

Superoxide Formation from Aqueous Reactions of Biogenic Secondary Organic Aerosols

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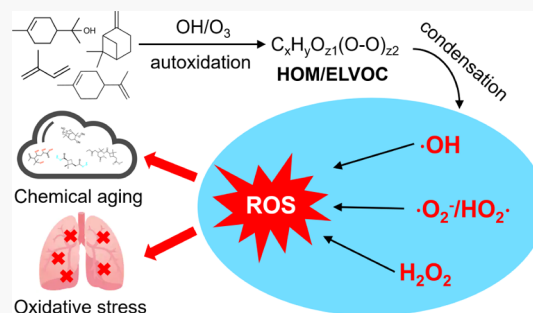


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ABSTRACT: Reactive oxygen species (ROS) play a central role in aqueous-phase processing and health effects of atmospheric aerosols. Although hydroxyl radical ($\cdot\text{OH}$) and hydrogen peroxide (H_2O_2) are regarded as major oxidants associated with secondary organic aerosols (SOA), the kinetics and reaction mechanisms of superoxide ($\text{O}_2^{\cdot-}$) formation are rarely quantified and poorly understood. Here, we demonstrate a dominant formation of $\text{O}_2^{\cdot-}$ with molar yields of 0.01–0.03% from aqueous reactions of biogenic SOA generated by $\cdot\text{OH}$ photooxidation of isoprene, β -pinene, α -terpineol, and d-limonene. The temporal evolution of $\cdot\text{OH}$ and $\text{O}_2^{\cdot-}$ formation is elucidated by kinetic modeling with a cascade of aqueous reactions including the decomposition of organic hydroperoxides, $\cdot\text{OH}$ oxidation of primary or secondary alcohols, and unimolecular decomposition of α -hydroxyperoxyl radicals. Relative yields of various types of ROS reflect a relative abundance of organic hydroperoxides and alcohols contained in SOA. These findings and mechanistic understanding have important implications on the atmospheric fate of SOA and particle-phase reactions of highly oxygenated organic molecules as well as oxidative stress upon respiratory deposition.



INTRODUCTION

Secondary organic aerosols (SOA) constitute a major fraction of ambient particulate matter and have significant impacts on global climate, air quality, and public health.^{1,2} Biogenic volatile organic compounds (VOCs), including isoprene and monoterpenes, have been identified as the primary precursors of SOA around the globe,³ including the Amazon region,⁴ China,⁵ and southeastern United States.⁶ The formation of SOA is initiated by multigenerational oxidation of VOCs and subsequent condensation of semivolatile oxidation products.^{3,7} Recent studies have revealed that highly oxygenated organic molecules (HOMs) and low volatility organic compounds generated by autoxidation substantially contribute to new particle formation and SOA growth.^{8,9} These compounds are found to be labile in the particle phase¹⁰ and a recent study suggested that particle-phase reactions need to be considered for full understanding of the atmospheric fate of HOMs.¹¹ Particle-phase chemistry and aqueous-phase processing involving oxidants and water-soluble organic compounds in cloud and fog droplets are very efficient pathways for the chemical transformation of SOA.^{12–14} These aging processes can lead to the change of particle properties including cloud condensation nuclei activity¹⁵ and absorption coefficient because of the formation of light-absorbing compounds.¹⁶

Reactive oxygen species (ROS), including the hydroxyl radical ($\cdot\text{OH}$), superoxide ($\text{O}_2^{\cdot-}$), hydroperoxyl radical ($\text{HO}_2^{\cdot}$), and hydrogen peroxide (H_2O_2), play a central role in chemical transformation of organic and inorganic compounds in the atmosphere.¹⁷ Substantial amounts of H_2O_2

were detected in ambient and laboratory-generated SOA, resulting from the hydrolysis of hydroxyhydroperoxides and peracids.^{18,19} $\cdot\text{OH}$, the most reactive form of ROS, was found to be released by decomposition of organic hydroperoxides,²⁰ peracids,²¹ and HOMs.²² Although $\cdot\text{OH}$ and H_2O_2 have been traditionally considered as the most important oxidants in aqueous droplets and thus studied extensively, additional oxidants have received growing attention. Singlet oxygen and organic triplet-excited state have emerged as new oxidants produced from dissolved organic compounds in atmospheric water.^{23,24} Redox reactions of quinones contained in aromatic SOA can lead to the formation of $\text{O}_2^{\cdot-}$.^{25,26} Previous studies have observed $\text{O}_2^{\cdot-}$ formation from biogenic-ozonolysis SOA as a minor component,^{20,26–28} however, the mechanism and kinetics of $\text{O}_2^{\cdot-}$ formation are poorly understood and rarely quantified.

Ambient SOA are found to have significant oxidative potential,^{2,29} which can be correlated with the formation of H_2O_2 and $\text{O}_2^{\cdot-}$ in epithelial-lining fluid,³⁰ inducing oxidative stress and adverse health effects upon inhalation and deposition in the human respiratory tract.^{2,31,32} ROS can

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exert drastic effects on biological tissues and cell components, subsequently causing acute airway inflammation and cardiopulmonary illnesses.^{31,33} Low levels of $O_2^{\bullet-}$ modulate various kinases or directly activate transcription factors to affect gene regulation in the nucleus;³⁴ however, excess $O_2^{\bullet-}$ formation is cytotoxic and induces a variety of diseases.³⁵ $O_2^{\bullet-}$ is also known as a crucial precursor of H_2O_2 , which can be further converted via Fenton (-like) reactions into $\bullet OH$.^{32,36} Given the atmospheric and physiological importance of ROS, it is critical to quantify kinetics and elucidate chemical mechanisms of the formation of different types of ROS from SOA in the aqueous phase. In this study, we observe substantial formation of $O_2^{\bullet-}$ by the SOA formed by $\bullet OH$ photooxidation of isoprene, β -pinene, α -terpineol, and D-limonene with the highest formation efficiency for the α -terpineol SOA. We found that the oxidation pathways (e.g., ozonolysis vs $\bullet OH$ photooxidation) and chemical composition of SOA play a critical role in determining ROS composition. Using a combination of laboratory experiments and kinetic modeling, we demonstrated that $O_2^{\bullet-}$ formation is caused by a cascade of aqueous reactions of biogenic SOA, involving the decomposition of organic hydroperoxides, $\bullet OH$ oxidation of primary or secondary alcohols, and unimolecular decomposition of α -hydroxyperoxyl radicals. To the best of our knowledge, this is the first study that explicitly addresses the mechanisms and kinetics of $O_2^{\bullet-}$ formation from biogenic SOA involving aqueous chemistry. These results have significant implications on chemical transformation of organic compounds in the atmosphere and adverse aerosol health effects in the human respiratory tract.

MATERIALS AND METHODS

SOA Formation, Collection, and Extraction. SOA particles were generated from dark ozonolysis and $\bullet OH$ photooxidation (referred as SOA_{O_3} and SOA_{OH} , respectively) of isoprene (Sigma-Aldrich, $\geq 99\%$), β -pinene (Sigma-Aldrich, $\geq 99\%$), α -terpineol (Arcos Organics, 97%), and D-limonene (Arcos Organics, 96%). Figure S1 shows the schematics of both oxidation systems. Briefly, SOA_{O_3} particles were produced in an oxidation 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 at 1 standard liter per minute (slm) through a commercial ozone generator (OzoneTech OZ2SS-SS). After the ozone concentration was stabilized, pure isoprene, β -pinene, α -terpineol, and D-limonene were injected into 5 slm of purge air flow separately using a syringe pump at a rate of $\sim 2 \mu L$ per minute. High concentrations ($2.2 \times 10^{15} \text{ cm}^{-3}$ for isoprene and $1.4 \times 10^{15} \text{ cm}^{-3}$ for β -pinene, α -terpineol, and D-limonene) of precursor and ozone ($1.8 \times 10^{14} \text{ cm}^{-3}$) were used to generate enough materials for analysis.

SOA_{OH} particles were generated in a 19 L potential aerosol mass (PAM) reactor.³⁷ 100–500 μL of VOC precursors (isoprene, β -pinene, α -terpineol, and D-limonene) were placed in an open 1.5 mL amber glass vial, which was kept inside a glass bottle prior to the PAM reactor. The precursors were then injected into the chamber using a 0.5 slm of carrier flow mixed with a 6 slm of humidified (Perma Pure humidifier, MH-110-12P-4) flow of purified air from a zero-air generator (model 7000, Environics). The $\bullet OH$ was generated through photolysis of water molecules by 185 nm UV radiation. The exposure time for the photooxidation of precursors in the PAM

reactor was about 3 min with a relative humidity around 30–40%. Despite the high $\bullet OH$ concentrations ($\sim 10^{11}$ – 10^{12} cm^{-3}) compared to ambient levels ($\sim 10^6 \text{ cm}^{-3}$), the PAM-generated SOA are found to be similar to ambient and chamber-generated SOA in terms of yield, oxidation state, hygroscopicity, and chemical composition.^{38–40} Additional advantages of the PAM reactor include shortened experimental timescales, ability to reach long photochemical ages, and minimized wall losses.⁴⁰

A scanning mobility particle sizer (SMPS, Grimm Aerosol Technik) was used to record the number concentrations and size distributions of SOA produced in the PAM reactor. The typical particle diameter of SOA_{OH} ranged from 30 to 500 nm, and the geometric mean diameter by mass varied from 70 to 120 nm. Particle sampling was initiated after the number concentrations stabilized. The SOA particles were collected on 47 mm-polytetrafluoroethylene filters (Millipore FGLP04700, 0.2 μm pore size) at a flow rate of 13 slm for 40 min and 5 slm for 3 h for SOA_{O_3} and SOA_{OH} , respectively.

The filter samples were extracted in 1 mL spin-trapping solutions (10 mM) or Milli-Q (deionized, resistivity = 18.2 $M\Omega/\text{cm}$) water for 7 min. The filter extracts were used for radical measurements or the H_2O_2 fluorometric assay, respectively. The mass difference before and after the extraction was regarded as the SOA dissolved in reagents, and an average molar mass of 200 g mol^{-1} was used for calculating the SOA molar concentrations in filter extracts. The SOA_{O_3} and SOA_{OH} concentrations were in the range of 1–16 mM and pH of SOA extracts varied between 4 and 6. At least three samples were prepared for each SOA_{O_3} and SOA_{OH} for EPR analysis and H_2O_2 measurement, respectively.

EPR Measurements. A continuous-wave electron paramagnetic resonance (CW-EPR) spectrometer (Bruker, Germany) coupled with a spin-trapping technique was used for free radical quantification. The spin-trapping agent used to capture free radicals generated upon aqueous reactions of SOA is 5-*tert*-Butoxycarbonyl-5-methyl-1-pyrroline-N-oxide (BMPO) (Enzo, $\geq 99\%$). After extraction, the filter extracts were incubated at a room temperature of 20 $^{\circ}\text{C}$, and a 50 μL aliquot was loaded into a 50 μL capillary tube (VWR) and inserted in the resonator of the EPR spectrometer at 10, 20, 60, 120, and 240 min from the start of aqueous reactions. The parameter sets for EPR measurements were a center field of 3515.0 G, a sweep width of 100.0 G, a receiver gain of 30 dB, a modulation amplitude of 1.0 G, a scan number of 10–50, attenuation of 12 dB, a microwave power of 12.6 mW, a modulation frequency of 100 kHz, and a conversion time/time constant of 5.12 ms. After obtaining the EPR spectra, SpinFit and SpinCount methods embedded in the Bruker Xenon software were applied to quantify BMPO-radical adducts²⁰ at each time point.

H_2O_2 Fluorometric Assay. A modified protocol⁴¹ was applied for the H_2O_2 measurement using a fluorometric H_2O_2 assay kit (MAK165, Sigma-Aldrich). 250 μL of DMSO and 1 mL of assay buffer were added to the red peroxidase substrate and horseradish peroxidase for reconstitution, respectively. The reagents were divided into ten sets of aliquots (25 μL of red peroxidase substrate, 100 μL of horseradish peroxidase, and 2 mL of assay buffer each). Prior to each analysis, one set of reagents was used to prepare 2 mL working solutions, consisting of 20 μL of red peroxidase substrate, 80 μL of horseradish peroxidase, and 1.9 mL of assay buffer. All H_2O_2 measurements were conducted within 2 h from the preparation

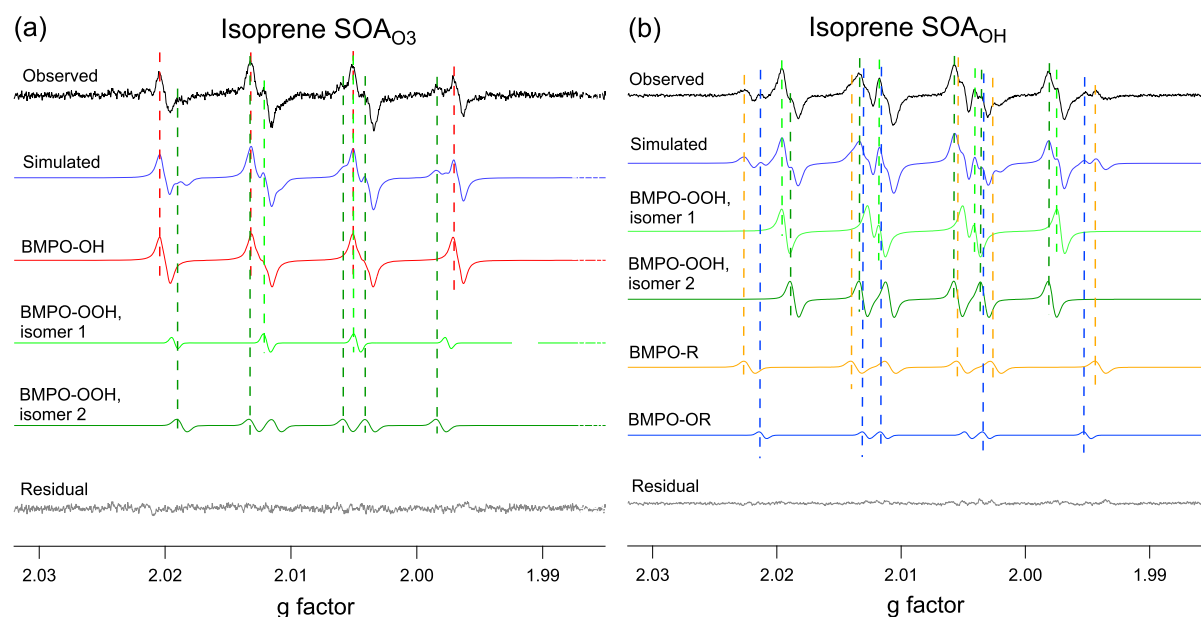


Figure 1. EPR spectra of BMPO-radical adducts from aqueous reactions of isoprene SOA generated from (a) dark ozonolysis and (b) $\bullet\text{OH}$ photooxidation. The observed spectra (black) are simulated (purple) and deconvoluted into BMPO-OH (red), BMPO-OOH isomer 1 (light green), BMPO-OOH isomer 2 (dark green), BMPO-R (yellow), and BMPO-OR (blue). Residual (gray) denotes the difference of observed and simulated spectra. Note that the two isomers of BMPO-OOH represent the *trans* or *cis* structures of the $-\text{OOH}$ group.

of working solutions because of the high instability of the probe. A calibration was performed using H_2O_2 standard concentrations ranging from 0.05 to 1.5 μM , which were prepared by diluting 30 wt % H_2O_2 (Sigma-Aldrich). The reaction vials (3 mL) consisted of 2.94 mL of solution (Milli-Q water + filter extracts) and 60 μL of working solution. The H_2O_2 yields from different SOA samples varied significantly and dilution factors were adjusted, so that the final H_2O_2 concentrations in the reaction vials were below 1.5 μM . All H_2O_2 measurements were conducted with a filter blank, with the same dilution factor as the samples. The addition of working solution was considered as the start of reaction, and the reaction vials were incubated at room temperature for 15 min until the measurement. The fluorescence of the reagents was measured using a spectrofluorophotometer (RF-6000, Shimadzu) at excitation and emission wavelengths of 540 and 590 nm, respectively.

Kinetic Modeling. A kinetic model was applied to simulate the simultaneous formation of $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$ by aqueous reactions of SOA using the reactions listed in Table S2. The reactions include chemical reactions of SOA components (R1–R7), ROS coupling reactions (R8–R16), and radical-trapping reactions by BMPO (R17–R21). SOA chemistry includes decomposition of organic hydroperoxides (ROOH), generating $\bullet\text{OH}$ radicals (R1),^{20,26} $\bullet\text{OH}$ oxidation of primary and secondary alcohols ($\text{R}_1\text{R}_2\text{CHOH}$) and subsequent reaction with O_2 to form α -hydroxyperoxyl radicals ($\text{R}_1\text{R}_2\text{C}(\text{O}_2)\text{OH}^{\bullet}$) (R2), decomposition of $\text{R}_1\text{R}_2\text{C}(\text{O}_2)\text{OH}^{\bullet}$ to generate $\text{HO}_2^{\bullet}$ (R3),^{42,43} $\bullet\text{OH}$ oxidation of ROOH (R4),⁴² $\text{R}_1\text{R}_2\text{C}(\text{O}_2)\text{OH}^{\bullet}$ (R5), and other SOA components (R6) and $\text{HO}_2^{\bullet}$ termination of $\text{R}_1\text{R}_2\text{C}(\text{O}_2)\text{OH}^{\bullet}$ (R7). The reaction yield of R3 (c_1) was also considered in the model. Rate coefficients of the decomposition of ROOH and $\text{R}_1\text{R}_2\text{C}(\text{O}_2)\text{OH}^{\bullet}$ as well as H-abstraction of $\text{R}_1\text{R}_2\text{CHOH}$ were assumed to be independent of the structures of R groups contained among different SOA, representing a major model assumption. This assumption is in line with the CAPRAM 3.0 model,⁴² in which

the rate constants of H-abstraction on alcohols vary within one order of magnitude regardless of carbon numbers and functionalities besides the hydroxy group. The radical composition profiles generated by different SOA are solely determined by the relative abundance of ROOH and $\text{R}_1\text{R}_2\text{CHOH}$ groups in SOA. Potential variation of these rate constants depending on R structures can be partly translated into uncertainties in molar fractions of ROOH and $\text{R}_1\text{R}_2\text{CHOH}$ as shown in Table S3.

The rate coefficients of ROS coupling reactions were obtained from literature values and the unknown rate coefficients and molar fractions of ROOH and $\text{R}_1\text{R}_2\text{CHOH}$ contained in SOA were determined using the Monte Carlo genetic algorithm (MCGA) to reproduce experimental data.⁴⁴ In the Monte Carlo search, input parameters were varied randomly within individual bounds: the boundaries of all reaction rate constants were generally constrained to within two orders of magnitude based on literature studies, while the ROOH/ $\text{R}_1\text{R}_2\text{CHOH}$ molar fractions were constrained to between 0.1 and 80%. As discussed in the main text, the determined rate coefficients and molar fractions are reasonable and in line with previous experimental measurements and modeling studies. The uncertainty of the reaction rates in Table S2 and the ROOH/ $\text{R}_1\text{R}_2\text{CHOH}$ fractions in Table S3 were obtained by running the MCGA numerous times (~ 40), which resulted in 20 parameter sets which reasonably captured the temporal trends of the experimental data. The 20 parameter sets were then used to plot 20 traces for the temporal formation of the BMPO adducts by each SOA, and the highest and lowest traces were selected as the upper and lower boundaries shown in Figure 3 for each SOA, respectively. Note that these boundaries do not necessarily correspond to the boundaries of each parameter in Tables S2 and S3. There is still relatively large uncertainty in the actual values of some parameters, as shown by the parameter ranges in Table S2; further measurements to quantify organic hydroperoxides and alcohols as well as dedicated kinetic

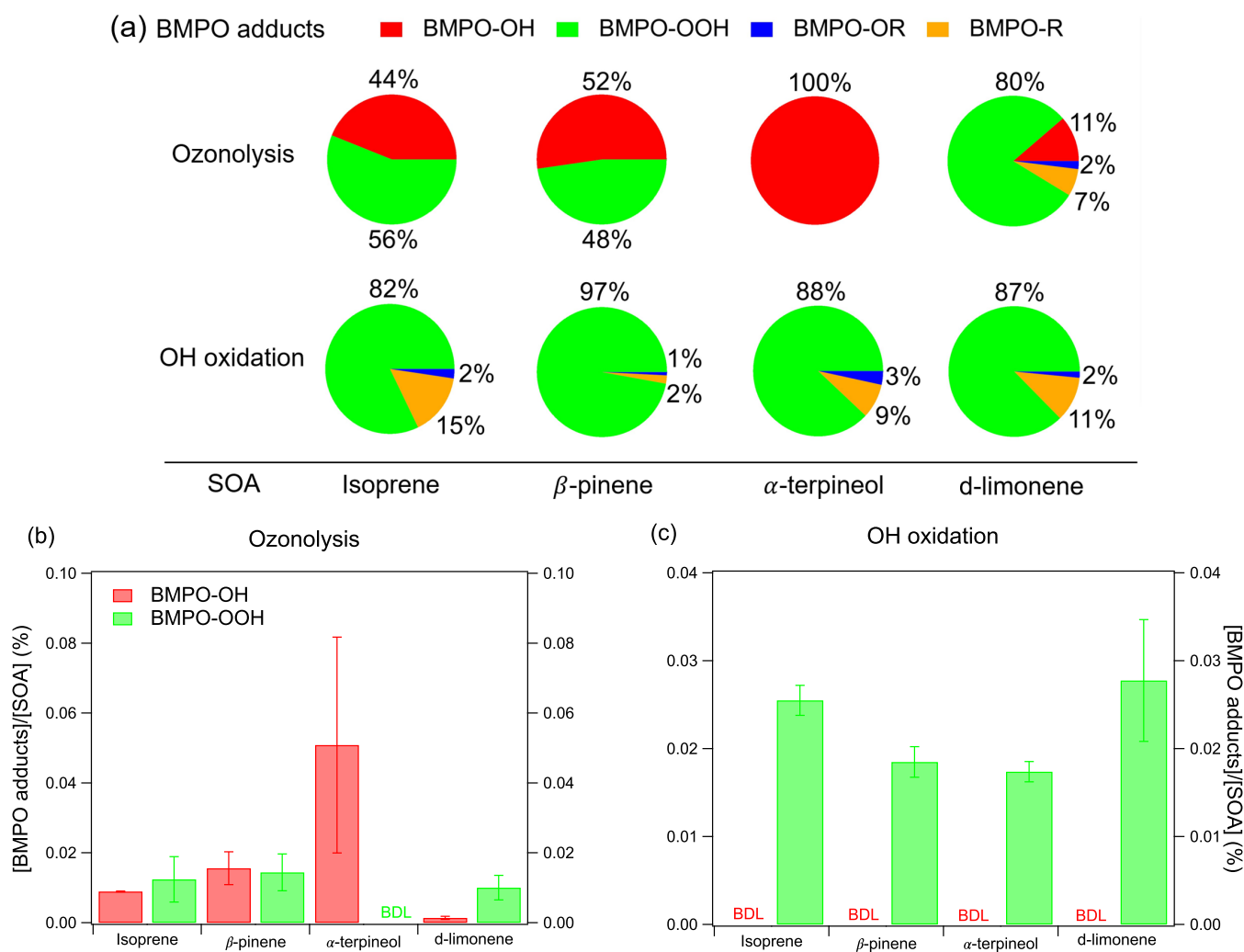


Figure 2. (a) Relative yields of BMPO-radical adduct from aqueous reactions of SOA generated by ozonolysis vs $\bullet$ OH photooxidation of isoprene, β -pinene, α -terpineol, and d-limonene. Molar yields of BMPO-OH (red) and BMPO-OOH (green) adducts generated by SOA from (b) dark ozonolysis and (c) $\bullet$ OH photooxidation after 20 min of aqueous reactions.

studies would be required for determination of these parameters.

The relative abundance of $\text{O}_2^{\bullet-}$ and $\text{HO}_2^{\bullet}$ in the aqueous solution is largely determined by pH. Tresp et al.⁴⁵ showed that at neutral pH (7.4), over 99.9% of BMPO-OOH was generated by BMPO reacting with $\text{O}_2^{\bullet-}$. In contrast, the pH of the SOA aqueous solutions obtained in this study ranged from 4 to 6. According to the Henderson–Hasselbalch equation with a pK_a value of 4.88 for $\text{HO}_2^{\bullet}$, $\text{HO}_2^{\bullet}$ would dominate over $\text{O}_2^{\bullet-}$ when the pH approaches 4, while $\text{O}_2^{\bullet-}$ and $\text{HO}_2^{\bullet}$ are in comparable amounts when the pH = $\sim$ 5. Therefore, BMPO trapping reactions of both $\text{O}_2^{\bullet-}$ and $\text{HO}_2^{\bullet}$ to form BMPO-OOH are considered (R18, 19).²⁸ The BMPO radical adducts (BMPO-OH, BMPO-OOH) can decay by self-decomposition or reactions with other radicals. Although self-decomposition half-life of BMPO-OH and BMPO-OOH in neutral solutions are known to be 30 min⁴⁶ and 23 min,⁴⁷ respectively, rate coefficients with radicals (e.g., $\bullet$ OH, $\text{O}_2^{\bullet-}$, organic radicals) leading to adduct decay are unknown. Thus, in this study, decay of BMPO-OH (R18) and BMPO-OOH (R21) are treated with pseudo-first-order rate coefficients. The estimated half-lives of BMPO-OH and BMPO-OOH are shorter than the literature values to be 14–24 min and 6–14 min, respectively,

indicating that decay of adducts by radicals are nonnegligible or lower pH may have impacted adduct stability.⁴⁸

RESULTS AND DISCUSSION

ROS Formation Efficiencies by SOA. Biogenic SOA were generated by both dark ozonolysis and $\bullet$ OH photooxidation (referred as SOA_{O_3} and SOA_{OH} hereafter) of isoprene, β -pinene, α -terpineol, and d-limonene. Particle water extracts were analyzed with electron paramagnetic resonance (EPR) spectroscopy coupled with a spin-trapping technique for the detection of free radicals. Figure 1 shows the observed EPR spectra of isoprene (a) SOA_{O_3} and (b) SOA_{OH} . The observed spectra were simulated and deconvoluted into spectra for different BMPO adducts with radicals including $\bullet$ OH, $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$, and carbon- and oxygen-centered organic radicals (BMPO-OH, BMPO-OOH, BMPO-R, and BMPO-OR, respectively). The EPR spectrum of isoprene SOA_{O_3} is dominated by a four-peak pattern, which can be attributed to BMPO-OH with a minor contribution from BMPO-OOH. In contrast, the major peaks in the EPR spectrum from isoprene SOA_{OH} represent BMPO-OOH with a minor contribution from carbon- and oxygen-centered organic radicals. Similar trends are observed for β -pinene and α -terpineol SOA, while d-

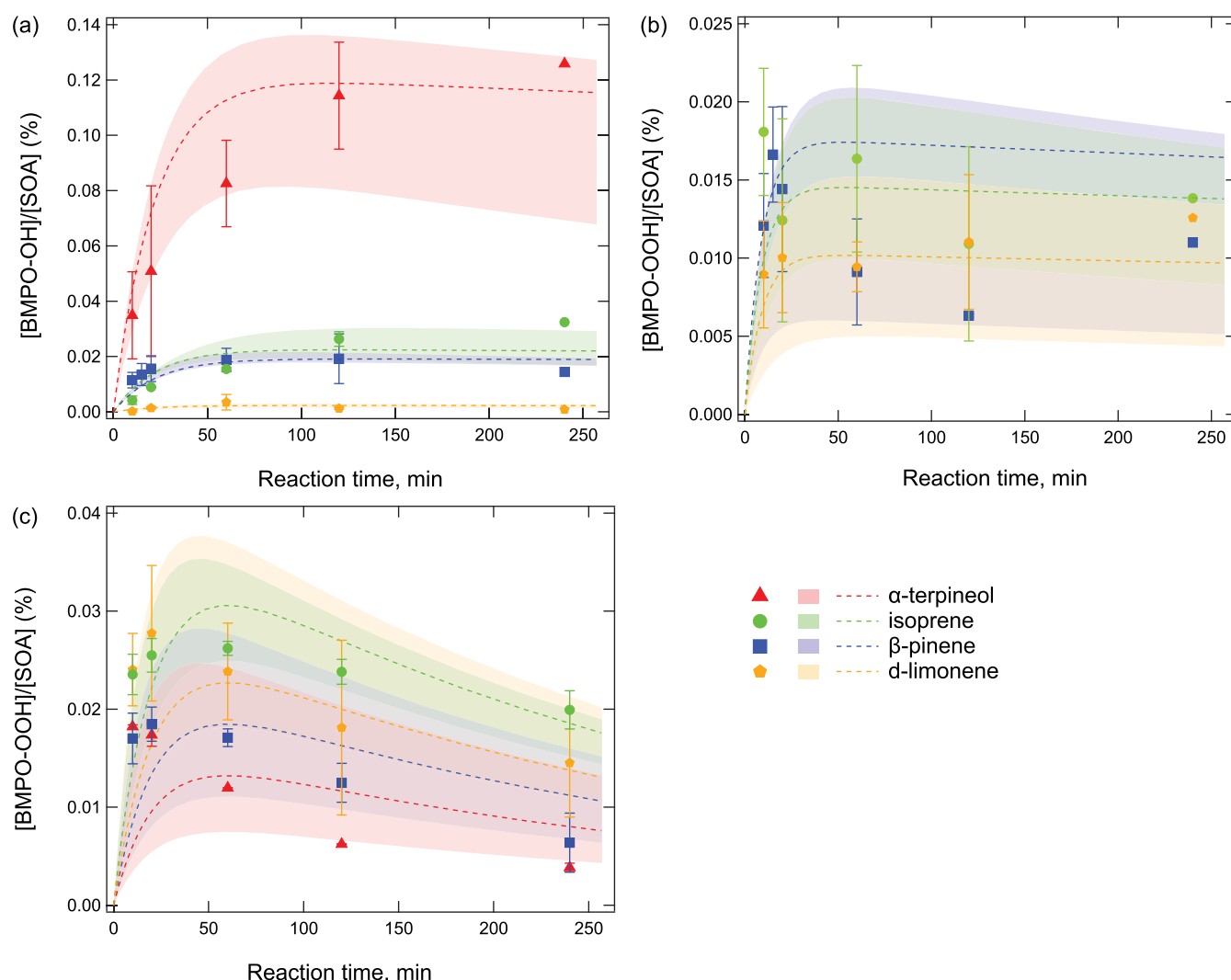


Figure 3. Temporal evolution of molar yields of (a) BMPO-OH and (b) BMPO-OOH adducts from aqueous reactions of SOA generated from dark ozonolysis (SOA_{O3}) and (c) BMPO-OOH adducts from SOA generated from $\bullet$ OH photooxidation (SOA_{OH}) of α -terpineol (red), isoprene (green), β -pinene (blue), and D-limonene (yellow). The markers are experimental data. The dashed lines represent the best fits of kinetic model with the shaded area denoting the modeling uncertainties. The $O_2^{\bullet-}/HO_2^{\bullet}$ formation from α -terpineol SOA_{O3} and $\bullet$ OH formation from all SOA_{OH} are below the detection limit.

limonene SOA mainly produces $O_2^{\bullet-}/HO_2^{\bullet}$ for both oxidation systems (Figure S2).

Integration of deconvoluted spectra allows us to quantify contributions from each radical species. Figure 2 shows quantifications of different types of radicals in water extracts of the SOA generated by ozonolysis or $\bullet$ OH oxidation of isoprene, β -pinene, α -terpineol, and D-limonene. Relative yields of BMPO-OH of isoprene and β -pinene SOA_{O3} after 20 min of reactions are 44 and 52%, respectively (Figure 2a), both of which further increase to >70% after 2 h (Figure S3a). This is in very good agreement with a previous study which demonstrated major OH formation from biogenic SOA formed by ozonolysis.²⁶ The α -terpineol SOA_{O3} generates $\bullet$ OH exclusively, while the D-limonene SOA_{O3} generates $O_2^{\bullet-}/HO_2^{\bullet}$ dominantly (80%) with minor contributions from $\bullet$ OH (11%) and organic radicals (7%). In contrast to major $\bullet$ OH formation by most of SOA_{O3}, more than 80% of radical species generated from SOA_{OH} are in the form of $O_2^{\bullet-}/HO_2^{\bullet}$. Figure 2b,c shows the molar yields or formation efficiencies of $\bullet$ OH and $O_2^{\bullet-}/HO_2^{\bullet}$ (molar concentration ratios of BMPO-radical

adduct to SOA) for SOA_{O3} and SOA_{OH}, respectively. α -Terpineol SOA_{O3} has the highest $\bullet$ OH formation efficiency with 0.06% followed by β -pinene and isoprene SOA_{O3}. All types of SOA_{OH} are found to have a similar $O_2^{\bullet-}/HO_2^{\bullet}$ formation efficiency of 0.018–0.03%.

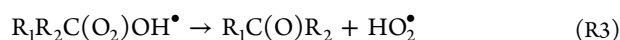
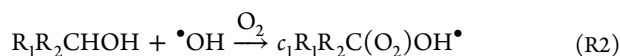
The molar yields of H₂O₂ from SOA were also quantified using a fluorometric H₂O₂ assay (Table S1). Isoprene SOA generally yields higher H₂O₂ compared to other types of SOA. The H₂O₂ yield from β -pinene SOA_{O3} ($1.8 \pm 0.3\%$) is comparable with results of Wang et al. ($1.3 \pm 0.9\%$),¹⁸ but around half of the amount reported by Tong et al. ($3.2 \pm 0.7\%$).²⁶ Isoprene SOA_{O3} generally produces higher H₂O₂ ($4.2 \pm 0.7\%$) compared to β -pinene SOA_{O3} ($1.8 \pm 0.3\%$), which are comparable with Tong et al.²⁶ ($8.0 \pm 0.8\%$ for isoprene SOA_{O3} and $3.2 \pm 0.7\%$ for β -pinene SOA_{O3}). For both oxidation systems with various precursors, the production of $O_2^{\bullet-}/HO_2^{\bullet}$ is tightly correlated with H₂O₂ formation with R^2 greater than 0.9 (Figure S4), indicating that $O_2^{\bullet-}$ is an important precursor of H₂O₂, or $O_2^{\bullet-}$ and H₂O₂ have similar types of source compounds. For β -pinene, α -terpineol, and D-

limonene SOA, the H_2O_2 yields from SOA_{O_3} are about one order of magnitude higher than those from SOA_{OH} . This is consistent with the reaction mechanism of ozonolysis, in which stabilized Criegee intermediates hydrolyze to form α -hydroxyhydroperoxides that can readily decompose into carbonyls and H_2O_2 .^{18,49,50}

The distinct profiles of ROS composition by SOA_{O_3} and SOA_{OH} reflect differences in chemical compositions and functionalities caused by different oxidation pathways. Monoterpene SOA from ozonolysis generally contain higher fractions of organic peroxides (12–65%) compared to those from photooxidation (6–18%),^{51,52} partly because organic hydroperoxides are decomposed with prolonged UV exposure.^{53,54} As ROOH can be a primary source of $\bullet\text{OH}$ radicals through decomposition,^{20,26} lower ROOH fractions should lead to minor contributions of $\bullet\text{OH}$ formation for SOA_{OH} . Detailed ROS formation mechanisms are discussed below to better understand how precursors and oxidation systems can affect ROS profiles.

Reaction Mechanism. The temporal evolution of $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$ formation from the aqueous reactions of SOA was measured. As shown in Figure 3a, the molar yields of BMPO-OH adducts from SOA_{O_3} increase over time and reach a steady state after approximately 2 h. In contrast, the molar yields of BMPO-OOH adducts from SOA_{O_3} (except α -terpineol SOA_{O_3} , which was below detection limit) reach their maximum concentrations within a short period of time (<30 min), followed by a slight decrease (Figure 3b). For SOA_{OH} , $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$ yields reach their maximum within 40 min, but decrease gradually over 4 h (Figure 3c). The BMPO-OH concentrations from all SOA_{OH} are below the detection limit. The highly distinct time-dependent profiles of $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$ formation lead to an interesting evolution of radical composition by SOA. For example, radical production from isoprene and β -pinene SOA_{O_3} is initially dominated by $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$, while $\bullet\text{OH}$ becomes dominant after 20 min (Figure S3a). In comparison, $\text{D-limonene SOA}_{\text{O}_3}$ and all types of SOA_{OH} (Figure S3b) are consistently dominated by $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$ (>70%) over 4 h.

To further elaborate the reaction kinetics and mechanism, a kinetic model was developed and applied to simulate the temporal evolution of $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$ radicals. The following reactions were implemented into the kinetic model for $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$ formation



$\bullet\text{OH}$ can be generated from the first-order decay of organic hydroperoxides (ROOH) (R1).^{20,26,55} Krapf et al.¹⁰ provided molecular evidence of the unimolecular decomposition of labile hydroperoxides in the condensed phase through the cleavage of the weaker O–O bond which must lead to $\bullet\text{OH}$ formation. In addition, direct $\bullet\text{OH}$ formation has been observed from the decomposition of cumene hydroperoxide²⁰ (common proxy of atmospheric ROOH) at room temperature and a recent study⁵⁶ and organic radicals. Note that $\bullet\text{OH}$ formation in R1 results from the decomposition of organic hydroperoxides without additional functionalities on the α -carbon, as the decomposition of α -hydroxyhydroperoxides leads to the formation of carbonyl and H_2O_2 instead of $\bullet\text{OH}$.⁵⁰

The generated $\bullet\text{OH}$ can abstract a hydrogen atom from α -carbon of primary or secondary alcohols to form α -hydroxyalkyl radicals ($\text{R}_1\text{R}_2\text{C}(\text{OH})^{\bullet}$), which immediately combine with dissolved O_2 to form α -hydroxyperoxyl radicals ($\text{R}_1\text{R}_2\text{C}(\text{O}_2)\text{OH}^{\bullet}$) (R2). These radicals can subsequently undergo unimolecular decomposition to form $\text{HO}_2^{\bullet}$ (R3).^{42,43} Note that this reaction is known to occur also in the gas phase.⁷

Note that $\bullet\text{OH}$ formation can be promoted in the presence of transition metal ions via Fenton(-like) reactions.^{57,58} To address this possible interference of metal contamination on radical formation, concentrations of Fe and Cu ions in the SOA extracts were measured using two highly sensitive spectrophotometric methods (ferrozine and bathocuproine methods,⁴¹ respectively). The results showed that they were both below the detection limits (10 ± 2 and 20 ± 5 nM for Fe and Cu ions, respectively). An additional control experiment was also conducted for measuring ROS formation from SOA extracts with and without a metal-chelating agent, diethylenetriaminepentaacetic acid, showing no significant difference, confirming the negligible impacts of potential metal contamination.

The kinetic model also considers a number of other reactions including $\bullet\text{OH}$ loss via reactions with SOA components, ROS coupling reactions, radical trapping by BMPO, and decay of BMPO-radical adducts (Table S2). Molar fractions of ROOH and $\text{R}_1\text{R}_2\text{CHOH}$ contained in SOA were estimated using the MCGA to reproduce experimental data.⁴⁴ The decomposition rate of ROOH estimated in this study ($(0.9\text{--}6.5) \times 10^{-5} \text{ s}^{-1}$) is in agreement with previous studies,^{20,28} and the lifetime of α -hydroxyperoxyl radicals (0.002–0.06 s) is also consistent with the aqueous chemistry model CAPRAM 3.0 (0.001–0.005 s).⁴² As shown in Figure 3, the modeling results show a good agreement with measurements within modeling uncertainties, indicating that the above reaction mechanisms are plausible for $\bullet\text{OH}$ and $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$ formation as they can explain the temporal evolution of distinct radical profiles depending on precursors and oxidation pathways. It should be noted that the decomposition rates involving hydroperoxides could be pH-dependent according to a recent study by Qiu et al.⁵⁹ Therefore, future studies are still warranted for the pH effects on ROS formation from SOA in the aqueous phase, where acidification (representative of aerosol pH) and neutralization (representative of physiological pH) are of interest and could both play a role in affecting the profiles of radical production.

The model-estimated molar fractions of ROOH in isoprene, β -pinene, and $\text{D-limonene SOA}_{\text{O}_3}$ are 6–25, 7–35, and 2–12%, respectively (Table S3), which are comparable with the peroxide mass fractions reported by previous studies for the same types of SOA (~ 30 , ~ 85 , and $\sim 2\%$, respectively),^{2,51,60,61} assuming that molar masses of peroxides and SOA components are the same. Note that the measured total peroxide contents include both organic peroxides (ROOR) and hydroperoxides (ROOH), which may explain the lower estimated fraction of ROOH in isoprene and β -pinene compared to literature values. In addition, it may imply that some ROOH may be more stable and do not decompose within the timescale of the experiment, as has been observed for isoprene hydroxyl hydroperoxide in a recent study.⁶² Significantly higher fractions of ROOH are estimated in the isoprene and β -pinene SOA_{O_3} compared to their corresponding SOA_{OH} (3–5% and 1–3%), leading to the major

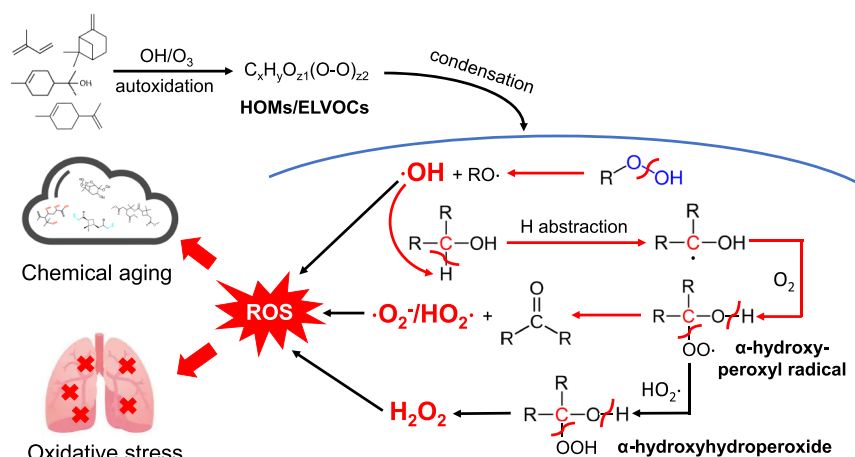


Figure 4. Implications of ROS formation by aqueous reactions of biogenic SOA. HOMs and extremely low volatility organic compounds (ELVOCs) are generated by gas-phase oxidation and autoxidation. After condensation, ROS including $\bullet\text{OH}$, $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$, and H_2O_2 can be generated via decomposition of organic hydroperoxides, $\bullet\text{OH}$ oxidation of primary or secondary alcohols, and unimolecular decomposition of α -hydroxyperoxyl radicals and α -hydroxyperoxyhydroperoxides in the aqueous phase. This process has significant implications for chemical aging of SOA in the atmosphere and oxidative stress upon respiratory deposition of SOA particles.

contribution of $\bullet\text{OH}$ formation in SOA_{O_3} . The molar fractions of $\text{R}_1\text{R}_2\text{CH}(\text{OH})$ in D -limonene SOA are estimated to be higher compared to ROOH , contributing to the $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$ -dominated profile for both D -limonene SOA_{O_3} and SOA_{OH} . Significant amounts of $\text{R}_1\text{R}_2\text{CH}(\text{OH})$ are predicted in most SOA (34–74%). Primary and secondary alcohols are generated via multigenerational gas-phase oxidation as shown in a number of previous experimental and theoretical studies as summarized in review papers.^{7,63} The α -terpineol SOA_{O_3} is estimated to contain a very small fraction of $\text{R}_1\text{R}_2\text{CH}(\text{OH})$ (0.1–1%), leading to the suppression of the $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$ formation. This is likely caused by the specific position of hydroxy groups in the α -terpineol: tertiary alcohol without α -H for abstraction and subsequently no formation of peroxy radicals. The predicted very low fraction of $\text{R}_1\text{R}_2\text{CH}(\text{OH})$ in α -terpineol SOA_{O_3} is consistent with previous experimental measurements,⁶⁴ showing that the primary products (>90%) from α -terpineol ozonolysis only contain tertiary alcohols.

Implications. This work elucidates ROS generation pathways from aqueous reactions of biogenic SOA as presented in Figure 4. Multigenerational atmospheric oxidation and autoxidation of biogenic VOCs by $\bullet\text{OH}$ and O_3 lead to the formation of highly functionalized and extremely low volatility organic compounds, HOMs, and ELVOCs.^{8,9} Most of these compounds contain alcohol and hydroperoxide functional groups. After condensation into the particle phase, a fraction of organic hydroperoxides (ROOH) decomposes to form $\bullet\text{OH}$, which can act as an ignition step for a cascade of ROS formation pathways. The e-folding times for the ROOH decomposition are estimated to be 4–30 h, which represent average lifetimes for different ROOH compounds; some of them may have shorter timescales,^{10,11} while others may be very stable.^{65,66} This decomposition process can be accelerated by photolysis^{53,54} and Fenton-like reactions of transition metal ions.^{20,28,62} We acknowledge a caveat of this work that the particle mass concentrations in the PAM reactor are much higher compared to ambient conditions, leading to more prominent condensation of semi-VOC. However, a recent study⁶⁶ found that the PAM reactor-generated α -pinene SOA contains substantial amounts of particle-phase HOMs, which is consistent with the gas-phase measurements in previous

studies.^{9,67,68} Although this study serves as a proof of concept and provide mechanistic insights into possible mechanisms of ROS formation, future studies are definitively warranted to investigate the ROS formation from SOA generated under conditions with lower oxidant and particle concentrations.

The $\bullet\text{OH}$ released during SOA decomposition can abstract hydrogen from primary or secondary alcohols ($\text{R}_1\text{R}_2\text{CH}(\text{OH})$) to form α -hydroxyalkyl radicals, which quickly react with dissolved oxygen to form α -hydroxyperoxyl radicals. Within milliseconds, α -hydroxyperoxyl radicals can undergo unimolecular decomposition to form $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$ radicals. Through $\text{HO}_2^{\bullet}$ termination, α -hydroxyperoxyl radicals form α -hydroxyalkyl hydroperoxides, which can decompose to generate H_2O_2 , another important ROS.^{50,69} Note that α -hydroxyalkyl hydroperoxides can form a stable complex with a water molecule, so the $-\text{O}-\text{OH}$ group is unlikely to be cleaved to yield $\bullet\text{OH}$ radicals.^{50,70} Other feasible pathways of H_2O_2 formation by SOA have also been discussed in the literature including hydrolysis of diacyl peroxides or peroxy acids,⁷¹ and the relative contributions of different H_2O_2 sources still warrant further studies.

Our findings demonstrate the importance of the interplay among different functionalities in determining radical production in the aqueous phase. The relative abundance of ROOH and $\text{R}_1\text{R}_2\text{CH}(\text{OH})$ can largely affect the compositions of $\bullet\text{OH}$, $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$, H_2O_2 , and organic radicals. It has been established that ROS play a central role in chemical transformation of organic and inorganic compounds in aqueous particles. Sources, sinks, and concentrations of ROS in atmospheric waters are still uncertain and it is still challenging to accurately predict their concentrations in atmospheric aqueous chemistry models.^{13,72} Implementation of molar yields of ROS by SOA determined in this study into models should improve quantification of ROS in aqueous droplets, which can then be compared with traditional ROS sources such as gaseous HO_x uptake and Fenton reactions to evaluate relative importance of different ROS formation pathways.

α -Terpineol and D -limonene are known as important indoor-relevant VOCs. α -Terpineol is a significant component of liquid cleaner/disinfectants and air fresheners and can be

emitted by some molds in the indoor environment, whereas D-limonene has been found in floor wax, all-purpose cleaners, and personal care products.⁷³ These terpenes are found in higher concentrations in indoor environments compared to outdoors and their oxidation can lead to substantial SOA formation indoors.⁷⁴ These compounds can also be transported to the outdoors, affecting ozone and SOA formation in the atmosphere.⁷⁵ α -Terpineol SOA_{O₃} and D-limonene SOA_{OH} show the highest formation efficiencies in the aqueous generation of $\cdot$ OH and O₂^{•−}/HO₂[•], respectively. Quantification of different types of ROS by SOA should be helpful for a better understanding of the aqueous-phase processing of chemical compounds in indoor and outdoor processes.

Upon inhalation and respiratory deposition of SOA particles, O₂^{•−} can be generated via redox reactions with lung antioxidants or can be released by macrophages after phagocytosis of inhaled particles in the lung-lining fluid.^{76,77} The antioxidant defense system can counteract ROS, however, excessive production of ROS can overwhelm antioxidant defenses and trigger or enhance oxidative stress, cell death, and biological aging.^{31,78} As direct measurements of ROS in the lung-lining fluid are challenging, implementation of formation efficiency of O₂^{•−} into the lung model^{30,32} will improve quantification of ROS in the lung-lining fluid for a better evaluation of the impact of biogenic SOA on oxidative stress and adverse health effects including asthma, allergies, and other respiratory diseases.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.0c07789>.

SOA chemistry and H₂O₂ fluorometric assay; H₂O₂ yields of aqueous reactions or SOA; chemical reactions and parameters in the kinetic model; molar fractions of ROOH and R₁R₂CHOH in SOA; schematics of dark ozonolysis and $\cdot$ OH photooxidation; EPR spectra of BMPO-radical adducts from aqueous reactions of SOA; temporal evolution of relative yields of BMPO-radical adducts from aqueous reactions of SOA; correlation of BMPO-OOH and H₂O₂ concentrations in aqueous reactions of SOA (PDF)

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Notes

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