Online Characterization Of Organic Aerosol By Condensational Growth Into Aqueous Droplets Coupled With Droplet Assisted Ionization

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ABSTRACT: Online analysis of ultrafine (<100 nm dia.) particles was performed by sending the aerosol through a condensation growth chamber (CGC) to create micrometer-size aqueous droplets that were subsequently analyzed by mass spectrometry with droplet assisted ionization (DAI). Three experiments are reported which illustrate key performance characteristics of the method and give insight into the ion formation process: size-selected cortisone particles, size-selected secondary organic aerosol (SOA) particles, and freshly nucleated SOA under atmospherically relevant conditions. In each case, SOA was produced by α -pinene ozonolysis. For size-selected cortisone particles between 30 and 90 nm dia. and SOA particles between 30 and 70 nm, the ion signal intensity was found to be approximately independent of particle size. This observation is attributed to formation of aqueous droplets in the CGC whose size distribution is independent of original particle size. A consequence of this behavior is that the sensitivity of molecular detection increases as the particle size decreases, and the method is particularly well suited for new particle formation studies under atmospherically relevant conditions, and mass concentrations on the order of 25 nm, 10⁴ m⁻³, 0.2 µg m⁻³ respectively. Mass spectra of freshly nucleated SOA could be explained by condensation of highly oxidized molecules (HOMs) that subsequently reacted in the particle phase. Size-selected SOA showed increasing oligomerization with increasing particle size, which is consistent with established particle growth mechanisms.

INTRODUCTION

Atmospheric aerosol, solid or liquid-like particulate matter suspended in air, is ubiquitous in the environment around us, affecting both human health and the environment. PM_{2.5}, particulate matter with an aerodynamic diameter less than 2.5 microns. can deposit in the respiratory tract potentially causing a variety of health issues after long-term exposure. Particulate matter also can pose increased risk if composed of toxic compounds. Therefore, it is important to understand atmospheric aerosol size and composition, as well as its evolution over time. Organic matter constitutes 20-90% of the atmospheric particulate mass,¹ with the majority being secondary organic aerosol (SOA) of a biogenic origin.² SOA is produced in the atmosphere by oxidation of volatile organic compounds (VOCs) by ozone, hydroxyl radicals, or nitrate radicals depending on location and time of day.3 A substantial portion of biogenic SOA is derived from oxidation of monoterpenes.^{2,4} The oxidation of α -pinene by ozone has been used extensively as a model reaction to study the formation and impact of SOA.5

Several online mass spectrometry methods have been developed to probe SOA composition including the aerosol mass spectrometer (AMS) which uses thermal desorption followed by electron ionization,^{6–8} the filter-inlet for gases and aerosols (FIGAERO) that has been interfaced to a time-of-flight (TOF) mass spectrometer with chemical ionization (CIMS),^{9,10} and extractive electrospray ionization (EESI) coupled to TOF or Orbitrap mass spectrometers.^{2,11–15} In the work presented here, droplet assisted ionization (DAI) is adapted for online aerosol analysis,^{16,17} and is shown to offer different measurement capabilities, especially in the nanoparticle size range.

DAI is an inlet ionization technique whereby molecular ions are produced directly within the atmospheric pressure inlet to the mass spectrometer, without the need for extensive sample preparation or the use of high voltages to induce ionization.¹⁶ The inlet consists of a simple temperature controlled stainless-steel capillary.^{16,17} Pressure and temperature gradients across the capillary cause liquid droplets in the gas flow to break up in a manner that produces molecular ions. The highest ion yields are obtained with aqueous droplets,¹⁷ and the sensitivity is sufficient for atmospheric aerosols, where the mass concentration can be lower than 1 μ g m⁻³. DAI shares some similarities to sonic spray ionization (SSI), where aerodynamic droplet breakup is used to create ions,¹⁸ and matrix assisted ionization (MAI), where clusters and/or particles containing the analyte and an added matrix compound are drawn off a substrate through the inlet.^{17,19,20} With DAI, the "matrix" is water solvent, and the temperature gradient from heating the capillary can enhance droplet breakup and ion formation beyond aerodynamic forces alone.

In this study, DAI is used for online organic aerosol analysis by adding water to the aerosol particles with a condensation growth chamber (CGC) located upstream of the capillary inlet. The CGC grows particles to a final droplet size that is to a first approximation independent of the original particle diameter. This setup confers some unique detection properties for DAI relative to AMS, FIGAERO and EESI. These properties are discussed in the context of atmospherically relevant organic aerosol analysis.



Figure 1. (A.1) Test aerosols are produced by atomization of a standard solution, with subsequent drying to remove solvent. (A.2) SOA is produced by α -pinene ozonolysis in a flow tube reactor, with subsequent removal of organic vapors. (B) Particle size-selection is performed with a differential mobility analyzer (DMA). (C) Aqueous droplets are formed from dry aerosol particles with a condensation growth chamber (CGC). (D) Droplets are analyzed by passing through a DAI capillary connected to a Waters Synapt G2-S mass spectrometer.

EXPERIMENTAL SECTION

Organic Aerosol Generation. Figure 1 shows the experimental workflow used for size-selection experiments. Cortisone was chosen as an aerosol standard owing to a high sensitivity of detection by DAI and a molecular structure that contains functional groups similar to those found in biogenic SOA. Cortisone powder was purchased from Sigma Aldrich (>98%, St. Louis, MO, USA) and was dissolved in Optima grade water purchased from Fisher Scientific (Hampton, NH, USA) at a concentration of 100 uM. The solution was atomized using a commercial atomizer (model ATM226, TOPAS, Dresden, Germany) to produce polydisperse aqueous aerosol droplets. The aqueous droplets were then sent through a series of four diffusion dryer tubes containing molecular sieves (Sigma, St. Louis, MO, USA) to remove water. The size distribution of the dry polydisperse cortisone aerosol measured with the scanning mobility particle sizer (SMPS, TSI Inc., Shoreview, MN, USA) had a median mobility diameter of 41.8 ± 0.5 nm, average number concentration of $5.4 \pm 0.2 \text{ x} 10^5$ particles cm⁻³, and average mass concentration of $128.9 \pm 0.7 \ \mu g \ m^{-3}$. Particle size selection was subsequently performed with a differential mobility analyzer (DMA; model 3085, TSI Inc., Shoreview, MN, USA) and a Polonium neutralizer (NRD, Grand Island, NY) preceding the DMA. Table S1 gives information about the size-selected aerosols including median diameter, number concentration, mass concentration and ion signal intensity.

For the α -pinene SOA, two different flow tube reactors (FTRs) were utilized depending on the experiment. In each case, the particle size distribution exiting the FTR was monitored with an SMPS.

Nucleation of α -pinene SOA with a low mass loading was performed using a 20 cm i.d., 150 cm long quartz FTR described elsewhere,²¹ with the following modifications. Gas flows were generated from a zero-air generator (737 series, Aadco Instruments, Cleveland, OH, USA). A total flow rate of 6 Lpm was sent through the FTR with the incoming flow split into two separate flows, the first flow providing a mixing ratio of α -pinene at 22 ppbv and the second flow providing the ozone at 250 ppbv. α -Pinene liquid was obtained from Sigma Aldrich (98%, St. Louis, MO, USA). Ozone was produced from a custom-built ozone generator by ultraviolet irradiation of a flow of zero air. The relative humidity inside the FTR was < 7% and no hydroxyl radical scavenger was added to the inlet air flows. The aerosol size distribution in the exiting flow was measured with an SMPS. Three separate experiments were performed, and the number and mass concentrations can be found in Table S2. For DAI analysis, 1 Lpm of the SOA was passed through a series of charcoal denuders to remove organic vapors and then sent to the CGC.

For particle size-selection experiments, SOA with a high mass loading was produced by α -pinene ozonolysis using a 2.22 cm i.d., 125 cm long Teflon-coated FTR described elsewhere.^{22,23} After mixing in the FTR, the α -pinene concentration was about 50 ppbv and the ozone concentration was about 6 ppmv, giving an SOA mass loading of about 1200 µg m⁻³. The reaction was performed under dry conditions (<7% RH) without hydroxyl radical scavenger. Table S3 gives information about the size-selected aerosols including median diameter, number concentration, mass concentration, and ion signal intensity.

Aqueous Droplet Generation. The cortisone and SOA aerosols were passed through a condensation growth chamber (CGC) to produce aqueous droplets. The CGC (adapted from a device obtained from Aerosol Dynamics Inc., Berkley, CA, USA)^{24,25} works by exposing the aerosol flow to a supersaturated water vapor, which causes liquid water to condense onto the particles. The CGC contains a laminar flow-through chamber, 13 mm i.d. and 293 mm long, that has a wick lining the inner wall of the chamber (bringing the flow through i.d. to 9.5 mm) made of nylon membrane filter media (1.2 micron pore size, Sterlitech, Kent, WA, USA). The wick is continuously saturated with water. The CGC chamber is comprised of three temperature-controlled regions. The first is the conditioner region that is set to 5°C. In the conditioner region the input aerosol flow is conditioned to a cool temperature and high relative humidity. The second region is the initiator region, set to 45°C where supersaturation of water vapor occurs to activate particle condensational growth where initial droplet growth occurs. The final region is the moderator region that is set at 10°C. The cooled walls of this region promote additional growth of the aerosol to produce aqueous droplets in the 1-3 μ m diameter size range that is independent of the size of the incoming (dry) aerosol particles.²⁴

Droplet Assisted Ionization. Molecular composition analysis was performed with a Waters Synapt G2-S quadrupole ion mobility time-of-flight mass spectrometer having an ion source region that was adapted for DAI. The DAI interface consists of a stainless-steel capillary tube (62 mm length, 1 mm o.d., 0.5 mm i.d.) that can be heated.^{16,17} The capillary is encased in a ceramic insulating jacket that contains 24-guage NiChrome wire for heating. The temperature is measured with a thermocouple probe and precisely controlled through the use of a custom-built temperature control box containing a solid-state relay (Omega, Stamford, CT, USA) and variable power supply. Droplets from the CGC enter through a Swage-lok assembly sealed to the DAI capillary inlet by a Teflon ferrule. All experiments in this study were performed with a 25°C capillary wall temperature, a mass spectrometer cone voltage of 40 V, and an offset voltage of 60 V. Mass spectra were collected in sensitivity-continuum mode and processed using the Waters Mass-Lynx software. The mass spectra shown in the figures were averaged over a 1-3 min period depending on the specific experiment performed. Blank sample subtraction for the size selection experiments was performed by atomization of pure water solvent and for the nucleation experiment by analyzing the air flow exiting the FTR without a-pinene gas added. In each case, the aerosol passed through the CGC prior to entering the capillary inlet.

RESULTS AND DISCUSSION

A key aspect of DAI, with implications for both potential aerosol applications and the mechanism of ion formation, is the dependence of ion signal intensity on the amount of analyte. For aerosol analysis, there are two important considerations. First is the mass flow of analyte through the inlet, which is determined by the mass concentration ($\mu g m^{-3}$) of analyte in the aerosol. Second is the particle size distribution of the aerosol. In our initial study of DAI, it was shown that the ion signal intensity scaled linearly with analyte mass concentration, provided that the size distribution of the aerosol remained constant.¹⁶ In a subsequent study, the role of droplet size was explored for liquid droplets composed of polypropylene glycol (PPG).¹⁷ In this experiment, PPG served both as the analyte and the solvent, and it was shown that the ion signal intensity scaled approximately with d^4 where d = droplet diameter. This result suggested that droplet size as well as analyte mass flow affects the ion signal. As discussed below, the experimental apparatus in the current study allowed the effect of analyte mass to be separated from droplet size.

The role of analyte mass was studied using a standard compound, cortisone, which has functional groups similar to those found in biogenic SOA. Figure 2 shows the DAI (+) mass spectrum of cortisone obtained with the experimental setup beginning with part A.1. of Figure 1. This mass spectrum was obtained by selecting 29 nm dia. dry cortisone particles with the DMA in part B of Figure 1, and then condensing water onto the particles using the CGC in part C of Figure 1. DAI was performed with a capillary wall temperature of 25°C (part D of Figure 1). The mass spectrum in Figure 2 is representative of other cortisone particle sizes as well. It consists of both protonated and cationized molecules, as well as clusters of two or three cortisone molecules. Cations are thought to arise from salt contamination from components such as glassware to prepare solutions, the atomizer, the solvent, and the CGC. Salt contamination has been noted previously.^{16,17} In separate MSMS experiments, the cluster ions were examined by ramping the collision energy.

Only a very low collision energy (< 10 eV) was needed to break apart the clusters, showing that they are noncovalently bound.



Figure 2. DAI (+) mass spectrum of the aqueous droplets generated from 29 nm size-selected cortisone particles. The mass spectrum was averaged over a 1-min period, and the base peak is $2x10^5$ counts per minute (cpm).

Figure 3 shows the dependence of ion signal intensity on size of the dry cortisone particles that were selected by the DMA in part B of Figure 1. All ions containing at least one cortisone molecule were summed to obtain the total signal intensity. The ion signal intensity is represented in two different ways. The right-hand scale along with the data points in red show the ion signal per cortisone particle as a function of particle diameter. These values were determined by dividing the absolute ion signal (counts per minute) by the flow rate of particles into the CGC and subsequently to the mass spectrometer (particles per minute). This plot shows that the ion signal per droplet hardly changes over the dry particle size range studied, even though the cortisone mass per droplet changes by almost two orders of magnitude. The left-hand scale along with the data points in black show the ion yield, defined as the fraction of molecules entering the mass spectrometer that are registered as ion counts. Here, the absolute ion signal was divided by the molecular flow (derived from the mass flow) of cortisone into the CGC. The ion yield is highest for the smallest cortisone particles and decreases substantially as the particle diameter increases.



Figure 3. Droplet ion signal vs. dry particle diameter for DAI analysis of size-selected cortisone particles. Error bars represent one standard deviation from the average signal intensity.

We interpret Figure 3 in the following way. As mentioned above, our previous work indicated that the ion signal intensity is droplet size dependent. In the current study, all droplets exiting the CGC were approximately the same size, independent of the original dry particle diameter entering the CGC.^{24–26} We reason that the number of gas phase ions formed during droplet breakup depends on the size of the droplet, not the concentration of solute within the droplet. For this reason, the experimental setup in Figure 1, which combines DAI analysis with a CGC that forms droplets of a uniform size, constitutes an ionization technique where the ion signal intensity scales with dry particle number concentration (at least in the ultrafine size range encompassed by Figure 3), rather than analyte mass flow. This characteristic of the CGC-DAI technique is fundamentally different from other online particle analysis methods such as AMS, FIGAERO, and EESI all of which respond linearly to aerosol mass concentration. Furthermore, the data in Figure 3 suggest that the CGC-DAI technique is especially well suited to particle formation and growth studies in the Aitken mode size range where the mass concentration is low but the number concentration can be high.

To illustrate this point, three nucleation experiments were performed where an important biogenic VOC, α -pinene, is oxidized by ozone in a flow tube reactor to form SOA. The reaction conditions are given in the Experimental Section, and the particle size distributions exiting the flow tube are given in Supporting Information. The aerosol produced by this reaction had median diameters, number concentrations, and mass concentrations on the order of 25 nm, 10⁴ particles cm⁻³, 0.2 µg m⁻³ respectively (Table S2). The data in Table S2 for the three experiments show that the DAI signal intensity correlates much more closely with number concentration than mass concentration. Since the DAI signal intensity responds to number concentration, its mass spectrum will be weighted toward the composition of particles near the middle of the size distribution. In contrast, mass spectra obtained with particle phase methods that respond to mass concentration will be strongly weighted toward the composition of particles in the high diameter tail of the size distribution.

Figure 4A shows the positive ion DAI mass spectrum of one α pinene derived SOA experiment obtained with a capillary wall temperature of 25°C. For the purpose of this proof-of-concept experiment, only ions below 300 m/z were considered in detail because ion signal intensities above this value did not meet our requirement for adequate signal-to-noise ratio.²³ Nonetheless, ion signal intensities below 300 m/z were quite strong and illustrate the sensitivity of the method. The mass spectrum in Figure 4A is qualitatively similar to those reported for similar experiments using EESI to analyze SOA with somewhat higher mass concentrations.¹³

Ions in Figure 4A consist of both protonated and sodiated molecular species. Molecular formulas were assigned to these ions in a similar manner to previous work.^{23,27,28} Peaks assigned a molecular formula were required to have a signal-to-noise ratio of 5 or greater, and the assigned formula m/z (including cation) had to be within 10 ppm of the measured m/z (most assignments had much smaller mass deviations). Initial assignments were made according to the following rules: O/C < 2 (number of oxygen to carbon atoms in the assignment), H/C between 0.4 and 3.0 (number of hydrogen to carbon atoms in the assignment), RDB-O between -10 and +10 (ring-to-double bond equivalent minus the number of oxygen atoms for the assignment). After these initial assignments were made, unreasonable formulas were identified and removed by hand.

Figure 4B summarizes the assigned molecular formulas from the mass spectrum in Figure 4A. Ions are represented by circles on a

grid of oxygen and carbon numbers in the assigned molecular formula. The radius of the circle is proportional to the ion signal intensity on a logarithmic scale. Multiple circles for a given number of oxygen and carbon atoms mean that multiple formulas exist with different numbers of hydrogen atoms. Note that the lack of formulas in the upper right corner of Figure 4B is a consequence of the 300 m/z cutoff in this study.



Figure 4. (A) DAI (+) mass spectrum of particles formed by α pinene ozonolysis (25 °C capillary wall temperature). The mass spectrum was averaged over a 3 min period, and the base peak intensity is 7.7 x 10⁴ cpm. (B) Assigned molecular formulas plotted on a grid of oxygen number and carbon number in the formula. The circle radii scale with the ion signal intensity on a logarithmic scale. Multiple circles for a given combination of oxygen and carbon atoms indicate different numbers of hydrogen atoms. Median diameter, number concentration, and mass concentration are 22 nm, 8x10³ cm⁻³, and 0.13 µg m⁻³ respectively (Table S2, Experiment 1).

The assigned formulas in Figure 4B include highly oxidized molecules (HOMs), most notably the $C_{10}H_{16}O_x$ series (ionic form shown in spectrum), which is highlighted in Figure 4A. This series has also been reported with EESI in a similar experiment.¹³ HOMs are noteworthy because they have been detected in the gas phase by CIMS and have been shown to play a substantial role in new particle formation and growth.^{29–33} Most HOMs in the gas phase have assigned formulas corresponding to monomer (C₈ to C₁₀) and dimer (C₁₈ to C₂₀) oxidation products of α -pinene, which has 10 carbon atoms. In contrast, the formulas in Figure 4B have carbon numbers across a wide range of values and are not constrained to relatively simple monomer and dimer products. Noteworthy first generation monomer products of α -pinene ozonolysis in Figure 4A include pinonaldehyde at 191 m/z [C₁₀H₁₆O₂Na]⁺, the base peak, norpinonaldehyde, 177 m/z [C₉H₁₄O₂Na]⁺, and pinanediol, 193 m/z [C₁₀H₁₈O₂Na]^{+.34–36} While these compounds are known to be produced in high yield from the ozonolysis reaction, their presence in Figure 4 is surprising since they are semivolatile and should not partition to the particle-phase under the conditions of this experiment.³⁷ Their presence in Figure 4 could be either a consequence of the physicochemical properties of the aerosol or an artifact of the CGC-DAI method. These possibilities are discussed below.

Physicochemical properties of the aerosol that are relevant to the product distribution in Figure 4 include the high viscosity of α-pinene SOA under the conditions of this experiment and the high reactivity of many ozonolysis products. It has been known for some time that SOA is highly viscous at low temperature and relative humidity.³⁸ α -Pinene SOA viscosity has been measured in the range from 10⁵ to higher than 10⁸ Pa s under dry conditions and temperatures near room temperature, denoting a semisolid state.³⁸ Restricted diffusion within a semisolid state may cause semivolatile compounds to become trapped within the particle phase through a kinetically controlled burying mechanism, as recently demonstrated by Vander Wall et al. (2020).³⁹ The semivolatile compounds in Figure 4 could have been produced in the gas phase and subsequently trapped within the growing particles, or they could have been produced directly in the particle phase where they remain trapped.

Scheme 1. Potential particle-phase reactions of hydroperoxides

Hydroperoxide Decomposition:

$$R_1 OOH \to R_1 O \cdot + \cdot OH \tag{1}$$

Isomerization/Decomposition of Alkoxy Radical:

$$R_1 O \cdot \rightarrow \cdot R_1 O H + \cdot (R_1 - C_x H_y O_z)$$
(2)
Isomerization Decomposition

Reaction of Hydroxyl Radicals:

$$R_2H + \cdot OH \to R_2 \cdot + H_2O \tag{3}$$

Hydrogen Abstraction:

$$\begin{pmatrix} \cdot R_1 O H \\ \cdot (R_1 - C_x H_y O_z) \\ \cdot R_2 \end{pmatrix} \xrightarrow{R_3 H} \begin{pmatrix} H R_1 O H \\ H (R_1 - C_x H_y O_z) \\ H R_2 \end{pmatrix} + R_3 \cdot (4)$$

Oligomerization:

 $R \cdot + R \cdot \rightarrow R - R \tag{5}$

where
$$R = R_1, R_2, or R_3$$

The SOA produced in our study is expected to be highly reactive. Peroxides are known to be abundant in SOA formed by α - and β -pinene oxidation, constituting between ~47 and ~85% of the bulk SOA mass.^{33,40-44} In the gas-phase, HOMs are produced by autooxidation, which efficiently forms hydroperoxide functionalities.^{29–33,43-45} Upon entering the particle phase, hydroperoxide-rich HOMs may decompose to produce hydroxyl radicals, alkoxy radicals and alkyl radicals, which can decompose further by the loss of small molecules or oligomerize to form much larger molecules.⁴⁶ Scheme 1 summarizes this wide range of processes. The net result is formation of products having carbon numbers across a wide range of values. Oxygen numbers of the products are generally

lower than the original HOMs owing to e.g. Equations 1 and 2 of Scheme 1. We suggest that these processes, which could in principle occur in either the gas or particle phase, contribute to the difference between the particle phase product distribution in Figure 4 and reported gas-phase distributions of HOMs.^{47–49} When viewed from the perspective of particle phase chemistry, the mass spectrum in Figure 4 provides evidence for substantial intermolecular reactivity within the particle phase, producing an interconnected oligomeric system. This reactivity may provide a molecular explanation for the high viscosity of the particle phase. Similarly, in a study by Pajunoja et. al. (2014), they determined that because their O:C ratio was 0.3, it is likely that the average composition of the SOA is small oligomers of second generation oxidation products.⁵⁰

An alternative possibility for the product distribution in Figure 4 is molecular decomposition either in the aqueous droplets produced by the CGC or during DAI analysis. The reactions summarized in Scheme 1 may occur within the aqueous droplets formed in the CGC prior to entering the mass spectrometer. While it is unclear in the current study to what extent this might occur, the transit time from the CGC to the DAI inlet is only about 1 s, meaning that such reactions must be very fast and would also be expected when using other characterization methods such as online EESI and off-line ESI. Many products in Figure 4 are related to each other by small molecule losses (e.g. -H₂O₂, -CO, -CO₂, -CH₂O₂, and -CH₂O) that could arise from ion decomposition inside the mass spectrometer. Previous MSMS studies have investigated how molecular ions from α -pinene SOA that contain hydroperoxide functionalities dissociate. ^{13,40} Loss of H₂O₂ has been reported as a specific marker for hydroperoxide functionalities⁴⁰ though several other dissociation routes exist. For example, Lee et al. (2020)¹³ performed MSMS on $C_{10}H_{16}O_4$ from α -pinene ozonolysis and reported several small molecule losses to give product ions having significantly lower oxygen numbers than the original molecule.¹³

Since the inlet capillary wall was held at 25 °C, droplet fission and ion ejection by DAI occurred at this temperature or below.⁵¹ However, ions exiting the capillary are effectively heated as they are accelerated through the ion optical system of the mass spectrometer. The amount of heating during ion transport can be estimated from the cortisone cluster ions in Figure 2. The relative intensities of these ions do not change with capillary wall temperature up to about 300 °C. Once the temperature increases above this value, cluster ions decrease in intensity relative to the monomer. Computational fluid dynamics modeling of the air flow inside the capillary shows that the maximum temperature of 300 °C, suggesting that heating in the ion optical system is also on the order of 150 °C, which is at the lower end of estimates reported in the literature for other mass spectrometer systems.⁵²

The negative ion DAI mass spectrum of this same nucleation aerosol (Table S2, Experiment 1) is shown in Figure 5A, and the corresponding oxygen number vs. carbon number plot is shown in Figure 5B. Several first-generation monomers of α -pinene ozonolysis are observed including, pinonic acid at m/z 183, [C₁₀H₁₅O₃]⁻, pinic acid at m/z 185, [C₉H₁₃O₄]⁻, and hydroxy-pinonic acid at m/z 199, [C₁₀H₁₅O₄]⁻. The C₁₀H₁₆O_x series is detected with oxygen numbers 3, 4, and 5, as shown in Figure 5A. HOMs are also prevalent in the negative ion mode spectra with oxygen atom count as high as 14 (Figure 5B). As discussed for the positive ion mass spectrum, the detection of ions over a wide range of carbon and oxygen atom numbers is likely the result of reactions summarized by the discussion above. Not surprisingly, the formulas identified from the negative ion mass spectrum are generally more highly oxidized than those identified from the positive ion mass spectrum.



Figure 5. (A) Online-DAI (-) mass spectrum of particles formed by α -pinene ozonolysis (25 °C capillary wall temperature). Base peak intensity is 2.1 x 10⁴ cpm. (B) Assigned molecular formulas from the DAI mass spectrum plotted on a grid of oxygen number and carbon number in the formula. The circle radii scale with the ion signal intensity on a logarithmic scale. Multiple circles for a given combination of oxygen and carbon atoms indicate different numbers of hydrogen atoms. The aerosol analyzed is the same as Figure 4.

In our previous work, we compared the amount of dissociation of a thermometer ion, p-methoxybenzylpyridinium, using DAI and ESI on the same mass spectrometer.¹⁶ We found that the survival yield of the thermometer ion was the same with the two ionization methods, suggesting that the amount of ion dissociation was characteristic of the mass spectrometer rather than the ionization method itself.¹⁶ In order to extend the DAI-ESI comparison to SOA, we performed a third type of experiment to characterize the particle size dependence of molecular composition. In this experiment, a flow tube reactor (A.2 in Figure 1) generated SOA particles that were size-selected with the DMA (B in Figure 1) and then analyzed by the CGC-DAI method (C and D in Figure 1). The results were then compared to the particle size dependence of DAI signal intensity for cortisone in Figure 3, and to our previous work using offline ESI-MS to characterize size dependent molecular composition.²³ Because of sensitivity limitations associated with offline analysis, the ESI study was performed with a high mass loading of SOA. These conditions were replicated for DAI analysis, even though the greater sensitivity of online analysis would have permitted a lower mass loading to be studied. In the offline ESI experiment, collection times of 1 hour to 1 day for individual size-selected samples

were required to obtain sufficient mass. In the online DAI experiments reported here, mass spectra were averaged over 3-min periods. Tables S3 and S4 give relevant data (particle diameter, number and mass concentrations, ion signal intensities, and ratios thereof) for three separate experiments that were performed.

DAI (+) mass spectra of size-selected α-pinene SOA from one representative experiment are shown in Figure 6. These mass spectra were obtained with a capillary wall temperature of 25 °C. Similar to the nucleation experiment, ions consisted of both protonated and sodium cationized species. Unlike the nucleation experiment, dimers and higher order oligomers are very intense in the size-selected mass spectra. This difference arises from the different SOA mass loadings of the two experiments. The high α -pinene and ozone mixing ratios in the size selection experiment enhance oligomer formation in the particle phase.^{36,37,45,47} In addition to the hydroperoxide reactions summarized in Scheme 1, these reactions may include aldol condensation, esterification, and/or anhydride formation, as well as others.^{46,53,54} It is important to note that the oligomers observed in Figure 6 are covalently bound, rather than the molecular clustering observed in Figure 2, as collision energies in excess of 20 eV are required to decompose the precursor ions.

The ion signal intensities for the size-selected SOA particles scale in a similar manner to those for cortisone in Figure 3. That is the signal intensity ratio scales more closely with number concentration ratio than mass concentration ratio. Details are given in the Figure 6 caption for Experiment 3 and in Table S4 for all three experiments.

A detailed analysis of the assigned molecular formulas from Figure 6 and the corresponding mass spectra from two replicate experiments show that molecular composition depends significantly on SOA particle size. We summarize these differences in three ways: oxygen-to-carbon ratio (O/C) of the particulate matter, average carbon oxidation state (\overline{OSc}) of the particulate matter, and the signal intensity ratio of higher order oligomers (assigned formulas with C₂₁ and above) to the total signal intensity. These measures are summarized in Table 1 for all three DAI experiments performed, and were also studied previously for offline ESI analysis of SOA produced by β -pinene ozonolysis.²³ Both O/C and $\overline{OS}c$ are higher for smaller particles than larger particles. In contrast, the fraction of ion signal intensity composed of higher order oligomers is lower for smaller particles than larger particles. These trends are the same as those reported previously for β -pinene SOA and are thought to arise from the same phenomenon.²³ Larger particles have a greater volume-to-surface-area ratio and therefore have a higher proportion of oligomers that formed in the particle phase. Since oligomerization generally involves water loss, the oxygen content of the organic matter decreases, as reflected by decreasing O/C ratio and OSc with increasing molecular size.^{23,32}

The extent to which hydrolysis takes place in the droplets produced by the CGC is unknown. However, as mentioned earlier, the time between droplet formation and analysis is short (1 s), which minimizes the effect of hydrolysis. The difference in molecular composition between the small and large size-selected particles cannot be explained simply by different hydrolysis rates of the droplets produced from each size particle, since the DAI results match those by offline ESI where there can be no difference in hydrolysis between the two particle sizes.²³

Table 1. Molecular Composition of Size Selected SOA

Approx. Particle Diameter (nm)	O/C Ratio (Mass Weighted)	<i>OS</i>_C (Mass Weighted)	Ratio of Oligo- mer to Total Ion Intensity
30	0.35 ± 0.01	-0.70 ± 0.03	0.68 ± 0.07
70	0.31 ± 0.01	$\textbf{-0.83}\pm0.02$	0.69 ± 0.02

 $O/C = \frac{\sum(O*SI)}{\sum(C*SI)}$ $\overline{OS}_{C} = 2 * \frac{\sum(O*SI)}{\sum(C*SI)}$ $\Sigma(H*SI)$ SI = signal intensity $\Sigma(C*SI)$ $\Sigma(C*SI)$



Figure 6. DAI (+) mass spectra of size-selected α -pinene SOA particles exiting the FTR for (A) 37 nm, and (B) 72 nm mobility diameters. Base peak intensities are $3x10^4$ and $8x10^4$ cpm respectively. The mass spectra were averaged over a 3-min period. The signal intensity ratio of A/B is 3 which more closely matches the number concentration ratio (6) than the mass concentration ratio (37).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Ion signal intensities and particle number/mass concentrations of size-selected cortisone aerosol (Table S1), the nucleation experiment (Table S2), and size-selected SOA particles (Tables S3 and S4)

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DEK and MVJ designed the project. DEK performed the experiments and analyzed the results. MJA and YZ contributed to DAI experiment and analysis. MST and DH assisted with flow tube experiments. ST assisted with data analysis. DEK wrote the manuscript, and all authors have approved the final version.

Notes

The authors declare no competing financial interest.

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TOC Figure:

