material to contribute to nucleation and particle growth. The trade-off between these two significant
45 temperature effects highlights a challenge in predicting new-particle formation in environments ranging from the
46 warm tropical surface to the outflow regions of deep-convective clouds. It also highlights the strong need to obtain
47 full experimental closure on the temperature dependent mechanisms responsible for this process.

48 Background

49 Previously, Stolzenburg *et al.* 2018²⁵ and Frege *et al.* 2018²⁶ have measured the composition of gas-phase products
50 and small charged clusters during new-particle formation from α -pinene over a range of temperatures in the Cosmic
51 Leaving OUtdoor Droplets (CLOUD) facility at CERN. Frege *et al.* 2018²⁶ used an atmospheric pressure interface
52 time-of-flight mass spectrometer (APi-ToF) to measure naturally charged ions, showing that low temperature (-25
53 $^{\circ}\text{C}$) favors formation of products with lower oxygen content and lower molecular weight compared to products formed
54 at high temperature ($+25$ $^{\circ}\text{C}$). Stolzenburg *et al.* 2018²⁵ combined measurements from a proton-transfer-reaction
55 mass spectrometer and a nitrate anion chemical ionization mass spectrometer (CIMS) to measure neutral gas-phase
56 species with a wide range of polarity and volatility, finding that products formed at low temperature (-25 $^{\circ}\text{C}$) have a
57 higher room-temperature saturation vapor pressure than products formed at high temperature ($+25$ $^{\circ}\text{C}$). Volatility in
58 this case was estimated using a simple composition-volatility relationship.^{25,27} Further, they modeled particle growth
59 using a dynamical Volatility Basis Set (VBS) to treat both the curvature (Kelvin) and condensed-phase mixing
60 (Raoult) effects on condensed-phase activity and were able to quantitatively reproduce particle growth rates derived
61 from a suite of microphysical instruments.

62 However, due to the lack of detailed composition and volatility measurements of the particles following new-
63 particle formation and condensational growth, it is not known whether measurements of particle-phase composition
64 will confirm our understanding of the temperature dependence of the gas-phase chemistry, or whether the particle
65 composition will show signs of subsequent condensed-phase chemistry. To answer those questions, here we present
66 real-time particle-phase composition measurements from a series of CLOUD experiments of new-particle formation
67 from pure α -pinene oxidation over a wide temperature range (-50 to $+25$ $^{\circ}\text{C}$) with atmospherically relevant precursor
68 concentrations. We use a Filter Inlet for Gases and Aerosols (FIGAERO) thermal desorption inlet on an iodide CIMS.
69 We first describe the overall response of the instrument to new-particle formation events in the CLOUD chamber,

70 then characterize the broad set of identified products, and finally show the progressive evolution of composition and
71 volatility of the products versus temperature in the two-dimensional volatility basis set.²⁷ Using direct temperature
72 programmed desorption, we infer volatility during new-particle formation, and confirm that covalently bound dimers
73 of α -pinene oxidation products are present in newly formed particles. Our objective is to investigate whether full
74 closure exists between the observed gas-phase species and concentrations, the observed particle growth rates, and the
75 observed condensed-phase composition at all temperatures.

76 **Materials and Methods**

77 **The CLOUD chamber**

78 The CLOUD chamber at CERN is a 26.1 m³ stainless steel chamber with precisely controlled temperature,
79 humidity and constituent gases. It is fed as a continuously stirred tank reactor with a flow of synthetic air formed
80 by mixing vapor from liquid nitrogen and liquid oxygen storage tanks. VOC gases are diluted to the required
81 concentration with pure air before entering into the chamber. The temperature in the chamber is controlled to a
82 precision of ± 0.1 °C over a broad range from -65 °C to 30 °C, and the chamber is mixed rapidly by inductively
83 coupled fans mounted at the top and bottom. Ions are controlled in three states (“neutral”, “galactic cosmic ray”, and
84 “beam”) via a switchable high-voltage clearing field and regulated exposure to a 3.5 GeV π^+ beam from the CERN
85 proton-synchrotron. A suite of real-time gas- and particle-phase instruments sample the chamber simultaneously,
86 collectively establishing a flushing time of approximately 1.5 h. More details can be found in Kirkby *et al.* 2011²⁸
87 and Duplissy *et al.* 2016.²⁹

88 Results presented here are from α -pinene oxidation experiments during the CLOUD-12 campaign in Fall 2017
89 under galactic cosmic ray conditions at four different temperatures: -50 °C, -25 °C, +5 °C and +25 °C. The α -pinene
90 concentration was 600 pptv for experiments at -50 °C, +5 °C and +25 °C, and 1200 pptv for the experiment at -25
91 °C (experiment at 600 pptv is not available). We held ozone at a constant 40 ppbv and performed all experiments
92 in the dark, and no hydroxyl radical scavenger was used. The chamber’s relative humidity (RH) was 90 % for
93 experiments at -50 °C and -25 °C and 38 % for experiments at +5 °C and +25 °C. We do not expect the difference
94 in humidity to significantly influence our results as RO₂-derived HOM formation shows limited RH dependence.³⁰ In
95 the chamber, the background concentration of nitrogen oxides was in the sub pptv range and the background sulfuric
96 acid concentration was lower than 5×10^4 cm⁻³.²⁸ For these experiments, we added no nitrogen oxides or sulfur
97 dioxide into the chamber and so these results represent NO_x-free “pure biogenic” organic conditions.

98 **FIGEARO chemical ionization mass spectrometer**

99 We used a chemical ionization mass spectrometer (CIMS) with a Filter Inlet for Gas and AEROSol (FIGAERO)
100 (Aerodyne Research Inc. & ToFwerk AG) to measure the nucleated particles from α -pinene oxidation. The FIGAERO-
101 CIMS, which has a sensitivity on the pg m⁻³ level, has been described in detail in Lopez-Hilfiker *et al.* 2014.³¹ In
102 brief, it measures gas-phase compounds while collecting particles on a Teflon filter in the inlet at a flow rate of

103 8 liters per minute. After particle collection, the FIGAERO switches to a particle thermal desorption mode in
104 which the filter is bathed in heated nitrogen carrier gas ranging from room temperature to about 160 °C following a
105 temperature program. Because the entire filter manifold is made of Teflon and thus has very low thermal conductivity,
106 it responds rapidly to the changing carrier-gas temperature. The thermally desorbed compounds from the collected
107 particles subsequently flow into an ion-molecule reactor and are measured by the downstream CIMS. Figure S1 shows
108 examples of thermal-desorption profiles of representative products identified from the experiments here. The gas-
109 phase sampling/particle collection time in our experiments was 30 minutes and the thermal desorption mode lasted
110 for 15 minutes before the instrument returned to the gas sampling and particle collection mode. Here we focus largely
111 on the particle-mode data.

112 We used iodide as the reagent ion as it can cluster effectively with low-volatility organic compounds.³² We
113 produced iodide ions by passing methyl iodide from a permeation source over a ²¹⁰Po foil. The long time-of-flight
114 (LTOF) mass spectrometer has a mass resolving power of up to 12,000 (Tofwerk AG). We collected data at 1 Hz and
115 averaged them to 0.1 Hz for post processing.

116 The temperature of the maximum desorption signal (T_{\max}) during the particle mode correlates with vapor
117 pressure and vaporization enthalpy,^{31,33} provided that compounds do not thermally decompose.³⁴ We performed
118 volatility calibrations by manually depositing an aliquot of a mixture of several known pure organic acids and fitting
119 the $1/T_{\max}$ (in K) of each calibrant with their sub-cooled liquid vapor pressure. We calibrated with the filter starting
120 at room temperature and show representative data in the Supporting Information. We use the calibration curve
121 to estimate the gas-phase saturation concentration of all the measured compounds by correlating $1/T_{\max}$ with their
122 saturation vapor pressure.

123 Results and Discussion

124 FIGAERO CIMS measurements of new-particle formation

125 We first present an example of a new-particle formation event in the CLOUD chamber from pure α -pinene
126 oxidation and show the corresponding FIGAERO particle-phase signals. In this event, the α -pinene concentration
127 was 600 pptv and the chamber temperature was -50 °C. In Figure 1a, we show the particle number size distribution
128 combining measurements from a nano-SMPS (TSI, Inc.) and a custom-made long-SMPS. This is a so-called “banana”
129 with time on the x-axis, mobility diameter on the (log) y-axis, and the number size distribution shown via colors;
130 the nucleation event in this case occurred somewhat before the earliest time shown and subsequent condensation
131 drove growth from roughly 3 nm to 30 nm over 4 h, made evident by the leading (upper) edge. This growth rate
132 of 8 nm h⁻¹ is typical of atmospheric new-particle formation events⁵ and indicates that condensable vapors in the
133 experiment were similar to those typical of the atmosphere. Because the FIGAERO provides a bulk mass measurement,
134 we show the corresponding particle volume distribution in Figure 1b. We highlight the particle collection periods in
135 the FIGAERO inlet with grey boxes (30 minutes each). For example, when we collected particles between 8:30 and
136 9:00 the leading edge was just over 20 nm, and data from the corresponding thermal desorption cycle appear between

137 9:00 and 9:15.

138 In Figure 1c we show representative data from the particle desorption cycles for a monomer product, $C_{10}H_{16}O_8-I^-$,
139 and a dimer product, $C_{20}H_{32}O_6-I^-$. Here we define monomer products as ions containing 10 or fewer carbon atoms
140 and dimer products as ions containing 11 to 20 carbon atoms. When there is sufficient mass loading (after 8 am
141 in this case), the peak signal for the dimer product always appears after the monomer product because it has a
142 lower vapor pressure. As the new-particle formation proceeds and particles grow to larger sizes, signals of both the
143 monomer and dimer products in the particle phase increase correspondingly in proportion to the particle volume.

144 We examined the size-dependence of total oxygen to carbon elemental ratio (O:C) during a new particle-formation
145 event and found no observable change in O:C versus particle size. There is thus no evidence from the FIGAERO
146 data that the particle composition changes significantly during an event. This may be because the time resolution
147 (45 minutes) of our data is not fine enough to capture the very beginning of the particle growth period where the
148 Kelvin effect is most critical,^{19,25} or simply that the signal to noise for particles smaller than 10 nm is insufficient to
149 resolve any composition differences. For the results we show in the rest of this paper, we use the data from the last
150 cycle for each experiment in order to maximize the signal to noise.

151 Our signal generally consists of a background that is nearly independent of temperature overlain by a well-defined
152 thermal desorption peak, as shown in Figure S4. To separate these we fit a linear background, as shown, and interpret
153 the peak area of the temperature-dependent peak above this background as the signal due to particles collected on
154 the filter during the sampling cycle. As we show in Figure S3, the sum of peak areas of all identified products in a
155 sampling cycle is proportional to the corresponding average SMPS mass. Further, during nucleation events with a
156 constant HOM vapor concentration (such as the event shown in Figure 1), the total signals of the first FIGAERO
157 cycle in which there are barely any particles in the chamber is generally well under 8% of maximum FIGAERO cycle.
158 For our quantitative analysis we use the signal from the end of each event, with maximum suspended volume; we
159 thus conclude that this signal is almost entirely due to collected particles, with little or negligible interference from
160 adsorbed vapors on the filter.

161 In Figure S5a, we correlate the FIGAERO signals with known mass concentration of a mixture of organic acids as
162 shown. In Figure S5b, we correlate the total particle-phase mass measured by the FIGAERO-CIMS and the average
163 integrated particle concentration during particle collection cycles under all temperatures, as measured by the SMPS.
164 The total particle mass from the FIGAERO correlates well with the SMPS mass, with an r^2 of 0.89. We find a ratio
165 of 1.6 between the inferred total mass based on filter calibrations (presuming a constant sensitivity of the I^- chemical
166 ionization) and the inferred mass based on the SMPS mass assuming a particle density of 1.4 g cm^{-3} . We have
167 observed correspondingly good correlation between the integrated FIGAERO signal and total particle volume during
168 a number of CLOUD campaigns.³⁵ This indicates that the overall sensitivity of the FIGAERO-CIMS to particle
169 loading is consistent across different experiments in our studies and that we are recovering a large fraction, if not all,
170 of the total available mass.

171 Measured products from FIGAERO-CIMS

172 In Figure 2, we show a representative mass-defect plot for particle-phase constituents from α -pinene oxidation
173 at +5 °C. We show mass-defect plots for all temperatures in Figure S6 in the Supporting Information. We are able
174 to clearly measure the monomers (C_{7-10} compounds) and dimers (C_{14-20} compounds) in the particle phase at all
175 temperatures in our experiments. Here we only show iodide adducts ($C_xH_yO_z \cdot I^-$), although a small portion of the
176 detected ions underwent iodide declustering.³² Due to the extremely low level of NO_x in the chamber (sub pptv), we
177 do not observe any signals from nitrogen containing species, consistent with NO_x -free conditions.

178 In Figure 2, we color code the symbols by oxygen number. In the monomer mass range, detected compounds
179 show $4 \leq n_O \leq 10$ at 5 °C. In the dimer mass range, the oxygen number varies from $5 \leq n_O \leq 13$. Products with
180 higher oxygen content may also exist as gas-phase products with up to 18 oxygens are detected by the nitrate-chemical
181 ionization mass spectrometer deployed in the same campaign (manuscript in prep). But the signals of these products
182 in the particle phase may be too low in our instruments to produce a reliable signal above the background. As shown
183 in Figure S6, as the temperature drops, the products shift progressively towards lower oxygen content in both the
184 monomer and the dimer bands. This is consistent with gas-phase observations from CLOUD-10 and CLOUD-11^{25,26}
185 that the rate of auto-oxidation is lower during new-particle formation at lower temperature, producing less oxidized
186 products at low temperature than at high temperature. In addition, lower temperature enhances condensation of
187 compounds with higher room-temperature saturation vapor pressures, which may be less oxygenated. For instance,
188 at +25 °C, for the $C_{10}H_yO_z$ series, the lowest oxygen content measured in the particle phase is O_6 while at, while at
189 -25 °C and -50 °C, the lowest oxygen content is O_3 , as shown in Figure S6. We shall discuss this more in the next
190 section.

191 As Figure 2 shows, we detected many dimer products in the thermal desorption data. This confirms that dimers
192 from α -pinene oxidation are covalently bounded, likely from $RO_2 + RO_2$ association reactions,³⁶ as they thermally
193 desorbed without evident fragmentation at temperatures as high as 130 °C in our instrument (also see Figure S1). We
194 did not detect any products in the trimer (C_{30}) or tetramer (C_{40}) mass ranges, though these species were observed as
195 naturally occurring ions by the APi-ToF-CIMS in prior CLOUD experiments.²⁶ This is consistent with these higher
196 mass ions being molecular clusters of covalently bound monomers and dimers that appear only as monomers and
197 dimers in the bulk particle thermal desorption data.

198 Volatility distributions of nucleated particles versus temperature

199 In Figure 3, we present the condensed-phase constituents at different temperatures within the two dimensional
200 volatility basis set (2D-VBS) introduced by Donahue *et al.* 2011.²⁷ The x-axis is the log of saturation concentration
201 ($C_{300\text{ K}}^*$) experimentally estimated using the thermal desorption profile measured at 300 K described in the Supporting
202 Information. We report volatility as C^* (and not C°) because our observations are over mixtures and thus implicitly
203 include activity coefficients. The y-axis is the observed oxygen to carbon ratio, O:C. Every datapoint is normalized
204 by the largest signal in the +25 °C data and the size of each datapoint signifies the signal level. The different

205 broad colored bands in the background represent the volatility classes of extremely low-volatility organic compounds
206 (ELVOC), low-volatility organic compounds (LVOC), semi-volatile organic compounds (SVOC) and intermediate-
207 volatility organic compounds (IVOC). We shift the volatility classes for the lower temperature experiments using
208 the Clausius-Clapeyron relation and the enthalpy of evaporation in Donahue *et al.* 2011²⁷ and Epstein and Donahue
209 2009³⁷ because the classes are fundamentally associated with atmospheric saturation ratios. Details of this calcu-
210 lation are in the Supporting Information. We also show the products aggregated into a 1D-VBS (C^* only) at four
211 temperatures in Figure S7 of the Supporting Information.

212 The counter-balancing effects of oxidation and temperature are evident in Figure 3, where to a great extent
213 the condensed-phase products remain in the LVOC range, with a tail extending into the ELVOC range. At +25
214 °C, most of the products have a 300 K saturation concentration lower than $1 \mu\text{g m}^{-3}$. As temperature decreases,
215 there is a progressive shift of both the monomer and dimer products towards higher 300 K (intrinsic) saturation
216 concentration and towards lower O:C. This is consistent with reduced formation of HOMs as observed by previous
217 gas-phase measurements.^{25,26} This also reflects the temperature effects on the saturation vapor pressure. Therefore,
218 the suppressed formation of compounds with lower volatility is compensated by the shift of the volatility classes at
219 lower temperatures, indicated by the shifted colored bands in Figure 3. For example, a compound with $\log C^* = 2$
220 at 300 K is an SVOC at +25 °C and +5 °C, but it is an LVOC at -25 °C and an ELVOC at -50 °C. This supports
221 the roughly constant particle growth below 10 nm observed across a wide range of temperatures by Stolzenburg *et*
222 *al.* 2018.²⁵

223 During low-temperature experiments, we used insulation to maintain the temperature between the chamber and
224 the instrument sampling/filter system. Still there may have been loss of higher-volatility compounds during the
225 low-temperature experiments. Therefore, our low-temperature measurements should be a lower bound of the signals
226 from the actual collected material. This could be why the -50 °C distribution does not extend through the LVOC
227 region, as the molecules at the LVOC-SVOC boundary are quite volatile at room temperature.

228 Further, some decomposition occurred during thermal desorption, and some observed monomers (blue symbols)
229 are actually products of dehydration³³ or decomposition of dimers;³⁸ these have volatilities (indicated by peak signal
230 temperatures) much lower than most of other monomer products as shown in the volatility space in Figure 3 and
231 instead appear within the dimer region. Despite these caveats, the evolution in both the volatility and the O:C
232 direction in the 2D-VBS as a function of temperature is clear, and most of the identified products have volatilities
233 based on peak thermal desorption temperature that are consistent with our broad estimates of their vapor pressures
234 based on their molecular formulae.²⁷

235 The volatilities used in prior nucleation and growth experiments on α -pinene oxidation were estimated based on
236 composition.^{19,25} The volatilities we show here in Figure 3 are directly measured based on peak desorption temper-
237 ature. However, the experimental conditions were similar during different CLOUD campaigns. Based on measured
238 vapor concentrations and estimated volatility distributions, Stolzenburg *et al.* 2018 were able to quantitatively repro-
239 duce the observed size-dependent growth rates at -25 °C, +5 °C and +25 °C (they did not reach -50 °C) using a
240 dynamical VBS model. Their results indicated that the condensing vapors remained just within the LVOC envelope

241 (approximately one order of magnitude to the left of the LVOC-SVOC dividing line at all temperatures). Here we
242 show direct confirmation of this result at the corresponding temperatures, though our particle phase composition
243 measurements with direct measurement of the volatility suggest that the demarcation is closer to the LVOC-SVOC
244 dividing line. This represents a strong agreement within approximately one order of magnitude in volatility (over a
245 range of many orders of magnitude).

246 Our particle-phase observations show that the molecules condensing to drive particle growth are progressively
247 more oxidized at elevated temperature, and also that there is a significant presence of covalently bound dimer species.
248 This confirms that the rate-limiting step for particle growth in this case is gas-phase formation of HOMs (rather than
249 subsequent particle phase chemistry) and is consistent with the rate-limiting step for nucleation itself being gas-phase
250 formation of dimers from RO₂ reactions, at least for T ≥ -25 °C. At -50 °C the products are dominated by products
251 with relatively low signals of auto-oxidation products, relatively low O:C, and low dimer formation; however, the
252 temperature is so low that even the mildly oxidized products are essentially ELVOCs capable of both nucleation and
253 growth. That in turn is consistent with very high overall secondary organic aerosol mass yields previously reported
254 for α-pinene oxidation at very low temperature.^{39,40} It also implies that at high altitudes, even slightly oxidized
255 compounds (e.g., first-generation products without auto-oxidation) may condense to facilitate new particle formation
256 and growth.⁴¹

257 Taken all results together, our study shows that lower temperature reduces the production of HOMs but at the
258 same time promotes condensation of less oxidized vapors to facilitate particle formation and growth. Our condensed-
259 phase volatility measurements are consistent with volatility distributions from growth rate calculation using gas-phase
260 observations. All told, the volatility distributions are consistent to within an order of magnitude (out of nearly 10) and
261 the growth rates are consistent to within ~30 %.²⁵ Further, we confirm a significant population of covalently bound
262 dimer species that survive thermal decomposition; these are thought to be critical for “pure biogenic” nucleation,
263 though subsequent growth is driven by monomer HOM species. Our results indicate that for the α-pinene oxidation
264 system, at least in the early stage of particle formation and growth under the typical loadings and conditions we
265 studied in the CLOUD chamber, gas-phase chemistry, instead of condensed-phase or heterogeneous reactions that
266 occur after low- or semi-volatile organics condense, is the dominant driver of the properties of biogenic SOA particles.

267 Associated Content

268 Supporting Information

269 Volatility measurements in the FIGAERO-CIMS, mass measurements in the FIGAERO-CIMS, shifts of volatility
270 classes as a function of temperature and supporting figures.

271 Acknowledgement

272 We thank the European Organization for Nuclear Research (CERN) for supporting CLOUD with important
273 technical and financial resources. This research has received funding from the U.S. National Science Founda-

274 tion under grants AGS-1801574, AGS-1801897, AGS-1649147 and AGS-1602086; the EC Horizon 2020 Programme
275 (Marie-Sklodowska-Curie Innovative Training Network “CLOUD-MOTION” No. 764991); European Unions Hori-
276 zon 2020 programme MC-COFUND Grant 665779; German Federal Ministry of Education and Research (No.
277 01LK1601A); ERC-Consolidator Grant NANODYNAMITE 616075; Horizon 2020 Marie Sklodowska-Curie Grant
278 656994 (“Nano-CAVa”); ERC Advanced “ATM-GP” grant No. 227463; and the Swiss National Science Foundation
279 Project 20FI20_159851, 200021_169090, 200020_172602 and 20FI20_172622. The FIGAERO-CIMS was supported by
280 an MRI grant for the U.S. NSF AGS-1531284 as well as the Wallace Research Foundation. Q.Y. was supported by a
281 Faculty for the Future Fellowship from the Schlumberger Foundation.

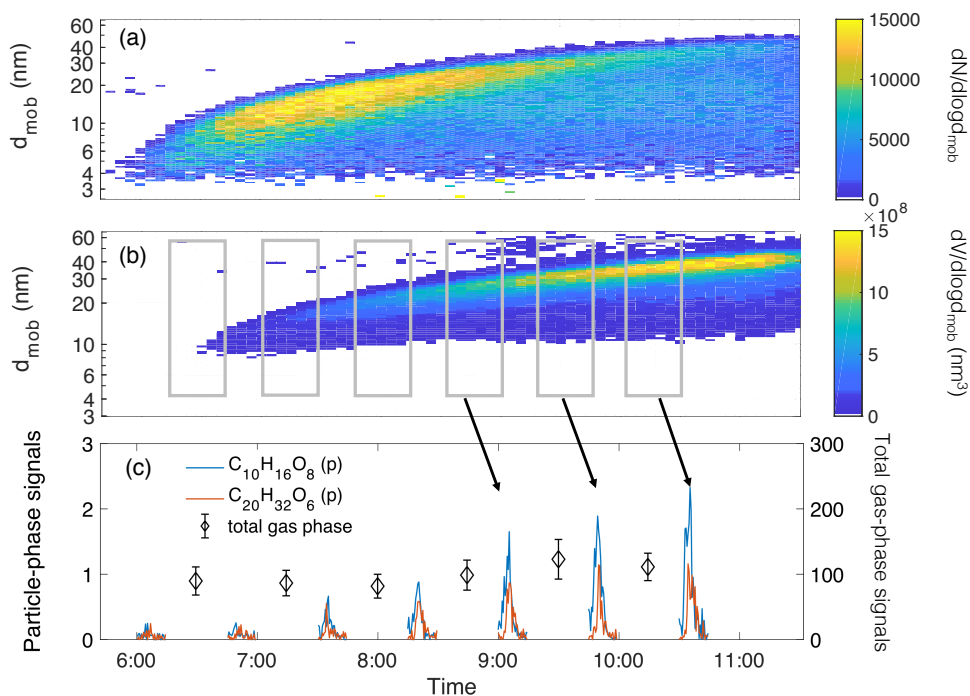


Figure 1: Example experiment performed with 600 pptv α -pinene and 40 ppbv ozone in the chamber at $-50\text{ }^{\circ}\text{C}$ and 90% RH. Panels (a) and (b) are merged size-distribution data measured by a nano-SMPS and a long-SMPS for the new-particle formation event. Panel (a) shows the number distribution and panel (b) shows the volume distribution. Time periods in the grey squares in (b) are the particle collection intervals (30 mins each) for the FIGAERO. The arrows indicate the corresponding signals during subsequent thermal-desorption cycles shown in panel (c). Each thermal desorption cycle lasts 15 min. The signals of a representative monomer (C_{10}) and dimer (C_{20}) product rise with total particle volume but remain roughly proportional, consistent with a constant particle composition. The gas phase was in a steady state during the experiment, as confirmed by the total gas-phase signal shown as black diamonds averaged over each gas-phase collection interval measured by the I^- CIMS. The constant gas phase signal and initially low filter desorption signal confirms that the FIGAERO filter signal represents the particle-phase composition.

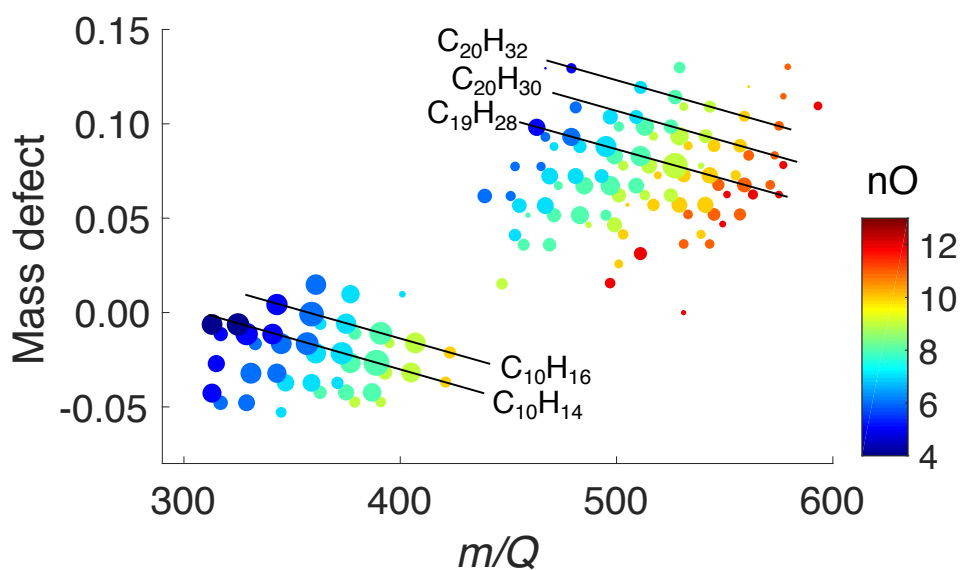


Figure 2: Mass-defect plot for nucleated particles at $+5\text{ }^{\circ}\text{C}$. Marker size corresponds to the square root of the ion signals, while color indicates number of oxygen atoms, as shown. We show the ions attached with I^- . The band between 300 and 450 Th is the “monomer” band of (largely) C_{10} species, while the band between 450 and 600 Th is the “dimer” band of (largely) C_{20} species. Each (slightly tilted) row corresponds to species with progressively more oxygen atoms, whereas each column corresponds to species with progressively more hydrogen atoms (almost entirely with an even hydrogen number).

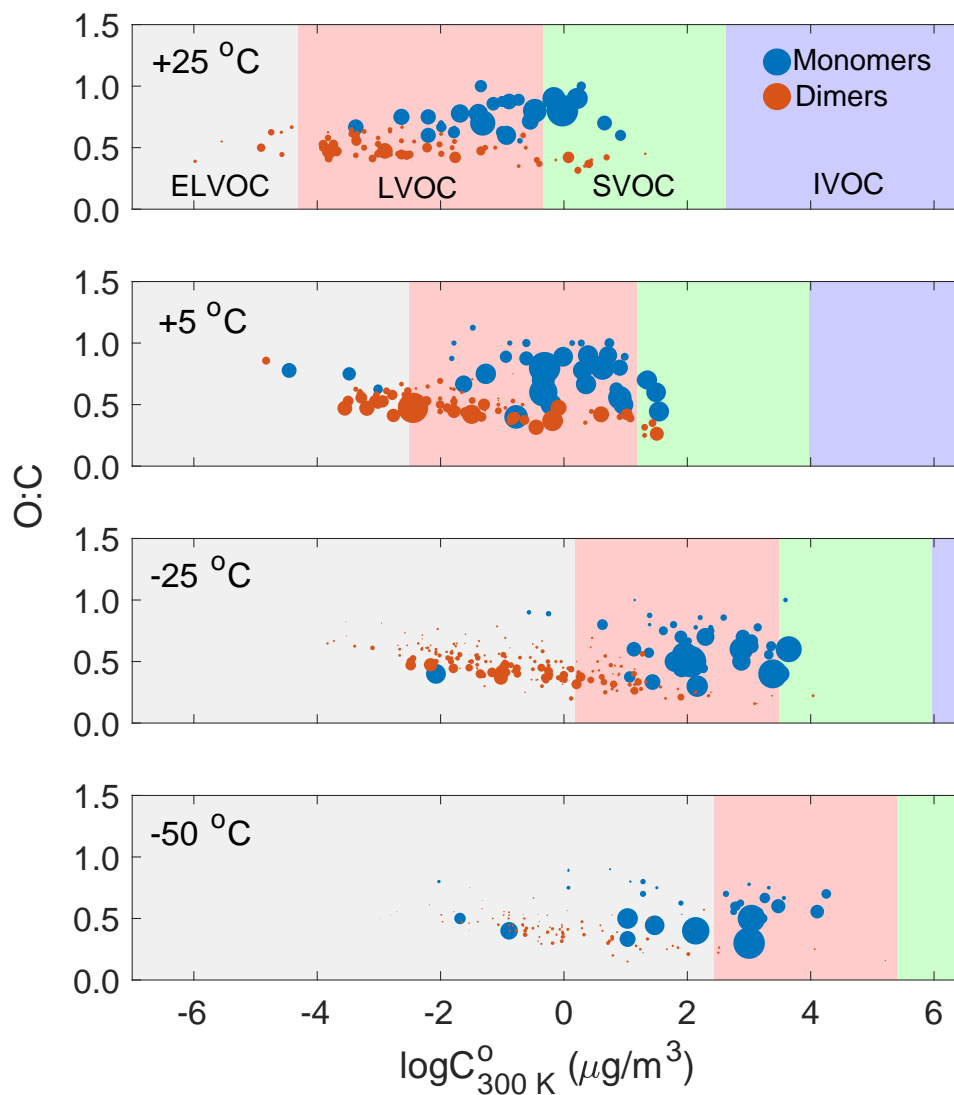


Figure 3: FIGAERO particle-phase data for α -pinene oxidation projected onto a 2D-VBS for the nucleated particles at CLOUD temperatures (from top to bottom) of +25 °C, +5 °C, -25 °C and -50 °C. Symbol colors differentiate monomers and dimers and symbol sizes are ion signals normalized by the highest signal in each temperature. The calibrated assessment of the volatility as $C^*(300\text{K})$ of the desorbed compounds is shown in the x axis. From left to right, the broad, colored bands in the background are volatility classes of extremely low-volatility organic compounds (ELVOC), low-volatility organic compounds (LVOC), semi-volatile organic compounds (SVOC) and intermediate-volatility organic compounds (IVOC). These classes are defined by actual volatility ($C^*(T)$) and so shift with temperature according to the Clausius-Clapeyron equation.

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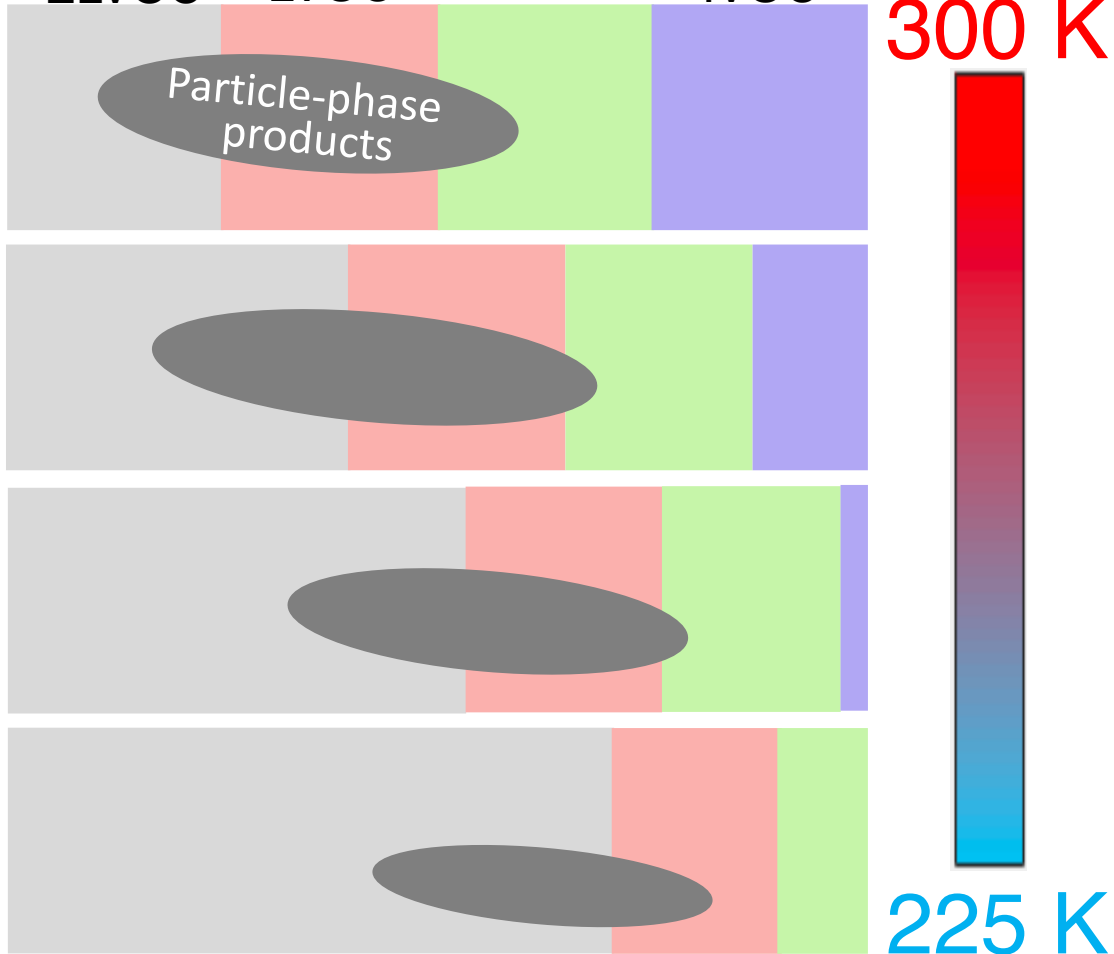
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