Environmental Science & Technology

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Isoprene Epoxydiol-Derived Sulfated and Nonsulfated Oligomers Suppress Particulate Mass Loss during Oxidative Aging of Secondary Organic Aerosol

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Cite This: *Environ. Sci. Technol.* 2022, 56, 16611−16620

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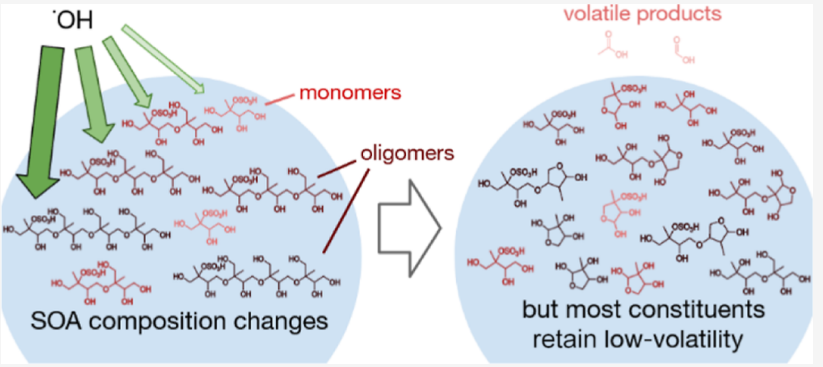

ABSTRACT: Acid-driven multiphase chemistry of isoprene epoxydiols (IEPOX) with inorganic sulfate aerosols contributes substantially to secondary organic aerosol (SOA) formation, which constitutes a large mass fraction of atmospheric fine particulate matter ($PM_{2.5}$). However, the atmospheric chemical sinks of freshly generated IEPOX-SOA particles remain unclear. We examined the role of heterogeneous oxidation of freshly generated IEPOX-SOA particles by gas-phase hydroxyl radical ($^{\bullet}OH$) under dark conditions as one potential atmospheric sink. After 4 h of gas-phase $^{\bullet}OH$ exposure ($\sim 3 \times 10^8$ molecules cm^{-3}), chemical changes in smog chamber-generated IEPOX-SOA particles were assessed by hydrophilic interaction liquid chromatography coupled with electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (HILIC/ESI-HR-QTOFMS). A comparison of the molecular-level compositional changes in IEPOX-SOA particles during aging with or without $^{\bullet}OH$ revealed that decomposition of oligomers by heterogeneous $^{\bullet}OH$ oxidation acts as a sink for $^{\bullet}OH$ and maintains a reservoir of low-volatility compounds, including monomeric sulfate esters and oligomer fragments. We propose tentative structures and formation mechanisms for previously uncharacterized SOA constituents in $PM_{2.5}$. Our results suggest that this $^{\bullet}OH$-driven renewal of low-volatility products may extend the atmospheric lifetimes of particle-phase IEPOX-SOA by slowing the production of low-molecular weight, high-volatility organic fragments and likely contributes to the large quantities of 2-methyltetrols and methyltetrol sulfates reported in $PM_{2.5}$.

KEYWORDS: *hydroxyl radical, fragmentation, revolatilization, atmospheric lifetime, methyltetrols, organosulfates, atmospheric multiphase chemistry*

1. INTRODUCTION

Secondary organic aerosol (SOA) derived from volatile organic compounds (VOCs) is estimated to comprise 70−90% of the organic mass in aerosols with aerodynamic diameters ≤2.5 μm ($PM_{2.5}$).[1] Isoprene, the most abundantly emitted reactive VOC,[2] oxidizes to form isoprene epoxydiols (IEPOX) under low-nitric oxide (NO) conditions,[3,4] and then produces SOA through acid-driven multiphase chemistry with inorganic sulfate ($Sulf_{inorg}$ = SO_4^{2-} + HSO_4^-) aerosol.[5−7] Riva et al.[8] recently demonstrated that when IEPOX is in excess during acid-driven reactive uptake onto acidic sulfate particles, 90% of $Sulf_{inorg}$ may be converted to organosulfates (OSs).

In isoprene-rich regions, the IEPOX-derived methyltetrol sulfates (MTSs) are among the most abundant compounds in $PM_{2.5}$,[9] contributing up to 13% of the total organic carbon in $PM_{2.5}$ collected in downtown Atlanta, GA,[10] up to 10% of OA

Received: May 4, 2022
Revised: October 27, 2022
Accepted: October 31, 2022
Published: November 15, 2022

mass at Look Rock, TN,[11] and Manaus, Brazil,[12] and up to 15% of total organic matter collected at Lake Michigan.[13] MTSs and other isoprene-derived OSs have also been measured in submicron particles in the upper troposphere,[14−16] cloud water,[17,18] and other forms of precipitation such as hailstones and rain.[19] The low volatility of IEPOX-derived OSs is thought to contribute to cloud formation[20,21] and lead to long atmospheric lifetimes of IEPOX-SOA, with removal only by particle deposition.[11,15] Though some atmospheric chemistry models include the formation of IEPOX-SOA, most assume that IEPOX-SOA and its particulate OSs remain unreactive.[22−25] A potential mechanism for the loss of OS-containing particle mass is •OH oxidation and fragmentation of the C_5 isoprene skeleton into lower-molecular-weight (MW) compounds that partition into the gas phase.[26−29] If volatilization as a result of heterogeneous •OH oxidation is substantial, it would impact the lifetime and effects of IEPOX-SOA. Furthermore, few studies[28−30] have attempted to estimate the extent and kinetics of revolatilization of isoprene- and terpene-derived SOA in the atmosphere.

During IEPOX reactive uptake, organics have been observed to "salt out" of the aqueous phase,[6,31,32] forming a viscous organic shell around an aqueous $Sulf_{inorg}$ core, which may affect its subsequent chemistry.[8,33−38] The organic shell slows the uptake of IEPOX into the aqueous phase[39,40] and facilitates the sequestration of IEPOX-derived organics in the surface region, increasing the probability of exposure to gas-phase oxidants such as •OH. Although IEPOX-derived SOA compounds appear to account for a large portion of isoprene-derived compounds in ambient SOA,[41,42] mechanisms of formation of many OSs and organic acids with clear isoprene signatures that have been measured in the atmosphere are unknown, making it difficult to account for them in atmospheric chemical transport models. Additionally, many IEPOX-SOA chemistry studies[8,39,43−45] have been conducted in the dark in the absence of •OH, a key atmospheric oxidant during the daytime.[46]

To our knowledge, three studies have examined the heterogeneous •OH oxidation of suspended IEPOX-SOA particles or of its individual constituents.[30,47,48] Experiments were conducted with residence times under five min and •OH levels of ~10^{11-13} molecules cm^{-3}, orders of magnitude higher than ambient-relevant •OH concentrations of around 10^6 molecules cm^{-3}.[49] These studies made significant progress in examining individual components of IEPOX-SOA. For example, in a previous study from our group, Chen et al.[48] proposed structures and plausible pathways for oxidation products derived from particulate 2-MTS previously reported in $PM_{2.5}$ from the upper and lower troposphere, as well as in cloud water and hailstones.[12,14,16−19,48] However, there remains a need for research on the heterogeneous •OH oxidation of the complete IEPOX-SOA particle mixture, including the characterization of key IEPOX-SOA constituents and their formation kinetics. The compositional changes of freshly generated IEPOX-SOA particles by aerosol aging mechanisms, such as heterogeneous •OH oxidation, remain uncertain and are the focus of this study.

2. EXPERIMENTAL METHODS

2.1. Smog Chamber Experiments. Experiments were conducted in a 10 m^3 indoor Teflon chamber at the University of North Carolina at Chapel Hill.[6] The chamber was flushed with zero air for ~12 h before each experiment to achieve background aerosol volume concentrations of <0.1 μm^3 cm^{-3}, measured by a scanning electrical mobility spectrometer (SEMS) consisting of a differential mobility analyzer (model 2002, BMI Inc.) coupled to a butanol mixing condensation particle counter (model 1710, BMI Inc.), and then humidified to ~50% relative humidity (RH) at 21 °C (see experimental conditions in Table S1). The RH and temperature were monitored by a dewpoint meter (Omega Engineering Inc.) at 5 s intervals. Background ozone (O_3) concentrations were below the limit of quantification (<2 ppb). O_3 was monitored at 10 s intervals by an O_3 analyzer (model 202, 2B Technologies). All experiments were conducted with minimal UV or visible light sources.

A custom-built atomizer was used to inject 90 ± 10 μm^3 cm^{-3} ammonium bisulfate (NH_4HSO_4) seed aerosol from an aqueous solution of 0.12 M NH_4HSO_4 (solution pH = 1.4; Atlas Scientific pH probe). After allowing the seed aerosol to stabilize for 30 min, 15 mg of authentic *trans*-β-IEPOX (synthesized in-house[50]) was injected into the chamber by passing heated nitrogen (67 °C) at 5 L min^{-1} through a glass manifold containing ethyl acetate solution until aerosol volume growth ceased (typically ~1 h after injection). •OH was generated by the reaction of ~2 ppm O_3 with tetramethylethylene (TME), injected at 280 mL min^{-1} from a 250 ppm cylinder with 5 L min^{-1} of sheath flow[51] for 4 h to sustain •OH concentration. SOA was collected from the chamber onto Teflon filters (0.2 μm pore size, PALL Corp.) for 1 h at a flowrate of ~12 L min^{-1} before and after oxidative aging. Control experiments with carbon strip denuders upstream of filters did not yield significantly different products or product distributions, indicating no additional SOA oxidation on filters during collection. In addition, 4 h aging experiments were conducted without the presence of •OH, with filters collected before and after nonoxidative aging.

Average •OH concentrations were estimated from initial O_3 and TME injection rate using a model based on the work of Lambe et al.[52] The •OH concentrations reported in Table S1 represents an upper bound estimate, as the model does not consider sinks for •OH.

IEPOX injection efficiencies ranged from 0.5 to 0.7 (~150−210 ppbv), as determined by the mass difference between the manifold pre- and post-injection using an analytical balance (Mettler Toledo model MS205DU).

2.2. Ambient $PM_{2.5}$ Collection. Field samples used in this work were collected during the 2013 Southern Oxidant and Aerosol Study (SOAS) at Look Rock, TN, USA[11] (analyzed 2019); during the summer of 2016 in Manaus, Brazil, as part of the Green Ocean Amazon field campaign[12] (analyzed 2018[48]); during the summer of 2017 in the Galápagos Islands, Ecuador[48] (analyzed 2019); and during the summer of 2021 in Research Triangle Park, NC, USA[53] (analyzed 2022). All four sites are typically isoprene-rich, low-NO atmospheres. Detailed information on sample collection, storage, and filter extraction is published elsewhere[8,48] and discussed in the Supporting Information. A 23 h $PM_{2.5}$ sample from Look Rock and a 24 h $PM_{2.5}$ sample from the Galápagos Islands containing the highest IEPOX-SOA mass (estimated by an Aerosol Chemical Speciation Monitor, Aerodyne, Inc., for Look Rock) were selected for reanalysis by HILIC/ESI-HR-QTOFMS. A 24 h $PM_{2.5}$ sample from Manaus was selected for reanalysis based on its low concentration of levoglucosan, indicating minimal biomass burning influence,[54] and a high concentration of MTSs.[12] A 23.5 h sample from Research

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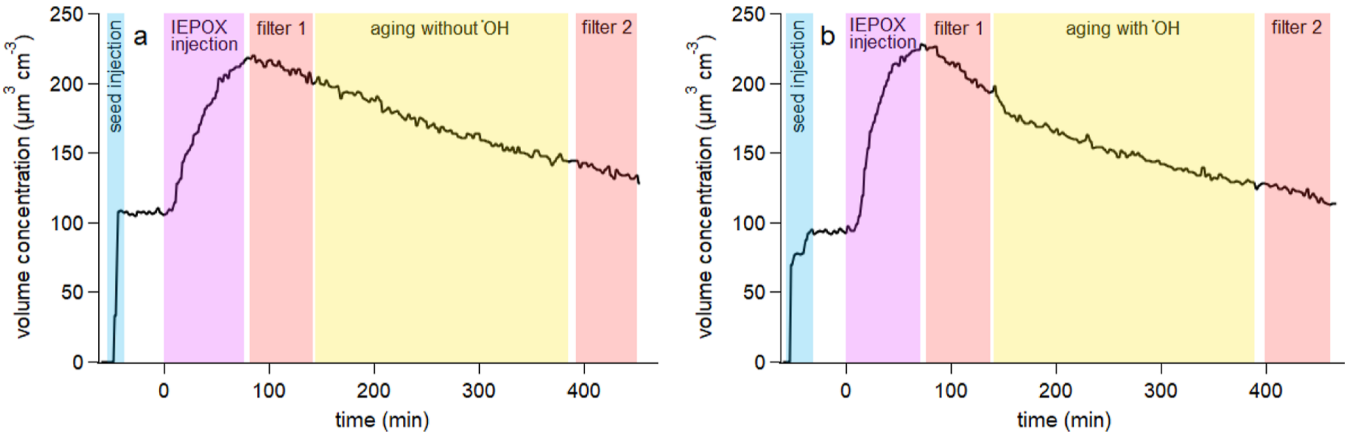
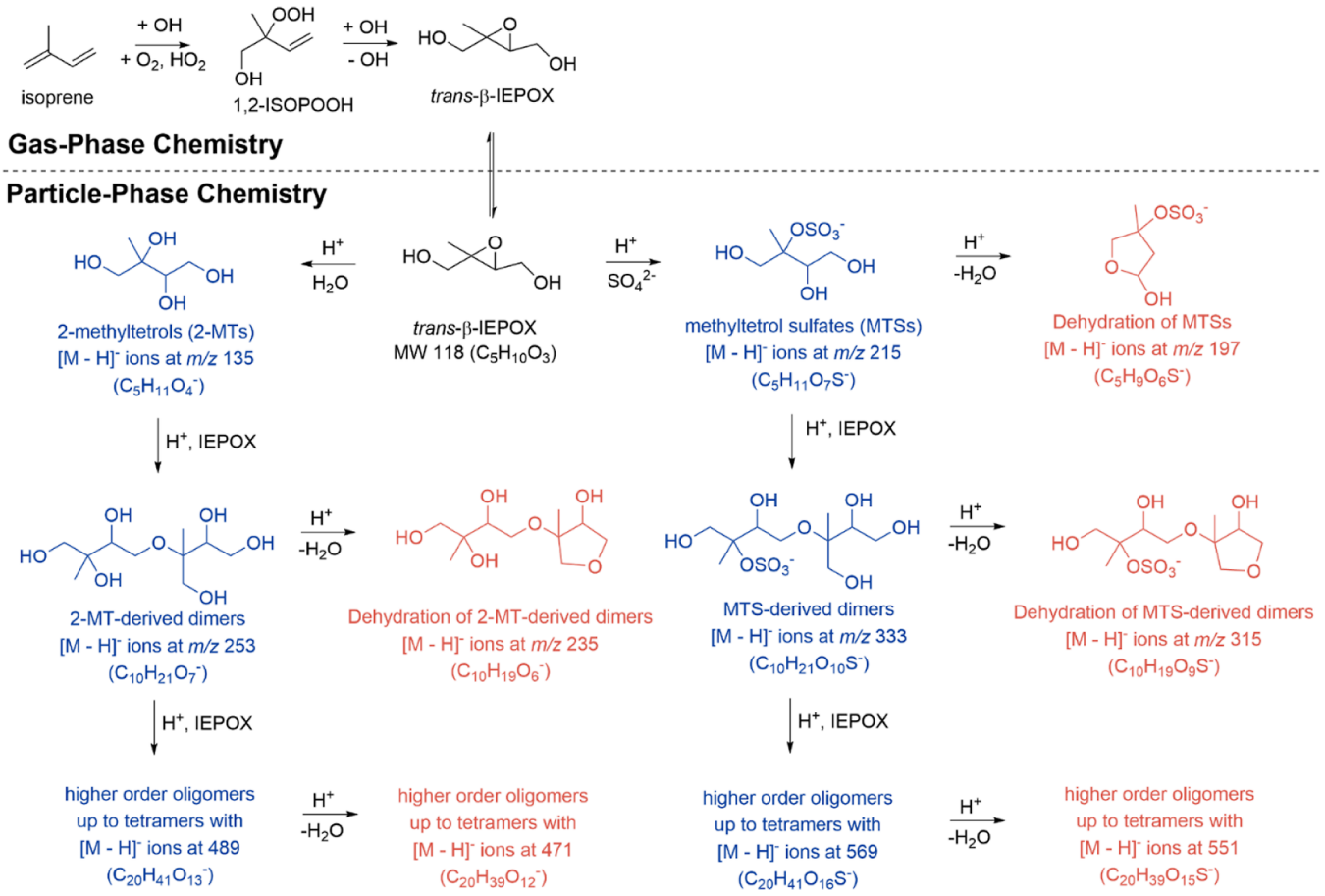


Figure 1. Time series of aerosol volume concentration for (a) representative 4 h of aging without an oxidant (Expt 7, Table S1) and (b) heterogeneous $^{\bullet}$OH oxidation (Expt 1, Table S1) of freshly generated IEPOX-SOA particles. Time is marked relative to the start of IEPOX injection. The $Sulf_{inorg}$ seed aerosol injection is shaded in blue; IEPOX injection is shaded in purple; filter collection periods is shaded in red; and TME injection or aging without OH is shaded in yellow. O_3 was injected once after the first filter collection, before TME injection.

Scheme 1. Particle-phase Production of 2-MT and MTS Monomers as well as Their Corresponding Oligomers, including Dehydration Products, in Freshly Generated IEPOX-SOA Particles. Nondehydrated Products are Highlighted in Dark Blue, and Dehydration Products are Highlighted in Red



Triangle Park was selected based on its high organic carbon concentration.[53]

2.3. Aerosol Chemical Characterization. All samples were extracted in methanol (Optima LC/MS Grade, Fisher Scientific) by 45 min sonication. The methanol filter extracts were dried under a gentle stream of high-purity nitrogen (Airgas) and reconstituted in 150 or 100 μL of 95:5 acetonitrile (ACN, optima grade, Fisher Scientific):17.8 MΩ Milli-Q water. We note that 2-methyltetrols (2-MTs), MTSs, and methyl sulfate have extraction efficiencies of 100 ± 2%, but other compounds have not been tested due to a lack of authentic standards. Filter extracts were analyzed by negative (−) ion mode hydrophilic interaction liquid chromatography coupled with electrospray ionization high-resolution quadru-

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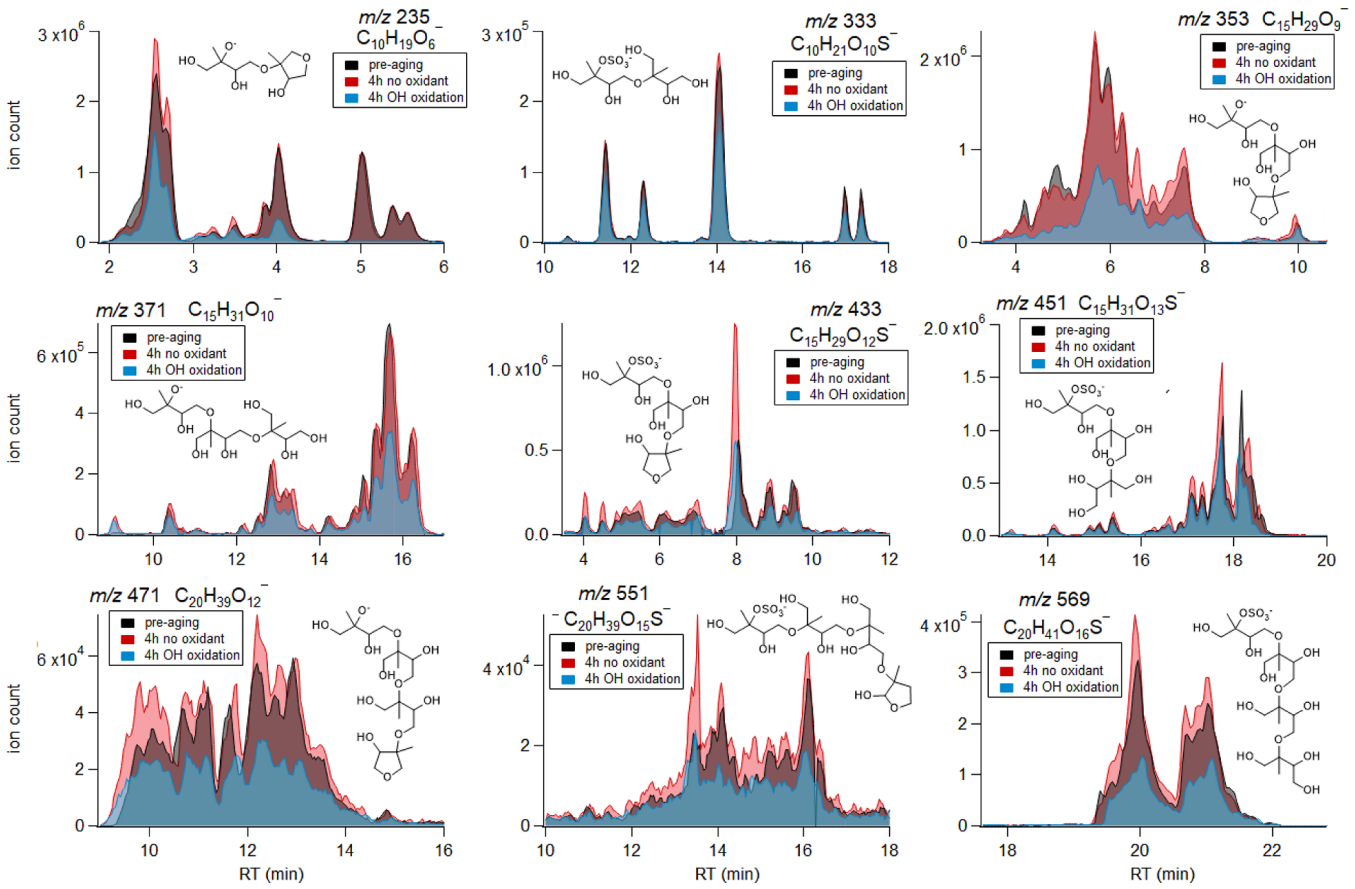

Figure 2. EICs of IEPOX-derived nonsulfated and sulfated oligomers detected by HILIC/ESI-HR-QTOFMS: pre-aging (black traces, Expt. 8, Table S1), 4 h of aging with no oxidant (red traces, Expt. 8, Table S1), and 4 h of aging with •OH (blue traces, Expt. 5, Table S1). Each signal is adjusted by the chamber particle volume integrated over the sampling period.

pole time-of-flight mass spectrometry (HILIC/ESI-HR-QTOFMS), as described by Cui et al.[12] and discussed in the Supporting Information. Data were analyzed using Agilent MassHunter Version B.06.00 Build 6.0.633.0 qualitative software. Duplicate filter samples collected in parallel from the same experiment (Expt. 6, Table S1) were used to compare our HILIC/(−)ESI-HR-QTOFMS method to reverse-phase liquid chromatography (RPLC) coupled to ESI-HR-QTOFMS operated in the negative ion mode (RPLC/(−)ESI-HR-QTOFMS). This was done to demonstrate that the HILIC/(−)ESI-HR-QTOFMS method has better chromatographic resolution of the high-order sulfated and nonsulfated oligomers in IEPOX SOA (Figure S1). Details of the RPLC/(−)ESI-HR-QTOFMS method are provided in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Minor SOA Mass Loss due to Heterogeneous •OH Oxidation. Figure 1 compares evolving aerosol volume concentrations with 4 h of aging without •OH (Expt 5, Table S1) and 4 h of heterogeneous •OH oxidation (Expt 1, Table S1) of freshly generated IEPOX-SOA. When gas-phase IEPOX was injected into the chamber, SEMS aerosol volume concentration increased rapidly as a result of acid-driven uptake of IEPOX. During the aging of IEPOX-SOA both with and without •OH, SEMS measurements indicate that the average size of the particles increased and the number concentration decreased, which is consistent with expected wall loss. We did not observe significant particle shrinkage or volume concentration loss expected from off-gassing of lower MW volatile products resulting from fragmentation of the C_5 IEPOX skeleton (see Figure S2). Minimal off-gassing indicates that most oxidation products remain within the particles during the 4 h •OH oxidation period.

3.2. Consumption of Oligomers and Production of Low-MW Oxidation Products. Scheme 1 shows that IEPOX is initially transformed into particulate 2-MTs, MTSs,[8,55] and the dehydration product detected as $[M-H]^-$ at m/z 197 ($C_5H_9O_6S^-$)[8,55] through acid-driven multiphase chemistry in the aqueous and acidic $Sulf_{inorg}$ phase.[5,7,8,12] Previous studies have also detected the rapid appearance of OS dimers at m/z 333 ($C_{10}H_{21}O_{10}S^-$),[5,8,12] dehydrated dimers at m/z 315 ($C_{10}H_{19}O_9S^-$),[8] and the nonsulfated analogues at m/z 253 ($C_{10}H_{21}O_7^-$)[5−8] and 235 ($C_{10}H_{19}O_6^-$),[8] as well as higher-order oligomers.[31,56]

With nonoxidative aging, oligomers and dehydrated derivatives containing up to four C_5 units (Figure 2) are generated in SOA by the sequential reaction of IEPOX with 2-MT and MTS.[32] We observe that the oligomers increase during aging in the absence of •OH, consistent with the report of Lin et al.[31] in which sulfated and nonsulfated oligomers containing up to ten C_5 units were identified. The formation of oligomers over time is further supported by measurements made by D'Ambro et al.[26,27] that link the nonoxidative aging of isoprene- and α-pinene-derived SOA with decreasing volatility. However, oligomers containing three and four C_5 units

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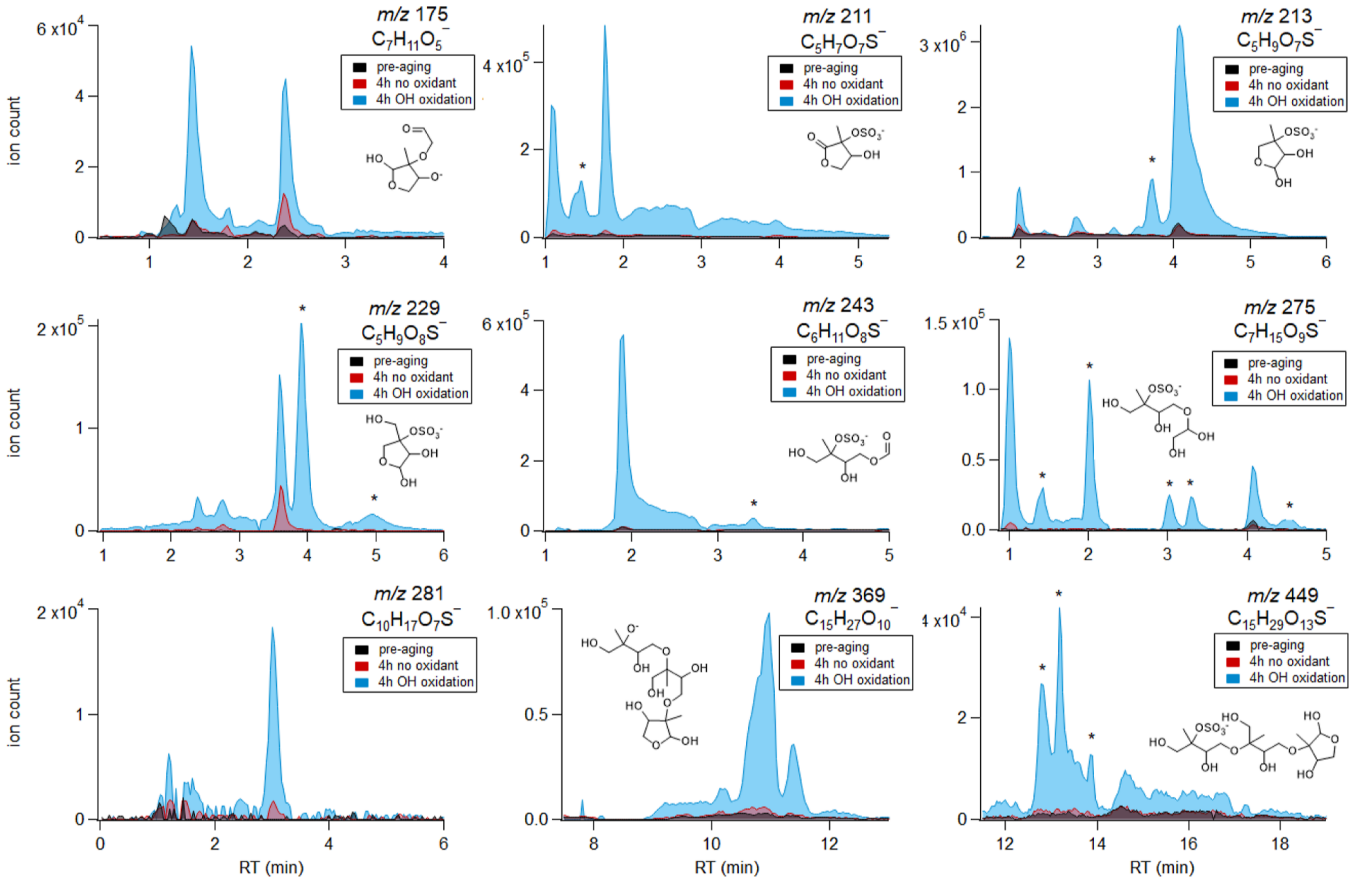

Figure 3. EICs of nine oxidation products of IEPOX-derived oligomers detected by HILIC/ESI-HR-QTOFMS: pre-aging (black traces, Expt. 8, Table S1), 4 h of aging with no oxidant (red traces, Expt. 8, Table S1), and 4 h of aging with •OH (blue traces, Expt. 5, Table S1). Peaks appearing only in •OH-aged samples are indicated by asterisks. Each signal is adjusted by the chamber particle volume integrated over the sampling period.

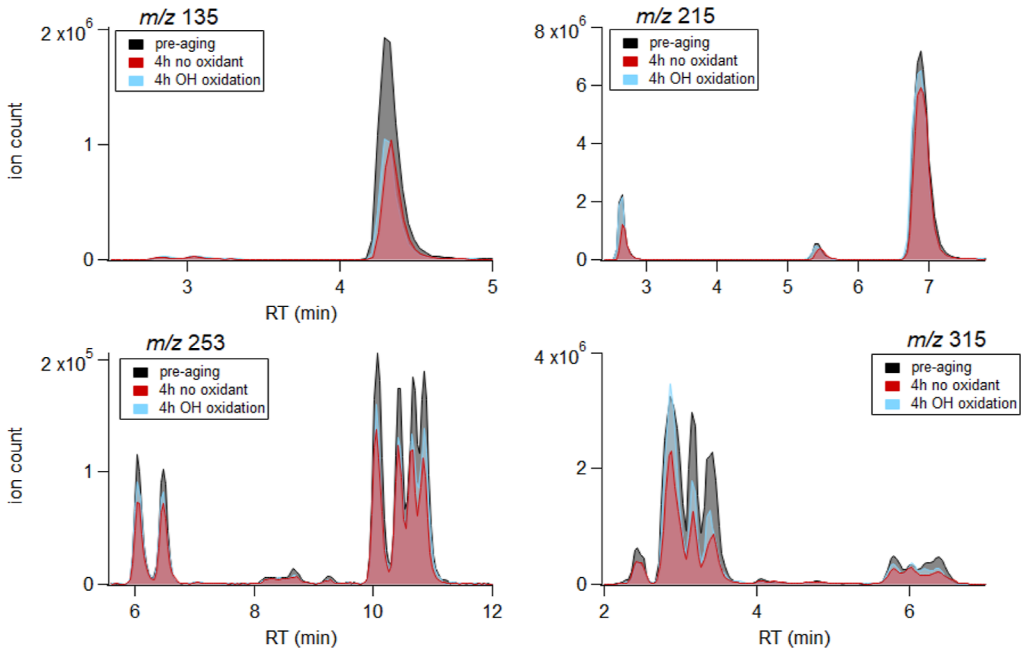

Figure 4. EICs of four precursor compounds detected by HILIC/(−)ESI-HR-QTOFMS: pre-aging (black traces, Expt 1, Table S1), 4 h of aging with no oxidant (red traces, Expt 5, Table S1), and 4 h of aging with •OH (blue traces, Expt 1, Table S1). Each signal is adjusted by the chamber particle volume integrated over the sampling period; samples have been diluted 100×.

decrease dramatically after 4 h of heterogeneous •OH oxidation, which is consistent with measurements made by Hall et al.[57] of α-pinene SOA. The behavior of the dimers is similar: *m/z* 235 and 333 decrease somewhat less during aging

https://doi.org/10.1021/acs.est.2c03200
Environ. Sci. Technol. 2022, 56, 16611−16620

with •OH compared to aging without •OH, with levels possibly maintained by oxidative breakdown of the higher oligomers. Scheme S1 provides an example of the fragmentation of an MTS-derived tetramer (m/z 569, $C_{20}H_{41}O_{16}S^-$) to yield the dimer m/z 333.

Products formed during 4 h of heterogeneous •OH oxidation are shown in Figure 3, and the formation pathways are proposed in Schemes S2,S3. Oxidation of the oligomers in Figure 2 is a potential contributor to products at m/z 211 ($C_5H_7O_7S^-$), 213 ($C_5H_9O_7S^-$), and 229 ($C_5H_9O_8S^-$), which were previously reported[48] from the heterogeneous oxidation of particulate 2-MTSs. Table S2 shows tentative structures for additional deprotonated molecules detected in the chamber experiments and ambient $PM_{2.5}$ samples, which are based on empirical formulas calculated from high-resolution mass data and the putative oxidation pathways shown in Schemes S2−S11.

A number of the heterogeneous oxidation products shown in Figure 3, generated during •OH aging, are also present at low counts in samples aged without oxidation, suggesting that there are alternative pathways to some products, possibly through acid-driven oligomer degradation. We note that in samples aged without oxidation, there are no ions with compositions compatible with peroxides or hydroperoxides, precluding particle oxidation by •OH from the decomposition of organic peroxides.[58,59]

3.3. Minimal Change in the Particulate Levels of MTSs, 2-MTs, and Dimers. Because MTSs are the most abundant IEPOX-SOA tracers and OSs in atmospheric fine particles,[5,7,12,42,56] MTSs should be the primary precursors to oxidation products under the conditions of the present study. Consistent with this expectation, we observe the same multifunctional OSs recently reported by Chen et al.[48] in a study of particulate MTS oxidation and propose the same heterogeneous oxidation pathways. Briefly, the reaction of alkyl peroxy radical (RO_2•) intermediates from H-abstraction and rapid addition of O_2 leads to OS products via Russell disproportionation,[60] Bennett−Summers reaction,[61] or β-scission of alkoxy radicals (RO•).[62,63] Acid-driven dehydration reactions can lead to methyl-tetrahydrofuran rings,[31] and H-abstraction α to an ether oxygen can lead to fragmentation, restoring one or more C_5 skeletons. A general mechanism based on the work of Chen et al.[48] is shown in Scheme S12, highlighting some important mechanisms in the production of SOA constituents discussed here. The formation of non-OS products observed can be explained by analogous reaction mechanisms in 2-MTs (Scheme S13).

However, the lack of consumption of monomers and certain dimers observed in our experiments does not support the high levels of products previously attributed to their oxidation by •OH.[48] Figure 4 shows that 2-MTs and MTSs decrease during aging, which is attributed to oligomerization, but the addition of •OH does not significantly increase their consumption. If the predominant process was the heterogeneous •OH oxidation of particulate 2-MTs and MTSs, off-gassing of volatile fragmentation products and substantial decreases in the levels of these compounds would be expected. The results displayed in Figure 4 therefore imply that the particulate 2-MTs and MTSs are either not being consumed or are being regenerated during •OH aging.

Recent studies[8,39] demonstrate that reactive uptake of IEPOX becomes limited as both an organic shell and the aqueous inorganic core of the particle become more viscous, precluding substantial further generation of initial uptake products (2-MTs, MTSs, and dimers) from gas-phase IEPOX. Hu et al.[30] demonstrated in an oxidation flow reactor (OFR) study that at high •OH concentrations (>10^{10} molecules cm^{-3}), the organic coating of IEPOX-SOA in ambient $PM_{2.5}$ maintains a barrier to the uptake of both IEPOX and OH, with the result that the SOA is resistant to mass loss by the production of high-volatility organic fragments. As regeneration from IEPOX would take place during aging without •OH, we do not observe it and conclude that further uptake of gas-phase IEPOX is not maintaining particulate MTS and 2-MT levels.

The dimers shown in Figure 4, in contrast to those shown in Figure 2, appear to increase during •OH aging compared to aging without •OH. We propose that monomers (and possibly lower-order oligomers) are regenerated via oxidative fragmentation of higher-order oligomers, such as those shown in Figure 2 to be heavily consumed during •OH oxidation. Possible pathways from a sulfated trimer observed by HILIC/ESI-HR-QTOFMS at m/z 451 ($C_{15}H_{31}O_{13}S^-$) to sulfated and nonsulfated monomers and dimers are proposed in Scheme S14.

3.4. Atmospheric Implications. Evidence from our chamber experiments suggests that oligomers are consumed during heterogeneous •OH oxidation, while monomers, for the most part, are not, despite the abundance of monomer products in our chamber samples. We observed species that could result from the •OH-driven fragmentation of sulfated and nonsulfated oligomers and dimers, based on the reaction pathways proposed here. We also failed to observe the particle shrinkage or volume concentration loss expected from the off-gassing of volatile low-MW fragmentation products of the C_5 IEPOX skeleton. Instead, we observed a pattern of shifting molecular species abundances that could be explained by fragmentation of sulfated and nonsulfated oligomeric species into lower-MW nonvolatile products, resulting in minimal loss of SOA mass during the timescale of our experiments. If particulate oligomers drive reactivity in IEPOX-SOA, not only might they regenerate monomers but they also could act as a sink for •OH, slowing monomer consumption. This combined effect could extend the apparent atmospheric lifetime of particulate 2-MTs and MTSs, explaining their high abundances previously reported in highly aged atmospheric $PM_{2.5}$ samples.[5,7,12]

In such atmospheric samples, we observe species with the same m/z and retention time patterns as those in chamber samples (see Figures S3−S5). Because the SOA studied here is exclusively the product of IEPOX uptake, some C_6−C_{10} compounds in ambient SOA that may have been previously misidentified as monoterpene-derived OSs can now likely be attributed to IEPOX.

Due to the similar RH,[64] pH,[64] and IEPOX/$Sulf_{inorg}$ ratios[8] between our chamber experiments and conditions in high-isoprene, low-NO_x atmospheres, we believe that, as in our chamber experiments, atmospheric IEPOX-SOA should be highly oligomerized. However, although their heterogeneous •OH oxidation products are observed in ambient SOA, high-order IEPOX-derived oligomers characterized in our freshly generated SOA samples are not. The dimers at m/z 253 and 333, which are highly abundant in freshly generated IEPOX-SOA particles, are detected at lower levels in ambient $PM_{2.5}$ samples than particulate 2-MTs, MTSs, and other oxidized isoprene-derived monomers; many trimers and tetramers

https://doi.org/10.1021/acs.est.2c03200
Environ. Sci. Technol. 2022, 56, 16611−16620

found in freshly generated IEPOX-SOA particles from our smog chamber studies were not detected in atmospheric $PM_{2.5}$ using the HILIC/(−)ESI-HR-QTOFMS method, nor were higher-MW oxidized products like m/z 369 and 467 that could decompose further.

Here, we assess ion abundance in atmospheric samples using the sample/blank EIC peak area ratio (see Table S2). Ions are considered to be present in an ambient sample only when the sample/blank ratio exceeds 3. Species more abundant in the atmosphere than in the chamber are predominantly sulfated monomer and dimer products, including some of the most abundant IEPOX products in all four of our atmospheric samples, m/z 211 and 281. Species more abundant in chamber samples are predominantly sulfated and nonsulfated oligomers, high-MW sulfated species, and low-MW nonsulfated species. We take these to be the IEPOX-SOA constituents that are consumed during oxidation or reactions with other constituents of ambient SOA, which has both oligomerized and oxidized for a longer period and contains other biogenic and anthropogenic reactive species.

While the fragmentation of isoprene-derived monomers generates volatile C_1−C_4 compounds, such as formic and acetic acid,[28,30,65] oligomers produce functionalized C_5−C_9 compounds with low vapor pressures.[51,66,67] The apparent $^{\bullet}$OH preference for oligomers extends the effective atmospheric lifetime of particulate monomers and the lifetime of IEPOX-SOA particulate matter as a whole, suggesting that the use of degradation rate constants from single-component studies in models will overestimate losses of IEPOX-SOA.[47,48] When particulate carbon remains in SOA longer, and thus becomes more oxidized, SOA may also become more efficient in cloud and ice nucleation.[68] Future work is needed to characterize the kinetics and quantify the products of the heterogeneous $^{\bullet}$OH oxidation of IEPOX-SOA mixtures in aerosol form in order to improve the prediction of their impacts on air quality and climate. This should also include a focus on obtaining gas-phase data to confirm the lack of revolatilization observed during this study as well as testing multiple pH and RH conditions relevant to different locations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.2c03200.

Additional methods; description regarding the LC/ESI-MS analysis; experimental conditions; proposed formulas and structures for IEPOX-SOA constituents; additional chromatograms for peak retention time stability and comparison of chamber and atmospheric samples; and oxidation reaction schemes leading to the observed m/z values (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was primarily funded by the National Science Foundation (NSF) under grant nos. AGS-1703535 (Surratt), AGS-2039788 (Surratt), AGS-1703019 (Ault), AGS-2040610 (Ault), and AGS-2001027 (Gold, Zhang). In addition, this

work was funded in part by the National Institute for Occupational Safety and Health (grant no. T42-OH008673), the National Institute of Environmental Health Sciences (grant no. P30ES010126), the Hong Kong Research Grants Council (Project ID: 2130626), and the William Neal Reynolds Fellowship of the Royster Society of Fellows at the University of North Carolina at Chapel Hill. The authors would like to thank Jin Yan for her help during the experiments and for helpful discussions. We thank Dr. William Vizuete and Tessa Szalkowski from the University of North Carolina at Chapel Hill for providing the $PM_{2.5}$ sample collected from the Galápagos field site. The authors would also like to thank Drs. Cristine M. D. Machado, Scot T. Martin, and Erickson O. dos Santos for providing the $PM_{2.5}$ sample collected from Manaus, Brazil, Central Amazonia; as well as John Offenberg for providing the $PM_{2.5}$ sample collected from Research Triangle Park, NC, USA.

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https://doi.org/10.1021/acs.est.2c03200
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