

The C₅–Alkene Triol Conundrum: Structural Characterization and Quantitation of Isoprene-Derived C₅H₁₀O₃ Reactive Uptake Products

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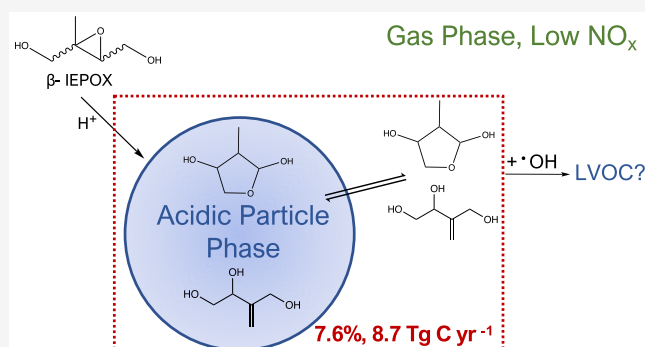
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Supporting Information

ABSTRACT: 2-Methyltetrols and C₅H₁₀O₃ compounds, referred to as “C₅–alkene triols,” are chemical tracers used to estimate isoprene-derived epoxydiol (IEPOX) contributions to atmospheric PM_{2.5}. For nearly two decades, “C₅–alkene triol” molecular structures and PM_{2.5} mass contributions have remained uncertain, and their origin as analytical artifacts is unclear. We synthesized C₅H₁₀O₃ reactive uptake product candidates (3-methyltetrahydrofuran-2,4-diol and 3-methylenebutane-1,2,4-triol) and investigated their behavior under conventional gas chromatography/electron impact–mass spectrometry (GC/EI-MS) with prior trimethylsilylation and, in parallel, by nondestructive hydrophilic-interaction liquid chromatography coupled with electrospray ionization interfaced to high-resolution quadrupole-time-of-flight mass spectrometry (HILIC/ESI-HR-QTOFMS). Using the synthetic standards, we confirmed their presence in laboratory-generated IEPOX SOA. In atmospheric SOA, both synthetic targets were confirmed and quantified by GC/EI-MS. Based on HILIC/ESI-HR-QTOFMS analysis of chamber-generated SOA, we estimate that ~10% of GC/EI-MS measured 3-methylenebutane-1,2,4-triol and ~50% of 3-methyltetrahydrofuran-2,4-diols are not analytical artifacts but arise from acid-driven particle-phase IEPOX isomerization. Significant quantities were also detected in impingers downstream from filters, demonstrating that “C₅–alkene triols” are semivolatile. Using chamber-derived yields, we tentatively estimate that atmospheric 3-methyltetrahydrofuran-2,4-diols and 3-methylenebutane-1,2,4-triol could contribute 8.7 Tg C yr^{−1}. To resolve their significance on air quality and climate, future studies should examine their gas-to-particle partitioning, yields, and atmospheric oxidation chemistry under varying environmental conditions.

KEYWORDS: IEPOX, secondary organic aerosol, multiphase chemistry, GC/MS, HILIC/ESI-MS



INTRODUCTION

Isoprene (2-methyl-1,3-butadiene) is the dominant biogenic volatile organic compound (BVOC) emitted into Earth's atmosphere at ~454 Tg C yr^{−1}, representing ~38% of the global VOC budget (roughly equivalent to methane emissions).^{1–3} During daytime under low-nitric oxide (NO) conditions, isoprene is primarily oxidized by atmospheric hydroxyl (OH) radicals to yield large quantities (115 Tg C yr^{−1}) of isomeric isoprene-derived epoxydiols (IEPOX; ~97% β-IEPOX and 3% δ-IEPOX isomers), which can undergo multiphase chemical reactions with existing acidic sulfate particles derived from anthropogenic sulfur emissions.^{3–6} The resultant SOA can contribute up to 40% of submicron particulate mass in isoprene-rich atmospheres, with levels projected to rise as climate change increases isoprene emissions and anthropogenic NO_x and SO₂ levels decrease due to future emissions controls.^{7–14}

IEPOX-derived C₅ polyols, including 2-methyltetrols and “C₅–alkene triols”, which we will refer to hereafter as “C₅H₁₀O₃ reactive uptake products” for structural accuracy, have been

employed as chemical tracers to investigate isoprene SOA composition and formation mechanisms.^{15,16} While 2-methyltetrols and methyltetrol sulfate esters have been definitively established as products of reactive uptake of IEPOX onto acidic seed aerosols,^{5,6,15,17,18} the origins, structures, and abundance of C₅H₁₀O₃ reactive uptake products remained uncertain due to the lack of authentic standards. Previous gas chromatography interfaced to electron impact–mass spectrometry (GC/EI-MS) analyses with prior trimethylsilylation of ambient aerosol using surrogate standards for quantitation indicate that the C₅H₁₀O₃ reactive uptake products exhibit concentrations roughly equivalent to 2-methyltetrols;^{19–21}

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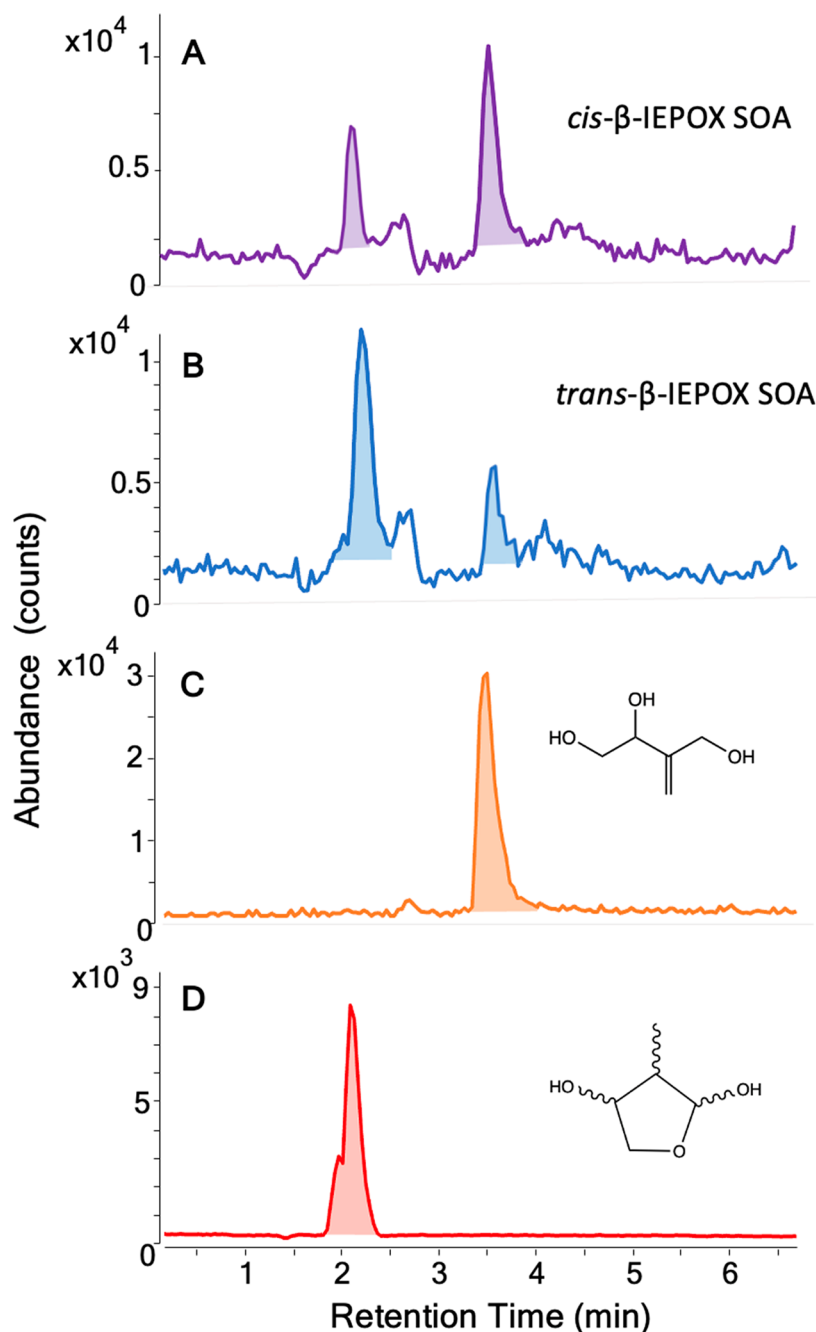


Figure 1. HILIC/(-)ESI-HR-QTOFMS EICs of $C_5H_9O_3^-$ at m/z 117, corresponding to $[M-H]^-$ ions of the $C_5H_{10}O_3$ reactive uptake products, including the 3-methylenebutane-1,2,4-triol (RT at 3.50 min) and 3-methyltetrahydrofuran-2,4-diol (RT at 2.08 min) in (A) laboratory-generated *cis*- β -IEPOX SOA, (B) laboratory-generated *trans*- β -IEPOX SOA, (C) 15 ppm 3-methylenebutane-1,2,4 triol standard, and (D) 100 ppm 3-methyltetrahydrofuran-2,4-diol standard. Note that HILIC does not resolve the four hemiacetal isomers.

however, differences in surrogate standard ionization efficiency may result in highly inaccurate quantitation.²²

Based on fragmentation patterns in GC/EI-MS analysis of trimethylsilyl (TMS) derivatized extracts of lab-generated SOA and ambient $PM_{2.5}$, *cis*- and *trans*-2-methyl-1,3,4-trihydroxy-1-butene and 3-methyl-2,3,4-trihydroxy-1-butene structures were proposed via acid-catalyzed ring-opening reactions of δ -IEPOX.¹⁵ Subsequent studies identifying δ -IEPOX as a minor IEPOX isomer discount this mechanistic pathway because it cannot account for observed levels of $C_5H_{10}O_3$ reactive uptake tracers in ambient fine aerosol ($PM_{2.5}$).^{15,23} Additionally, nuclear magnetic resonance spectrometry

(NMR) analysis of IEPOX isomerization in acidic bulk solution has demonstrated formation of isomeric 3-methyltetrahydrofuran-2,4-diols, the favored tautomers of the 2-methyl-1,3,4-trihydroxy-1-butene isomers, suggesting these two silyl enol ethers as possible artifacts of the derivatization procedure.²⁴

Chamber and field studies using alternative analytical techniques, such as the Filter Inlet for Gases and Aerosols coupled to a Chemical Ionization Mass Spectrometer (FIGAERO-CIMS), instead suggest that observed $C_5H_{10}O_3$ reactive uptake products are substantially artifacts from the decomposition of methyltetrol sulfate esters and oligomeric

sulfated and nonsulfated SOA components during thermal GC/EI-MS analysis.^{25,26} A comparison of nondestructive chemical analysis of IEPOX SOA by hydrophilic interaction liquid chromatography coupled with electrospray ionization interfaced to high-resolution quadrupole time-of-flight mass spectrometry operated in the negative ion mode (HILIC/(−)ESI-HR-QTOFMS) with GC/EI-MS by Cui et al. confirmed that a substantial proportion of observed C₅H₁₀O₃ uptake product tracers are thermal decomposition products of 2-methyltetrol sulfate esters formed during GC/EI-MS analysis.²⁷ However, the HILIC/(−)ESI-HR-QTOFMS analysis was optimized for highly polar anionic sulfate esters and neutral polyols such as the 2-methyltetrols.²⁷ Less polar compounds, such as the C₅H₁₀O₃ reactive uptake products, could have escaped detection because of short elution times and a lack of sensitivity in (−)ESI-MS analyses.

Several studies suggest that isoprene-derived C₅-polyols partition into the gas phase following in-particle formation from multiphase chemistry of IEPOX.^{28–31} In fact, gaseous C₅H₁₀O₃ reactive uptake tracers have been reported at field sites in the Southeastern U.S., Central Amazonia, and Eastern China, but analyses used protocols which are subject to thermal decomposition artifacts.^{30,31} Partitioning into the gas phase would be an important component of the atmospheric lifecycle of C₅H₁₀O₃ reactive uptake products, as revolatilized compounds may be oxidized in the atmosphere into low-volatility organic species, constituting a hitherto unrecognized source of isoprene-derived SOA.

To address the persistent questions regarding structure, origin, and quantitation of the C₅H₁₀O₃ reactive uptake products, we synthesized putative uptake products and established their structures as isomeric 3-methyltetrahydrofuran-2,4-diols and, unexpectedly, 3-methylenebutane-1,2,4-triol. We optimized the HILIC/(−)ESI-HR-QTOFMS protocol to unequivocally identify their structures in laboratory-generated IEPOX SOA as well as to determine their behavior and extent of artifact formation during GC/EI-MS analysis with prior trimethylsilylation. We then used our insights for parallel quantitation of C₅H₁₀O₃ reactive uptake tracers by GC/EI-MS in extracts of laboratory-generated IEPOX SOA and demonstrated partitioning into the gas phase. Importantly, we have confirmed the presence of the synthesized structures in ambient PM_{2.5} collected from Research Triangle Park (RTP), North Carolina (NC), U.S.

MATERIALS AND METHODS

Synthesis. 2-Methyltetrols, 2-Methyletetrol-sulfates, *cis*-/*trans*- β -IEPOX. A diastereomeric mixture of racemic 2-methyltetrol sulfates, diastereomeric mixtures of racemic 2-methyltetrols, and racemic *cis*- and *trans*- β -IEPOX were synthesized by published procedures.^{32–34}

3-Methylenebutane-1,2,4-triol and 3-Methyltetrahydrofuran-2,4-diol. 3-Methylenebutane-1,2,4-triol and 3-methyltetrahydrofuran-2,4-diol were synthesized by routes developed in-house. Synthetic details (Schemes S1 and S2) and characterization by NMR (Figures S1–S4) are presented in the Supporting Information (SI).

Laboratory-Generated *cis*-/*trans*- β -IEPOX SOA. SOA was generated by the reactive uptake of *cis*- and *trans*- β -IEPOX onto acidic sulfate seed aerosol using the 10-m³ Teflon indoor chamber facility located at the University of North Carolina at Chapel Hill. The detailed procedures for SOA generation, controls, and extraction were adapted from Cui et al.²⁷ and are

outlined in the SI. Experiments (Table S1) were carried out under dark and humid (50–54% relative humidity, RH) conditions, with IEPOX/inorganic sulfate ratios mirroring typical summer conditions in the Southeastern U.S.³⁵ Filter and impinger samples were collected for particle- and gas-phase chemical analysis, respectively.

Ambient PM_{2.5} Collection at RTP, NC. PM_{2.5} samples were collected onto prebaked quartz fiber filters in RTP, NC during September 2021 as described in the SI. Sampling conditions are summarized in Table S2.

Offline Mass Spectrometric Analysis of Laboratory-Generated and Ambient SOA. Laboratory-generated and ambient aerosol samples were analyzed by GC/EI-MS, and in parallel by HILIC/(−)ESI-HR-QTOFMS, with instrument conditions adapted from Cui et al.²³ and outlined in the SI. Additionally, retention times (RTs), linear range (L. range), coefficient of determination (R²), limits of detection (LOD), limits of quantification (LOQ), Teflon filter extraction efficiency, and impinger recovery efficiency of five replicate standard injections are described in Tables S3 and S4 for HILIC/(−)ESI-HR-QTOFMS and GC/EI-MS, respectively.

RESULTS AND DISCUSSION

HILIC/(−)ESI-HR-QTOFMS Analysis of Chamber-Generated IEPOX SOA. C₅H₁₀O₃ reactive uptake products were detected and quantified by HILIC/(−)ESI-HR-QTOFMS in laboratory-generated *cis*- and *trans*- β -IEPOX SOA. Extracted ion chromatograms (EICs) are shown in Figure 1 and corresponding mass spectra in Figure S5. The mass-to-charge ratio of (*m/z*) 117, corresponding to [M−H][−] ions, with an extraction width of *m/z* ± 0.02 was used to generate the EICs of the C₅H₁₀O₃ reactive uptake products. The detection of 3-methyltetrahydrofuran-2,4-diols and 3-methylenebutane-1,2,4-triol in chamber-generated IEPOX SOA by HILIC/(−)ESI-HR-QTOFMS analysis indicates that both compounds are definitively products of reactive uptake onto existing acidic sulfate aerosol. Formation mechanisms from the isomerization of β -IEPOX are proposed in Scheme S3.

cis- β -IEPOX uptake chamber experiments performed in triplicate and analyzed by HILIC/(−)ESI-HR-QTOFMS yielded an average of 3.52 ± 1.91 $\mu\text{g m}^{-3}$ of particulate 3-methyltetrahydrofuran-2,4-diol and 0.41 ± 0.21 $\mu\text{g m}^{-3}$ of particulate 3-methylenebutane-1,2,4-triol. Five *trans*- β -IEPOX uptake chamber experiments yielded an average of 4.41 ± 2.36 $\mu\text{g m}^{-3}$ of particulate 3-methyltetrahydrofuran-2,4-diol and 0.19 ± 0.07 $\mu\text{g m}^{-3}$ of particulate 3-methylenebutane-1,2,4-triol. Particulate concentrations of the well-established 2-methyltetrol sulfate esters and 2-methyltetrols tracers formed in the β -IEPOX uptake experiments exceeded those of the C₅H₁₀O₃ reactive uptake products: 24.43 ± 15.48 and 13.61 ± 7.56 $\mu\text{g m}^{-3}$, respectively.

Concentrations of C₅H₁₀O₃ reactive uptake products in ambient PM_{2.5} samples collected in RTP, NC, were below quantifiable limits of the HILIC/(−)ESI-HR-QTOFMS method. The detection of standards in laboratory-generated SOA but not ambient aerosol can be attributed to differences in the conditions of formation and SOA concentrations between the two sample types. RH during ambient aerosol sampling at RTP (75 ± 3.4%) was significantly higher than in chamber experiments (52 ± 1.8%). Because isomerization reactions of IEPOX, which form the C₅H₁₀O₃ reactive uptake products, are most favorable under dry, acidic conditions, an increase in RH is likely to explain a decrease in product

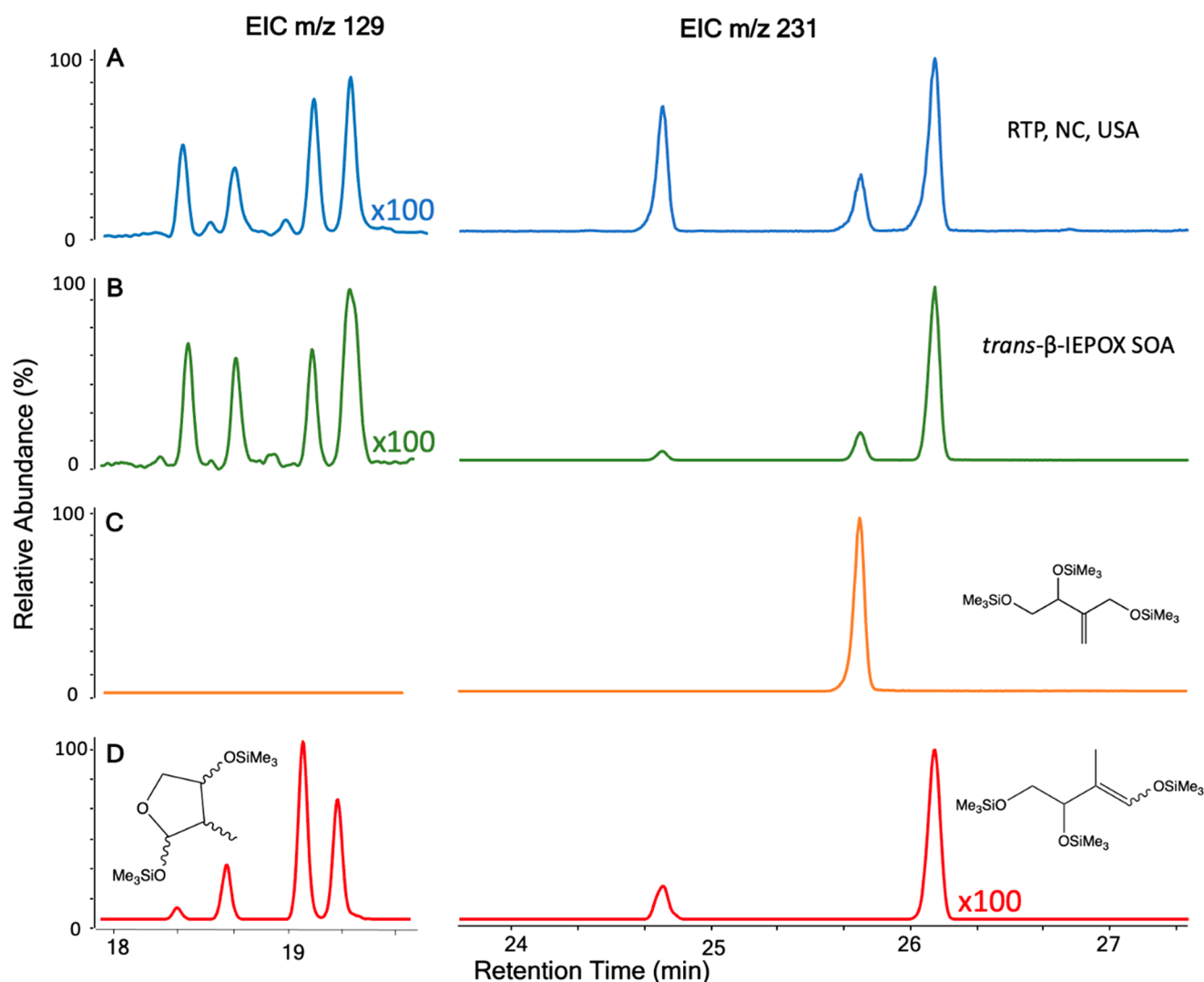


Figure 2. GC/EI-MS EICs at m/z 129, corresponding to bis-TMS ester derivatives (RTs at 18.4, 18.6, 19.1, and 19.3 min) and at m/z 231, corresponding to tris-TMS ester derivatives (RTs at 24.8, 25.8, and 26.1 min), from (A) PM_{2.5} collected in RTP, NC, during September 2021; (B) laboratory-generated *trans*- β -IEPOX SOA; (C) the 3-methylenebutane-1,2,4-triol standard and (D) the 3-methyltetrahydrofuran-2,4-diol standard. The y-axes of EICs at m/z 129 in panels A and B are magnified $\times 100$, indicating that artifacts (EICs at m/z 231) predominate. Trimethylsilylation of *trans*- β -IEPOX SOA yields predominantly the single isomer at 26.1 min. Note also different isomer distributions of ambient and synthetic hemiacetals.

yields.²⁴ Future measurements of ambient and chamber-generated SOA under a variety of atmospheric conditions are necessary to determine the impact of RH and aerosol pH, which in turn affect the aerosol phase state and morphology of IEPOX SOA, on C₅H₁₀O₃ reactive uptake product yield.^{35,36} Differences in aerosol mass concentration may also contribute to discrepancies between observations in ambient versus laboratory-generated aerosol. The higher organic particulate concentrations in the chamber ($430 \pm 82 \mu\text{g m}^{-3}$) promote increased partitioning into the particle phase compared to the more dilute ambient SOA ($7.7 \pm 1.8 \mu\text{g m}^{-3}$), which could shift the gas-to-particle phase equilibrium.³⁷ Thus, for semivolatile species like C₅H₁₀O₃ reactive uptake products, only a low concentration may remain in the particle phase following atmospheric gas-to-particle phase partitioning, potentially causing particulate concentrations to be below instrument detection limits.

GC/EI-MS Analysis of Ambient and Chamber-Derived SOA. Having established the structures of 3-methylenebutane-

1,2,4-triol and 3-methyl-tetrahydrofuran-2,4-diols as multi-phase chemical products of IEPOX by HILIC/(−)ESI-HR-QTOFMS analysis, we investigated their behavior under the derivatization GC/EI-MS protocol to evaluate the likelihood and extent of artifact formation by thermal decomposition. EICs at m/z 231 were used to identify and quantify the three tris-TMS C₅H₁₀O₃ reactive uptake product derivatives eluting at 24.8, 25.8, and 26.1 min,¹⁵ while EICs at m/z 129 were used to identify bis-TMS derivatives eluting at 18.4, 18.6, 19.1, and 19.3 min. Figure 2 shows the structures of TMS derivatives of synthesized C₅H₁₀O₃ reactive uptake products and compares the GC/EI-MS EICs to ambient aerosol and laboratory-generated β -IEPOX SOA.

GC/EI-MS analysis of 3-methylenebutane-1,2,4-triol yields a single tris-TMS isomer, eluting at 25.8 min. Figure S6 shows that the mass spectral fragmentation pattern of the tris-TMS derivative of the authentic standard exactly matches the ambient aerosol collected from RTP, NC.

A small amount (<15%) of the 3-methyltetrahydrofuran-2,4-diol standard tautomerizes to the ring-opened tris-TMS ester under derivatization conditions, yielding *cis*-/ *trans*-3-methylbut-3-ene-1,2,4-triols, corresponding to the isomers eluting at 24.8 and 26.1 min. The mass spectral fragmentation patterns of the tris-TMS derivatives of the authentic standard exactly match those of the corresponding peaks in the PM_{2.5} samples from RTP, NC, shown in Figure S6. The remaining fraction (>85%) of the 3-methyltetrahydrofuran-2,4-diol standard forms isomeric bis-TMS derivatives, eluting between 18.4 and 19.4 min. Because there is a substantial energy barrier associated with ring opening of the hemiacetal 3-methyltetrahydrofuran-2,4-diol, derivatization under standard protocol yields predominantly the bis-TMS esters.^{38,39} Identical behavior under the derivatization protocol is observed in lab-generated β -IEPOX SOA and in PM_{2.5} from RTP, NC; however, in these samples, the tris-TMS ester predominates. The discrepancy between the behavior of the 3-methyltetrahydrofuran-2,4-diol standard and lab-generated and ambient SOA samples can be attributed to the thermal decomposition of 2-methyltetrol sulfates (and likely oligomers thereof) during GC/EI-MS analysis, as demonstrated by Cui et al.²⁷

Because authentic standards were previously unavailable for quantitation of C₅H₁₀O₃ reactive uptake products, 2-methyltetrols have been traditionally employed as surrogate standards.^{19–21,40} To determine whether 2-methyltetrols are appropriate surrogates for analysis of tris-TMS C₅H₁₀O₃ reactive uptake derivatives (i.e., exhibit comparable ionization efficiencies), tris-TMS derivatives in PM_{2.5} samples collected from RTP, NC, were quantitated using authentic standards, and concentrations were compared with quantitation using the 2-methyltetrol standards. The tris-TMS tautomers of the 3-methyltetrahydrofuran-2,4-diols quantitated using the respective authentic standards were on average 85.5% higher than when quantified by the 2-methyltetrol proxy. The concentration of tris-TMS 3-methylenebutane-1,2,4-triol quantified using the authentic standard was, on average, 64.9% higher than when quantified using 2-methyltetrols. However, note that the tris-TMS derivatives are largely artifacts in origin. Thus, the 2-methyltetrols are not suitable proxies for tris-TMS derivatives of C₅H₁₀O₃ uptake products, and since the tris-TMS derivatives are largely artifacts, they are not desirable tracers for C₅H₁₀O₃ uptake products.

The extent of thermal decomposition of methyltetrol sulfates as well as other sulfated and nonsulfated oligomers during derivatization GC/EI-MS analysis was quantified by comparing concentrations of C₅H₁₀O₃ reactive uptake products in laboratory-generated β -IEPOX SOA measured by GC/EI-MS to measurements using the nondestructive HILIC/(–)ESI-HR-QTOFMS protocol. Table S5 suggests that approximately 87% of 3-methylenebutane-1,2,4-triol and 48% of the sum of 3-methyltetrahydrofuran-2,4-diol isomers measured by GC/EI-MS in β -IEPOX SOA are thermal decomposition artifacts. Thus, the remaining 13% and 52% of signals, respectively, can be attributed to the reactive uptake of β -IEPOX isomers under the Southeastern U.S. atmospheric conditions mimicked in this study.

Detection of Gas-Phase C₅H₁₀O₃ Reactive Uptake Products in Laboratory-Generated β -IEPOX SOA. The U.S. EPA OPERA Model estimates that the C₅H₁₀O₃ reactive uptake products are semivolatile, with vapor pressures of 1687 and 2297 $\mu\text{g m}^{-3}$ for 3-methylenebutane-1,2,4-triol and 3-methyltetrahydrofuran-2,4-diol, respectively.⁴¹ Thus, these

compounds are expected to revolatilize from the particle phase into the atmosphere. Here, gas-phase C₅H₁₀O₃ reactive uptake products present in chamber experiments during reactive uptake of *trans*- β -IEPOX, the predominant IEPOX isomer,²³ were collected in duplicate with subsequent analysis by GC/EI-MS. Breakthrough measurements of 2- and 3-methyltetrol sulfates by HILIC/(–)ESI-HR-QTOFMS verified only negligible amounts of particulate breakthrough. Thus, impinger samples were free of thermally labile sulfated precursors which could contribute decomposition artifacts upon GC/EI-MS analysis. GC/EI-MS EICs of *m/z* 231 shown in Figure S7 reveal that the tris-TMS derivative of 3-methylenebutane-1,2,4-triol exhibits substantial gas-phase concentrations ($3.0 \pm 1.70 \mu\text{g m}^{-3}$), 15 $\times$ more abundant than in the particle phase. Similarly, 3-methyltetrahydrofuran-2,4-diol ($5.96 \pm 2.64 \mu\text{g m}^{-3}$) was also detected in the impinger sample, with gas-phase concentrations approximately 1.3 $\times$ greater than its particle-phase concentration. Results suggest that 3-methylenebutane-1,2,4-triol and 3-methyltetrahydrofuran-2,4-diol partition into the gas phase after initial formation in the particle phase from the multiphase chemistry of IEPOX. Although measurements are limited to laboratory-generated *trans*- β -IEPOX SOA under the specified chamber conditions, results provide important evidence for significant revolatilization of C₅H₁₀O₃ reactive uptake products: a process which is not considered in chemically explicit atmospheric modeling of isoprene oxidation.^{20,42–45}

Total yields of 3-methylenebutane-1,2,4-triol and 3-methyltetrahydrofuran diols were estimated from β -IEPOX uptake chamber experiments, with calculations outlined in the SI. Under the chamber conditions examined here (50% RH, seed pH 1.5), β -IEPOX yields 1.8% 3-methylenebutane triol (0.1% particle phase, 1.7% gas phase) and 5.8% 3-methyltetrahydrofuran-2,4-diol (2.5% particle phase, 3.3% gas phase) upon reactive uptake onto acidic sulfate seed aerosol. Given that global IEPOX production is estimated to be 115 Tg C yr^{–1}, C₅H₁₀O₃ reactive uptake products could contribute approximately 8.7 Tg C yr^{–1} to the atmosphere, which is the total that exists in both the gas and particle phases.³

Atmospheric Implications. “C₅-alkene triol” structures have been confirmed as 3-methylenebutane-1,2,4-triol and isomeric 3-methyltetrahydrofuran-2,4-diols by HILIC/(–)ESI-HR-QTOFMS. We propose the abbreviation “C₅H₁₀O₃ reactive uptake products” or the use of respective chemical names replace the term “C₅-alkene triols” for a more accurate representation of the structures.

Conventional derivatization GC/EI-MS protocol for measurement of C₅H₁₀O₃ uptake products lacks accuracy because the tris-TMS analytes are largely artifacts of thermal decomposition and the protocol completely neglects quantitation of the hemiacetal bis-TMS derivatives. Additionally, the use of 2-methyltetrols as a proxy standard for the tris-TMS derivatives significantly underestimates tris-TMS derivative concentrations. Our results are consistent with FIGAERO–CIMS studies suggesting that C₅H₁₀O₃ uptake tracers measured by GC/EI-MS are largely artifacts of thermal decomposition of methyltetrol sulfate esters (or oligomers).^{25–27}

Nondestructive HILIC/(–)ESI-HR-QTOFMS analysis shows low particle-phase yields of 3-methylenebutane-1,2,4-triol and 3-methyltetrahydrofuran-2,4-diols in laboratory-generated β -IEPOX SOA. However, we report evidence that yields may be greatly enhanced by taking into account

partitioning into the gas phase following particle-phase formation from the multiphase chemistry of IEPOX. This revolatilization process has important atmospheric implications, as the unsaturated 3-methylenebutane-1,2,4-triol may be readily oxidized by gas-phase OH radicals to form low-volatility organic species that represent a hitherto unrecognized contribution to SOA. Models of isoprene-SOA formation and distribution should be more accurately parametrized to account for semivolatile $C_5H_{10}O_3$ uptake product formation, and thus IEPOX uptake coefficients should likewise be re-examined to account for partitioning of uptake products into the gas phase since previous iodide-CIMS measurements could not differentiate these isomeric products from IEPOX.^{46–48}

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.estlett.2c00548>.

Detailed synthesis procedures, experimental protocol for smog chamber generation of SOA, 1H , ^{13}C , HSQC and HMBC MNR spectra, GC/EI-MS and HILIC/(-)ESI-HR-QTOFMS method and spectra, discussion of quality control measures, and yield calculation estimation (PDF)

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Notes

The authors declare no competing financial interest.

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