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Rapid growth of organic aerosol nanoparticles over a wide tropospheric temperature range

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28Nucleation and growth of aerosol particles from atmospheric va-29pors constitutes a major source of global cloud condensation nu-30 clei (CCN). The fraction of newly-formed particles that reaches CCN 31sizes is highly sensitive to particle growth rates, especially for par-32ticle sizes below 10 nm where coagulation losses to larger aerosol 33particles are greatest. Recent results show that some oxidation prod-34ucts from biogenic volatile organic compounds are major contribu-35tors to particle formation and initial growth. However, whether oxi-36dized organics contribute to particle growth over the broad span of 37tropospheric temperatures remains an open question, and quantita-38tive mass balance for organic growth has yet to be demonstrated at 39any temperature. Here, in experiments performed under atmospheric 40conditions in the CERN CLOUD chamber, we show that rapid growth 41of organic particles occurs over the range from -25°C to +25°C. The 42lower extent of auto-oxidation at reduced temperatures is compen-43sated by the decreased volatility of all oxidised states. We could re-44produce the measured growth rates using an aerosol growth model 45based entirely on the experimentally-measured gas-phase spectra of 46oxidized organic molecules using two complementary mass spec-47 trometers. We show that the growth rates are sensitive to particle 48curvature and display a clear acceleration as the particles increase in 49size, corresponding to a Kelvin diameter of 4.8 \pm 0.8 nm at 300 K, ex-50plaining widespread atmospheric observations that particle growth 51rates increase in the single-digit-nm size range. Our results demon-52strate that organic vapours can contribute to particle growth over 53a wide range of tropospheric temperatures from molecular cluster 54sizes onward. 55

56 aerosol particles | nanoparticle growth | atmospheric aerosol formation 57 | CERN CLOUD experiment

The global budget of cloud condensation nuclei (CCN) has a 60 significant impact on the Earth's radiative balance, as it affects 61 the albedo and the lifetime of clouds. New particle formation 62 by gas-to-particle conversion is the largest source of CCN (1). Especially the early steps of particle growth between 1-10 nm determine the survival chance of freshly formed particles and therefore their climatic relevance (2, 3). The major vapours driving particle growth are sulfuric acid and, maybe more importantly, low volatility organics resulting from the oxidation of volatile organic compounds (VOCs) (4). Monoterpenes are an important class of atmospheric VOCs with copious emissions from vegetation (5). They are quickly oxidized in the atmosphere and through a subsequent auto-oxidation process

Significance Statement

Aerosol particles can form and grow by gas-to-particle conversion and eventually act as seeds for cloud droplets, impacting the global climate. Volatile organic compounds emitted from plants are oxidized in the atmosphere and the resulting products drive particle growth. We measure particle growth by oxidized biogenic vapors with a well-controlled laboratory setup over a wide range of tropospheric temperatures. While higher temperatures lead to increased reaction rates and concentrations of highly oxidized molecules, lower temperatures allow additional, but less oxidized, species to condense. We measure rapid growth over the full temperature range of our study, indicating that organics play an important role in aerosol growth throughout the troposphere. Our finding will help to sharpen the predictions of global aerosol models.

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The authors declare no conflict of interest.

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rapidly form highly oxygenated molecules (HOMs), which con-125126stitute a large source of low-volatility species in the atmosphere 127(6). Recent studies have shown that HOMs from the ozonolysis 128of the predominant monoterpene α -pinene are able to form 129(7) and efficiently grow particles from cluster sizes onward (8). 130Model simulations suggest that they are major contributors 131to particle formation on a global scale (9). Moreover, the 132impact of HOMs on initial particle growth might explain the 133observations of accelerating growth rates between 1-10 nm 134during particle formation events (10) by a multi-component 135Kelvin effect (8, 11), also known as nano-Köhler theory (12). 136This is because HOMs span a wide range of volatilities (13)137and, with increasing particle size, more and more low-volatile 138species can contribute to the growth process.

139In contrast to sulfuric acid in combination with ammo-140nia or amines, where growth proceeds close to the kinetic 141limit (14), the characteristics of growth driven by organics 142are governed by the resulting volatilities of the wide variety 143of oxidation products. Therefore, temperature likely plays a 144decisive role as the saturation concentration has a steep expo-145nential temperature-dependence as described by the Clausius-146Clapeyron relation. Additionally, a recent study has shown 147that temperature crucially influences the chemical composition 148of the initially formed molecular clusters in α -pinene ozonolysis 149(15). Therefore, the contribution of biogenic organics to new 150particle formation might be strongly sensitive to temperature. 151This, in turn, may significantly influence the importance of 152new particle formation at high altitudes (16) and in outflow 153regions of deep-convective clouds, e.g. over the Amazon Basin 154(17-19).

155Here we investigate in the CLOUD chamber (20) the effect 156of temperature on the production of oxygenated molecules 157and subsequent particle growth from dark α -pinene ozonolysis at three different temperatures $(-25^{\circ}C, +5^{\circ}C, and +25^{\circ}C)$ 158159for various precursor concentrations. The resulting volatility 160distributions are inferred by combining two types of chemical-161ionisation high resolution mass spectrometers (21, 22) using 162different ionization techniques in order to obtain a detailed 163representation of the gaseous oxidation products. Together 164with the precision measurement of particle growth rates (23)165this allows identification of the underlying processes and their 166temperature dependence responsible for initial growth in bio-167genic ozonolysis systems (See Methods for details about the 168experimental setup, measurement procedures and used instru-169mentation). 170

171 172 **Results**

Observed gas phase mass spectrum. Fig.1 shows mass defect 173plots from the Nitrate-CI-APi-ToF (Nitrate-CI) (21) and the 174PTR3-ToF (PTR3) (22) during three representative exper-175iments at three different temperatures. For all three cases, 176we averaged the observed gas-phase concentrations C^{v} over a 177period where comparable particle growth rates are measured 178with a DMA-train (23) and the α -pinene ozonolysis rate is 179similar with $[k(T) \cdot ap \cdot O_3] \sim 1.4 - 2.0 \cdot 10^6 \text{cm}^{-3} \text{s}^{-1}$. 180

181 The mass defect plots for all temperatures show the typical 182 pattern of HOMs (8). Two bands can be identified, one repre-183 senting monomers (n_c =6-10, 100-400 Th) and one representing 184 dimers (n_c =16-20, 400-600 Th); molecules with increasing 185 oxidation state are found towards the lower right of the panels. 186 Apparently, the PTR3 introduces more than 200 previously



Fig. 1. Mass defect of all measured neutral oxidized organic compounds versus the nominal mass to charge ratio of three representative experiments, at $+25^{\circ}$ C (A), at $+5^{\circ}$ C (B) and at -25° C (C), all with a similar α -pinene ozonolysis reaction rate. Diamonds represent molecular ions measured by the PTR3 and circles compounds measured by the Nitrate-Cl, both taking the different reagent ions into account. The size of the symbols is proportional to the logarithm of the measured concentration and the color is related to the volatility class as defined in Fig. S3. 207 208 209 210 211 212 213

undetected molecular ion signals, not only HOMs, which are 215 usually specified by their high O:C ratio (>0.7 for monomers), 216 but mostly compounds towards lower oxidation states. 217

As temperature decreases, the intensity of the majority 218 of the peaks drops, especially for compounds with a high 219 oxidation state and with a high detection efficiency in the 220 Nitrate-CI. This is similar to the observations by (15), where 221 a significant decrease in O:C ratio of the nucleating charged 222 clusters was observed during the same set of experiments. 223

In Fig.1, the symbol color for peaks with an identified 224composition corresponds to a broad temperature-dependent 225classification of their volatility, based on the carbon and oxygen 226numbers of the individual compounds (see Supporting Infor-227mation for detailed information on the volatility classification 228 and its temperature dependence). We place them in four gen-229eral groups, according to their saturation mass concentration 230 C^* : extremely low volatility compounds (ELVOC, $\log_{10} C^* \leq$ -2314.5), low volatility compounds (LVOC, $\log_{10} C^* = (-4.5, -0.5]$), 232semi-volatile compounds (SVOC, $\log_{10} C^* = (-0.5, 2.5]$) and in-233termediate volatility compounds (IVOC, $\log_{10}C^*>2.5)$ (13). 234Compounds in the ELVOC and LVOC ranges have been shown 235to contribute to nanoparticle growth (8). Comparing this clas-236sification for the three different temperatures clearly indicates 237the importance of the compounds observed by the PTR3. At 238-25°C, large quantities of LVOC compounds can be observed 239by the usage of this additional ionization technique. 240

Observed volatility distribution within a volatility basis set 242 (**VBS**). As volatilities of organic compounds observed in the 243 atmosphere vary by more than 10 orders of magnitude, it is 244 convenient to simplify considerations of gas-to-particle partitioning by grouping compounds together within a volatility basis set (13, 24). Within this framework, the volatility 247 bins are separated by one decade in C^* at 300 K, and for 248

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[cm⁻³] 250CV/C PTR3 108 251Nitrate-CI Concentration 107 252106 253254105 ₿ +5°C 255E 10⁹ ELVOC svoc 256CV/C* >14 257Concentration 107 258106 25926010 -25°C ELVOC 261E 10⁹ E 10⁸ LVOC รงดด 262C^v/C^{*} > 1 ◀ 263Concentration 107 264106 26526610 ⁵ -5 -4 -3 -2 -1 log₁₀(C*[μg m⁻³]) -7 -10 -9 -8 -6 Ò 1 267268269Fig. 2. Volatility distributions for representative experiments with similar α -pinene 270ozonolysis rate, (A) $+25^{\circ}$ C, (B) $+5^{\circ}$ C and (C) -25° C. The green and blue bars show summed molecular ions observed in the Nitrate-CI and PTR3, respectively. The 271highest and lowest bin are overflow bins. Volatility bins are defined at 300 K, shifted 272

IVOC

SVOC

IVC

+25°C ELVOC

and widened according to their corresponding temperature. The resulting saturation 273mass concentration is defined on the x-axis, while $\log_{10} C_{300K}^*$ is specified by white numbers. Additionally, the bins in supersaturation with $C^v/C^* > 1$ are found left of 274275the indicating arrow.

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other temperatures the binned distribution is shifted towards 278lower saturation mass concentrations. The saturation mass 279concentration of oxidized organics should follow the Clausius-280281Clapeyron relation at a constant evaporation enthalpy $\Delta H_{\rm vap}$, which in turn is linked to C^* at 300 K (13) (see Supporting 282Information for details). 283

Fig.2 shows the resulting binned volatility distribution of all 284observed organic gas-phase compounds for the three represen-285tative experiments of Fig.1. Due to the observed comparable 286growth rates of the three examples, the gas-particle partition-287ing is expected to be comparable, which is confirmed by the 288 289similarity of the observed total volatility distribution over the 290ELVOC and LVOC ranges. However, it is important that this 291is only the case due to the additional observed compounds by 292the PTR3, which, in agreement with Fig.1, mainly detects less oxygenated molecules with $n_0 \leq 7$. Earlier work on growth 293of nucleated particles from α -pinene oxidation at $+5^{\circ}C$ em-294ploying only a Nitrate-CI found that the measured HOMs 295296could only explain a fraction of the growth and speculated that the nitrate detection efficiency was progressively lower for 297 less polar (and hence more volatile) species (8). We confirm 298the missing fraction and find that the PTR3 detects many 299new compounds not measured by the Nitrate-CI, independent 300 of temperature. At low temperature, fewer polar functional 301 groups are required for a compound to have a low volatility, 302and thus at +5 °C and even more significantly at -25 °C (Panel 303 304 (B) and (C) respectively) these species observed by the PTR3 contribute substantially in the LVOC and even ELVOC range. 305306

Particle growth measurements. We measured growth rates 307during the experiments with a DMA-train over two different 308 309 size-intervals, 1.8 - 3.2 nm and 3.2 - 8 nm (see Methods for 310 details). Fig.3 shows the measured growth rates versus several gas-phase variables. Panel (A) and (B) show the correlation 311with the estimated reaction rate of the α -pinene ozonolysis dur-312ing the growth rate measurement. Higher reaction rates, and 313 hence higher product concentrations, lead to higher growth 314rates, following an exponential relation $m(T, d_p) \cdot [\mathbf{k}(T) \cdot \mathbf{ap} \cdot \mathbf{O}_3]^q$ 315(see Supplementary Information for details). For a given α -316pinene ozonolysis reaction rate we find lower growth rates at 317smaller sizes. The smaller size range also shows a more signifi-318 cant temperature dependency: the growth rates are higher at 319low temperatures at a given reaction rate. This indicates that 320 the ozonolysis products at the three different temperatures 321have different properties influencing their ability to condense 322323from molecular cluster sizes onward.

Fig.3 panel (C) and (D) show the measured growth rates 324versus the total HOM signal observed in the Nitrate-CI only, 325along with a kinetic curve showing the growth rate if all 326measured HOMs condensed irreversibly (25). The growth 327 rates of the three different temperatures are clearly separated, 328 but condensation at the kinetic limit for HOMs would give 329almost identical values. Thus, the total HOM concentration 330 331observed in the Nitrate-CI cannot fully describe the observed growth at any temperature. At $+25^{\circ}$ C several HOMs measured 332by the Nitrate-CI are classified as SVOC and might not be 333 able to condense, and at -25°C the Nitrate-CI measures only 334a small fraction of the less oxygenated α -pinene oxidation 335 products responsible for particle growth (see Fig.2). 336

337 Therefore, panels (E) and (F) of Fig.3 show the growth rates versus a sum, combining both mass spectrometers, over all 338 VBS bins in supersaturation for a given particle size, i.e. with 339 $S = K(D_p) \cdot C_{\text{VBS bin}}^v / C_{\text{VBS bin}}^* > 1.$ A Kelvin-term $K(D_p) =$ 340 $10^{D_{K10}/D_p}$ accounts for the curvature of the particles, slowing 341growth of smaller particles. With this simple approach, it 342is possible to bring the growth measurements at these three 343 different temperatures into reasonable agreement, aligning 344 the data points roughly parallel to the kinetic line. This 345approach only accounts for bins in supersaturation, which 346should condense almost kinetically. Especially for the larger 347 size-interval, the measured growth rates are slightly higher 348 than the supersaturated kinetic limits for all temperatures. 349However, some VBS bins below supersaturation will contribute 350 as well by gas-particle partitioning, which is not considered in 351this simple approach. 352

353Comparison with an aerosol growth model. Aerosol growth is 354 modeled with the same framework as used in (8). However, 355 the model was adopted to take real time measured VBS-356distributions from both mass spectrometers as input, without 357 any adjustments of unknown charging efficiencies (see Sup-358porting Information for details). 359

The most important remaining unknown in the condensation equations is the Kelvin-term and the Kelvin-diameter, describing the curvature effect for the condensation onto the smallest particles:

$$D_{K10} = \log_{10}(e) \cdot \frac{4\sigma M}{RT\rho}$$
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[1] 365
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However, the observed size-dependence and especially the 367 growth measurements at diameters $< D_{K10}$ should provide 368 a direct constraint on the curvature effect. For the three 369 representative experiments, we find the best agreement with 370 $D_{K10}(T) = (4.8 \pm 0.8) \cdot (300 \,\mathrm{K} \cdot T^{-1})$ nm, which could corre-371spond to a surface tension of $\sigma = 0.03$ N m⁻¹, a molecular 372



Fig. 3. Growth rates measured by the DMA-train in two size intervals (1.8-3.2 nm, panels (A),(C),(E) and 3.2-8 nm, panels (B),(D),(F)) versus several gas phase variables.453Representative experiments are highlighted. On the x-axis, panel (A) and (B) show the reacted α-pinene rate, panel (C) and (D) show the HOMs observed in the Nitrate-CI and panel (E) and (F) show the amount of condensable material determined by the temperature dependent volatility basis set. Colors in all plots indicate the run temperatures, purple corresponds to -25°C, green to +5°C and red to +25°C. In panel (A) and (B) the light yellow areas shows the range of growth rates of the other size-interval to demonstrate the observed lower growth rates at small diameters. In panels (C)-(F), the gray area illustrates the range of uncertainty on the kinetic condensation limits drawn as solid colored lines. In panel (E) and (F) the error on the sum over the VBS-distribution is determined from the 1 decade uncertainty in the volatility definition.453453454455455456456457456458457458458

mass of M = 320 g mol⁻¹ and a density of $\rho = 1400$ kg m⁻³. values typical for a LVOC HOM. Fig.4 shows the resulting predicted growth rates and their size-dependence in comparison with the measurements. The agreement between modeled and measured growth rate at the smallest sizes is within the uncertainties of the measurements. Other values for D_{K10} , e.g. $D_{K10}(300K) = 3.75$ nm, used previously, lead to a significant overestimation of the observed growth rates at the smallest diameters for all temperatures. Another reason for the higher D_{K10} could be an underestimation of the volatility of the most oxygenated compounds (26). Above 5 nm, the model agrees well with the observations at all temperatures. Considering the 1 decade uncertainty in saturation mass concentration (see Supporting Information for details), we achieve reasonable mass balance for growth of freshly nucleated particles between 2 and 30 nm over a wide range of conditions.

Although there is no disagreement of the model with the measurements, within the uncertainties, there are several contributions that we have not considered. First, some condensable compounds might still be undetected by the two used ionization-chemistries. Additionally, fragmentation of molecules within the instruments might disturb the volatility estimate. Second, as well the temperature dependence of organic volatilities is subject to uncertainties (11). Third, we do not model any particle phase reactions, such as oligomerisation. 423Reactive uptake is thought to be more important at larger 424particle sizes (27), again in part because of the Kelvin effect 425(28).426

427Conclusion

429 Organics play a leading role in atmospheric new particle for-430 mation and growth and thus govern the global budget of 431 CCN. VOC oxidation products in the atmosphere make up 432 a substantial portion of condensing vapors causing growth 433 of existing particles. Because oxidized organics span a wide 434 range of volatilities, temperature is a crucial parameter. We

460have shown that the combination of two mass spectrometers. 461both using different ionization techniques, and consideration 462of the volatility distribution of the measured compounds, here 463with a volatility basis set, gives a sufficient constraint of the 464 gas-phase products, to comprehensively describe growth over 465a wide temperature range. The measurements are in good 466 agreement with an aerosol growth model and for the first time 467 a direct estimate of the Kelvin diameter for organics of 4.8 468 nm could be inferred. 469

Temperature influences the growth by organics from dark 470 α -pinene ozonolysis in several ways via competing processes. 471This is illustrated in Fig.5, where the oxidation products con-472taining 4 oxygen atoms are compared to the oxidation products 473containing 10 oxygen atoms with respect to their average satu-474ration mass concentration and the measured concentration for 475three experiments with a comparable α -pinene ozonolysis reac-476tion rate. While for both groups of compounds the volatility 477 decreases with decreasing temperature, the measured con-478centrations increase with increasing temperature for the O_{10} 479monomers at similar α -pinene ozonolysis reaction rates. This 480 is due to the temperature dependence of the unimolecular auto-481oxidation reactions. It is highly likely that the intramolecular 482H-atom transfer reactions have significantly higher activation 483 energies than radical-radical termination reactions, and so it is 484 reasonable that the extent of auto-oxidation will increase with 485increasing temperature (29). As these intramolecular reactions 486have to occur several times in order to form higher oxygenated 487molecules, measured concentrations of O_{10} compounds drop 488 significantly as temperature decreases. 489

Our precision measurement of particle growth rates across 490 the critical size range from 2 - 30 nm reveal that organic 491 condensation drives particle growth at a similar rate over a 492 wide temperature range, when the precursor oxidation rate is 493 held constant. This is due to counterbalancing temperature-494 dependent effects: lower volatility but also less extensive oxy-495 genation at lower temperature. The competing processes 496



Fig. 4. Modeled and measured growth rate versus particle diameter. (A) $+25^{\circ}C$ at 518increasing α -pinene ozonolysis reaction rates (~1.7-2.3 $\cdot 10^{6}$ cm⁻³s⁻¹) (B) +5°C at increasing reaction rates (\sim 1.2-1.8 $\cdot 10^{6}$ cm $^{-3}$ s $^{-1}$) (C) -25 $^{\circ}$ C at constant reaction 519rates ($\sim 1.9 \cdot 10^6$ cm⁻³s⁻¹). The thick black lines indicates the modeled total growth 520rate and the dashed black lines indicate the associated uncertainty resulting from a 521 \pm one bin shift of the VBS-distribution. The contribution of the different bins of the 522VBS-distribution is illustrated by the colored areas, where white numbers and the color 523code represent the saturation mass concentration at 300 K for all three cases. The contribution below the thick gray line is from bins with $C^{v} > C^{*}$. For the measured 524growth rates, red diamonds show the DMA-train (shown as well in Fig.3) and blue 525circles other instruments (see Supporting Information for details). The capped black 526errorbar shows the statistical uncertainty of the single measurements, while the gray 527errorbar gives the 50 % systematic uncertainty of the appearance time method.

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530described in Fig.5 are thus of the same order of magnitude. This suggests a crucial role for organics in aerosol growth 531across the wide temperature range of the troposphere. Not 532only due to higher emission and ozonolysis reaction rates, but 533534also due to rapid auto-oxidation to highly oxygenated states, organics can influence aerosol growth dramatically in warm 535regions. However, due to the strong drop in volatility of even 536537modestly oxygenated organic products at low temperature, organics can drive aerosol growth also in cold regions, e.g. at 538high altitudes and the sub-arctic. Global aerosol models there-539fore need to implement robust descriptions of these processes, 540541not only considering the first order rate constants of ozonolysis 542and OH reactivity, but rather a more detailed description of 543organic chemistry and its temperature dependence. Precision 544measurements with a complementary set of mass spectrome-545ters and particle-size-distribution measurements in the crucial region below 10 nm provide important constraints for model 546 predictions of the contribution of gas-to-particle conversion to 547the global budget of cloud condensation nuclei. 548

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550 Materials and Methods

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The CLOUD chamber. The CERN CLOUD chamber is a 26.1 m³ electro-polished stainless steel vessel, surrounded by a thermal housing capable of stabilizing temperature in a range from -65 °C to +100 °C with ± 0.1 K precision (30). The chamber is equipped with a gas control system achieving extremely high purities by mixing boil-off nitrogen and boil-off oxygen at the atmospheric ratio of 79:21. Highly pure trace gases can be precisely added at the ppt level. Before the start of the experiments the chamber was heated to



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Fig. 5. Overview over the competing processes and their temperature dependence. The left panel shows the summed measured concentration of the O_4 and O_{10} monomer (C_{6-10}) compounds. The right panel shows the averaged saturation mass concentration of the same groups of compounds. Data are taken from three experiments with comparable α -pinene ozonolysis reaction rate. The sketch on the left panel illustrates the higher measured concentrations at higher temperatures, especially of highly oxygenated products. The sketch on the right panel shows that growth at cold temperature can proceed already with the condensation of lower oxygenated products due to the decrease in volatility.

100 °C and rinsed with ultra-pure water for cleaning. This assured operation at contaminant levels of less than $5 \cdot 10^4 \text{ cm}^{-3} \text{ H}_2 \text{SO}_4$ and total organics below 150 pptv (15, 20).

A high-voltage field of ± 30 kV can be applied between two electrode grids, located at the top and bottom of the chamber. The electric field sweeps out all ions from the chamber allowing for ion-free experiments. If the field is switched off, ions are created by the impact of galactic cosmic rays and decay products from ambient radioactivity.

591Experiments were conducted as follows: At 38 % relative humidity, with no SO_2 and no NO_x present in the chamber, stable ozone 592concentrations of 30-40 ppb were established. Under dark condi-593tions, i.e. without any additional OH radical production mechanism 594except from the ozonolysis itself, the high-voltage field was switched 595on, to perform experiments under neutral conditions first. Injection of α -pinene initiated the ozonolysis reaction and the subsequent 596formation of particles. After steady-state α -pinene concentrations 597 were reached and particle growth was measured up to at least 10 598nm, the high-voltage field is switched off. Ions now present in the 599chamber lead to a significant increase in nucleation rate (7). There-600 fore two growth rate measurements can eventually be performed 601 as the size-distribution will show two growing particle populations. Moreover, the second measurement is almost independent of chang-602 ing gas concentrations as the steady-state is already reached during 603 the neutral experiments. As no significant effect on growth due to 604 the different ionization conditions was found all measurements are 605 treated equally in this study. 606

Measurement of particle growth. Apparent particle growth rates are
inferred from particle-size-distribution measurements with the ap-
pearance time method (10), as it was done in previous comparable
studies (8, 14). Particle-size-distributions are measured by sev-
eral sizing instruments optimized for a certain size range. Each
instrument was thereby treated separately but we found comparable
results in the overlapping regions for all presented experiments (See
Supporting Information for details).607
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613 Key part of this study is the precision measurement of particle-614size-distributions in the size range between 1.8-8 nm by a newly developed instrument, a DMA-train (23). It uses six differential 615 mobility analyzers in parallel with the classified size fixed for every 616 device. Subsequent detection of the size-selected aerosol is done by 617 the usage of six condensation particle counters. As no scanning is 618 involved, high counting statistics at a single size is achieved, pro-619 viding unprecedented high sensitivity to low number concentrations 620 in the crucial sub 10-nm range.

621 **Gas-phase measurements.** Gas phase compounds were measured 622 by high-resolution mass spectrometry. For this study two differ-623 ent instruments with two different chemical ionisation techniques 624 neutral gas phase species present during the α -pinene ozonolysis 625 experiments.

626 Using an atmospheric-pressure-interface, the rather selective ionization technique of a chemical-ionisation mass spectrometer 627 using nitrate $(HNO_3)(NO_3^-)$ as the reagent ion (21) was used to 628 obtain a very clean spectrum of HOMs (6). The broad ionization 629 efficiency of H₃O⁺-water clusters was deployed in a novel proton-630 transfer-reaction time-of-flight mass spectrometer to ionize VOCs as well as semi-volatile organic compounds (SVOCs) and HOMs (22). 631 While the Nitrate-CI is calibrated to the response of H_2SO_4 , the 632 response of the PTR3 to HOMs is assumed to behave comparably 633to Butanon (22). Inlet loss corrections for HOMs have to be applied 634 to both instruments and are adjusted for the PTR3 to give good 635overlap for peaks observed in both instruments (see Supporting Information for details). 636

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641 642 ACKNOWLEDGM

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745 Supporting Information (SI)

Appearance time method for growth rate determination. Particle
growth rate measurements were performed with the appearance
time method, which can be used especially in chamber experiments,
where a clear front of a growing particle population can be identified
during most nucleation experiments.

The particle-size distribution was measured by a comprehensive set of four different instruments. Below 2.5 nm, a particle size magnifier in scanning mode was used (31). The size range between 1.8-8 nm was covered by a DMA-train (23). Above 8 nm a scanning mobility particle sizer system, TSI nano-SMPS model 3982, measured up to 65 nm (32). Additionally, a neutral cluster and air ion spectrometer (NAIS) measured between 3-42 nm (33). Considering the analytical specific distribution binned

Considering the evolution of particle size-distribution binned into different size-channels, the signal in each size-channel is fitted individually with a four parameter sigmoid function using a leastsquare algorithm:

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$$S_{d_p}(t) = \frac{a-b}{1+(t/t_{app})^d} + b,$$
 [S1]

 $\begin{array}{l} 762 \\ \text{where a and b represent the background and plateau value of the} \\ 763 \\ \text{sigmoid function respectively, d is a parameter for the steepness} \\ 764 \\ \text{of the rising signal and $t_{\rm app}$ is the time at which the 50 \% value} \\ 765 \\ \text{between plateau and background is reached.} \end{array}$

A representative fit for a 3.2 nm size channel of the DMA-train is 766 shown in Fig. S1 (A). All size-channels are cross-checked manually 767 after the automated fitting and a statistical error of $t_{\rm app}$ is estimated 768from the covariance of the fit-result. The values obtained for t_{app} 769 can be plotted against the corresponding diameter as shown in Fig.S1 (B). A linear fit with an orthogonal distance regression is 770 used to take into account both the uncertainties of t_{app} and of the 771diameter of the size-channels. The resulting value of the slope and 772 its associated error can be interpreted as an apparent particle growth 773rate and its statistical uncertainty. However, this growth rate does not necessarily represent the growth caused by pure condensation, 774as it omits coagulation and, in chamber experiments, wall losses, 775 which both alter the particle size-distribution (34). Therefore, a 776 systematic uncertainty of the method is estimated to be 50 % (35). 777 For the DMA-train two size-intervals for the growth rate mea-778surement were defined: One between 1.8-3.2 nm and one between 3.2-8 nm. The choice of the size-intervals is arbitrary but proofed to 779 be representative to show differences between early and later growth. 780 In (8) it was shown that growth driven by biogenic organics shows 781only a minor size-dependence above 5 nm, i.e. the upper growth 782rate size-interval of the DMA-train is representative for growth >5783nm.

Absolute HOM concentration measurements using Nitrate–
CI-APi-ToF. The Nitrate-CI-APi-ToF (Nitrate-CI) uses negative nitrate, (HNO₃)(NO₃⁻), as reagent ion (36), which shows high





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charging efficiencies towards H_2SO_4 and HOMs. The concentration 807 of a HOM species is estimated via 808

$$[\text{HOM}_i] = C \cdot T_i \cdot \text{SL}_{\text{HOM}_i} \cdot \ln \left(1 + \frac{[\text{HOM}_i \cdot \text{NO}_3^-]}{\sum_{j=0}^2 [\text{NO}_3^- \cdot (\text{HNO}_3)_j]} \right) \begin{bmatrix} \text{S2} \\ \text{810} \\ \text{811} \\ \text{812} \end{bmatrix}$$

Here $[HOM_i \cdot NO_3^-]$ is the background corrected peak area which 813 is normalized to the intensity of the main reagent ions. To obtain 814 a quantitative concentration, three factors are applied: First, a 815 calibration factor C, which is inferred from a calibration using sul-816 furic acid (37) and assuming that all detected HOMs have the same ionization efficiency (6). Second, a mass dependent transmission 817 efficiency T_i of the APi-ToF can be inferred in a seperate experiment 818 by depleting the reagent ions with several perfluorinated acids (38). 819Third, sampling line losses $\mathrm{SL}_{\mathrm{HOM}_i}$ are estimated assuming laminar 820 flow diffusional losses in the sampling lines (39) with a diffusion coefficient of HOMs scaling with the molecular mass M_i of the 821 compound via $D[\text{cm}^2\text{s}^{-1}] = 0.31 \cdot M_i^{-1/3}$ at 278 K, determined from 822 wall loss measurements in the CLOUD chamber. As the sampling 823 lines of the Nitrate-CI are thermally insulated, for other experiment 824 temperatures $D \propto (T/278K)^{1.75}$ is assumed. As the compounds 825 detected by the Nitrate-CI are mostly classified ELVOC or LVOC 826 in the temperature range of this study, we can assume that they all 827 get lost irreversibly to sampling line walls due to diffusion.

Absolute concentration measurements of oxidized organics using 829 **PTR3-ToF.** The PTR3-ToF (PTR3) uses $(H_3O^+)(H_2O)_n$ clusters 830 as reagent ions, ionizing α -pinene as well as first and higher order 831 oxidation products by proton transfer or ligand switch reactions 832 (22). A contact minimized laminar flow inlet system with core sampling is used to transfer the sample air into the tripole reaction 833 chamber operated at 80 mbar and reduces transmission losses. The 834 $(H_3O^+)(H_2O)_n$ cluster ion distribution can be regulated by a radio-835 frequency-amplitude applied to the tripole rods without influencing 836 the reaction time. Increased pressure in the reaction region and 837 longer reaction times compared to traditional PTR instruments yield a 500 fold increased sensitivity to a broad range of organics. 838 At the operating conditions of the PTR3, secondary reactions of 839 ionized species with the most abundant neutral VOCs in the sample 840 gas are limited to less then one percent at the highest measurable 841 concentrations. The new instrument bridges the gap between pre-842 cursor measurements at ppbv level to HOM measurements at sub ppt level, complementing atmospheric pressure CIMS techniques. 843

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A quadrupole interfaced Long-ToF mass spectrometer (TOFW-844 ERK AG, Thun, Switzerland) is providing the high mass resolving 845 power needed to separate isobaric compounds. We obtained more 846 than 1500 individual mass peaks, excluding isotopes, during α -847 pinene ozonolysis experiments. A multi-peak fitting algorithm is applied to separate the major compounds and assign chemical sum 848 formulas. Extracting the relevant signals is done omitting all masses 849 rising less than 3σ above chemical background noise during ozonol-850 ysis measurements and removing peaks with possible uncertainties 851 caused by interference of higher neighboring peaks. $(H_3O^+)(H_2O)_n$ clusters are known to be soft ionization reagent ions. Nevertheless 852 we cannot exclude completely fragmentation of some ionized HOMs 853 loosing most likely H₂O especially when containing an (-OOH) 854 group. 855

The PTR3 was calibrated with a gas standard containing 1 856 ppm of 3-hexanone, heptanone and α -pinene in nitrogen, which was dynamically diluted by a factor of 1000 in VOC-free air to 857 contain 1 ppbv of each compound. Duty cycle corrected counts 858 per second dcps are used in order to compensate for the mass-859 dependent transmission of the TOF mass spectrometer (dcps(i) =860 $cps(i) \cdot (101/m_i)^{1/2}$) (22). For 3-hexanone and heptanone we ob-861 tained a sensitivity which is in agreement with the calculated sensi-862 tivity taking into account the duty cycle corrected $(H_3O^+)(H_2O)_n$ regent ion count rates, the pressure and the reaction time in the 863 reaction chamber (80 mbar; 3 ms) and using $2 - 3 \cdot 10^{-9} \text{cm}^3 \text{s}^{-1}$ 864 as a fast reaction rate constant close to the collisional limit value. 865 Consequently, only lower end product concentrations can be given.

In a previous α -pinene ozonolysis study PTR3 results showed quantitative agreement for several HOMs with the Nitrate-CI (22). The authors estimated 80 % inlet losses for low-volatile molecules 868



Fig. S2. Quantitative comparison of selected peaks observed in both mass spectrometers and its temperature dependence for three representative runs with similar α -pinene ozonolysis rate. The correction for PTR3 compounds to account for sampling line losses and the additional 80 % wall loss inside the PTR3 ion source are displayed by the hatched area.

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889 with $n_{\rm O} > 5$, bringing the two instruments into reasonable quanti-890 tative agreement for common molecular ion signals. However, the 891 assumption for the Nitrate-CI, that all detected molecules get lost 892 on contact with sampling line walls, does not hold for all substances measured by the PTR3. In the transition from SVOC to LVOC 893 the partitioning of substances between inlet line walls and sample 894 gas is temperature dependent. We therefore extended the approach 895 of (22) with our knowledge about an approximate volatility of the 896 measured compounds. Assuming that all molecules in the LVOC 897 and ELVOC range get lost by diffusion (the diffusion coefficient of a molecule is estimated similar to the Nitrate-CI) according to 898 (39), we can apply a temperature dependent loss-correction for the 899 sampling line losses, which is split up into three sections: 900

$$\eta_{\text{tot}} = \eta_{\text{line,int}}(T) \cdot \eta_{\text{line,ext}}(298\text{K}) \cdot \eta_{\text{PTR3}}(310\text{K})$$
[S3]

902 We account for losses at the sampling line within the CLOUD cham-903 ber $\eta_{\text{line,int}}$ at chamber temperature T, as well as losses occurring at 904 the sampling line outside the chamber at room temperature $\eta_{\text{line,ext}}$ 905 (as it was not thermally insulated) and losses within the PTR3 906 instrument heated to 37° C η_{PTR3} . Therefore, for each sampling 907 section other molecules might be subject to losses according to their 908

Comparison of the used mass spectrometers. The considerations of 909 the two previous sections result in the comparison for data obtained 910in three representative experiments at three different temperatures 911 which is shown in Fig.S2, where $\eta_{\text{line,int}}$ and $\eta_{\text{line,ext}}$ are calculated 912assuming diffusional losses similar to the Nitrate-CI and $\eta_{\rm PTR3}$ is estimated to correct for the 80% discrepancy found in (22). For 913higher oxygenated molecules the agreement between both mass 914spectrometers is in a reasonable range including the additional loss 915term η_{PTR3} for losses within the PTR3 ion source and inlet. This 916 indicates that the loss in measured concentration from $+25^{\circ}C$ to 917 -25°C for the three experiments at similar initial precursor oxidation rates is caused by the reduced reaction rates of the auto-oxidation 918 process. For lower temperatures and lower oxidized states (n_{O} 919= 4/5/6) a discrepancy between the instruments gets significant. 920 However, even at elevated temperatures, the Nitrate-CI is only 921detecting a small fraction of all oxidation products with $n_O = 5/6$ 922observed by the PTR3. Therefore it is concluded that the increasing discrepancy is likely due to a lowered sensitivity of the Nitrate-CI 923for such compounds. The ionization efficiency in the Nitrate-CI 924depends on the relative binding energy of a $(HNO_3)(NO_3^-)$ cluster 925compared to a $(Analyte)(NO_3^-)$ cluster (40). A relative shift in 926 binding energies at lower temperatures that favors $(HNO_3)(NO_3^-)$ 927clustering instead of $(Analyte)(NO_3^-)$ clustering, could explain the 928observed decrease of signal for the lower oxidation states for the 929Nitrate-CI. The higher oxidation states however are unaffected because the $(HOM)(NO_3^-)$ clustering is generally very strong and 930

will always dominate the $(HNO_3)(NO_3^-)$ clustering, which explains 931 the good agreement of the two instruments for higher oxidized 932 states. 933

Growth rate parametrization. Growth rates were parametrized in Fig.3 (A) and (B) by the simple exponential relation $GR=m(T, d_p)$. $[k(T) \cdot ap \cdot O_3]^q$, to express the correlation between growth rate and α -pinene ozonolysis reaction rate. While the coefficients $m(T, d_p)$ depend on temperature and size-range of the growth rate measurement, q is chosen to be independent of both. A minimum least-square regression yields the results presented in TableS1. 938

Size-Range	m(+25°C)	m(+5°C)	m(-25°C)	q
1.8-3.2 nm	1.12·10 ⁻⁷	2.09·10 ⁻⁷	$2.67 \cdot 10^{-7}$	1.21
3.2-8.0 nm	$2.66 \cdot 10^{-7}$	$3.12 \cdot 10^{-7}$	$3.57 \cdot 10^{-7}$	1.21

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Table S1. Resulting parameters from least-square regression for the growth rate parametrization of Fig.3 (A) and (B) by the simple exponential relation $GR = m(T, d_p) \cdot [k(T) \cdot ap \cdot O_3]^q$.

950Volatility of HOMs. Direct measurements of volatilities of individualHOM are extremely challenging as they are difficult to synthesizeand the vapour pressures are too low for current volatility measurement techniques. To overcome this problem, vapour pressurescan be inferred by several model calculations, like so-called groupcontribution methods (41) or parametrizations according to theoxidation state (13). In this study a combined approach is applied.We use a volatility parametrization according to the carbon

We use a volatility parametrization according to the carbon $n_{\rm C}^i$ and oxygen $n_{\rm O}^i$ number of the specific molecule *i*. This is based on two general observed trends that increasing carbon and increasing oxygen number lower the volatility of oxidized organic molecules. Thus, these quantities are linked to volatility, expressed as the logarithm of the saturation mass concentration $\log_{10} C_i^*$ for compound *i*: 957 958 959 960 961 962

$$\log_{10} C_i^*(300K) = \left(n_{\rm C}^0 - n_{\rm C}^i\right) \cdot b_{\rm C} - n_{\rm O}^i \cdot (b_{\rm O} - b_{\rm add}) - 2 \frac{n_{\rm C}^i n_{\rm O}^i}{n_{\rm C}^i + n_{\rm O}^i} \frac{963}{964}$$
[S4] 965

where the parameter $n_{\rm C}^0 = 25$ is the baseline carbon backbone for a volatility of 1 μ g m⁻³ without the addition of any functional groups. $b_{\rm C}=0.475$ is the roughly half decade decrease in volatility per carbon atom and $b_{\rm O}=2.3$ is the more than two decade decrease in volatility per oxygen atom assuming an average of (=O) and (-OH) groups. $b_{\rm CO}$ is a non-linearity term. More details can be found in (13).

However, other functionalities e.g. hydroperoxides (-OOH) and 972 covalently bound dimers are not included in $b_{\rm O}$, but are both 973 abundant in HOMs from α -pinene ozonolysis. To account for these 974specific attributes, a representative set of proposed products (8,26) with known structure is analyzed with the group contribution 975method SIMPOL (41). The results are fitted with Eq. S4 including 976 a free parameter b_{add} altering the effect of oxygen b_O . Monomer 977 and dimer products are fitted separately allowing this parameter to 978 include the covalent binding. The resulting parametrisation at 300 979 K is shown in Fig. S3. The free parameter yields $b_{add} = 0.90$ for monomers and $b_{\rm add} = 1.13$ for dimers. Accordingly, for any α -pinene 980 ozonolysis product with unambiguously identified composition, a 981 volatility can be calculated. 982

However, computed volatilities from group-contribution methods generally tend to underestimate vapour pressures at low vapour pressures. A recent study investigating the volatility of α -pinene oxidation products with quantum-chemical based model calculations found large deviations due to intramolecular H-bonds (26). These deviations were significant especially for highly oxygenated monomers and dimers, while the agreement for the higher volatilities was much better. 982983983984985986987988

This study focuses on the temperature dependence of the volatilities which is described by: 990

$$\log_{10} C^*(T) = \log_{10} C^*(300K) + \frac{\Delta H_{\text{vap}}}{R \ln(10)} \left(\frac{1}{300} - \frac{1}{T}\right) \quad [\text{S5}] \quad \begin{array}{c} 991\\992 \end{array}$$



1005Fig. S3. Volatility model used in this study. For a representative set of proposed1006products from α -pinene ozonolysis the known structure is used to calculate the
volatility by the group-contribution method SIMPOL or are directly measured by
(42, 43). Results are fitted with the proposed relationship from (13) including a free
parameter for the oxygen dependence.

 $\begin{array}{c} 1009 \\ 1010 \end{array}$

1011 The evaporation enthalpy ΔH_{vap} can be linked to the saturation 1012 mass concentration at 300 K log₁₀ $C^*(300K)$ according to (13) and 1013 combined with (44):

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$$\Delta H_{\text{vap}} \left[\text{kJ mol}^{-1} \right] = -5.7 \cdot \log_{10} C^* (300K) + 129$$
 [S6]
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The correlation between volatility at 300 K and the evaporation 1016 enthalpy ΔH_{vap} is very comparable for approaches like (44), (13) 1017 and (26). Moreover, the shift in volatility due to temperature in this study is most important for oxygenated compounds with 1018 volatilities around $\log_{10} C^*(300K) \approx 0,$ at the transition between 1019 LVOC and SVOC. For those molecules also the predictions of the 1020 volatility between the different methods don't differ drastically 1021(26). Therefore, we assume an overall uncertainty of the volatility 1022description of ± 1 bin (i.e. 1 decade in $C^*(300K)$ for volatility distributions within a volatility basis set). This uncertainty is 1023 shown Fig.3 panel (E) and (F) and gives the method uncertainties 1024 in Fig.4. 1025

1026Aerosol growth model. The measured VBS-distributions can be used to model aerosol growth. The modeling framework is based on the 1027 one used in (8) but simplified for the input of direct VBS-distribution 1028 measurements. Starting from a VBS-distribution at t = 0 the growth 1029of a monodisperse population of nucleated particles at an initial 1030size of 1.2 nm mobility diameter is modeled. Every VBS bin is 1031 treated like a single surrogate molecule having the properties of the averaged mass and concentration of the bin. It is assumed that the 1032 measured gas-phase concentrations are in steady-state with losses 1033 to particles and chamber walls. The condensation flux $\phi_{i,p}$ of every 1034VBS bin i should then follow: 1035

$$\phi_{i,p} = N_p \cdot \sigma_{i,p}, \cdot k_{i,p} \cdot F_{i,p}$$
[S7]

1036 ${\cal N}_p$ gives the number concentration of particles of a given size. 1037 $\sigma_{i,p} = \pi/4(d_p + d_i)^2$ is the particle-vapor collision cross-section 1038including the diameter of the monodisperse particle population d_p 1039 and mass-diameter of the VBS bin d_i . $k_{i,p} = \alpha_{i,p}\nu_{i,p}\beta_{i,p}$ is the deposition rate of vapor molecules at surface, with $\alpha_{i,p}$ the mass 1040 1041 accommodation coefficient, $\nu_{i,p} = (8RT/(\pi\mu_{i,p}))^{1/2}$ the center of mass velocity for particle and vapor (with the reduced mass 1042 $\mu_{i,p} = (M_i M_p)/(M_i + M_p))$ and $\beta_{i,p}$ the correction factor for non-continuum dynamics (45). $F_{i,p}$ is the driving force of condensation, 1043 1044closely related to the saturation ratio S_i of the VBS bin by $F_{i,p} =$ 1045 $C_i^0(S_i - X_{i,p}\gamma_{i,p}K_{i,p})$. This driving force of condensation for a 1046 VBS bin i gives the difference between gas phase activity S_i and particle phase activity $(X_{i,p}\gamma_{i,p}K_{i,p})$, which includes the Raoult 1047 term $X_{i,p}\gamma_{i,p}$ to account for the mixture effect of the particles and 1048

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the Kelvin-term $K_{i,p} = \exp(4\sigma M/(RT\rho d_p))$ accounting for the curvature effect of the particle surface. The model assumes an ideal mass based solution, i.e. the condensed phase activity is the mass fraction $X_{i,p}$ and hence $\gamma_{i,p} = 1$. Therefore we use C* as saturation mass concentration throughout this study, as $C^* = \gamma_{i,p}C^0$. Solving the share endenseting equations for the measured 1059

Solving the above condensation equations for the measured evolution of the VBS-distribution assuming this distribution always reflects a steady-state between production from α -pinene ozonolysis and wall losses and following the growing monodisperse aerosol population, yields a diameter versus time evolution which can be connected to a growth rate. 1059 1060 1061 1062 1063

Besides from the different input VBS-distributions at different temperature, only the Kelvin-term and the collision-frequency include a temperature dependence.

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