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Chemical Characterization of Secondary Organic Aerosol from Oxidation of Isoprene Hydroxyhydroperoxides

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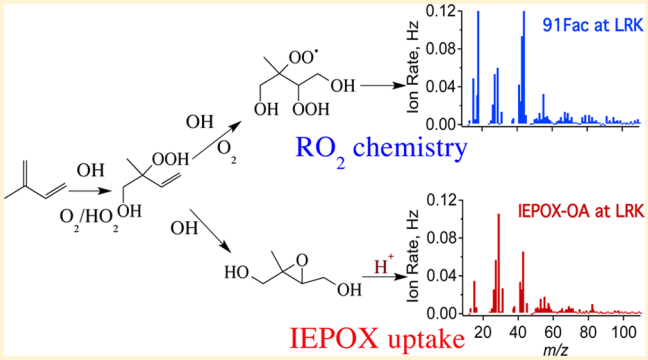
Supporting Information

ABSTRACT: Atmospheric oxidation of isoprene under low-NO_x conditions leads to the formation of isoprene hydroxyhydroperoxides (ISOPOOH). Subsequent oxidation of ISOPOOH largely produces isoprene epoxydiols (IEPOX), which are known secondary organic aerosol (SOA) precursors. Although SOA from IEPOX has been previously examined, systematic studies of SOA characterization through a non-IEPOX route from 1,2-ISOPOOH oxidation are lacking. In the present work, SOA formation from the oxidation of authentic 1,2-ISOPOOH under low-NO_x conditions was systematically examined with varying aerosol compositions and relative humidity. High yields of highly oxidized compounds, including multifunctional organosulfates (OSs) and hydroperoxides, were chemically characterized in both laboratory-generated SOA and fine aerosol samples collected from the southeastern U.S. IEPOX-derived SOA constituents were observed in all experiments, but their concentrations were only enhanced in the presence of acidified sulfate aerosol, consistent with prior work. High-resolution aerosol mass spectrometry (HR-AMS) reveals that 1,2-ISOPOOH-derived SOA formed through non-IEPOX routes exhibits a notable mass spectrum with a characteristic fragment ion at m/z 91. This laboratory-generated mass spectrum is strongly correlated with a factor recently resolved by positive matrix factorization (PMF) of aerosol mass spectrometer data collected in areas dominated by isoprene emissions, suggesting that the non-IEPOX pathway could contribute to ambient SOA measured in the Southeastern United States.



INTRODUCTION

The largest mass fraction of atmospheric fine particulate matter ($PM_{2.5}$, aerosol with aerodynamic diameters ≤2.5 μm) is generally organic, dominated by secondary organic aerosol (SOA) formed from the gas-phase oxidation of volatile organic compounds (VOCs). Although SOA contributes a large portion (20−90%) of the total $PM_{2.5}$ mass, current models continue to under-predict SOA mass.[1−3] However, recent studies have demonstrated that incorporating reactive uptake of organic species to acidic wet aerosols, such as isoprene epoxydiols (IEPOX), improves agreement with observations.[4,5] Biogenic VOCs (BVOCs), such as isoprene and monoterpenes, are typically the most abundant SOA precursors, especially in regions of dense terrestrial vegetation.[4]

Isoprene (2-methyl-1,3-butadiene, C_5H_8) is the most abundant nonmethane hydrocarbon emitted into the troposphere with emissions exceeding 500 Tg yr^{-1}.[7] The principal atmospheric degradation pathway of isoprene is oxidation by hydroxyl (OH) radical,[8−10] which along with oxidation by nitrate (NO_3) radical and ozone (O_3), accounts for up to 50% of the SOA budget.[11] OH-initiated oxidation of isoprene produces organic peroxy radicals (RO_2) that under low-NO_x conditions, subsequently react with hydroperoxy radicals (HO_2) and form different isomers of isoprene hydroxyhydroperoxides (ISOPOOH). Recent studies have shown that of the ISOPOOH isomers, two are atmospherically important: the 2-hydroperoxy-2-methylbut-3en-1-ol (1,2-ISOPOOH) and the 2-hydroperoxy-3-methylbut-3en-1-ol (4,3-ISOPOOH).[12,13] ISOPOOH can subsequently react with OH radicals and lead to the production of isoprene epoxydiols (IEPOX) at yields greater than 75%.[12]

SOA formation from acid-catalyzed particle-phase reactions of IEPOX has been previously demonstrated.[15−21] IEPOX-derived SOA tracers, such as 2-methyltetrols, C_5-alkene triols, IEPOX-derived organosulfates (OSs), IEPOX-derived

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oligomers, have been chemically characterized in both laboratory-generated SOA and atmospheric $PM_{2.5}$ samples.[16,17,22−26] IEPOX-derived SOA has been observed to account for up to 33% of the total fine organic aerosol (OA) mass collected during summer in downtown Atlanta, GA.[27] Similar levels of isoprene-derived SOA have been recently observed at other field sites across the southeastern US,[27−32] and in other biogenic-rich areas.[33,34]

Although IEPOX is the main product of ISOPOOH oxidation, recent studies have reported the formation in the gas phase of highly oxidized compounds.[12,13] Krechmer et al.[13] recently demonstrated that gas-phase reaction products from ISOPOOH photooxidation could be comparable to the maximum SOA potential of the highly oxidized compounds identified from the oxidation of monoterpenes.[35] This underlines the potential atmospheric significance of SOA formation arising from ISOPOOH oxidation. Although the photooxidation of isoprene forms IEPOX in high yield, the rate of its reactive uptake under atmospheric conditions is slow,[19,20] and may be significantly reduced by the presence of organic coating on pre-existing inorganic aerosols.[36] Moreover, it has recently been shown that IEPOX reactive uptake may only account for half the aerosol formed from isoprene oxidation under low NO conditions.[38] Thus, recent studies emphasize the fact that either gas-phase oxidation of IEPOX or ISOPOOH through a non-IEPOX route (i.e., reactive uptake) could lead to SOA formation and potentially contribute to a significant fraction of the isoprene-derived SOA budget.

In this study, we investigate the oxidation of authentic 1,2-ISOPOOH synthesized in-house[28] in the presence of sulfate aerosol of varying acidity under different relative humidity (RH) conditions, with a focus on the chemical characterization of the resultant SOA constituents. Filters collected from indoor smog chamber experiments were analyzed by ultra performance liquid chromatography interfaced to a high-resolution quadrupole time-of-flight mass spectrometer equipped with electrospray ionization (UPLC/ESI-HR-QTOFMS), gas chromatography interfaced to an electron impact-mass spectrometer (GC/EI-MS), and assayed by an iodometric-spectrophotometric method to measure total organic peroxides.[24,39] Selected filters were also extracted and aerosolized into a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS). Finally, $PM_{2.5}$ samples collected from a ground site at Look Rock (LRK), TN, during the 2013 Southern Oxidant and Aerosol Study (SOAS), were chemically characterized, to supplement the PM_1 characterization by an Aerodyne Aerosol Chemical Speciation Monitor (ACSM), for evaluation of the contribution of ISOPOOH-derived SOA to the OA sampled at LRK. Comparison of laboratory and field data supports the potential importance of ISOPOOH oxidation as contributing to the isoprene-derived SOA budget through a non-IEPOX route.

■ EXPERIMENTAL SECTION

Chamber Experiments. Nineteen experiments were performed in the 10−m^3 Teflon indoor environmental smog chamber at the University of North Carolina. The details of experimental setup and analytical techniques used in this work have been described previously.[16,17,40] Briefly, experiments were carried out at room temperature (296 ± 1 K) in the dark and at low- (<5%) and high-RH (50−55%). Experimental conditions are summarized in Supporting Information (SI) Table S1. Prior to each experiment, the chamber was flushed continuously with clean house air for ∼24 h until the particle mass concentration was <0.01 $\mu g\ m^{-3}$ to ensure that there were no pre-existing aerosol particles. Aerosol size distributions were continuously measured using a differential mobility analyzer (DMA, Brechtel Manufacturing Inc. (BMI), model 2002) coupled to a mixing condensation particle counter (MCPC, BMI model 1710) in order to monitor aerosol number, surface area, and volume concentration within the chamber. Chamber flushing also reduced O_3 and VOC concentrations below the detection limit (<1 ppb for ozone). The O_3 concentration was monitored over the course of experiments using an UV photometric analyzer (Model 49P, Thermo-Environmental). Temperature and RH in the chamber were continuously monitored using a dew point meter (Omega Engineering, Inc.).

Acidified (ABS) or nonacidified (AS) ammonium sulfate seed aerosols were generated by nebulizing aqueous solutions of 0.06 M $(NH_4)_2SO_4$ (aq) + 0.06 M H_2SO_4 (aq) or 0.06 M $(NH_4)_2SO_4$ (aq), respectively. As previously determined by Riva et al.,[36] the aerosol acidity of the ABS seed aerosols used in this work is comparable to range of acidity of ambient aerosols recently characterized in the southeastern US.[37] Seed aerosols were introduced into the Teflon chamber prior to VOC injection. A known amount of 1,2-ISOPOOH (∼50 or 300 ppb; SI Table S1) was introduced into the chamber by passing a heated nitrogen (N_2) stream through a heated glass manifold (40−50 °C) for 90 min. A complete description of the 1,2-ISOPOOH synthesis is described in the SI text; NMR data were published previously that demonstrated high purity (>99%).[28] OH radicals were formed by ozonolysis of tetramethylethylene (TME, Matheson) in the absence of light, as described in previous studies.[43−45] O_3 (1.4−1.6 ppm) was introduced into the chamber using an O_3 generator (model L21, Pacific ozone) and was followed by addition of a continuous flow of TME (1×10^9 molecules $cm^{-3}\ s^{-1}$). Controls in the absence of TME were performed to determine the effect of O_3 on ISOPOOH oxidation. Similar concentration of O_3 was used and diethyl-ether was injected by the same procedure to serve as an OH radical scavenger.[41,42] The concentration of OH radicals generated under the conditions in this work was calculated to be $3-4 \times 10^6$ molecules cm^{-3}, consistent with previous work.[43] Once aerosol volume concentrations stabilized, SOA was collected onto 47 mm diameter Teflon filters (1.0-μm pore size, Tisch Environmental, EPA $PM_{2.5}$ membrane) at a sampling flow rate of ∼15 L min^{-1} for 60−90 min to characterize particle-phase reaction products.

Ambient $PM_{2.5}$ Collection. $PM_{2.5}$ samples were collected during the 2013 Southern Oxidant and Aerosol Study (SOAS) campaign from 1 June to 17 July 2013 at Look Rock, TN (LRK).[28] This site is strongly influenced by isoprene emissions,[6] and isoprene oxidation appears to be one of the main SOA contributors.[28] $PM_{2.5}$ samples were collected onto prebaked 8 × 10 in Tissuquartz Filters (Pall Life Sciences) by high-volume $PM_{2.5}$ air samplers (Tisch Environmental) operated at 1 $m^3\ min^{-1}$ using two sampling protocols described in detail elsewhere.[28] A total of 123 filters from LRK were analyzed to evaluate the contribution of ISOPOOH-derived SOA on the isoprene-derived SOA budget.

Aerosol-Phase Chemical Characterization. Chemical characterization of SOA from gas- phase oxidation of 1,2-ISOPOOH was performed by UPLC/ESI-HR-QTOFMS (6520 Series, Agilent) operated in both negative and positive ion modes and by GC/EI-MS (Hewlett-Packard, 5890 Series II). Operating conditions have been described in detail elsewhere.[16,17] Filters collected from smog chamber experi-

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ments were extracted with 22 mL of high-purity methanol (LC-MS CHROMASOLV-grade, Sigma-Aldrich) by sonication for 45 min. The methanol extracts were then blown dry under a gentle N_2 (g) stream at ambient temperature.

For UPLC/ESI-HR-QTOFMS analysis, dried extracts were reconstituted with 150 μL of a 50:50 (v/v) solvent mixture of methanol (LC-MS CHROMASOLV-grade, Sigma-Aldrich) and high-purity water (Milli-Q, 18.2 MW). Five μL and ten μL aliquots were injected onto the UPLC column (Waters ACQUITY UPLC HSS T3 column, 2.1 × 100 mm, 1.8 μm particle size) and eluted at a flow rate of 0.3 mL min^{-1} with a solvent mixture of methanol containing 0.1% acetic acid or 0.1% ammonium acetate (LC-MS CHROMASOLV-grade, Sigma-Aldrich) and water containing 0.1% acetic acid or 0.1% ammonium acetate (LC-MS CHROMASOLV-grade, Sigma-Aldrich) for negative and positive ion modes, respectively. A mixture of 2-methyltetrol sulfate esters ($C_5H_{11}O_7S^-$) and 3-pinanol-2-hydrogen sulfate ($C_9H_{13}O_6S^-$) were used as surrogate standards to quantify OSs. 1,2-ISOPOOH ($C_5H_{12}O_3Na^+$) was used as surrogate standard to quantify multifunctional hydroxyhydroperoxide compounds and oligomers in positive mode. Maleic acid ($C_4H_3O_4^-$; > 99%, Sigma-Aldrich) was used to quantify acidic compounds identified in negative ion mode.

For GC/EI-MS analysis, dried filter extracts were trimethylsilylated by addition of 100 μL BSTFA + trimethylchlorosilane (99:1 (v/v), Supleco) and 50 μL pyridine (Sigma-Aldrich, 98%, anhydrous). The mixture was heated for 1 h at 70 °C and analyzed within 24 h following trimethylsilylation. Analyses were performed by GC/EI-MS at 70 eV (Hewlett 5890 Packard Series II gas chromatograph interfaced to a HP 5971A Series mass selective detector, Econo-CapTM-ECTM-5 column, 30 m × 0.25 mm × 0.25 μm). Isoprene-derived SOA tracers were quantified using the authentic 2-methyltetrol and 2-methylglyceric acid standards synthesized in-house.[28]

Filters collected from field studies were extracted using the protocols described above; however, prior to drying, extracts were filtered through 0.2-μm PTFE syringe filters (Pall Life Science, Acrodisc) to remove insoluble particles or quartz filter fibers.

High-Resolution Aerosol Mass Spectrometry of Aerosolized Standard and ISOPOOH-SOA. High-resolution mass spectra of synthesized 1,2-ISOPOOH and ISOPOOH-SOA were acquired using an Aerodyne aerosol mass spectrometer equipped with a high-resolution time-of-flight mass spectrometer (HR-ToF-AMS).[46] ISOPOOH-SOA was collected on particle filters and then extracted by sonicating the filters in 50 mL of methanol for 10 min. The methanol solutions of the standard and the SOA were atomized using a constant output atomizer (TSI, Inc.). The polydisperse aerosol particles generated from atomization were passed through a charcoal denuder to remove the methanol solvent and then directly sampled into the HR-ToF-AMS. High-resolution AMS spectra were analyzed using the standard AMS data analysis software packages SQUIRREL (Version 1.56D) and PIKA (Version 1.15D).

ACSM NR-PM_1 Characterization. Fine ambient aerosol was sampled from the rooftop of the air-conditioned building at the LRK site during the 2013 SOAS campaign. ACSM operation parameters followed those of previous studies.[27,28] Briefly, the ACSM scanning rate was set at 200 ms amu^{-1} and data were averaged over 30 min intervals. Data were acquired using ACSM DAQ version 1438 and analyzed using ACSM Local version 1532 (Aerodyne Research, Inc.) within Igor Pro 6.3 (Wave-Metrics). Mass resolution, heater bias voltage, ionizer voltage, and amplifier zero settings were checked and adjusted daily. A collection efficiency (CE) of 0.5 calculated based on Middlebrook et al.[47] was applied to the ACSM data in order to accommodate composition-dependent CE.

Total Aerosol Peroxide Analysis. The total amount of organic peroxides in the ISOPOOH-derived SOA was quantified using an iodometric-spectrophotometric method adapted from Surratt et al.,[24] which was originally based on Docherty et al.[39] Briefly, a 50:50 (v/v) mixture of methanol and ethyl acetate was used rather than pure ethyl acetate. Calibration and measurements were performed at 470 nm using a Hitachi U-3300 dual beam spectrophotometer. 1,2-ISOPOOH was used as the standard for quantification of organic peroxides formed from ISOPOOH oxidation. The method was validated using benzoyl peroxide (BPO) and molar absorptivity from the calibration curves were determined to be ~600 (1,2-ISOPOOH) and ~825 (BPO), which is in excellent agreement with the values previously reported for the BPO.[24,39]

■ RESULTS AND DISCUSSION

In this study we investigate the SOA formation from the oxidation of 1,2-ISOPOOH by OH radicals at varying aerosol acidity and RH. Experiments were carried out in the dark with generation of OH radicals by ozonolysis of TME. Although TME is a convenient dark source of OH radicals,[43−45] O_3 could potentially react with the double bond of 1,2-ISOPOOH. Hence, control experiments were performed in absence of TME with 1.5−1.6 ppm of O_3 either with or without diethylether as an OH scavenger and ABS or AS seed particles at low-RH (SI Table S1). As shown in SI Figure S1 and Table S1, SOA formation is significantly reduced in the absence of TME, confirming that 1,2-ISOPOOH-derived SOA is dominated by OH-initiated oxidation in this work. The presence of OH scavenger further suppressed SOA formation from 1,2-ISOPOOH in the absence of TME, indicating the generation of OH radicals from ISOPOOH ozonolysis.

The levels of SOA observed under the conditions employed in this work indicate a potential contribution of ISOPOOH oxidation to SOA formation. Significant gas-phase formations of highly oxidized multifunctional compounds (HOMs) have been identified recently and could potentially contribute in new particle formation,[13,48] such compounds could participate in SOA formation observed in the experiments performed without seed aerosols. The presence of water has a weak impact on SOA formation; indeed no significant difference was observed between the experiments performed under low- and high-RH conditions using AS particles (SI Table S1). Comparison of aerosol growth using ABS and AS particles reveals that acidity increases SOA formation as demonstrated in many previous studies, especially during the oxidation of isoprene.[15,24,25,42,49,50] Acid-catalyzed multiphase reactions, such as reactive uptake of epoxide intermediates,[15−17,19,20,51,52] were identified as major pathways to explain the enhancement of SOA mass due to the presence of acidic aerosols. A smaller effect was observed for experiments performed under high-RH conditions and could be attributed to dilution of aerosol acidity by additional particle water.[19]

Chemical Characterization of Aerosol-Phase Reaction Products. SOA was chemically characterized by UPLC/ESI-HR-QTOFMS operated in both negative and positive ion modes and by GC/EI-MS. Figure 1 presents the contributions

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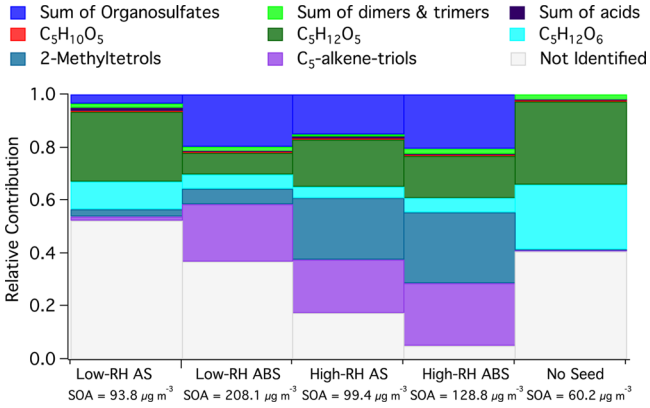

Figure 1. Relative mass contributions of 1,2-ISOPOOH-derived SOA tracers quantified by GC/EI-MS and UPLC/ESI-HR-QTOFMS in filters collected from different experiments. ABS and AS correspond to experiments performed using acidified and nonacidified particles, respectively, under low- (<5%) and high-RH (50−55%). No seed represents experiments performed without initial injection of AS seed particles under low-RH conditions. Reported concentrations of seeded experiments correspond to the average mass concentrations of the different experiments listed in SI Table S1.

of different chemical classes of SOA constituents identified under the different conditions used in this work. Mass of individual aerosol-phase compounds and sum of SOA constituents were divided by the total mass of SOA formed from 1,2-ISOPOOH oxidation using an aerosol density of 1.25 g cm^{-3}.[10] SI Tables S2 and S3 summarize the ISOPOOH-derived SOA products identified by UPLC/ESI-HR-QTOFMS operated in positive and negative ion modes, respectively. C_5-alkene triols quantified by GC/EI-MS were likely products from decomposition of high-MW oligomers formed by IEPOX reactive uptake. Their masses contribute to the total IEPOX-derived SOA. However, since the main goal of this work is focused on non-IEPOX SOA (particularly the hydroperoxides), UPLC/ESI-HR-QTOFMS is more suitable for the detection and quantification of the SOA products due to its soft ionization and availability of isoprene hydroperoxide standards. Total organic peroxide aerosol concentrations, presented in SI Table S1, reveal that organic peroxides account for a significant fraction of the SOA mass measured in different experiments. Masses determined by iodometric-spectrophotometric technique are in fairly good agreement with the total masses of organic peroxides quantified by UPLC/ESI-HR-QTOFMS (Figure 1 and SI Table S1).

$C_5H_{12}O_5$ and $C_5H_{12}O_6$ are the two major multifunctional hydroxyhydroperoxides identified in the particle phase and are tentatively assigned to isoprene trihydroxyhydroperoxide (ISOPTHP) and the isoprene dihydroxydihydroperoxide (ISOP(OOH)$_2$), respectively. Both products have been identified in the gas phase using an Aerodyne high-resolution time-of-flight chemical ionization mass spectrometer (HRToF-CIMS) equipped with an atmospheric pressure nitrate-ion (NO_3^-) ionization source.[13] In addition Liu et al.[53] have reported the presence of HOMs such as ISOPTHP and ISOP(OOH)$_2$ in the particle phase using a HRTOF-CIMS coupled with a filter inlet for gases and aerosols (FIGAERO HRToF-CIMS). As shown in Figure 1, these products together contribute ∼55% of the SOA mass formed in absence of seed aerosol, suggesting that HOMs such as ISOP(OOH)$_2$ could participate in SOA formation, which was also highlighted in previous work.[13,53] Significant concentrations of both products were also measured in ISOPOOH-derived SOA formed using seed particles, particularly AS aerosol under low-RH conditions. AS aerosols effloresce at RH < 5%,[54] and heterogeneous processes such as acid-catalyzed aqueous-phase reactions are significantly reduced.[16,17,19,20] Therefore, larger concentrations of multifunctional hydroxyhydroperoxides observed at low-RH might be due to slower/lack of heterogeneous processes that lead to the decomposition of HOMs. ABS aerosol and/or the presence of water in particles significantly reduced (up to a factor of 3) the concentrations of particle-phase hydroperoxides (i.e., ISOPTHP and ISOP(OOH)$_2$), suggesting that hydroxyhydroperoxide compounds undergo further particle-phase reactions through decomposition or hydrolysis reactions.[55,56]

Krechmer et al.[13] estimated that $C_5H_{10}O_5$ could be a significant contributor to SOA formation: however, low concentrations of this reaction product were measured under the conditions used in this work. A C_5 epoxy product $C_5H_{10}O_5$ can be ruled out because contributions by such a product should be absent under acidic conditions and concentrations of $C_5H_{10}O_5$ appear similar in all experiments. Indeed, significant acid-catalyzed reactive uptake of epoxide products have been demonstrated in previous studies.[15,16,51,52,57,58] Therefore, due to its presence in particle phase, $C_5H_{10}O_5$ was tentatively assigned to isoprene dihydroxy-carbonyl hydroperoxide, which is consistent with the formation of substituted hydroperoxide products as discussed by St. Clair et al.[12] It is important to note that Liu et al.[53] did not observe $C_5H_{10}O_5$ in a large yield in ISOPOOH-derived SOA, suggesting that $C_5H_{10}O_5$ could be volatile, which could explain its small presence in particle phase.

Fifteen oligomers were identified in the particle phase in all experiments, and their concentrations are reported in Figure 2 and SI Figure S2. However, chemical mechanisms leading to oligomers are unclear. Reaction mechanisms involving hemiacetal/acetal formation initiated by hydration of a carbonyl have been proposed[24,56,59] and formation of the oligomers was strongly dependent on acidity and particulate water. In addition, we cannot rule out the possibility that these oligomers could be formed through peroxyhemiacetal formation as recently demonstrated in prior work.[60,61] Consistent with these reports, concentrations of $C_{10}H_{20}O_6$, $C_{10}H_{22}O_7$, $C_{10}H_{22}O_8$ and $C_{15}H_{32}O_{11}$ identified in 1,2-ISOPOOH-derived SOA reported here are significantly enhanced by the presence of either acidified aerosol or water. For example, Lin et al.[16] identified the large formation of $C_{10}H_{22}O_7$ from the acid-catalyzed reactive uptake of IEPOX onto ABS aerosols. Concentrations of other oligomeric products (e.g., C_8−C_9) are, however, reduced in the presence of wet aerosols, suggesting that these compounds might undergo further heterogeneous reactions, such as hydrolysis, leading to other products such as organosulfates (OSs). Krechmer et al.[13] did not observe oligomer formation in the gas-phase, which suggests that oligomerization reactions may not occur in the gas-phase. It is important to note that oligomers were also measured in the experiments performed in the absence of seed particles, suggesting that heterogeneous reactions may also occur during uptake/condensation on organic aerosol as previously observed from the photooxidation of isoprene.[24,59] Formation of oligomers could occur via esterification, aldol condensation and/or hemiacetal reactions as summarized by Nguyen et al.[59] Hence, the identified compounds, such as 2-methylglyceric acid or HOMs, might undergo further heterogeneous reactions to form the observed C_8−C_{15}

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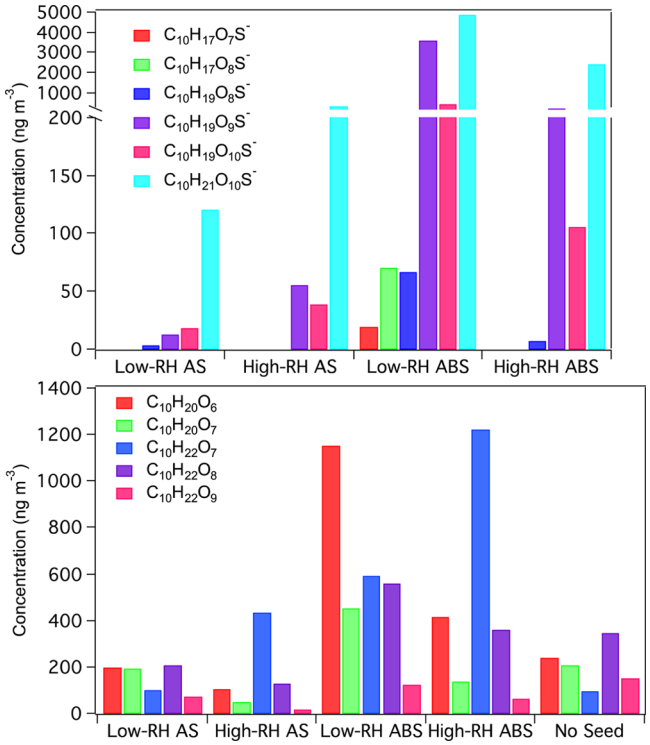

Figure 2. Concentrations of C_{10}-OS-dimers and C_{10}-dimers in SOA formed from the gas-phase oxidation of 1,2-ISOPOOH. ABS and AS correspond to experiments performed using acidified and nonacidified particles, respectively, under low- (<5%) and high-RH (50−55%). No seed represents experiments performed without initial injection of AS seed particles under low-RH conditions.

oligomeric compounds. Due to the lack of standards for these compounds, quantification was performed using 1,2-ISOPOOH as a surrogate standard, resulting in potential uncertainties for the estimated concentrations of these oligomers.

Formation of OSs (up to ∼20% of the mass of SOA under acidic conditions) was identified in all experiments performed in the presence of sulfate aerosols (Figure 1). Negative ion UPLC/ESI-HR-QTOFMS analysis of filter extracts provides excellent sensitivity for the detection of OSs, which yield intense $[M-H]^-$ ions,[26,62] and show characteristic product ions at m/z 80 ($SO_3^{\bullet/-}$), 81 (HSO_3^-) or 97 (HSO_4^-) in MS^2 spectra. Concentrations, retention times, and accurate mass measurements of observed OSs are proposed in SI Table S3 and Figure 2 and SI Figure S3. IEPOX-OS ($C_5H_{11}O_7S^-$) was the predominant OS identified in the oxidation of 1,2-ISOPOOH under all conditions, and has been previously identified from the reactive uptake of IEPOX onto sulfate aerosols.[16,25,63] Among the identified OSs, parent ions at m/z 139, 153, 197, 213 were previously observed in the oxidation of isoprene by OH radical and/or ozone.[25,42] However, the presence of ISOP(OOH)$_2$-OS ($C_5H_{11}O_8S^-$; m/z 231) in SOA has not been previously reported, and thus, could be used as a tracer for 1,2-ISOPOOH-derived SOA through a non-IEPOX route. Two isobaric parent ions with the composition $C_5H_{11}O_8S^-$ were found. Both exhibit a loss of bisulfate (m/z 97) as the base peak fragment ion, which is characteristic of OSs with a labile proton β to the sulfate group.[64]

Seventeen parent ions containing 6−20 carbons were observed (SI Table S3) in ISOPOOH-derived SOA under all conditions and are tentatively identified as OSs by characteristic product ions at m/z 80 or 97 in their MS^2 spectra. Some of the corresponding unsulfated ions are present in positive mode, which might support the importance of particle- phase reactions. More work is needed to identify the structures and elucidate the chemical reactions leading to such oligomers.

Formation of highly oxidized products, such as OSs, demonstrates the importance of heterogeneous processes, such as reactive uptake of epoxides onto ABS aerosols, in SOA formation.[15,17,51,65,66] OSs may also be formed by nucleophilic substitution of organic nitrates by sulfate,[57,67] heterogeneous oxidation of unsaturated compounds involving sulfate anion radicals,[68−70] or nucleophilic oxirane ring opening. In absence of light, sulfate radicals could be formed from the reaction of sulfate ions with OH radicals.[71] Although heterogeneous oxidation of sulfate ions by OH radicals is unlikely, OH radicals could be generated by decomposition of hydroperoxides in aerosol water.[72] Heterogeneous chemistry of gas-phase organic peroxides has been suggested to explain the formation of certain OSs and tetrols.[22,42] Hence, acid-catalyzed perhydrolysis of hydroperoxides followed by reaction with sulfate ions could explain the formation of some OSs such as ISOP(OOH)$_2$-OS.

Reaction Mechanism. The reaction of OH radicals with 1,2-ISOPOOH can, in principle, proceed via four pathways: H atom abstraction from OOH or C−H or OH addition to the double bond at C_1 or C_2. St. Clair et al.[12] have recently reported that addition reactions dominate over the OH abstraction reactions, and OH addition to the double bond was calculated at yields greater than 85%. Scheme 1 presents proposed reaction mechanisms that yield the identified or tentatively proposed products of the reaction of 1,2-ISOPOOH with OH radicals. OH addition yields large formation of *cis*/*trans*-β-IEPOX (∼71%),[12] which undergoes further oxidation reactions or leads to IEPOX-derived SOA products in the presence of ABS aerosols.[15−17,57,63] OH addition also leads to isomeric RO_2 radicals: $C_5H_{11}O_6^\bullet$ (RO_2-1 and RO_2-2) with yields of 10% and 29%, respectively.[12] It is, however, important to mention that the calculated yields reported by St Clair et al.[12] underpredict the formation of *cis*/*trans*-β-IEPOX, and thus, might overestimate the formation of RO_2-1 and −2. H-shift between the hydroperoxide (ROOH) and RO_2 radical were calculated by St. Clair et al.[12] to be very fast; however, the calculations suggest that RO_2 radicals are favored on secondary carbons.

RO_2-2 can react with HO_2 and generate ISOP(OOH)$_2$, which has been identified as a major ISOPOOH-derived SOA product. Formation of ISOPTHP could be explained by self- and cross-reactions of the RO_2 radicals formed from the initial oxidation (OH/O_2) of ISOPOOH and/or RO_2 radicals generated from TME ozonolysis.[22] The self- and cross-reactions of RO_2-2 radicals could also lead to the formation of the corresponding alkoxy radical (RO), which further fragments and forms a C_2-hydroperoxide ($C_2H_4O_3$) product. RO_2-1 radical, which is the main RO_2 radical formed from 1,2-ISOPOOH oxidation, could react with HO_2 and yield ISOP(OOH)$_2$. In addition, RO_2-1 could also undergo self- and cross- reactions via the "'radical channel'" to form an RO radical and via the "'molecular channel'" leading to the formation of the corresponding alcohol (ISOPTHP) and carbonyl ($C_5H_{10}O_5$).[73] RO radicals can also fragment and generate more volatile species.[12,14] Yields of H abstraction from CH_2 are lower than 7%;[12] however, even though minor, this

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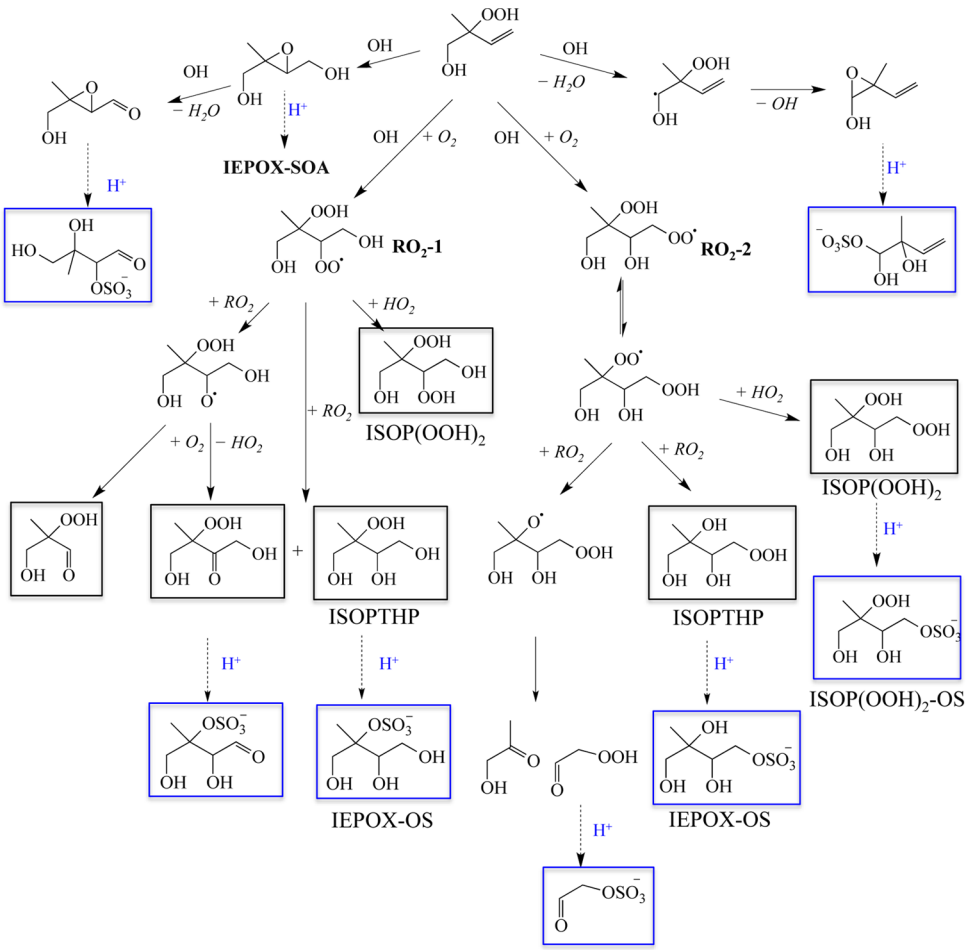
Scheme 1. Proposed Mechanism for ISOPOOH Oxidation Indicating Likely Reaction Pathways for the Formation of Main Identified Products[a]



[a]Identified OSs are boxed in blue, whereas other major ISOPOOH-derived SOA constituents are boxed in black. This work builds on prior gas-phase studies by St. Clair et al.,[12] Krechmer et al.,[13] and Bates et al.,[14] thus providing a more direct link between gas- and particle-phase chemistry.

pathway could lead to the formation of an epoxide ($C_5H_8O_2$).[14,74]

Reactive uptakes of epoxides have been demonstrated to be a major OS formation pathway during the photooxidation of isoprene.[15,25,57] IEPOX-OS is identified as the predominant OS under all conditions in this investigation and its formation is assumed to result from the reactive uptake of IEPOX. Formation of $C_5H_9O_6S^-$ could also be explained by the reactive uptake of an epoxide ($C_5H_8O_2$) proposed by St. Clair et al.[12] IEPOX could also further react in the presence of OH radicals to an epoxy-hydroxy-aldehyde ($C_5H_8O_3$) (Scheme 1), which would yield $C_5H_9O_7S^-$ by reactive uptake onto sulfate aerosols. However, this pathway could be considered minor, because the reactive uptake of IEPOX onto acidic particles will dominate over the reaction with OH. In addition, the potential for acid-catalyzed perhydrolysis of hydroperoxides, such as ISOPTHP and $C_5H_{10}O_5$, followed by reaction with sulfate could also contribute in the formation of IEPOX-OS and $C_5H_9O_7S^-$. Acid-catalyzed perhydrolysis of ISOP(OOH)$_2$ followed by reaction with sulfate anion radicals could be a possible route to form ISOP(OOH)$_2$-OS (Scheme 1), which to our knowledge was identified here for the first time.

Atmospheric Implications. AMS mass spectra of SOA generated from the gas-phase oxidation of 1,2-ISOPOOH are presented in Figure 3 and SI Figure S4. The mass spectra reveal a prominent fragment ion at m/z 91 that resemble mass spectra of PMF factor from ambient OA measurements.[28,33] The ratio of m/z 91 to m/z 82 ion fractions (f_{91}: f_{82}) is 2−4 in mass spectra of 1,2-ISOPOOH-derived SOA generated in experiments using nonacidified aerosol. It is important to mention that fragment ion at m/z 82 is the signature of reactive uptake of IEPOX.[16,27] Therefore, enhancement of the intensity of m/z 82 fragment ion (f_{91}: f_{82} ~ 0.7) in mass spectra of 1,2-ISOPOOH-derived SOA from experiments using acidified aerosol (SI Figure S4) was expected due to the formation of IEPOX-derived SOA products.[16,19,20,27] The fragment ion at m/z 91 was previously proposed as peroxide tracer with an elemental formula of $C_3H_7O_3^+$ from isoprene photooxidation under low-NO_x and low-RH conditions;[24] however, this composition was not verified by high-resolution AMS. A recent study using the HR-ToF-AMS established $C_7H_7^+$ as the composition of the intense ion at m/z 91 in laboratory experiments of β-pinene oxidation.[75] The HR-ToF-AMS measurements of 1,2-ISOPOOH-derived SOA in this work reveal that the fragment ion at m/z 91 is also associated with the $C_7H_7^+$ formula. Potential sources of $C_7H_7^+$ from this SOA system include thermal decomposition of dimers and oligomers on the vaporizer, thermally enhanced combination reactions on

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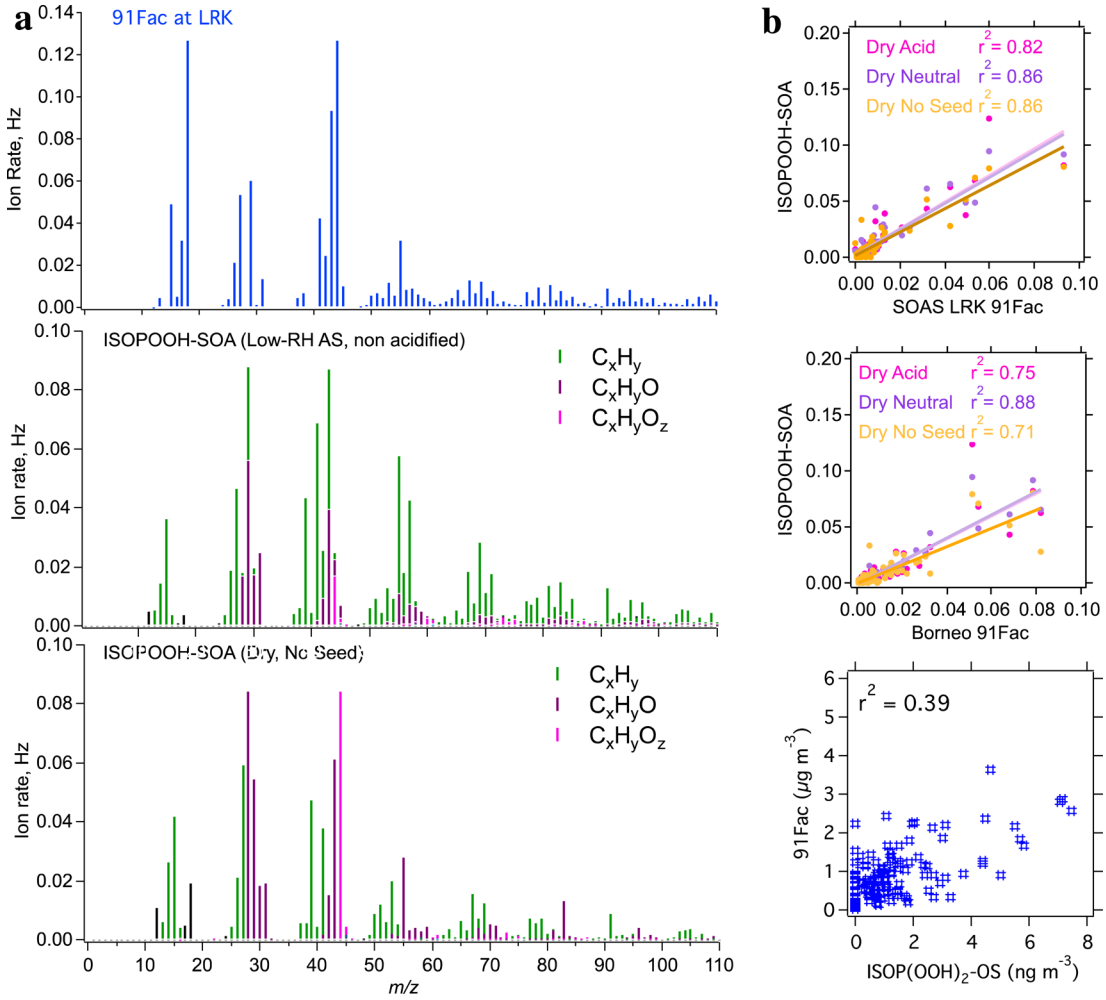

Figure 3. (a) Mass spectra of 91Fac resolved from PMF analysis of OA measured at LRK during the 2013 SOAS campaign using the ACSM, ISOPOOH-derived SOA generated from gas-phase oxidation of 1,2-ISOPOOH with AS (nonacidified) particle and without seed aerosol (No Seed) in the UNC dark indoor smog chamber under low-RH conditions, respectively. (b) Correlations of 91Fac factor from LRK and Borneo with laboratory-generated ISOPOOH-derived SOA, and 91Fac factor from LRK versus ISOP(OOH)$_2$-OS quantified in filters collected at LRK during SOAS campaign.

AMS vaporizer and ionizer surfaces, and/or radical/ion recombination within the plumes of evaporating particles.

The mass spectra of 1,2-ISOPOOH-derived SOA are strongly correlated (r^2 = 0.7−0.9) with the ambient PMF factor referred to as 91Fac from LRK,[28] and Borneo.[33] Stronger correlations ($r^2 \sim 0.9$) are found between ISOPOOH-derived SOA generated from experiments using nonacidified aerosol and 91Fac factor than other factors (Figure 3 and SI Figure S5). Furthermore, a moderate correlation ($r^2 \sim 0.4$) between 91Fac and ISOP(OOH)$_2$-OS from LRK site indicates that ISOPOOH-derived SOA could contribute to 91Fac production in isoprene-dominated areas. A recent study attributed nighttime oxidation chemistry of monoterpenes to the production of less-oxidized oxygenated organic aerosol (LO-OOA).[30] We found that the 91Fac factor was not correlated ($r^2 \leq 0.1$) with monoterpene-derived OSs ($C_{10}H_{17}O_5S^-$, $C_9H_{14}NO_8S^-$, $C_{10}H_{16}NO_7S^-$, and $C_{10}H_{16}NO_{10}S^-$),[26] or with known monoterpene-derived organonitrates ($C_{10}H_{16}NO_5^-$ and $C_{10}H_{14}NO_6^-$),[75] suggesting that oxidation chemistry of monoterpenes was likely not influential in 91Fac factor production observed at the LRK site during the 2013 SOAS campaign. In addition, diurnal variation observed during the SOAS campaign shows two increases at noon and in the evening,[28] suggesting that 91Fac production in early summer was influenced by two different sources/chemistries. The rise of 91Fac at noon is, however, larger than in the evening and dominated the 91Fac production during the whole summer. An increase at noon likely indicates formation of 91Fac from photo-oxidation chemistry and might support contribution of ISOPOOH oxidation in the 91Fac.[76] Furthermore, at the SOAS Centerville, AL field site, several ISOPOOH-derived SOA tracers were observed, including ISOP(OOH)$_2$, ISOPTHP, $C_5H_{10}O_5$, $C_5H_{10}O_6$, as well as the nitrate analogue of the $C_5H_{12}O_6$, $C_5H_{11}NO_7$, in the particle phase (SI Figure S6) utilizing the online FIGAERO HRToF-CIMS, which has been described for this specific deployment in detail previously.[77] This instrument also detects these same tracers in independent chamber experiments of ISOPOOH and isoprene photo-oxidation using AS seed, similar to the *low-RH AS* and *No seed* experiments described herein where acid catalyzed IEPOX multiphase chemistry is suppressed.[53] That two independent measurement methods show substantial aerosol concentrations of molecular tracers of ISOPOOH derived RO_2 chemistry in independent chamber experiments and separate field measurement sites provides strong support for the broad importance of this SOA formation pathway.

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This study highlights the potential of ISOPOOH oxidation in atmospheric SOA formation. PMF analysis at the LRK site indicates that the SOA linked to ISOPOOH chemistry (91Fac factor) and the SOA formed from IEPOX (IEPOX-OA factor) account for 18% and 32% of the total OA mass, respectively. Hence, isoprene chemistry represent about 50% of the OA mass measured at LRK during the 2013 SOAS campaign.[28] Although ISOPOOH-derived SOA through a non-IEPOX route likely contributes to 91Fac at LRK during the SOAS campaign, we cannot rule out the contribution of other potential sources, which were not identified in this study. At CTR, 91Fac was suggested to be dominated by monoterpene chemistry since its diurnal variation peaks at night.[30] However, contribution of isoprene-derived SOA at CTR was significantly lower compare to LRK (18% of total OA mass),[30] with non-IEPOX derived SOA was estimated to contribute up to 2% of the total OA mass.[13] In addition, some differences in the chemical composition of ISOPOOH oxidation products between the present work and Krechmer et al.[13] might explain the discrepancies between LRK and CTR observations. First, the AMS spectra obtained from the oxidation of 1,2-ISOPOOH (Figure 3) in this study and 4,3-ISOPOOH (SI Figure S3 in Krechmer et al.[13]) appear different. Second, Krechmer et al.[13] estimated that $C_5H_{10}O_5$ could be an important SOA precursor, whereas it was in low abundance in our experiments. Finally, these significant differences likely suggest that yields of condensing SOA between 1,2-ISOPOOH and 4,3-ISOPOOH[13] are different and might contribute to an underestimation of the SOA formed from the oxidation of 1,2-ISOPOOH. Therefore, our estimation is likely an upper limit for non-IEPOX derived SOA.

The ISOPOOH-derived SOA through a non-IEPOX pathway revealed in this study and others,[13,53] may represent an important missing source of SOA from isoprene oxidation in low-NO_x (pristine) environments. Future studies should systematically investigate the photochemical aging of ISOPOOH-derived SOA in order to evaluate its potential contribution to the formation of more oxidized OA that has been observed at several sites throughout the southeastern U.S. region.[28,30]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b02511.

> Details of the 1,2-ISOPOOH syntheses can be found in the SI text. The tables provide a summary of experimental conditions as well as a summary of the different compounds identified in ISOPOOH-derived SOA by UPLC/ESI-HR-QTOFMS using negative and positive modes. Figures S1 and S2 present quantification of identified compounds. Figure S3 shows the mass spectra of laboratory ISOPOOH derived SOA generated from the oxidation of 1,2-ISOPOOH using ABS aerosol. Figure S5 reports the correlations of the PMF factors from LRK and Borneo with ISOPOOH derived SOA. Figure S6 shows diurnal profiles of ISOPOOH-derived SOA tracers observed at CTR (PDF)

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Notes

The authors declare no competing financial interest.

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