Stability of α-Pinene and d-Limonene Ozonolysis Secondary Organic Aerosol Compounds Towards Hydrolysis and Hydration

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Keywords: particulate matter, chemical aging, water vapor, liquid water, monoterpenes, mass spectrometry

ABSTRACT

Secondary organic aerosol (SOA), formed through the gas-phase oxidation of volatile organic compounds (VOCs), can reside in the atmosphere for several days and sometimes for weeks. The formation of SOA takes place rapidly, often within hours after VOC emissions, and SOA can then undergo much slower physical and chemical processes throughout its lifetime in the atmosphere. Water, in the form of water vapor, aerosol liquid water, and cloud and fog water, can strongly impact the composition of SOA by altering formation and short-term aging mechanisms; however, less is known about how water impacts long-term SOA aging. The goal of this work is to systematically explore the effects of water on the chemical composition of α-pinene and d-limonene SOA during long-term aging processes. SOA samples were generated in an oxidation flow reactor and collected on foil substrates. Samples were aged in the presence of water vapor at 97% relative humidity for 7-14 days or an aqueous solution for 1-2 days, then analyzed with direct infusion electrospray ionization high resolution mass spectrometry to gain insight into the chemical composition of SOA before and after aging. The patterns of peak intensities and observed molecular formulas were examined for evidence of water-driven chemistry. We found that chemical composition of the SOA did change during long-term exposure to water vapor and liquid water, but the extent of the change was surprisingly small. This indicates that the exposure to water is not a strong driver of long-term aging processes compared to other mechanisms of aging for the monoterpene SOA studied.

INTRODUCTION

Atmospheric aerosols are solid or liquid particles suspended in air that affect climate through their interactions with solar radiation and their ability to change cloud albedo. They scatter and absorb solar radiation, diminishing visibility, and also contribute to adverse health effects as aerosol particles are small enough to penetrate deep into the lungs and other organs, causing a variety of cardio-respiratory illnesses.[1,2] These effects are experienced on local, regional, and global scales because aerosols persist long enough to be transported hundreds of kilometers from their source.[1]

Organic aerosols account for a dominant fraction of aerosols in the lower troposphere, with significant implications on the energy budget of the Earth and human health.[3] Primary organic aerosols are directly emitted, whereas secondary organic aerosols (SOA) are formed through chemical reactions in the atmosphere involving volatile organic compounds (VOCs), which are emitted from both biogenic and anthropogenic sources.[3] These reactions include the gas-phase oxidation of VOCs followed by condensation, heterogeneous oxidation of VOC oxidation products on particle surfaces, and aqueous processing in cloud or fog droplets. Atmospheric residence time for SOA can vary from minutes to weeks,[4] and during this time various physical and chemical changes can occur within the particle depending on the environmental conditions.[5] Due to the large variability of sources, chemical constituents, and transformations, SOA formation and aging processes are one of the leading sources of uncertainty in aerosol radiative forcing in global climate models, making them one of the least understood components of atmospheric aerosols.[6]

In the atmosphere, SOA are exposed to different forms of water including water vapor, organic-phase water, aerosol liquid water, and cloud and fog droplets, which can promote reactions and result in changes in chemical composition, vapor pressure, and solubility.[7] The amount of water aerosols can interact with varies in atmosphere, in which water can either act as solvent or a solute. While cloud and fog droplets typically contain liquid water with low amounts of solutes and dispersed insoluble particles, the state of water in aerosols is dependent on the relative amount of organic and inorganic compounds. Under dry conditions, water is present as a thin film on particle surfaces. At higher relative humidity (typically greater than 80%), particles with soluble organics and inorganics contain concentrated aqueous solutions of inorganics and may also contain water molecules dispersed in the organics phase. For example, ammonium sulfate particles coated with

SOA are known to phase separate into a deliquesced ammonium sulfate core and organic-rich shell containing water.[8]

Hydrolysis, in which a water molecule is used to break a chemical bond, is one of the most common reactions that can occur in the presence of water. The hydrolysis of single bonds can result in fragmentation of larger compounds into smaller molecules.[9–12] These compounds can lead to an increase in SOA volatility, decrease in SOA solubility, and may lead to the loss of material from organic particles by evaporation. Conversely, the hydration of compounds containing a double bond, such as carbonyls, can result in the addition of hydroxyl group and/or lead to oligomers with higher-molecular weights and lower volatility through hydrolysis, and thus do not readily evaporate from the particles[13–15]

Hydrolysis and hydration of several classes of SOA compounds has been studied from the perspective of atmospheric chemistry over the last few years. Epoxides undergo hydration, which can be catalyzed by ammonium ions and acids, leading to compounds with lower volatility and higher solubility.[9–12] Diacyl peroxides, formed through the gas-phase RO_2 + RO_2 reactions, have been shown to hydrolyze in humid conditions and contribute to the formation of carboxyl and ester groups.[16] α-acyloxyalkyl hydroperoxides, a class of ester hydroperoxides formed through the reaction between organic acids and stabilized Criegee intermediates, were shown to undergo rapid hydrolysis in the aqueous phase.[17] Atmospherically relevant anhydrides can undergo hydration. For example, phthalic anhydride was found to be taken up into the particle phase and then add water to form phthalic acid.[18] Nucleophilic reactions can occur during the hydrolysis of lactones, resulting in ring opening products.[19,20] There have been numerous studies on organonitrates, which have been shown to hydrolyze in humid conditions, especially in the presence of acids.[21–27] Dicarbonyls, such as glyoxal and methylglyoxal, can easily partition into the aqueous phase and undergo hydration, resulting in oligomer formation.[13–15] Oxaloacetic acid has been shown to decarboxylate with a lifetime of 5 hours in pure water and 1 hour in ammonium sulfate aerosols.[28] However, not all potentially hydrolysable compounds undergo hydrolysis due to kinetic limitations. For example, levoglucosan, a molecular marker for biomass combustion, can be hydrolyzed by acid catalysis to form α-D-glucose. However, levoglucosan was found to be stable with respect to hydrolysis and did not degrade over a period of 10 days.[29]

The work cited above focused on the hydrolysis and hydration of model organic compounds in the presence of atmospherically relevant acids and salts at varying pH levels. Systematic experiments on simultaneous hydrolysis and hydration of complex mixtures of compounds present in SOA have not been carried out. Previous studies of aqueous photochemistry of SOA suggested that hydrolysis of SOA compounds may occur even in the absence of catalysts,[30–32] but studying the hydrolysis was not the primary objective of those studies. In some cases, SOA compounds appeared to decay slowly in dark conditions. However, these experiments only lasted a few hours whereas the lifetime of aerosols can be up to days and weeks.[31] Additionally, understanding the chemical processes, or the lack thereof, that can occur during aging could potentially simplify future experiments. For example, the stability of SOA compounds would indicate that experimentalists can still garner reliable results even if samples were not immediately analyzed, or changes in the composition of SOA would suggest that results may be skewed if the sample was left out for a long period of time. The goal of this work is to explore the effects of water vapor and liquid water on the chemical composition of SOA compounds from the ozonolysis of monoterpenes during long-term aging processes. Based on previous results,[30–32] we hypothesize that the composition of SOA will significantly change upon aging in water vapor and liquid water for extended period of time (1-2 weeks and 1-2 days, respectively). Evidence of water driven chemistry was determined by monitoring changes in peak patterns and molecular formulas of lab-generated SOA before and after aging using electrospray ionization mass spectrometry (ESI-MS). This study focuses on lab generated particles and do not contain other constituents such as inorganic species. Therefore, the findings presented in this study pertains to mostly in remote locations. Our results suggest that SOA from the ozonolysis of monoterpenes remain relatively stable with respect to hydrolysis and hydration, indicating that this process is not the main aging mechanism of SOA.

MATERIALS AND METHODS

SOA Generation. SOA samples from α-pinene and d-limonene ozonolysis were produced in a ~20 L continuous flow reactor under dry and dark conditions. Prior to each experiment, the reactor was purged with zero air (Parker 75-62 purge gas generator). Ozone was introduced into the reactor by flowing pure oxygen through a commercial ozone generator (OzoneTech OZ2SS-SS) at 0.5 SLM (standard liters per minute). Pure liquid α-pinene or d-limonene was evaporated into ~5 SLM flow of zero air using a syringe pump at a constant rate of ~2 μL min^{-1}. The estimated initial mixing ratios of ozone and VOC were 10 ppm and 60 ppm, respectively, so the reaction was oxidant

limited. High concentrations of precursor and oxidant were used to generate enough SOA material, typically in the milligram range, for the analysis described below. Under the ozone-limited conditions, the oxidation for endocyclic double bond in d-limonene is favored, and the exocyclic double bond may survive the oxidation.[33] Previous studies have found that different initial concentrations of VOC and oxidant lead to different yields and ROS profiles and intensities,[34,35] so the conclusions of this paper should only be applied to underoxidized conditions of SOA formation. SOA was collected onto a foil substrate on Stage 7 (0.32-0.56 μm) of a micro-orifice uniform deposit impactor (MOUDI, model 110R) at a flow rate of ~30 SLM (5.5 SLM from the flow tube + 25 SLM make-up air) to create a uniform deposition of particles on the substrate.

Aging by exposure to water vapor followed by low-resolution mass spectrometry analysis. A list of experiments done to understand SOA aging by exposure to water vapor is outlined in Table S1. The first series of experiments was done by exposing SOA to humidified air for a prolonged period of time. A saturated slurry of K_2SO_4 (6 g salt and 50 mL of water) was prepared and added to a glass jar, serving as the relative humidity (RH) aging chamber. A segment of the foil substrate was placed on a petri dish floating on top of the saturated solution to expose the SOA sample to humid conditions, while the remaining substrate was kept frozen as a control. Based on the saturation vapor pressure of K_2SO_4, the headspace was maintained at 97.3 ± 0.45 % RH.[36] The RH aging chamber was sealed with a Parafilm^{TM} M film and wrapped in foil to block light exposure and left undisturbed for 1-2 weeks. The foil substrate was then removed from the aging chamber and frozen until analyzed by mass spectrometry.

SOA aged by water vapor was analyzed using a Xevo TQS quadrupole mass spectrometer with an ESI source in negative ion mode. The mass spectrometer was operated using the following parameters: source cone voltage, 50 V; cone gas flow, 150 L/h; capillary voltage, 2.21 kV; source temperature, 120 ºC; desolvation temperature, 500 ºC; desolvation gas flow 1000 L/hr. Samples were extracted using a 1:1 mixture of water and acetonitrile, placed on a shaker for ~10 min, and then injected into the ESI-MS by direct infusion. All samples described were in their respective solvent for up to 3 hours between extraction and analysis.

Aging by exposure to water vapor followed by high-resolution mass spectrometry analysis. Subsequent experiments with water vapor aging relied on a modified protocol (Figure S1). Each SOA substrate was split into three (instead of two) equal segments. One segment was aged in a

desiccator at RH <2% for 1-2 weeks; another segment was aged in the RH aging chamber for 1-2 weeks; finally, the last segment was frozen until analyzed by mass spectrometry. The goal of these additional experiments was to distinguish between hydrolysis and hydration reactions (by comparing samples aged at room temperature under dry and humid conditions) and spontaneous aging chemistry that does not require water (by comparing frozen samples with those aged at under room temperature dry conditions). Note that, very fast hydrolysis and hydration processes are difficult to study because water is ubiquitous in the atmosphere, we are primarily interested in slower processes involving water. For these and subsequent experiments, we used a high-resolution mass spectrometer equipped with a direct infusion electrospray ionization source (ESI-HRMS). Following the aging protocols, aged samples and frozen control were extracted using a 1:1 mixture of water and acetonitrile, placed on a shaker for ~10 minutes, and then promptly analyzed using high resolution mass spectrometry**.** The Thermo Scientific Q Exactive Plus Orbitrap mass spectrometer was operated in negative ion direct infusion mode with a spray voltage of 2.5 kV and resolving power (m/Δm) of 1.4 x 10^5. A mass spectrum of the solvent was also collected to correct for the background in the spectra of SOA before and after aging.

Peak *m/z* values and abundances were extracted from the raw mass spectra using the Decon2LS program, (https://omics.pnl.gov/software/decontools-decon2ls), and then processed with in-house software. Peaks corresponding to molecules with ^{13}C atoms or obvious impurities and ion fragments, including any peaks with *m/z* < 100, were removed. Peaks with a solvent/sample ratio of more than 0.1 were also removed. The peaks were assigned in two stages, first to internally calibrate the *m/z* axis with respect to the expected peaks, and then re-assigned after minor corrections (<0.001 *m/z* units). Mass spectra from different samples were clustered by molecular formulas of the neutral compounds, $C_cH_hO_o$, in which deprotonation was assumed to be the main ionization mechanism.

Aging in liquid water followed by high-resolution mass spectrometry analysis. After observing only a limited change in the mass spectra of SOA exposed to water vapor, the next series of experiments examined water driven chemistry of SOA in liquid water. In the initial protocol, half of the foil substrate containing SOA was extracted using 10 mL of nano-pure water, resulting in a mass concentration of 50-100 μg/mL. The solution was placed on a shaker for ~10 min, left

undisturbed for 1-2 days, and then analyzed with high resolution mass spectrometry. The other half of the substrate was kept frozen and was dissolved before analysis.

A modified protocol was later adopted to check whether aging in solution was specific to water or could happen in an organic solvent (Figure S1). A SOA fraction was first separated into three equal segments. One segment was extracted and aged in 5 mL of nano-pure water, another segment was extracted and aged in 5 mL of acetonitrile, and the last segment was placed in a freezer until analysis. The appropriate amount of nano-pure water and/or acetonitrile was added to the samples so that the final solvent was a 1:1 mixture of water and acetonitrile, resulting in a mass concentration of 50-100 μg/mL. The high-resolution mass spectrometry analysis was done as described above. A detailed list of experiments done to understand SOA aging in liquid water can be found in Table S1.

RESULTS

Composition of SOA before aging. Figure 1 (panels a,c) shows low-resolution mass spectra of the fresh α-pinene SOA before aging by exposure to water vapor, where peaks are normalized to the sum of the peak abundances in each spectrum. The mass spectra of the fresh α-pinene SOA are similar in the overall structure to previous mass spectra reported for α-pinene SOA.[30,31] The monomer (< 250 Da) and dimer regions (250-450 Da) are clearly evident in each spectrum, and correspond to products containing one and two oxygenated α-pinene units, respectively. The five most abundant monomer peaks have molecular weights of 170, 172, 184, 186, and 200 Da, which most likely correspond to pinalic acid, terpenylic acid, pinonic acid, pinic acid, and 10-hydroxypinonic acid, respectively.[37,38] The most abundant dimer peaks have molecular weights of 326, 338, 354, 368 and 370 Da, all of which were observed in previous studies, including a recent study that investigated high-molecular weight dimers esters in α-pinene ozonolysis and the boreal forest field studies in Hyytiälä, Finland.[39,40] Repeated α-pinene SOA experiments were done and analyzed using ESI-HRMS to confirm these results. The HRMS mass spectra showed similar patterns and abundant monomer and dimer peaks, so they are not shown here.

Figure 2 shows high-resolution mass spectra of the fresh α-pinene and d-limonene SOA before aging in liquid water, where peaks are normalized to the combined peak abundance. The mass spectra of the fresh α-pinene and d-limonene SOA were similar to the previous results reported

for α-pinene and d-limonene ozonolysis with distinct distribution of peaks in the monomer and dimer region in each spectrum. The high resolution of the mass spectrometer makes it possible to unambiguously determine molecular formulas but makes no distinction between isobaric compounds. Formulas corresponding to $C_9H_{14}O_3$ (pinalic and limonalic acid), $C_{10}H_{16}O_3$ (pinonic and limononic acid), $C_9H_{14}O_4$ (pinic and limononic acid) and $C_{10}H_{16}O_4$ (10-hydroxypinonic and 7OH-limononic acid) are the most abundant peaks in the monomer range, as seen in previous studies.[39–42] The most likely identities for these products appear in parenthesis next to the formulas. The three strongest peaks in the dimer range are $C_{19}H_{30}O_6$ (MW of 354), $C_{19}H_{30}O_5$ (MW of 338), and $C_{19}H_{28}O_7$ (MW of 368) for α-pinene SOA and $C_{19}H_{30}O_7$ (MW of 370), $C_{19}H_{30}O_8$ (MW of 386), and $C_{20}H_{32}O_8$ (MW of 400) for d-limonene SOA. These peaks in the dimer range have also been observed in the fresh α-pinene SOA and d-limonene SOA in previous studies.[39–41]

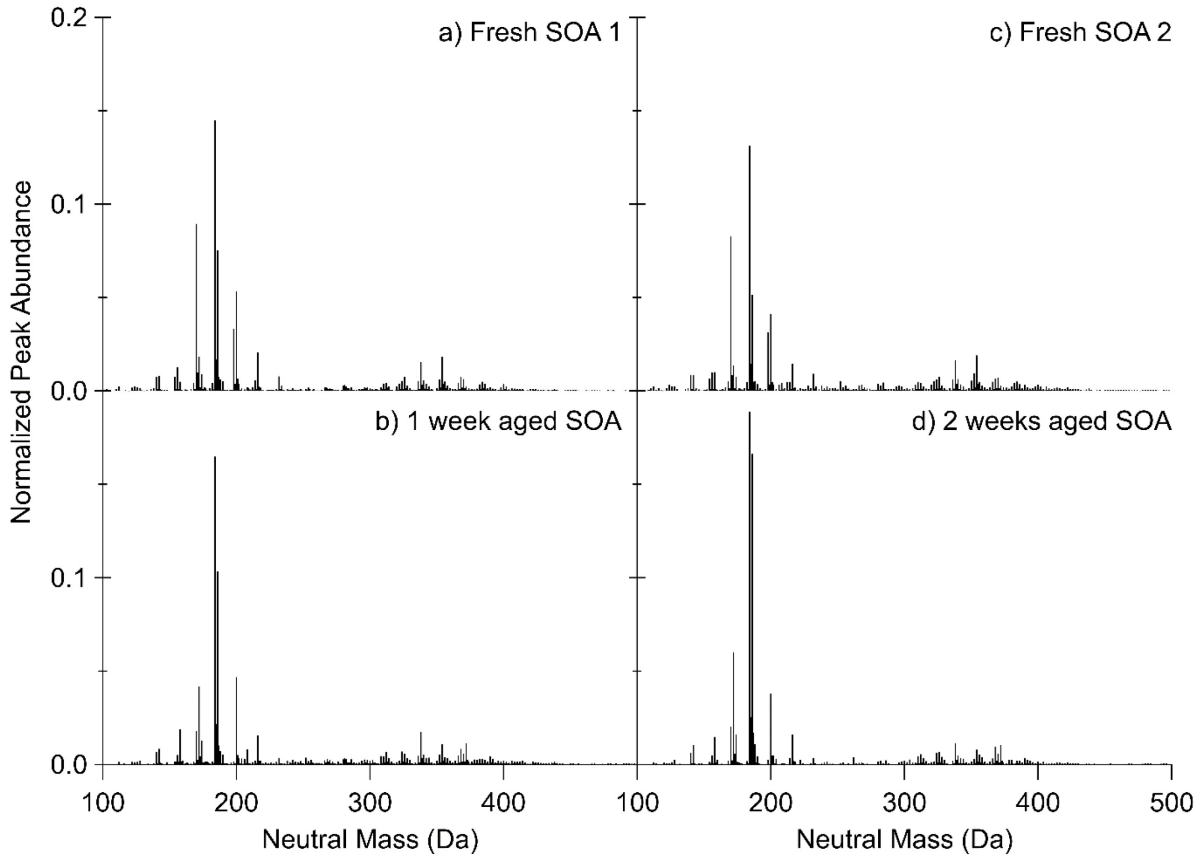


Figure 1. ESI-MS mass spectra of fresh α-pinene SOA (a,c) and α-pinene SOA in the presence of water vapor for 1 (b) and 2 (d) weeks. Peaks were normalized to the combined peak abundance.

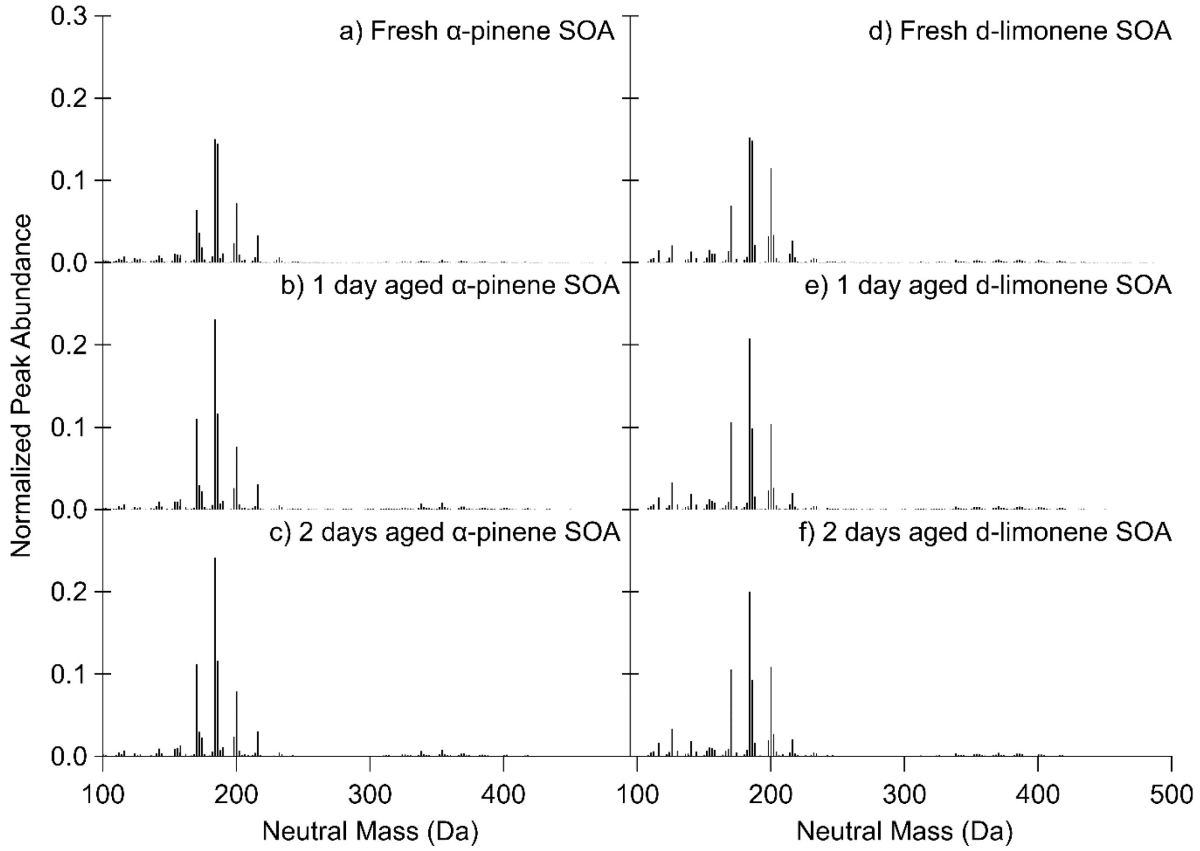


Figure 2. ESI-HRMS mass spectra of fresh α-pinene (a) and d-limonene (d) SOA and α-pinene and d-limonene SOA after aging in liquid water for 1 (b,e) and 2 (c,f) days. Peaks were normalized to the combined peak abundance.

Aging by exposure to water vapor. Comparing the fresh α-pinene SOA and aged α-pinene SOA in Figure 1 shows there are only subtle changes in the peak pattern indicating that water driven chemistry does not result in large changes in the chemical composition in α-pinene SOA, even after 2 weeks of exposure. To take a closer look at the changes in the peak patterns, difference spectra were created by subtracting the spectra of SOA before aging from the spectra of SOA after aging. The resulting difference spectra in Figure 3 confirm that aging α-pinene SOA by exposure to water vapor for 1 week and 2 weeks did not produce drastic changes in chemical composition. None of the major peaks disappeared completely, and no new major peaks appeared after aging. There is no evidence for effective hydrolysis of dimers into monomers which would have resulted in systematically negative differences in the dimer region. The peak abundances did change with a good level of reproducibility between the independently prepared 1-week and 2-week samples (panels 1 and b in Figure 3). Peaks that increased after aging had molecular weights of 172, 184, and 186 Da, which most likely correspond to terpenylic acid, pinonic acid, and pinic acid,

respectively. On the other hand, peaks at 170 and 198 Da showed slight decreases after aging for 1 and 2 weeks. A list of the major peaks that changed after aging by exposure to water vapor can be found in Table 1.

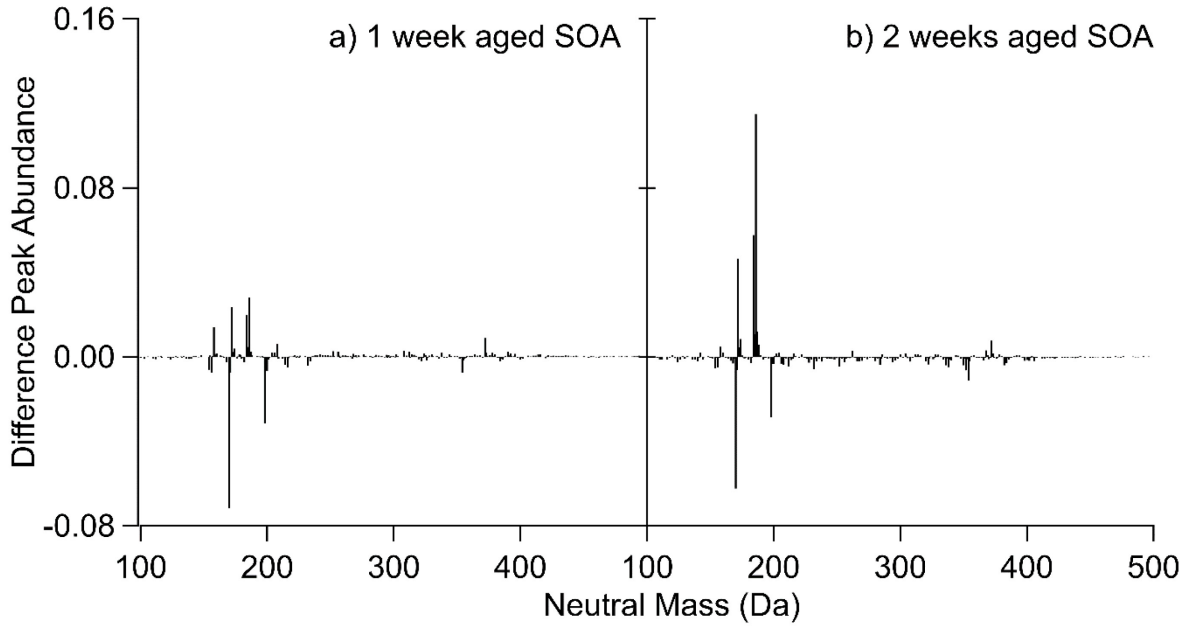
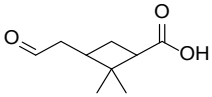
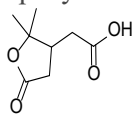
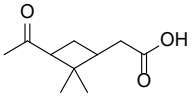
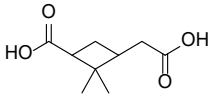
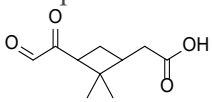


Figure 3. Difference low-resolution mass spectra of α-pinene SOA aged for 1 and 2 weeks by exposure to water vapor. Positive and negative peaks represent compounds that increased and decreased after aging by exposure to water vapor, respectively.

Table 1. Major compounds in α-pinene SOA that changed after aging by exposure to water vapor. Ratios > 1 indicate that the corresponding peak increased with aging while ratios < 1 suggest that the peak decreased after aging.

Observed MW (Da)	Likely Structure	Aged:Fresh Ratios	
		Aged for 1 Week	Aged for 2 weeks
170	Pinalic Acid 	0.20	0.25
172	Terpenylic acid 	2.30	4.38
184	Pinonic Acid 	1.14	1.44
186	Pinic Acid 	1.37	3.23
198	Oxopinonic acid 	0.05	0.08

In follow up experiments, α-pinene SOA samples were also aged in dry room-temperature conditions to serve as a comparison to aging under humid conditions. The difference high-resolution mass spectra of the fresh α-pinene SOA and aged α-pinene SOA in dry conditions (Figure S2 and S3) also indicate that the changes in peak patterns are subtle. Furthermore, peak abundances appeared to change regardless of the presence of water. For example, peaks with molecular weights of 172.074 Da ($C_9H_{14}O_3$, pinalic acid), 184.109 Da ($C_{10}H_{16}O_3$, pinonic acid), and 186.089 Da ($C_9H_{14}O_4$, pinic acid), increased by similar amounts after both dry and humid air aging. Peaks with molecular weights of 170.094 Da ($C_8H_{12}O_4$, terpenylic acid) and 198.089 Da ($C_{10}H_{14}O_4$, oxopinonic acid) decreased under both dry and humid conditions. A list of the major peaks that changed after aging in dry and humid conditions can be found in Tables S2 and S3. The oxopinonic acid peak is notable as it exhibited one of the largest changes in relative abundance decreasing by a factor of three after aging in dry air and by more than an order of magnitude after

aging in humid air. The rest of the aged:fresh ratios ranged from ~0.2 to ~4, i.e., within one order of magnitude.

Aging in liquid water. Figure 2 shows the high-resolution mass spectra of fresh α-pinene and d-limonene SOA and the corresponding mass spectra of SOA aged in liquid water for 1 and 2 days. The aged SOA still had a distinct distribution of peaks in the monomer and dimer regions in each spectrum. Comparing the fresh SOA to the aged SOA in Figure 2, the composition of the SOA did change, but the extent of the change was again relatively small. For example, the dimer region was still clearly discernable in the mass spectra. Similar to the results with the water vapor aging described above, this indicates that liquid water does not produce large chemical composition changes in dissolved SOA.

The α-pinene and d-limonene SOA products before and after aging in liquid water are compared using difference mass spectra in Figure 4. Similar to the SOA aged by exposure to water vapor, there are no drastic changes in a majority of the relative peak abundances indicating that a change in phase state of water does not result in large changes in the chemical composition of SOA. Table 2 lists the major peaks that changed after aging in liquid water for 1-2 days. $C_9H_{14}O_3$ (pinalic and limonalic acid), $C_{10}H_{16}O_3$ (pinonic and limononic acid) increased after aging in liquid water while $C_9H_{14}O_4$ (pinic and limononic acid) acid shows a slight decrease after 1-2 days. The aged:fresh relative peak abundance ratios range from 0.6 to 1.7, i.e., less than a factor of two difference. $C_8H_{12}O_4$ (terpenylic acid) decreased after aging in liquid water, but $C_8H_{12}O_4$ (limonalic acid) increased after aging in liquid water. Similarly, $C_{10}H_{16}O_4$ (10-hydroxypinonic acid) increased after aging in liquid water, but $C_{10}H_{16}O_4$ (7OH-limononic acid) deceased after aging in liquid water. However, the extent of these are relative small as the relative peak abundance ratios ranged from ~0.8-1.8.

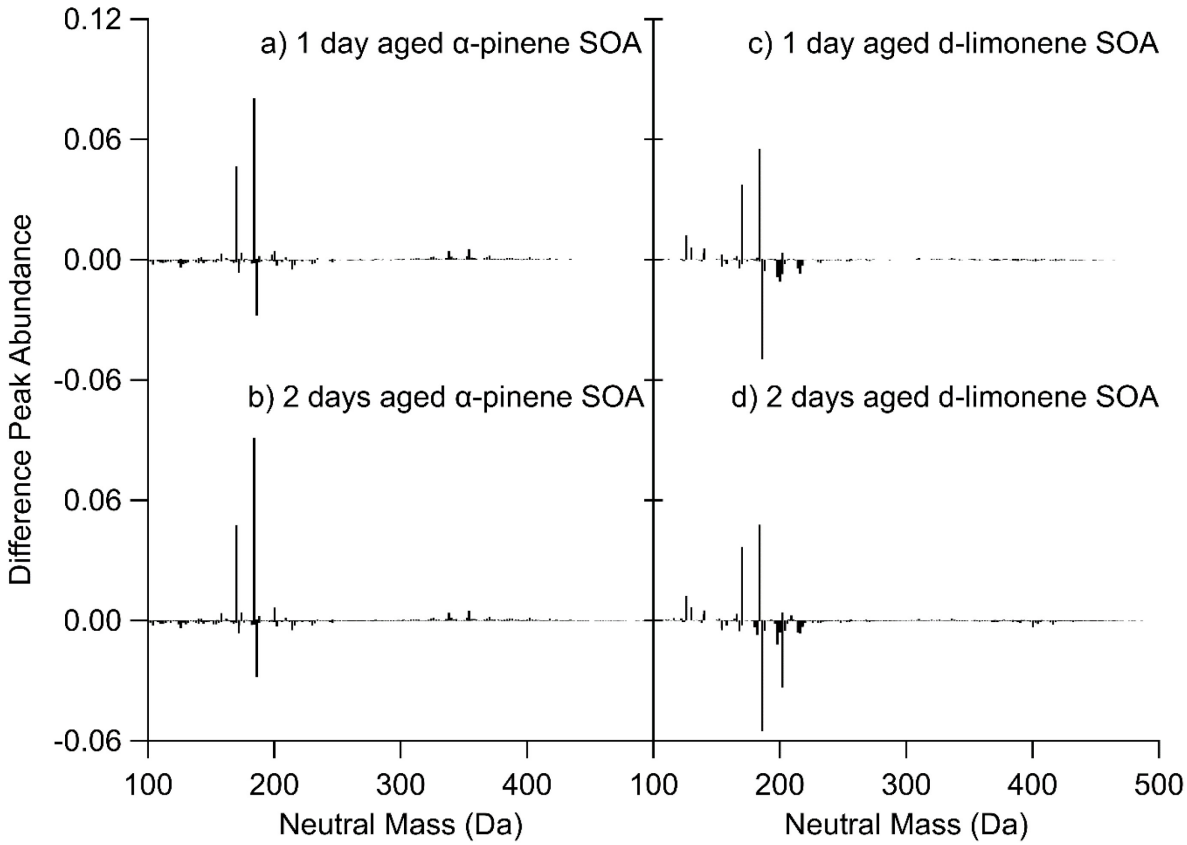


Figure 4. Difference high-resolution mass spectra of α-pinene and d-limonene ozonolysis SOA aged in liquid water for 1 and 2 days. Positive peaks represent compounds that increased after aging in water and negative peaks presents compounds that decreased after aging in water.

Table 2. Major compounds in α-pinene and d-limonene SOA that changed after aging in liquid water. Ratios > 1 indicate that the correspond peak increased with aging while ratios < 1 suggest that the peak decreased after aging.

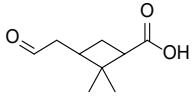
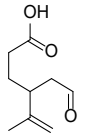
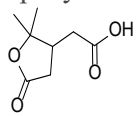
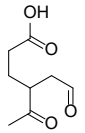
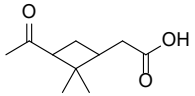
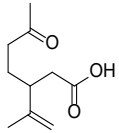
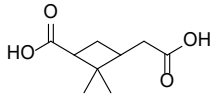
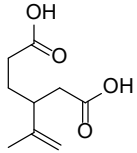
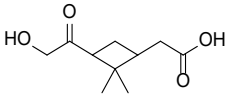
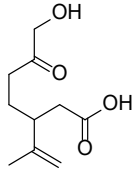
		Suggested Structures		Aged:Fresh Ratios			
Observed MW (Da)	**Molecular Formula**	**α-pinene SOA**	**d-limonene SOA**	**α-pinene SOA 1 day aged**	**α-pinene SOA 2 days aged**	**d-limonene SOA 1 day aged**	**d-limonene SOA 2 days aged**
170.094	$C_9H_{14}O_3$	Pinalic Acid 	Limonalic Acid 	1.72	1.74	1.54	1.52
172.074	$C_8H_{12}O_4$	Terpenylic acid 	Limonalic acid 	0.81	0.82	1.41	1.89
184.109	$C_{10}H_{16}O_3$	Pinonic Acid 	Limononic Acid 	1.54	1.61	1.36	1.31
186.089	$C_9H_{14}O_4$	Pinic Acid 	Limonic Acid 	0.81	0.80	0.66	0.63
200.105	$C_{10}H_{16}O_4$	10-hydroxypinonic acid 	7OH-limononic acid 	1.06	1.09	0.90	0.95

Figure S4 and S5 contrasts difference mass spectra that compare the effect of α-pinene SOA aging in acetonitrile and water. Again, the changes in peak patterns are subtle. The peak corresponding to 170.094 Da ($C_9H_{14}O_3$, pinalic acid) increased after aging in acetonitrile and compounds that had molecular weights of 184.109 Da ($C_{10}H_{16}O_3$, pinonic acid) and 186.089 Da ($C_9H_{14}O_4$, pinic acid). A list of the major peaks that changed after aging in dry conditions can be found in Table S4 and S5, with the aged:fresh relative peak abundance ratios range from 0.6 to 1.3. Of the compounds listed, pinonic acid is the most interesting one as it showed opposite effects in acetonitrile (slight decrease) and water (slight increase).

DISCUSSION

While direct infusion ESI mass spectrometric techniques are not quantitative, the absence and presence of peaks and changes in peak abundances between samples are suitable indicators of the differences in composition. The subtle changes in the mass spectra in both the SOA aged by exposure to water vapor and the SOA aged in liquid water imply that most of the compounds remained stable with respect to hydrolysis and hydration. None of the peaks were completely removed by hydrolysis and hydration, and no new major peaks appeared after aging, indicating that the distribution of compounds in the SOA stayed approximately the same between the fresh and aged samples. Major peaks in both low and high-resolution mass spectra did change as the aged SOA to fresh SOA ratio ranged between ~0.05-4. As the samples were analyzed in triplicate and the mass spectra of the replicates were reproducible, this allows relative certainty that the differences between the fresh and aged samples were due to measurable differences in the composition of the samples after aging.[43]

The mass spectra of the controls helped determine whether the changes resulted due to the presence of water vapor or liquid water or whether the changes in the mass spectra resulted from chemistry that did not need water to occur. The major peaks that changed in the SOA aged by exposure to water vapor and the SOA aged in dry air were similar. For example, compounds that had molecular weights of 172.074 Da ($C_9H_{14}O_3$), 184.109 Da ($C_{10}H_{16}O_3$), and 186.089 Da ($C_9H_{14}O_4$) increased after aging, while compounds that decreased after aging had molecular weights of 170.094 ($C_8H_{12}O_4$) and 198.089 ($C_{10}H_{14}O_4$). However, the extent of change was larger in the SOA aged by exposure to water vapor as noted by the aged:fresh ratios. The changes in the mass spectra after SOA aged in liquid water and in acetonitrile were also slightly different. For example, pinic acid

($C_9H_{14}O_4$) decreased slightly after aging in liquid water, but remained essentially unchanged after aging in acetonitrile. Additionally, the peak that corresponds to pinonic acid ($C_{10}H_{16}O_3$) increased after in liquid water but decreased after aging in acetoniltrile. This indicates that some of the differences in the fresh SOA and aged SOA in liquid water were likely due to the presence of a water. Overall, the difference mass spectra for the controls and the SOA aged by exposure to water vapor and in liquid water were relatively subtle.

Our initial hypothesis that the long term aging of SOA would lead to significant changes in the chemical composition was prompted by the findings by Romonosky et al. (2017).[31] Using direct-infusion ESI-MS, they observed that the SOA dimer region decreased by ~30% and some peaks in the monomer peaks increased by ~20-50% in the mass spectrum when leaving α-pinene SOA from ozonolysis in water undisturbed for 4 h in the dark as a control.[31] Additionally, aging the SOA in water led to a decrease in the average O:C ratio and average molecular weight, which made the SOA compounds more volatile.[31] Based on the observations of Romonosky et al., we fully expected that aging the SOA in liquid water for as long as two days should have led to a large change in the dimer and trimer region in the mass spectrum. However, in this study there were only subtle changes in the mass spectrum with the most notable changes from the monomeric compounds. The SOA generations methods from this study and the Romonosky et al. (2017) paper could potentially be responsible for the differences in results. SOA in Romonosky et al. (2017) was generated in a 5 m^3 chamber, in which ozone was in excess. In this study, SOA was generated in a flow tube reactor, in which VOC precursor was in excess. As previously mentioned, the oxidant:VOC ratio used in experiments can lead to different SOA composition with diverse physical and chemical properties. For example, in the case of d-limonene, experiments with excess d-limonene would favor a selective oxidation of the endocyclic double bond whereas experiments with excess ozone would completely oxidize both the endocyclic and exocyclic double bonds.[33] Figure S6 shows a Van Krevelen diagram of fresh a-pinene SOA from Romonosky et al. (2017) compared to this study. The size of the markers in each plot is scaled to the normalized intensity. The compounds between the two studies share similar compounds that have comparable O:C and H:C ratios. However, the main difference between the fresh a-pinene SOA is that there are higher intensities of compounds with a larger O:C in Romonosky et al. compared to this study indicating that the sample was more oxygenated. Again, this likely due to initial conditions used in SOA formation, in which VOC was in excess in this study and ozone was in excess in the Romonosky

et al. rather than aging in the presence of ozone as the composition of α-pinene ozonolysis SOA remains pretty stable after oxidative aging.[44,45] Many reactions are accelerated in acidic environments. For example, aldol condensation, polymerization, gem-diol reactions, dehydration, and esterification are catalyzed by acids and results in oligomers and dimers. Due to the nature of the excess oxidant environment in which the chamber was ran, the SOA that was collected most likely had higher fraction of carboxylic acids, which would explain the higher of compounds with a larger O:C illustrated in Figure S6. Thus, the high fraction of carboxylic acids would lower the pH when the sample was dissolved in water and therefore promoting acid catalyzed reactions leading differences in the mass spectra when aged in water. Additionally, other studies have shown the initial concentration of oxidant and VOC can lead to disparities in mass concentrations and ROS profiles, which could indicate that the SOA compositions are not the same.[34,35] Both studies are atmospherically relevant. Romonosky et al. is more applicable to the outdoor atmosphere, in which SOA is formed in a VOC-limited environment. This study, on the other hand, pertains mostly to the indoor atmosphere. The off gassing by wood products as well as the increase use of terpenoids in cleaning products and air fresheners would results in elevated concentrations of these compounds that exceeds the concentration of ozone.[46–48] Due to differences in initial conditions, it likely that the composition of SOA used in this study and the Romonosky et al. (2017) differ, which could results in varying degrees of hydrolysis and hydration.

D'Ambro et al. (2018), examined isothermal evaporation of α-pinene ozonolysis SOA by collecting a spot of SOA material on a filter, leaving the material exposed to a flow of humidified nitrogen at room temperature for up to 28 h, and then examining the chemical composition of the remaining material by thermal desorption mass spectrometry.[49] They observed significant loss of SOA compounds from the filter, with 50-70% of organics lost after 24 hours. Unlike previous studies of SOA particle evaporation rates, which were shown to be strongly affected by RH, D'Ambro et al. observed only a weak dependence of the SOA material loss rate on RH, which could be specific to filter-based aging experiments because it takes longer for collected SOA on the filter to take up water.[49] While most of their observations could be explained by evaporation, they had to assume that oligomers in SOA can reversibly decompose with decompaction rates ranging from 10^{-5} to 10^{-4} s^{-1} depending on the method of SOA preparation. Our aging experiments were carried out in small sealed volumes to help suppress evaporation, but it is likely that some evaporative loss took place in our vapor aging experiments. To account for that, we normalized

the mass spectra to highlight relative changes in composition after aging. Our observations support the general conclusions of D'Ambro et al. (2018) that exposure to water vapor does not have a strong effect on the composition of the SOA (evaporative loss is more important). The control experiments, in which SOA was exposed to dry instead of humid air, produced comparable changes in mass spectra to those under humid conditions.

SUMMARY AND IMPLICATIONS

Different forms of water including water vapor, aerosol liquid water, organic-phase water, and cloud and fog water can promote reactions that result in changes in chemical properties within SOA. This environment is particularly important when understanding the aging of compounds in aerosols which spend days to weeks in the atmosphere. We analyzed the effect long-term aging has on the chemical composition of model SOA prepared by ozonolysis of α-pinene and d-limonene. Our initial expectation was that aging SOA derived from ozonolysis by exposure to water vapor and liquid water would result in changes in the monomeric and dimeric compounds through hydrolysis and hydration of oligomeric compounds. While the presence of water lead to changes in the chemical composition of these aerosols, the extent of these changes was relatively small, suggesting that hydrolysis and hydration is not a major aging mechanism in the atmosphere (at least for these types of SOA). Further investigation on the pH dependence of hydrolysis and hydration reactions in SOA are next logical step in the study.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on XXX at DOI:XXXX. It contains a summary of all aging experiments (Table S1), an illustration of the aging protocol (Figure S1), difference HRMS for α-pinene SOA aged under dry and humid conditions (Figure S2, S3 and Tables S2, S3), difference HRMS for α-pinene SOA aged in liquid acetonitrile and water (Figure S4, S5 and Tables S4, S5), and a Van Krevelen diagram of fresh a-pinene SOA (Figure S6).

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Author Contributions

The experiments and data analysis were conceived by CW and SAN, and carried out by CW and DV. The manuscript was written by CW with contributions from all the co-authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

This work was supported by US National Science Foundation grant AGS-1853639. CW acknowledges support from the Ridge to Reef NSF Research Traineeship, award DGE-1735040. The high-resolution mass spectrometer instrument used in this work was purchased with grant NSF CHE-1920242, and the low resolution mass spectrometer was purchased with grant NSF CHE-1337080. The authors thank Natalie R. Smith for help with using the high-resolution mass spectrometer.

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