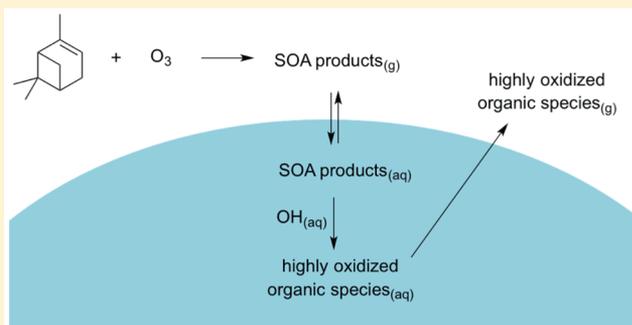


Effects of Condensed-Phase Oxidants on Secondary Organic Aerosol Formation

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S Supporting Information

ABSTRACT: In this study we investigate the hypothesis that oxidants present within atmospheric particles can promote the formation of highly oxidized organic aerosol (OA) via oxidation reactions in the condensed phase. Secondary organic aerosol (SOA) was generated from the ozonolysis of α -pinene and isoprene in an environmental chamber, with seed particles systematically varied in order to assess the effects of condensed-phase oxidant levels on SOA loading and composition. The effects of particle phase (aqueous vs dry), condensed-phase oxidant source (none vs H_2O_2 vs Fenton chemistry), and irradiation (none vs UV) were all examined. For experiments conducted with aqueous particles but without any added oxidants, UV irradiation resulted in a small but measurable enhancement in the oxygen-to-carbon ratio (O/C). OA formed in the presence of aqueous oxidants was substantially more oxidized, with the highest oxidant concentrations leading to OA with an O/C as high as 1.4 for α -pinene and 2.0 for isoprene, strongly suggesting the formation of oxalate. High aqueous oxidant levels also resulted in increased loss of carbon from the condensed phase. This OA was more oxidized than in any other ozonolysis experiment reported to date, indicating that, when present, aqueous oxidants can have a dramatic effect on SOA formation. However, oxidant concentrations within atmospheric aqueous particles remain poorly constrained, making it difficult to assess the impacts of aqueous-phase oxidation on the loadings and oxidation state of atmospheric OA.



INTRODUCTION

A significant fraction of atmospheric organic aerosol (OA) is made up of highly oxidized material.^{1–3} Ambient measurements indicate that this highly oxidized OA can form rapidly in the atmosphere, over time scales of ~ 1 – 3 days.⁴ However, laboratory and model studies typically have difficulty reproducing the rapid formation of highly oxidized OA from traditional gas-phase oxidation.^{2,3} Models aimed at reproducing the formation of OA as measured in field studies tend to predict aerosol that is less oxidized than ambient secondary OA (SOA) at a given loading,^{5–7} or that requires formation time scales longer than those observed in the field.⁸ Similarly, most laboratory experiments are unable to generate highly oxidized OA from gas-phase oxidation at atmospherically relevant oxidant exposures.^{3,9–11} One exception is the recent observation of the rapid formation of highly oxidized, extremely low-volatility organic compounds formed from multiple RO_2 isomerization reactions.^{12,13} However, such a mechanism is unlikely to account for the gradual aging observed in field studies,¹ suggesting that other mechanisms also play a role in the formation of highly oxidized OA in the atmosphere.

One potential pathway for the formation of highly oxidized OA involves the further oxidation of condensed-phase organic species, such as those in the atmospheric aqueous phase (e.g.,

deliquesced particles).^{14–17} It is well-established that the chemistry of atmospheric particulate matter may be influenced by the presence of aqueous oxidants, such as the hydroxyl radical (OH), which can be taken up from the atmosphere or chemically formed from processes such as photolysis of nitrate, nitrite, or hydrogen peroxide (H_2O_2), or Fenton-type reactions between H_2O_2 and Fe(II) .^{14,17–21} Recently, experiments conducted in bulk aqueous solutions have shown that the oxidation of water-soluble species by aqueous hydroxyl radicals leads to the rapid formation of highly oxidized organic material.^{22–28} More recently, oxidation within submicron particles has also been shown to affect OA loadings and composition. The presence of condensed-phase oxidants (generated from Fenton chemistry) leads to decreased SOA yields,^{29,30} but also increases the oxidative uptake of gas-phase species.³¹ Recently we oxidized single-component aqueous organic aerosol particles using Fenton chemistry,²² and found evidence for multiple generations of aqueous oxidation, as well

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Table 1. Reaction Conditions and Results for All SOA Experiments

expt	precursor	seed	% RH	initial O/C	Δ O/C after H ₂ O ₂ ^a	Δ O/C after UV ^b	yield			carbon yield		
							initial	after H ₂ O ₂	after UV	initial	after H ₂ O ₂	after UV
1	α -pinene	dry AS	<11	0.69	(0.02) ^c	0.02	0.27	(0.26) ^c	0.25	0.17	(0.16) ^c	0.15
2	α -pinene	dry AS	<5	0.59	0.01	0.01	0.26	0.26	0.25	0.18	0.18	0.17
3	α -pinene	aq AS	74–77	0.59	(0.01) ^c	0.05	0.19	(0.16) ^c	0.16	0.13	(0.11) ^c	0.10
4a	α -pinene	aq AS	84–87	0.62	–0.01	0.09	0.18	0.15	0.14	0.12	0.10	0.09
4b ^d	α -pinene	aq AS	74–77	0.56	0	0.07	0.16	0.13	0.12	0.11	0.09	0.08
5	α -pinene	dry FS	<4	0.76	0.06	0.04	0.13	0.13	0.08	0.08	0.07	0.04
6	α -pinene	aq FS	79–83	1.08	(0.07) ^c	0.05	0.12	(0.12)	0.06	0.06	(0.06) ^c	0.03
7	α -pinene	aq FS	83–86	1.15	0.20	–0.07	0.12	0.11	0.02	0.06	0.05	0.01
8	isoprene	dry AS	<11	0.81	<i>e</i>	0.01	0.038	<i>e</i>	0.036	0.022	<i>e</i>	0.021
9	isoprene	aq FS	70–77	1.60	0.37	–0.75	0.020	0.023	0	0.007	0.007	0

^aRelative to initial O/C. ^bRelative to O/C after H₂O₂ addition. ^cParentheses indicate experiments to which H₂O₂ was not added; for these, reported values indicate measurements taken at the same time point as in the experiments with added H₂O₂. ^dReplicate of expt 4a. ^eUV irradiation was initiated earlier than in expt 9, so there is no dark “after H₂O₂” measurement taken at the same time point as in expt 9.

as the partitioning of oxidation intermediates out of the condensed phase. As a result of all these studies, it is clear that chemistry within the aqueous phase can be an efficient pathway for the formation of highly oxidized organic material in simple model systems. However, the role that such reactions play in aerosol formation in the ambient atmosphere is unclear, given complexities associated with gas–particle partitioning, oxidant levels and distributions, and the large number of organic species present.

Here we expand our previous work on aqueous oxidation to more atmospherically relevant OA systems, spanning a broader range of condensed-phase oxidation conditions. Rather than starting with a single organic molecule in the condensed phase, we generate SOA (a complex mixture of condensable products) from the gas-phase ozonolysis of biogenic VOCs. As in our previous work, aqueous oxidation is carried out within deliquesced submicron particles, which provide partitioning conditions that are more representative of the atmosphere than bulk aqueous solutions.²² The oxidant levels within the particles, as well as the phase of the particles, are systematically varied by the use of different seed types and reaction conditions, whereas the gas-phase oxidants are kept constant. Condensed-phase oxidation of the SOA is examined using a number of schemes, including not only Fenton chemistry, which was recently studied by Chu et al.,^{29,30} but also UV irradiation, H₂O₂, and H₂O₂ + UV. Measurements focus on the effect of condensed-phase oxidation on the chemical composition of the aerosol, specifically the degree of oxidation of the particulate carbon, as well as on aerosol yield (the fraction of carbon in the condensed phase at the end of the experiment). We emphasize that while particle-phase oxidant levels are varied by specific changes to photochemical conditions (e.g., UV irradiation, H₂O₂ addition, and initiation of Fenton chemistry), our goal is not to investigate the detailed effects of these specific mechanisms under atmospheric conditions. Instead, the primary objective of this study is to examine the overall effect that oxidation occurring within aerosol particles can have on the amount and the degree of oxidation of particulate carbon.

MATERIALS AND METHODS

SOA was formed from the ozonolysis of biogenic hydrocarbons (α -pinene and isoprene) under a number of different seed and humidity conditions, allowing for the systematic variation of

oxidant levels within the particles. Gas-phase oxidative conditions were kept essentially constant from experiment to experiment, ensuring that any differences in chemistry were driven by differences in condensed-phase oxidation only. As described below, parameters that were varied include the phase of the particles (aqueous vs dry, via the variation of relative humidity, RH), (2) the source of condensed-phase oxidants (none vs H₂O₂ vs Fenton chemistry), and (3) irradiation (dark vs UV lights). The conditions for each experiment, provided in Table 1, are described in detail below.

Experimental Setup. The reactor and experimental protocols have been previously described elsewhere.²² Here we briefly highlight key features and important changes for this present study. All experiments were carried out in the MIT chamber, a 7.5 m³ Teflon bag run in semibatch mode at 20 °C, filled with pure compressed air (Aadco), with relative humidity (RH) controlled by a bubbler containing Milli-Q water. Deliquesced seed particles were introduced by directly atomizing a 1 g L^{−1} solution of either ammonium sulfate (AS, Sigma-Aldrich, >99.0%) or iron(II) sulfate heptahydrate (FS, Alfa Aesar, >99.999% metals basis) into the chamber for 0.5–1 h. This generated a seed volume of between 5.5 × 10¹⁰ and 1.7 × 10¹¹ nm³ cm^{−3}, depending on the RH and seed type. During atomization, 20 ppb of (−)- α -pinene (1.0 μ L, Sigma-Aldrich, 98%) or 400 ppb of isoprene (13.5 μ L, Sigma-Aldrich, 99%) was injected through a septum into a 1/4 in. o.d. stainless steel line with ~1 LPM of clean air flow. A nonreactive dilution tracer (2.0 μ L of hexafluorobenzene, Sigma-Aldrich, >99%) was also injected. After an initial mixing time of at least 20 min, SOA formation was initiated by introduction of an excess of ozone (80–100 ppb for α -pinene, ~900 ppb for isoprene), generated by sending 1.5 LPM of clean air through a corona discharge ozone generator (Enaly). This also generated a small amount of NO_x (<5 ppb for α -pinene, <25 ppb for isoprene). An OH scavenger was not used in these experiments. For some experiments (nos. 2, 4a, 4b, 5, 7, and 9), once the SOA precursor had reacted away (~3 h for α -pinene, ~5 h for isoprene), hydrogen peroxide (6.0 μ L of 30% w/w H₂O₂ in water, Alfa Aesar) was added to the gas phase, for an estimated concentration of ~270 ppb in the gas phase and (assuming Henry's Law partitioning) ~27 mM H₂O₂ in the aqueous particles.³² Aqueous [H₂O₂] may be somewhat different from this value, but any deviations from Henry's Law partitioning are not expected to significantly impact the conclusions of this

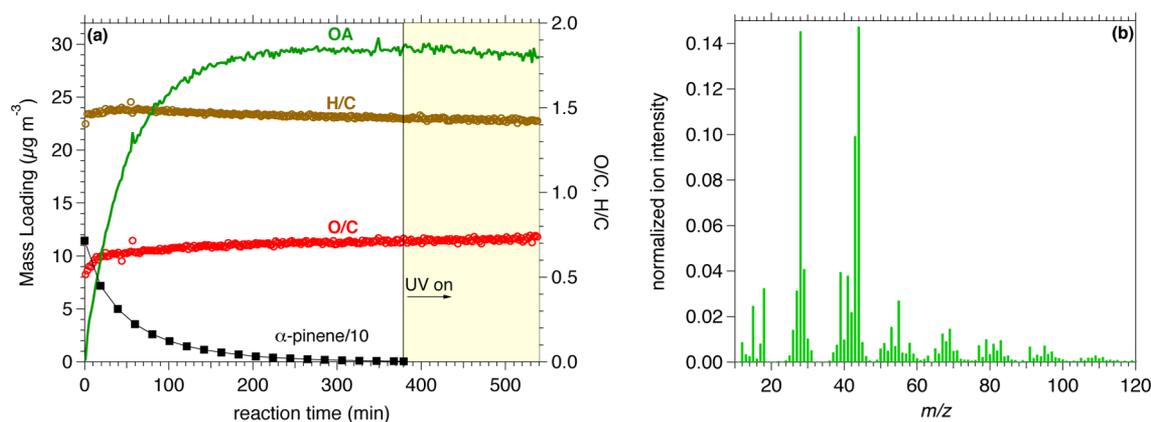


Figure 1. Results for the baseline experiment, formation of SOA from ozonolysis of α -pinene in the presence of dry AS seed (expt 1): (a) mass concentrations of organic aerosol and α -pinene, and SOA elemental ratios; (b) average organic aerosol mass spectrum.

work. The purpose of the H_2O_2 addition was to initiate Fenton chemistry, as in our previous study;²² however, as described in the [Results and Discussion](#) section, it was found that H_2O_2 is not necessary to initiate such chemistry, and therefore, it was added only for some experiments. Once the reactions appeared to have gone to completion (~ 6 h for α -pinene, ~ 10 h for isoprene), two banks of 24 black lights were turned on to assess the photoreactivity of the reaction products and the effects of any condensed-phase photochemistry.

Instrumentation. A high-resolution time-of-flight aerosol mass spectrometer (AMS, Aerodyne Research Inc.) was used to measure the aerosol chemical composition, and a scanning mobility particle sizer (SMPS, TSI Inc.) was used to measure the aerosol size distribution, volume, and number concentration. All reported AMS data were collected in V-mode. Concentrations of α -pinene, isoprene, and hexafluorobenzene were monitored using gas chromatography with flame ionization detection (GC-FID, SRI). We also monitored NO_x (Horiba Inc.), ozone (2B Tech), and temperature and relative humidity (Vaisala).

The AMS measures the total mass of chemical families, such as organic, sulfate, and ammonium,^{33,34} as well as the elemental composition of the organic aerosol, namely, the hydrogen-to-carbon ratio (H/C) and the oxygen-to-carbon ratio (O/C).^{35,36} All H/C and O/C values reported here were calculated using the recently developed “improved-ambient” method.³⁷ The SOA mass yield (Y) and carbon yield (Y_C) are calculated from eqs 1 and 2, respectively

$$Y = \frac{\Delta c_{\text{OA}}}{\Delta \text{HC}} \quad (1)$$

$$Y_C = \frac{\Delta c_{\text{OC}}}{\Delta \text{HC}_C} = \frac{12\Delta c_{\text{OA}}}{(12 + 16\text{O/C} + \text{H/C})\Delta \text{HC}_C} \quad (2)$$

in which Δc_{OA} and Δc_{OC} are the wall-loss- and dilution-corrected increases in organic aerosol mass concentration (discussed below) and organic aerosol carbon mass concentration, and ΔHC and ΔHC_C are the dilution-corrected decreases in the total mass concentration and carbon mass concentration of the reacted hydrocarbon (α -pinene or isoprene). The wall-loss corrections do not include loss of vapors to the Teflon chamber walls, and therefore, our yields may be underestimated somewhat. An accurate determination of Δc_{OA} is challenging because of uncertainties in the particle seed density, hygroscopicity, and AMS collection efficiency of

FS particles (all of which are likely to be different than those of AS), as well as the relative detection of water in the AMS and SMPS. Details of the determination of Δc_{OA} from SMPS and AMS data in light of these complications are given in the [Supporting Information](#). The hydrocarbon concentration is corrected for dilution using the measured hexafluorobenzene decay rate,³⁸ and particle concentrations are corrected for wall loss and dilution using a fitted decay rate (see SI).³⁹ The GC-FID calibration factors were determined by averaging the peak area across experiments conducted within a given time period and setting it equal to the initial concentration ($114 \mu\text{g m}^{-3}$ for α -pinene or $1135 \mu\text{g m}^{-3}$ for isoprene).

RESULTS AND DISCUSSION

Experimental conditions and key results for each experiment are provided in [Table 1](#). Experiments 1–7 used α -pinene as the SOA precursor, oxidized in the presence of dry AS seed (expts 1–2), aqueous AS seed (expts 3–4), dry FS seed (expt 5), or aqueous FS seed (expts 6–7). Experiments 8 and 9 used isoprene as the precursor, in the presence of dry AS seed (expt 8) or aqueous FS seed (expt 9). All “dry” experiments were run at $\text{RH} < 11\%$, below the efflorescence RH of AS, ensuring the seed particles were solid; “aqueous” experiments were run at $70\% < \text{RH} < 87\%$, above the deliquescence RH, ensuring that seed particles contained liquid water. The level of oxidation of the OA is described in terms of O/C, for the straightforward comparison with other studies. Other metrics for oxidation, namely H/C and the average carbon oxidation state ($\overline{\text{OS}}_C \approx 2 \times \text{O/C} - \text{H/C}$), exhibit similar changes; values are given in the [Supporting Information](#). The “initial” values in [Table 1](#) for O/C, yield, and carbon yield were measured just prior to the addition of H_2O_2 ($t = 3$ h for α -pinene, $t = 5$ h for isoprene). Also given are the yield, carbon yield, and change in O/C 3–5 h after the addition of H_2O_2 ($t = 6$ h for α -pinene, $t = 10$ h for isoprene), and then 3–5 h after UV irradiation ($t = 9$ h for α -pinene, $t = 15$ h for isoprene). Measurements for those experiments in which H_2O_2 was not added are indicated by parentheses. Some replicates (e.g., expts 4a and 4b) were carried out in order to examine the run-to-run variability between experiments, which in some cases was found to exceed the measurement variability within a given experiment. This is likely the result of small unintentional differences in experimental conditions (e.g., seed concentrations, RH, or flushing time) between replicates; however, these differences do not affect the overall results.

α -Pinene SOA with Dry AS Seed. Results for expt 1 (the ozonolysis of α -pinene in the presence of dry AS) are shown in Figure 1. SOA formation in this experiment occurs in the absence of any added condensed-phase oxidants, and therefore represents the baseline degree of oxidation against which other experiments are compared. Figure 1a shows the mass concentrations of α -pinene and SOA, as well as the O/C and H/C of the SOA, and Figure 1b shows the organic mass spectrum of the SOA. Oxidation begins immediately following the addition of ozone ($t = 0$), producing SOA with an O/C of ~ 0.7 , and H/C of ~ 1.5 . This is more oxidized than SOA generated from α -pinene ozonolysis in previous studies,^{3,37} possibly due to differences in oxidative conditions (such as the VOC/O₃ ratio or the use of an OH scavenger). However, this difference does not affect the relative enhancement in oxidation between experiments, nor the overall conclusions of this work. Most of the α -pinene reaction and SOA formation is completed within ~ 3 h. Exposure to UV light leads to no appreciable change to the elemental ratios or organic mass loading. In a similar experiment in which ~ 270 ppb H₂O₂ was added prior to UV irradiation (expt 2), a similar degree of oxidation was observed (Table 1), again with no change to O/C upon UV exposure. This indicates that photolysis of gas-phase H₂O₂ has no measurable effect on the SOA generated. (SOA experiments that use H₂O₂ as an OH source generally involve concentrations of H₂O₂ that are at least 10 times higher than the present levels;⁴⁰ the lower concentrations here likely explain the lack of any observed oxidation.) These two dry AS experiments have the highest measured yields of all the α -pinene experiments. These are higher (by nearly a factor of 2) than previously reported yields for α -pinene ozonolysis at this range of OA loadings;^{36,37} again, this may be a result of different experimental conditions, such as higher seed concentrations or the absence of an OH scavenger.

α -Pinene SOA with Aqueous AS Seed. Experiments 3, 4a, and 4b probed the formation of SOA in the presence of aqueous AS seed. Experiment 3 differed from expts 4a and 4b in that it involved no addition of H₂O₂; expts 4a and 4b were replicates in order to assess run-to-run variability. Results show some variability, with initial O/C and yield values differing by $\sim 10\%$. However, the absolute changes to these values upon addition of H₂O₂ or UV are essentially the same in both cases, indicating that this variability does not affect the observed aging chemistry.

In all cases (expts 3, 4a, and 4b), the initially formed SOA had, to within the apparent run-to-run variability, the same degree of oxidation as in the dry case. However, unlike with dry AS, there was an increase in O/C upon exposure to UV. This can be seen in Figure 2a, which shows O/C before and after UV irradiation for all the AS seed experiments. It is clear from Figure 2a that UV increases the rate of oxidation in the aqueous AS experiments, but has no effect in the dry AS experiments. This is likely due to the UV-initiated production of aqueous oxidants from the photolysis of SOA molecules⁴¹ or other ozonolysis products. For example, organic peroxides, which can generate OH radicals upon photolysis, make up ~ 20 – 50% by mass of α -pinene ozonolysis SOA.^{42,43} The increase in O/C was greater when H₂O₂ was added (expts 4a and 4b), presumably because of additional oxidant formation from the photolysis of aqueous H₂O₂ to OH. Because H₂O₂ did not enhance oxidation in the dry AS experiment, it is unlikely that gas-phase oxidants are responsible for this increased oxidation.

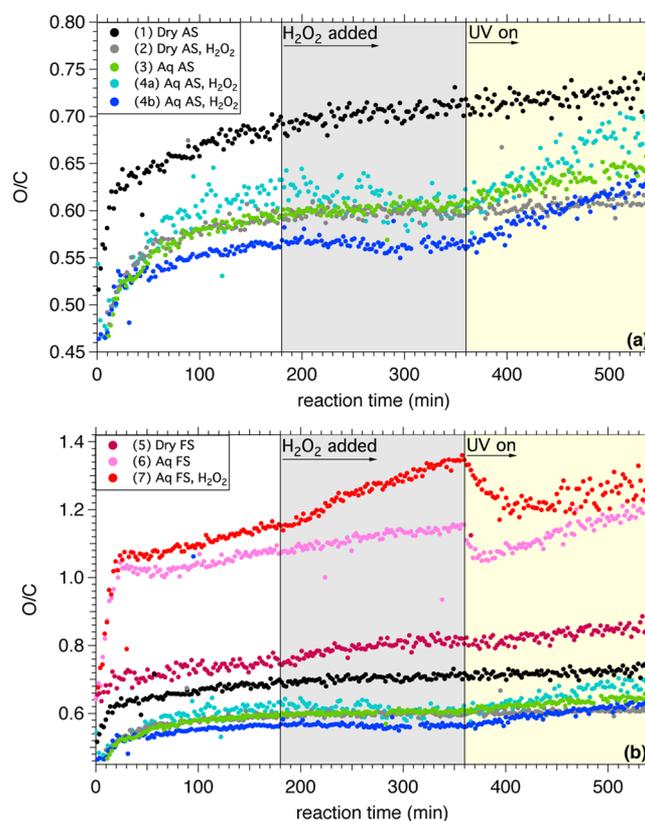


Figure 2. Effect of H₂O₂ addition and UV irradiation on O/C for α -pinene ozonolysis experiments: (a) AS seed only (expts 1–4b), (b) image zoomed out to show all α -pinene ozonolysis experiments (AS seed and FS seed, expts 1–7).

The SOA yields in the presence of aqueous AS seeds are ~ 35 – 50% lower than those in the presence of dry AS seeds. This might result from a loss of water from the aqueous particles upon dissolution of the condensable organic species. Since the yield calculations assume no change in particulate water content during an experiment (see SI), this lower particle volume would be assumed to be from a smaller amount of condensed organic material, and thus result in an underestimate of yield for the aqueous AS experiments. Cocker et al. also measured lower yields for α -pinene ozonolysis with aqueous AS than with dry AS.⁴⁴ This may also have resulted from changes in particulate water, which were not directly measured in that experiment.

α -Pinene SOA with Aqueous FS Seed. As shown in Table 1 and Figure 2b, the SOA formed in the presence of aqueous FS seed (expts 6 and 7) is dramatically more oxidized than the SOA formed with AS seed. Figure 3a shows the mass concentration of OA and α -pinene, and the OA elemental ratios for expt 6. Prior to UV irradiation, the organic material reaches an O/C > 1.1 and H/C < 1.1 , with a mass spectrum (Figure 3b) dominated by m/z 44 (CO₂⁺), an ion fragment that indicates the presence of highly oxidized species. Blank experiments demonstrate that this high level of oxidation is not influenced substantially by background organic material in the chamber or seed (see Supporting Information). UV irradiation leads to a rapid loss of organic material from the condensed phase, likely from the photolysis of oxidation products to smaller volatile species, which then partition out of the condensed phase. The initial sharp decline in O/C upon UV irradiation suggests that the products undergoing

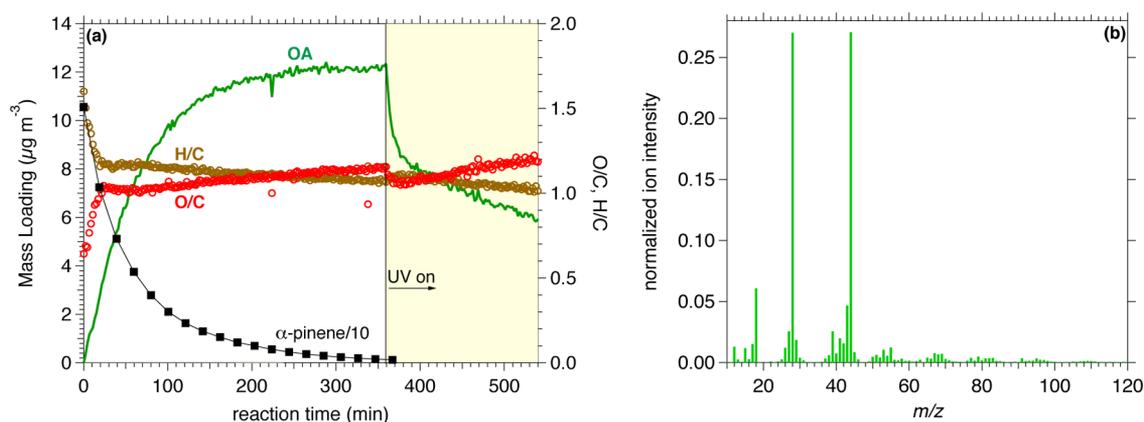


Figure 3. Results for the formation of SOA from ozonolysis of α -pinene in the presence of aqueous FS seed (expt 6): (a) mass concentrations of organic aerosol and α -pinene, and SOA elemental ratios, and (b) average organic mass spectrum prior to UV irradiation.

photolysis are the most highly oxidized species. Both the organic mass spectrum (Figure 3b) and the rapid decay of OA mass during irradiation are consistent with the presence of oxalate,^{45,46} which is both highly oxidized (O/C = 2) and subject to rapid photolysis when present as an iron(III) complex.⁴⁷ Oxalate also appeared to be a major product in our earlier study of the aqueous-phase oxidation of polyols,²² and has been measured in various oxidation studies involving bulk aqueous solutions,^{23,27,48} underscoring its importance as an aqueous-phase oxidation product. Following the initial decline, O/C begins to rise, indicating that UV in the FS experiments also leads to increased concentrations of aqueous oxidants, possibly from photo-Fenton chemistry, leading to further oxidation of the nonoxalate particulate organic species.

For the first 3 h of oxidation, the conditions in expts 6 and 7 were identical. Therefore, the differences in initial O/C (1.08 vs 1.15) are again attributed to run-to-run variability, likely from minor differences in experimental conditions (e.g., from differences in seed loadings or water content). Regardless, the addition of H_2O_2 in expt 7 appears to accelerate the oxidation chemistry (Figure 2b), increasing the rate at which O/C rises, and leading to a higher degree of oxidation and a greater loss of organic material upon photolysis. To our knowledge, the SOA generated in expts 6 and 7 is more oxidized than that from any other ozonolysis system reported to date, including those in which the SOA was further aged.^{3,9,11,49}

The immediate production of highly oxidized organic material indicates that aqueous oxidants are generated as soon as SOA formation begins, in high enough concentrations that the condensed-phase oxidation is rapid relative to the initial gas-phase chemistry (i.e., with ozonolysis as the rate-limiting step). In order to better characterize the oxidative conditions within the particles, we repeated expt 7 with an aqueous OH tracer (adonitol, a C5 polyol) added to the seed particles. (Details of this experiment are given in the Supporting Information.) With the assumption that the dominant aqueous oxidant is the hydroxyl radical, and with k_{OH} of $1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$,¹⁸ the rate of adonitol decay implies a maximum $[\text{OH}]_{\text{aq}}$ of $\sim 3.3 \times 10^{-13} \text{ M}$ during ozonolysis, and $\sim 2.5 \times 10^{-12} \text{ M}$ after the addition of H_2O_2 . These correspond to high aqueous-phase concentrations ($>10^8$ molecules OH per cm^3 solution), which are consistent with some modeled values of $[\text{OH}]_{\text{aq}}$ in ambient deliquesced particles ($\sim 10^{-12} \text{ M}$),¹⁸ but much higher than the concentrations inferred in other studies

($\sim 10^{-15} \text{ M}$).^{17,19} This uncertainty in ambient $[\text{OH}]_{\text{aq}}$ is discussed in the Conclusions section.

The rapid, immediate oxidation of the SOA upon the addition of ozone also indicates that Fenton-type chemistry can occur even in the absence of H_2O_2 . Such chemistry requires the presence of an oxidant, which could be either the ozone used to drive the SOA-formation chemistry, or reactive oxygen species (ROS) generated in the ozonolysis reaction. To investigate these two possibilities, an additional experiment was run in which ozone and aqueous particles composed of FS and erythritol were added to the chamber; since erythritol does not react with ozone, only ozone (and not ozonolysis products) is available to initiate Fenton-type chemistry. No oxidation of erythritol was observed, indicating that the Fenton-type chemistry occurring in the α -pinene experiments was initiated by ROS produced by ozonolysis, such as HO_2 , RO_2 , ROOH , or stabilized Criegee intermediates. A proposed general reaction scheme for the ozonolysis of α -pinene in the presence of FS seed is shown in Figure 4.

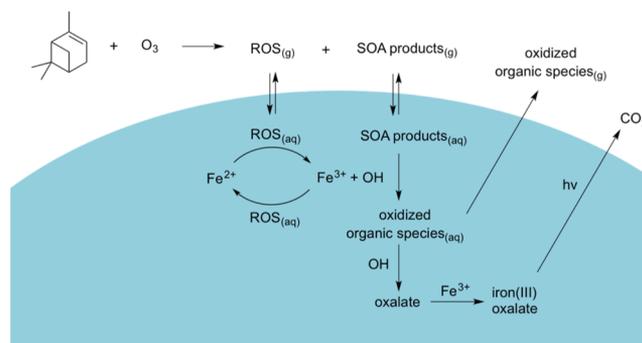


Figure 4. Proposed reaction scheme for ozonolysis of α -pinene in the presence of aqueous FS seed. Following the gas-phase reaction of ozone and α -pinene, water-soluble organic products and reactive oxygen species (ROS) partition into the condensed phase. ROS react with dissolved Fe(II) to initiate Fenton-type chemistry and produce aqueous hydroxyl radicals (OH). The organic products then undergo further oxidation by OH within the particles. Some of this oxidation leads to smaller volatile products that partition out of the particles. Oxalate is retained in the condensed phase due to complexation with iron; the iron(III) oxalate complex (and possibly other oxidized products as well) undergoes photolysis to gas-phase products. The addition of H_2O_2 accelerates the formation of highly oxidized OA by increasing $[\text{ROS}]$ and therefore the rate of $[\text{OH}]_{\text{aq}}$ production.

α -Pinene SOA with Dry FS Seed. In order to determine the effect of FS in dry aerosol, an additional experiment was conducted with FS seed and H₂O₂ at low RH (expt 5). This represented an intermediate case, with SOA that is somewhat more oxidized than for dry AS seed, but still substantially less oxidized than for aqueous FS seed (Table 1, Figure 2b). As with the aqueous FS experiment, UV irradiation led to some loss of organic mass from the condensed phase, suggesting that some oxidized photolabile products had been formed. However, the lower degree of oxidation relative to the aqueous FS experiments points to the importance of the aqueous phase for the generation of oxidants. The exact reason for the higher level of oxidation than in the AS experiments is not clear, but could be due to some oxidation chemistry at the particle interface, and/or the presence of a small amount of water in or on the particles. These results differ somewhat from those of Chu et al., who observed higher levels of oxidation with aqueous AS than dry FS;²⁹ this discrepancy may be due to differences in oxidative conditions (OH vs ozone, continuous irradiation vs irradiation near the end of the experiment) or in the initial water content of the seed particles.

On average, the FS experiments have lower yields than the AS experiments, with a greater difference between carbon yields than mass yields (due to the high oxygen content in the organic material formed with FS seed). This suggests that aqueous oxidation results in some fragmentation to smaller products (Henry's Law constants $<10^5$ M atm⁻¹) that partition out of the condensed phase, as we observed previously for the aqueous oxidation of polyols within aerosol particles.²² These yield comparisons assume that the fresh SOA formed on dry AS has the same density as the oxidized SOA formed on aqueous FS; however, it is possible that the oxidized SOA may be denser than that. If instead of the base-case density of 1.4 g cm⁻³ we use an upper-limit density of 1.9 g cm⁻³ (that of solid oxalic acid) for the FS experiments, calculated yields from the FS experiments increase by a factor of 1.4, and thus are not significantly lower than those in the aqueous AS experiments. While these uncertainties complicate the detailed comparison of yields, the difference in densities is likely smaller than this, suggesting that the presence of aqueous oxidants likely leads to the increased loss of carbon to the gas phase.

Mixed-Seed α -Pinene Experiment. In order to further investigate the process by which highly oxidized aerosol is formed in the presence of FS, α -pinene was initially oxidized in the presence of aqueous AS seed (generating less-oxidized SOA, as in expt 3), and then FS seed was introduced into the chamber. Results (changes to O/C and H/C with time) are shown in Figure S1. The initial SOA resembled that produced in the other aqueous AS experiments (O/C \sim 0.7, H/C \sim 1.5). However, as soon as FS seed particles were added, the SOA underwent further oxidation, generating oxidized OA with a final O/C of 1.15 and H/C of 1.05. As with the other aqueous FS experiments, UV irradiation led to the loss of organic material to the gas phase.

These results suggest that SOA products are able to partition out of the initial particles and into more reactive aqueous particles where they can undergo further oxidation. Alternatively, oxidants generated within the reactive aqueous particles could also escape to the gas phase and partition into unreactive particles, causing additional oxidation. While it is possible that some coagulation of unreactive and reactive particles occurs, this is expected to be slower than partitioning, since estimated partitioning time scales for the present

conditions are <5 min,⁵⁰ whereas coagulation time scales are on the order of 1–2 h.⁵¹ Therefore, it appears that partitioning plays a key role in this additional oxidation, and more generally that this condensed-phase oxidation chemistry can convert less-oxidized SOA components (such as those typically generated in chambers) to more highly oxidized species, as suggested in previous work.^{22,29,31}

Isoprene SOA Experiments. Only two isoprene oxidation experiments were carried out (expts 8–9); the purpose was largely to determine whether such highly oxidized SOA can be formed from precursors other than α -pinene. As shown in Table 1, the isoprene experiments yielded results similar to the α -pinene experiments. Ozonolysis of isoprene with dry AS seed (expt 8) produced reasonably oxidized SOA (O/C = 0.8). As with α -pinene ozonolysis, the SOA composition did not change over the course of the experiments and was not affected by exposure to UV. Isoprene SOA formed with aqueous FS seed and H₂O₂ (expt 9) was extremely oxidized, reaching an O/C of 2.0, again with a mass spectra that closely resembles that of oxalate.^{45,46} Thus, the enhancement in the degree of oxidation when SOA is formed in the presence of aqueous-phase oxidants is not unique to α -pinene. As in the α -pinene experiments, and in our previous studies with polyols,²² the increased oxidant levels from dark Fenton chemistry led to a decrease in total particulate organic mass. Isoprene SOA formed in the presence of aqueous oxidants had a 47% lower yield and 68% lower carbon yield (or 29% lower yield and 55% lower carbon yield assuming an upper-limit SOA density of 1.9 g cm⁻³). Again, this loss of carbon upon further oxidation likely occurs via fragmentation to volatile products that then partition out of the condensed phase. As with α -pinene SOA, exposure to UV results in the rapid loss of organic matter, except here nearly all of the SOA is lost to the gas phase via photolysis. This is consistent with the material having been almost fully converted to oxalate in these experiments.

Comparison with Previous Results. Results from this study, which systematically examined how condensed-phase oxidation affects SOA amount and chemistry, are reasonably consistent with previous studies examining the effects of condensed-phase oxidative processes on SOA. In particular, our Fenton results generally agree with those of Chu et al., who found that, for the photooxidation of α -pinene using NO_x and HONO, aqueous FS seeds resulted in an enhanced degree of oxidation and decreased yields.^{29,30} Our observation that irradiation leads to the oxidation of SOA generated in the presence of aqueous AS seeds is also consistent with the results of Wong et al., who showed that the oxidation of α -pinene ozonolysis SOA upon UV irradiation was most dramatic at high RH.⁵² However, that study, as well as others,^{43,52,53} found that UV irradiation also leads to the loss of SOA particle mass at low ($<10\%$) RH, whereas in our experiments irradiation had no effect on dry particles, and in fact did not affect mass yields for any AS experiments. While the exact reasons for such differences are unclear, they may arise from differences in experimental parameters, such as the UV wavelengths used and the initial degree of oxidation (O/C) of the SOA prior to irradiation. Regardless, the present results and those of Wong et al.⁵² suggest that the effects of photolysis on SOA amount and composition are enhanced for aqueous systems, possibly due to differences in oxidant formation and/or the viscosity of the SOA material.

CONCLUSIONS AND IMPLICATIONS

Our results indicate that the presence of aqueous oxidants can lead to the rapid, efficient oxidation of SOA. Such aqueous-phase oxidation also results in a loss of aerosol mass, implying that aqueous oxidation can act as a sink for SOA, via fragmentation to smaller gas-phase products. In particular, Fenton-type chemistry (from the interaction of Fe(II) and reactive oxygen species) within aqueous particles oxidizes SOA extremely rapidly, resulting in the formation of organic aerosol that is substantially more oxidized than that normally generated in chamber SOA experiments.

Because the primary oxidants in the aqueous FS experiments are presumably OH radicals, these general results may not be unique to iron-containing particles, but instead may be applicable to any deliquesced particles containing aqueous OH. We note, however, that the FS experiments were carried out under intensely oxidizing conditions (with $[\text{OH}]_{\text{aq}}$ as high as 2.5×10^{-12} M), in part because the concentration of soluble iron used in these experiments was far higher than is found in ambient particles. The applicability of the present results to atmospheric oxidation processes depends critically on how such condensed-phase oxidant levels relate to those found in deliquesced aerosol particles under ambient conditions. The rapid formation of extremely highly oxidized OA, more oxidized than is normally found in ambient aerosol, suggests that ambient $[\text{OH}]_{\text{aq}}$ levels are not normally as high as those in our experiments. Unfortunately, ambient levels of aqueous OH have never been measured, and thus are very uncertain. Concentrations can be estimated from models of aqueous-phase chemistry, but predicted $[\text{OH}]_{\text{aq}}$ exhibits very high model-to-model variability. For example, the CAPRAM 3.0i multiphase mechanism predicts levels above 10^{-12} M,¹⁸ similar to the concentrations accessed in our experiments; however, other box models predict that the high concentrations of organic material within aqueous aerosol greatly suppresses $[\text{OH}]_{\text{aq}}$, such that radical chemistry within aqueous submicron particles is essentially negligible.^{16,17} Further, it is likely that there exist additional, poorly characterized sources and sinks of aqueous OH (such as the generation of OH from organic material¹⁶) that are not currently included in models. Thus, the concentrations of aqueous OH within atmospheric particles, which ultimately determine the importance of aqueous-phase oxidation reactions, are essentially unconstrained at present. This points to the critical need for the improved characterization of ambient levels of aqueous-phase oxidants, via detailed studies of individual oxidant sources and sinks, and ideally the direct measurements of oxidant concentrations, within the atmospheric aqueous phase.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.5b06160.

Details of the calculation of Δc_{OA} , the measurement of background signal, and the estimation of $[\text{OH}]_{\text{aq}}$ as well as the measurements of H/C and $\overline{\text{OS}}_{\text{C}}$ (Table S1) and evolving elemental ratios in the AS+FS mixing experiment (Figure S1) (PDF)

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Notes

The authors declare no competing financial interest.

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