SUPPORTING INFORMATION

Heterogeneous Hydroxyl Radical Oxidation of Isoprene Epoxydiol-Derived Methyltetrol Sulfates: Plausible Formation Mechanisms of Previously Unexplained Organosulfates in Ambient Fine Aerosols

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1. Oxidation flow reactor description

The Oxidation flow reactor (OFR) used in the experiments is a horizontal 13-L glass cylindrical chamber (46 cm in length and 22 cm in inner diameter) that can be employed in photo-oxidation mode to form hydroxyl radical (•OH), as described previously. Ozone (O₃) was produced from external irradiation of zero air flow with a mercury lamp (λ=185 nm) at 1 L min⁻¹ into the OFR. The O₃ concentration downstream of the PAM reactor was monitored every 10 s by an O₃ analyzer (2B technologies, Model 202). A humidifying flow generated by passing 2 L min⁻¹ zero air through a humidified Nafion tube (Perma Pure LLC, Model FC100-80-6-MSS-01) was added to the flow entering the OFR. The atomizer output (3 L min⁻¹), O₃ (1 L min⁻¹) and humidifying flows (2 L min⁻¹) were combined with a dry zero air flow at 1 L min⁻¹ to make up a total flow of 7 L min⁻¹, corresponding to a plug flow residence time of 128 s. •OH was generated by irradiating O₃ in the reactor flow with four mercury lamps (λ_max=254 nm) (BHK, Inc.) shielded in Teflon-coated quartz cylinders. The •OH exposure (molecule cm⁻³ s) in the OFR was varied by changing the UV light intensity by stepping the lamp voltages in the range of 0 to 110 V. The O₃ concentration downstream of the OFR was monitored every 10 s by an O₃ analyzer (2B technologies, Model 202). Relative humidity (RH) and temperature of the flow exiting the OFR were measured by a HOBO RH-temperature sensor (Onset Computer Corp.) recording every 5 s. RH, temperature, O₃ concentration, residence time of the gas, and known reaction rate constants from the literature were used to derive •OH exposure levels at each voltage setting based on a modeling method described elsewhere.¹,²

As shown in Table S1, a 1.04 mM aqueous solution of 2-methyltetrol sulfate (2-MTS) ammonium salt was used for Experiments (Expts) 1-3. For Expt 4, the atomizing solution was acidified to a sulfuric acid concentration of 1.22 mM. For Expt 5, IEPOX-derived SOA was pre-
generated in a 10-m³ indoor smog chamber at UNC under ~60% RH following published procedures, and directed into the OFR for heterogeneous ‘OH oxidation. The flow exiting the base of the reactor was passed through a carbon strip denuder (Sunset Lab) and an O₃ scrubber filled with O₃ destruct catalyst (Carulite 200 Catalyst, Carus) before being directed to downstream sampling devices. Real-time aerosol size distributions, total particle number, surface area (Sₐ) and volume concentrations were measured with a scanning electrical mobility spectrometer (SEMS) consisting of an electrostatic classifier (BMI Inc.) and a mixing condensation particle counter (MCPC, BMI Inc., Model 1700).

2. Authentic 2-MTSs standard

A diastereomeric mixture of racemic ammonium 2-MTSs ((2R,3S)/(2S,3R)- and (2S,3S)/(2R,3R)-1,3,4-trihydroxy-2-methylbutan-2-yl sulfates) was prepared following a published procedure. The purity of the standard was determined to be 60.2% by proton nuclear magnetic resonance (¹H NMR) spectroscopy. The impurities were determined to be methyl sulfate (CH₃O⁵⁻) and ammonium sulfate along with C₂-C₄ compounds that also appear in our proposed oxidation schemes including ions at m/z 201(C₄H₉O₆S⁻), 183 (C₄H₆O₆S⁻) and 153 (C₃H₅O₅S⁻). Using available standards (methyl sulfate and ammonium sulfate (Sigma Aldrich)), methyl sulfate was determined to comprise 25.9% of the sample (w/w) by hydrophilic interaction liquid chromatography interfaced to electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (HILIC/ESI-HR-QTOFMS) and ammonium sulfate was determined to comprise 4.5% by ion chromatography (IC), with C₂-C₄ compounds accounting for the residual mass. It is possible that these OS impurities undergo ‘OH oxidation contributing to the overall radical pool. However, they do not account for the major OS ions reported in this work. Although an increase in inorganic sulfate signal was observed by IC for samples after heterogeneous ‘OH
oxidation, we could not definitively conclude that increased inorganic sulfate is attributable to 2-MTSs due to significant presence of methyl sulfate, which easily fragments into formaldehyde and sulfate radical ion upon \( \cdot \text{OH} \) oxidation.\(^5\) We suspect that the yield of inorganic sulfate from 2-MTSs is lower than that from 3-MTSs because multiple cascading steps of reactions following the scission pathway would be required to generate sulfate radical ion from a tertiary sulfate like 2-MTSs. Future study on inorganic sulfate yield from 2-MTSs is needed.

3. Ambient PM\(_{2.5}\) sampling and site information

**Look Rock, Tennessee, Southeastern U.S.** Southeastern U.S. PM\(_{2.5}\) samples were collected from a site at Look Rock, Tennessee, USA from 1 June to 17 July 2013 during the 2013 Southern Oxidant and Aerosol Study (SOAS) onto quartz filters. The sampling site and aerosol collection procedures have been previously described.\(^6\) The 23-hour sample (17 June, 8 am - 7 am 18 June, local time) selected for reanalysis by the HILIC/ESI-HR-QTOFMS in the present study corresponds to the highest IEPOX-derived SOA mass measured by Aerosol Chemical Speciation Monitor (ACSM, Aerodyne, Inc.). IEPOX-derived SOA (IEPOX-OA) measured by the ACSM was resolved by Positive Matrix Factorization (PMF) analysis.\(^6\)

**Manaus, Brazil, Central Amazonia.** PM\(_{2.5}\) samples from Central Amazonia were collected onto quartz filters at the University School of Technology of the Amazonas State University in Manaus, Brazil from August to September (dry season), 2016. Filter sampling and storage procedures have been previously described.\(^4\) The 24-hour sample selected for reanalysis (24 September 2016) by the HILIC/ESI-HR-QTOFMS is minimally influenced by biomass burning (lowest measured levoglucosan concentration) and has the highest MTS concentration.\(^7\)

**Galápagos islands, Ecuador.** PM\(_{2.5}\) samples from the Galápagos Islands, Ecuador, were collected on the rooftop of Galápagos Science Center (GSC) at Isla San Cristobal over a 10-day period in
July 2018. The sampling site and aerosol collection procedures will be described in a forthcoming manuscript. Briefly, a 23-hour aerosol sample (19 July, 11:35 am – 10:24 am, 20 July, local time) selected for analysis by the HILIC/ESI-HR-QTOFMS method was collected onto a pre-baked quartz filter (8.5 × 11 inches, Pallflex Tissuquart Filters, 2500 QAT-UP grade, Pall Laboratory) using a high-volume PM$_{2.5}$ (HiVol) air sampler (TE-6070V-BL, Tisch Environmental). The HiVol was located on the second floor of a two-story building near Instituto Nacional de Meteorologia e Hidrologia (INAMHI) meteorological station (0.9000° S, 89.6000° W) and operated at an average flow rate of 1.19 m$^3$ min$^{-1}$ over the sampling period. Quartz filters were pre-baked at 550 °C and sealed in antistatic bags with two packets of silica gel prior to collection. After sampling, filters were immediately stored in situ in a −20 °C freezer until they were transported to UNC in a cooler on ice. At UNC, filters were stored under dark conditions in a −20 °C freezer until chemical analyses.

4. Sample preparation for laboratory and field aerosol samples

A 50 μL aliquot of each PILS aqueous sample was withdrawn and diluted in 950 μL acetonitrile (ACN, HPLC grade, Fisher Scientific) shortly after collection in order to achieve the solvent composition of the organic mobile phase. Diluted PILS and dry filter samples were stored in the dark at −20 °C prior to HILIC/ESI-HR-QTOFMS analysis within 48 hours. Blank and sample filters collected from both laboratory experiments and field sites (37 mm-diameter punches from the original Hi-Vol quartz filters) were individually submerged in 22 mL methanol (Optima LC/MS, Fisher Scientific) and sonicated for 45 minutes. Extracts were filtered into pre-cleaned scintillation vials through PTFE syringe filters (Agilent Technologies, 0.2-m pore size) to remove filter fibers, and gently blown dry under a high-purity N$_2$ stream at room temperature. Before drying laboratory filter samples, 10 mL of each filter extract were transferred into another pre-
cleaned scintillation vial and blown dry for subsequent IC analysis. Dried extracts from each filter were reconstituted in 0.3 mL 95:5 (v/v) acetonitrile (ACN, HPLC grade, Fisher Scientific) Milli-Q H$_2$O prior to HILIC/ESI-HR-QTOFMS and 0.5 mL Mili-Q H$_2$O prior to IC analysis, respectively. If necessary, additional dilutions with 95:5 (v/v) ACN:H$_2$O were made for each reconstituted HILIC/ESI-HR-QTOFMS sample to ensure a 2-MTSs concentration within the linear calibration range (0.01–1 µg mL$^{-1}$).

5. Offline HILIC/ESI-HR-QTOFMS analysis for laboratory and field aerosol samples

Organosulfates (OS) were characterized by HILIC/ESI-HR-QTOFMS using an Agilent 6500 Series UPLC system equipped with an ESI source interfaced to an Agilent 6250 Series Accurate Mass Q-TOFMS operated in negative ion mode using instrumental conditions described in Cui et al.$^4$ Briefly, A 5-µL or 25-µL aliquot of each standard or sample was injected, respectively, onto a Waters ACQUITY UPLC ethylene bridged hybrid amide (BEH-Amide) column (2.1 × 100 mm, 1.7 mm particle size, Waters) at 35 °C. The mobile phases consisted of aqueous eluent (A) 0.1% (w/w) ammonium acetate in Milli-Q H$_2$O, and organic eluent (B) 0.1% (w/w) ammonium acetate in a 95:5 (v/v) ACN:Milli-Q H$_2$O, both adjusted to a pH of 9.0 with NH$_4$OH (TraceMetal Grade, Fisher Scientific). Eluent A was held at 0% for 4 min, then increased to 15% over 16 min and held constant until 24 min, decreased to 0% from 24 min to 25 min, and held constant until 30 min. ESI-HR-QTOF-MS mass spectra were recorded over the range $m/z$ 60 to 1000. At the beginning of each analysis period, the mass spectrometer was calibrated using a commercially available ESI-L low-mass concentration tuning mixture (Agilent Technologies) in 95:5 (v/v) ACN:Milli-Q H$_2$O. QTOF-MS mass axis calibration was conducted in the low mass range ($m/z$ 50–1700) and high-resolution mode (4GHz). Seven compounds were used for calibration: $m/z$ 68.9958, 112.9856, 301.9981, 601.9790, 1033.9881, 1333.9689, and 1633.9498. The acetic acid adduct of
hexakis (1H,1H,3H-tetrafluoropropoxy) phosphazene (m/z 980.0164), purine (m/z 119.0363), and leucine enkephalin (m/z 554.2620) were continuously infused for real-time mass axis correction.

Data was analyzed by Mass Hunter Version B.06.00 Build 6.0.633.0 software (Agilent Technologies).

6. IC analysis for laboratory aerosol samples

A 25-μL aliquot of each laboratory sample reconstituted in H₂O was analyzed by an anion exchange IC system (ICS 3000, Thermo Fisher) equipped with an IonPac AS11-HC guard column (2×50 mm, Thermo Scientific) and anion-exchange column (2×250 mm, Thermo Scientific) at a flow rate of 0.4 mL min⁻¹. The temperature of the conductivity detector (Dionex) interfaced to the IC was set at 35 °C. The 35-min potassium hydroxide (KOH) eluent program utilized for the IC was as follows: KOH was increased from 1 mM to 30 mM KOH from 0 to 25 min, then ramped to 84 mM KOH from 25 to 30 min, decreased to 1 mM until 30.1 min and held constant until 35 min. The product assignment of chromatographic peaks eluting at different times is based on calibrated retention orders of authentic standards as previously described.³

7. Heterogeneous ‘OH oxidation kinetics of 2-MTSs

The ‘OH-initiated decay of 2-MTSs follows an exponential trend and is fitted to an exponential function to obtain an effective second-order heterogeneous ‘OH rate constant (k)⁹:

$$\ln \frac{C}{C_0} = -k [OH] t$$  \hspace{1cm} \text{(Eqn. S1)}

where \(C_0\) is the concentration of 2-MTSs before oxidation, \(C\) is the concentration of 2-MTSs at a given ‘OH exposure, [OH] is the gas-phase concentration of the ‘OH, and \(t\) is the reaction time.

The product of [OH] and \(t\) is ‘OH exposure (molecule cm⁻³ s). The \(k\) for the 2-MTSs was then determined to be \(4.87 \pm 0.64 \times 10^{-13}\) cm³ molecule⁻¹ s⁻¹. It should be noted that the heterogeneous OH reaction rate reported here is for aerosol particles with a surface-weighted diameter of 119 ±
4 nm. The effective heterogeneous kinetics are dependent on factors such as particle size and particulate 2-MTSs mass fractions. Due to these potential limitations, the rate reported here is an approximation, and should only be used as such.

Based on the kinetic data, the e-folding lifetime of 2-MTSs against heterogeneous 'OH oxidation, \( \tau \), can be estimated using Eqn. S2.\(^{10}\)

\[
\tau = \frac{[\text{2-MTOS}]}{[\text{2-MTOS}]} = \frac{1}{k[\text{OH}]} \quad \text{(Eqn. S2)}
\]

Using a 24-h averaged 'OH concentration of \(1.5 \times 10^6\) molecule cm\(^{-3}\),\(^{11}\) the \( \tau \) of 2-MTSs was calculated to be 16±2 days. Longer e-folding lifetimes of 39 days in SE US and 79 days in Amazon were estimated assuming 24-h averaged 'OH concentrations \(0.6 \times 10^6\) molecule cm\(^{-3}\) in SE US and \(0.3 \times 10^6\) molecule cm\(^{-3}\).\(^{12,13}\) However, the lifetime would be much shorter in urban areas where 'OH concentrations are elevated: 5.9 days assuming an OH concentration of \(4 \times 10^6\) molecule cm\(^{-3}\),\(^{14}\) and 2.2 days assuming \(1.1 \times 10^7\) molecule cm\(^{-3}\) which is the average daily maximum reported for Beijing in Summer 2006.\(^{15}\) In fact, the two C\(_5\)-OS oxidation products of 2-MTSs (at \(m/z\) 211 and 213) were the most abundant C\(_5\) species measured in Beijing during 2016 summertime and shown to have a strong correlation with 2-MTSs (\(R^2 = 0.77\)).\(^{16}\) This agrees well with our proposed mechanisms and suggests that a region influenced by both anthropogenic and biogenic emissions with elevated 'OH concentrations is conductive to the formation of these heterogeneous 'OH oxidation products. Note that the heterogeneous 'OH oxidation rate constant determined here is presumably for homogeneous 2-MTS aerosols. Given that the phase state of the 2-MTS particles is likely to be semisolid when RH is less than 80%,\(^{3,17}\) the effect of RH on this reaction is likely to be minimal during daytime RH conditions in the Southeastern US and the Amazon rainforest. Due to the low-volatility of 2-MTSs and salting out to core-shell morphology in mixed organic-inorganic aerosols,\(^3\) it seems likely that 2-MTOSs will remain at the aerosol
surface to be oxidized by •OH at a faster rate to yield the previously unexplained OSs. Overall, the heterogeneous •OH oxidation processes of 2-MTSs are reasonably fast and should be considered in large-scale models in order to better understand the transformation and abundance of these atmospheric particulate OSs.

8. Microscopy Imaging

Morphology of 2-MTS aerosols characterized by both atomic force microscopy (AFM) at atmospheric pressure and scanning electron microscopy (SEM) under vacuum confirmed that 2-MTS aerosols used in the heterogeneous •OH oxidation experiments are homogeneous spheres. The operating conditions for AFM and SEM are described in prior publications. For sample collection, 3-stage microanalysis particle sampler (MPS-3, California Measurements, Inc.) with size cuts of 5.0, 2.5, and 0.4 μm was operated at 2.1 L min⁻¹ and only stage 3 (size cut of 0.4 μm) was used in the present work. Aerosol particles were impacted onto silicon wafer substrates (Ted Pella, Inc.) and carbon-type-b Formvar-coated copper transmission electron microscopy (TEM) grids for analyses using SEM and AFM, respectively. Samples were stored in sealed plastic vials at room temperature prior to analyses. 2-MTS aerosols were imaged in 5x5 μm regions by an AFM (Anasys Instruments) in tapping IR mode using a gold coated microfabricated silicon probes (Bruker, Santa Barbara, CA) at ambient laboratory temperature (~23 °C), pressure, and RH (~36%). SEM analysis of 2-MTS aerosols collected onto TEM grids was performed by a FEI Helios 650 Nanolab-Dualbeam electron microscope equipped with a high angle annular dark field (HAADF) detector operated at an accelerating voltage of 10.0 kV and a current of 0.80 nA under vacuum conditions (10⁻³ to 10⁻⁵ Pa).

9. Heterogeneous •OH oxidation mechanism of 2-MTSs
Heterogeneous 'OH oxidation of organic aerosols proceeds through two general processes: functionalization and fragmentation.\textsuperscript{19,20} The branching ratio between these pathways affects aerosol loading, composition and volatility. Key to both processes is the fate of peroxyl radicals (RO\textsuperscript{2}\textbullet{}), which form from reaction of organic molecules with 'OH followed by addition of O\textsubscript{2}. The first-generation RO\textsuperscript{2}\textbullet{} can self- and/or cross-react with a second RO\textsuperscript{2}\textbullet{} in a chain termination reaction yielding an intermediate tetroxide (RO\textsubscript{4}R) followed by disproportionation through three reaction channels (R1a - R1c). The resulting products are ketones (R’C(O)R), alcohols (ROH), and alkoxy radicals (RO').\textsuperscript{21-23} While R1a and R1b result in functionalized products, the RO' formed by R1c leads to fragmentation through β-scission.

\begin{align*}
\text{RO}\textsuperscript{2}\textbullet{} + R'O\textsuperscript{2}\textbullet{} &\rightarrow ROH + R'C(O)R + O_2 & (\text{R1a}) \\
\text{RO}\textsuperscript{2}\textbullet{} + R'O\textsuperscript{2}\textbullet{} &\rightarrow 2R'C(O)R + H_2O_2 & (\text{R1b}) \\
\text{RO}\textsuperscript{2}\textbullet{} + R'O\textsuperscript{2}\textbullet{} &\rightarrow RO' + R'O' + O_2 & (\text{R1c})
\end{align*}

Russell observed equal yields of alcohols and ketones from reactions of RO\textsuperscript{2}\textbullet{} generated from oxidations of arylalkyl hydrocarbons through a cyclic RO\textsubscript{4}R transition state.\textsuperscript{24} Later, Bennett and Summers showed that the condensed phase reactions of alkane-derived RO\textsuperscript{2}\textbullet{} via a non-cyclic transition state favored ketones over alcohols at room temperature with the yield of alcohols increasing with temperature.\textsuperscript{25} The early studies are based on reactions of specific compounds and recent studies indicate the yields of alcohols, ketones and RO' vary depending on molecular structures of the precursor and the reaction temperature.\textsuperscript{20,26,27} For ease of presentation, we refer to the formation of alcohols as Russell reactions as R1, the formation of ketones as Bennett-Summers reactions as R2 and the β-scission of RO' as R3 in the proposed reaction schemes (Schemes S1-S4). Note that when both RO\textsuperscript{2}\textbullet{} are tertiary, only RO' formation is possible due to the
lack of an \( \alpha \) hydrogen.\textsuperscript{26} Available experimental rate coefficients between tertiary \( \text{RO}_2^* \) were shown to be slow relative to the reactions with primary and secondary \( \text{RO}_2^* \).\textsuperscript{26,28}

Two criteria were the basis of initial screening of the HILIC/ESI-HR-QTOFMS data for OSs: 1) ions that fragmented to bisulfate anion (\( \text{HSO}_4^- \), \( m/z \) 97) from available auto MS/MS data; and 2) ions that show increased abundance following 'OH exposure. Based on these criteria, the parent ions of OS products in Table S2 were identified. Abundant OS ions were detected at \( m/z \) 231 (\( \text{C}_5\text{H}_{11}\text{O}_8\text{S}^- \)), 229 (\( \text{C}_5\text{H}_9\text{O}_8\text{S}^- \)), 213 (\( \text{C}_5\text{H}_9\text{O}_7\text{S}^- \)) and 211 (\( \text{C}_5\text{H}_7\text{O}_7\text{S}^- \)) as discussed in the main text. An important observation discussed here is that the 1,5-\( \text{H} \) Shift of \( \text{RO}_2^* \) has been demonstrated as a plausible mechanism for \( \text{RO}_2^* \) in the condensed-phase.\textsuperscript{29} A 1,5-\( \text{H} \) shift of the \( \text{C}_2 \)-methyoxyl radical (Scheme S2) could result in the isomeric cyclic hemiacetals of ions detected at \( m/z \) 229 (\( \text{C}_5\text{H}_9\text{O}_8\text{S}^- \)). The further oxidation of the hemiacetals produces isomeric cyclic lactones detected at \( m/z \) 227 (\( \text{C}_5\text{H}_7\text{O}_8\text{S}^- \)), different from those formed in Scheme S6. In addition, several \( \text{C}_2-\text{C}_4 \) OS ions are proposed as heterogeneous 'OH oxidation products through \( \text{RO}_2^* \) formation from four first-generation \( \text{RO}_2^* \) transients followed by \( \beta \)-scission. In Scheme S3, \( \text{C}_4\text{H}_7\text{O}_8\text{S}^- \) (\( m/z \) 199) is formed directly from one of the two \( \beta \)-scission pathways of the first-generation \( \text{C}_3-\text{RO}_2^* \). The second \( \beta \)-scission pathway forms a \( \text{C}_3-\text{RO}_2^* \) which gives rise to a newly reported OS, \( \text{C}_3\text{H}_7\text{O}_6\text{S}^- \) (\( m/z \) 171) through Russell disproportionation. Scheme S4 yields \( m/z \) 171 from the first generation \( \text{C}_4-\text{RO}_2^* \) precursor. The structure proposed for \( m/z \) 171 is a sulfate hemiacetal, suggested to be unstable toward hydrolysis under conditions of HILIC separation.\textsuperscript{30} However, sulfate acetals are known in carbohydrate chemistry\textsuperscript{31,32} and cyclic sulfate hemiacetal metabolites have been analyzed by reverse phase HPLC.\textsuperscript{33-35} In Scheme S4, \( \text{C}_4\text{H}_7\text{O}_7\text{S}^- \) (\( m/z \) 199) is formed either via Russel disproportionation or Bennett-Summers reactions of the \( \text{C}_4-\text{RO}_2^* \) generated from \( \beta \)-scission of the \( \text{C}_4-\text{RO}_2^* \). The assigned structure of \( \text{C}_4\text{H}_7\text{O}_7\text{S}^- \) (\( m/z \) 199) formed in both Schemes S3 and S4 is 2-.
methylglyceric acid (2-MG OS) as discussed in the main text. In Scheme S5, \( m/z \) 171 is proposed to react via further abstraction of an \( \alpha \)-hydrogen and elimination of \( \text{HO}_2^- \) from the \( \text{O}_2 \) adduct to yield a \( \text{C}_3 \)-sulfate hemiacetal at \( m/z \) 169 (\( \text{C}_3\text{H}_5\text{O}_6\text{S}^- \)). The short retention time (RT) of \( m/z \) 169 on the HILIC column suggests that this ion is not lactic acid sulfate, which has been previously identified in ambient aerosols\(^{30,36,37} \) and supports the proposed mechanism and the assigned structure. This may serve as a plausible mechanism to explain the detection of this ion as a \( \text{C}_3 \) hydroxyketone OS in isoprene ozonolysis in the presence of acidified sulfate aerosols. An additional oxidation of \( m/z \) 171 generates a long retention time ion at \( m/z \) 185 consistent with a carboxylic acid retaining the sulfate hemiacetal functionality.

In Scheme S7, a 1,2-H-shift of the \( \text{C} \)-centered radical from Scheme S2 followed by \( \beta \)-scission leads to glyoxal sulfate at \( m/z \) 139 (\( \text{C}_2\text{H}_3\text{O}_5\text{S}^- \)), which undergoes further oxidation to sulfated glycolic acid at \( m/z \) 155 (\( \text{C}_2\text{H}_5\text{O}_6\text{S}^- \)). Alkyl 1,2-H-shifts have large energy barriers and are generally unfavorable. However, carbon substituents can appreciably lower the barrier, particularly when delocalization of electron density to substituent \( p \)-orbitals is possible as would be the case in this\(^{38,39} \) \( \beta \)-scission of the \( \text{C} \)-centered radical in the \( \text{C}2-\text{C}3 \) direction leads to the \( \text{C}2 \) sulfate ester of glyceraldehyde at \( m/z \) 169 (\( \text{C}_3\text{H}_5\text{O}_6\text{S}^- \)), an isobar of the sulfate hemiacetal ion proposed in Scheme S5. Further oxidation of glyceraldehyde sulfate leads to the \( \text{C}2 \) sulfate ester of the carboxylic acid at \( m/z \) 185 (\( \text{C}_3\text{H}_5\text{O}_7\text{S}^- \)), an isobar of the \( m/z \) 185 ion in Scheme S5.

The ions at \( m/z \) 185 (\( \text{C}_3\text{H}_5\text{O}_7\text{S}^- \)) and 155 (\( \text{C}_2\text{H}_5\text{O}_6\text{S}^- \)) detected in the aged 2-MTS aerosol samples have RTs >22 min (Figure S3A-D, Table S2), indicating that the products have both carboxylic acid and sulfate groups. The EIC of the ion \( m/z \) 139 (\( \text{C}_2\text{H}_5\text{O}_5\text{S}^- \)), shows two low intensity peaks (Figure S3A - D), supporting \( \text{cis/trans} \) isomers of the enol tautomeric form. The EICs of \( m/z \) 169 also show two peaks (Figure S3A-D), consistent with the presence of isobars.
predicted in Schemes S5 and S7. The EIC of m/z 171 shows two peaks. The proposed sulfate
hemiacetal structure does not have geometric isomers, ruling this out as a possible explanation.
Stable rotamers resulting from hindered rotation about C1-C2 bond or an isobaric structure may
account for the EIC. A sulfate ester of glycerol would have the correct composition, but there does
not appear to be a plausible route to such a product. It should be noted that the elution time of the
ion at m/z 185 is after 24 min, which is during mobile phase re-equilibration. Although day-to-day
variations in RTs are possible, this indicates incomplete elution prior to gradient switching, leaving
room for future improvement of our HILIC method.

An OS product, C₄H₇O₆S⁻ (m/z 183), could potentially form based on our proposed
mechanism (Scheme S4), with a structure identical to that proposed for oxidation of methyl vinyl
ketone and methacrolein³⁷,⁴⁰–⁴² and the ozonolysis of isoprene⁴³ in experimental studies. The
HILIC/ESI-HR-QTOFMS trace shows an ion at m/z 183 (C₄H₇O₆S⁻) eluting with an early
retention time (RT ~ 1.3 min), which is consistent with a structure that contains a carbonyl, sulfate
and hydroxyl groups.⁴⁴ However, high background levels of this ion were detected in lab-generated
2-MTS aerosols and IEPOX SOA aerosols before exposure to •OH, and the ion abundance
decreased with increasing •OH exposure. Hence, we are not able to conclude definitively that
C₄H₇O₆S⁻ (m/z 183) is solely derived from 2-MTSs in our experiments.

While heterogeneous OH oxidation products (e.g., m/z 211 and 213) of particulate 2-MTSs
(m/z 215) can also react with OH, their low yields within the studied OFR conditions suggest that
their later-generation oxidation products were below HILIC/ESI-HR-QTOFMS detection limits.
In ambient environments where 2-MTSs are the dominant particulate OSs, it is not unreasonable
to expect the later-generation oxidation products have a minor contribution to total OSs and OA
in PM$_{2.5}$. Future work should synthesize some of the heterogeneous oxidation products identified
from the present study (e.g., m/z 211 and 213) to systemically assess their reactivities against heterogeneous OH oxidation and hydrolysis relative to 2-MTSs. Due to high concentrations of 2-MTSs used in our lab studies and typically observed in PM$_{2.5}$, future work should also examine if secondary chemical processes, such as 2-MTS reactions with RO• or sulfate radical anions (SO$_4^{2-}$), also lead to multifunctional OSs.

The HILIC/ESI-QTOFMS analysis of PM$_{2.5}$ field samples collected at Look Rock, TN, USA, Manaus, Brazil, and Galápagos Islands, Ecuador is consistent with proposed mechanisms. RTs of major OS ions match those of the chamber-generated samples from heterogeneous 'OH oxidation of 2-MTS aerosols and IEPOX SOA aerosols (Figures 3A-D, S2, S3A-D). Quantification of OSs formed is difficult due to a lack of authentic standards and warrants future synthesis work. A quick estimation of OS abundance relative to parent OS (2-MTSs) can be derived if the response factors for all OSs are assumed the same (Figure S6). After exposure to 'OH equivalent to 2-week atmospheric aging (at 'OH concentration of 1.5 × 10$^6$ molecule cm$^{-3}$), the summed ratios of the four C$_5$ OS products (m/z 211, 213, 229, and 231) to 2-MTSs is ~ 0.1 for laboratory OFR experiments, comparable to the three ambient samples (~0.15, ~0.14, and ~0.1 for Galapagos, Look Rock, and Manaus, respectively). Differences observed between HILIC traces of OS ions in laboratory samples and field samples are expected because of variation in 'OH concentrations at different sampling locations changes the extent of 2-MTSs oxidation, variations in aerosol acidity likely influence product and isomer distribution. We encourage researchers to revisit available LC data along with other collocated measurements to look for the oxidation products reported in this work and resolve how these factors may impact the amounts of OSs observed in ambient PM$_{2.5}$.
Since atmospheric PM$_{2.5}$ is typically acidic,$^{46}$ an experiment conducted with the atomizing solution of 2-MTSs spiked with sulfuric acid (Expt. no. 4 in Table S1) was conducted to probe the dependence on acidity. The resulting isomeric peaks for different OS ions resolved by HILIC were distinctly different compared to the neutral seed experiments (Expt. no.1-3 in Table S1). For CsH$_9$O$_7$S$^-$ (m/z 213), peak 1 (RT = 1.75 min) and peak 4 (RT = 3.07 min) were greatly enhanced (Figure S2). The abundance of peak 1 (RT = 2.28 min) for CsH$_9$OsS$^-$ (m/z 229) was enhanced relative to peak 2 (RT = 3.17 min). Peak 1 of CsH$_7$O$_7$S$^-$ (m/z 211) eluting at 1.22 min was also enhanced. These data give additional insights into the eluting patterns for field samples. Even when starting from a single species, such as authentic 2-MTSs, heterogeneous ‘OH oxidation chemistry quickly becomes very complicated as more oxidation products and isomers are formed. Future studies need to elucidate the branching ratios for the products of first- and later-generation RO$_2$• self-/cross- reactions, as well as the dominant isomers of OS products and their dependence on aerosol acidity and morphology. A better understanding in the reaction kinetics and product/isomer distribution will help parameterize this chemical process, which is currently lacking in air quality and climate models. Although OSs were exclusively measured and reported to be the main heterogeneous OH oxidation products of 2-MTSs in this work, the formation of other compounds such as alcohols or acids that would be expected as scission products are not evident by the analytical technique used and may warrant further examination.
Table S1. Experimental Conditions of Heterogeneous ’OH Oxidation Experiments.

<table>
<thead>
<tr>
<th>No</th>
<th>Aerosol Type&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Exposure&lt;sup&gt;b&lt;/sup&gt;</th>
<th>RH (%)</th>
<th>T (°C)</th>
<th>Sampling Method</th>
<th>Offline Analytical Techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2-MTSs</td>
<td>O₃ + UV</td>
<td>60.5</td>
<td>21.5</td>
<td>PILS Filter</td>
<td>IC HILIC/ESI-HR-QTOFMS</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SEMS</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2-MTSs</td>
<td>O₃ + UV</td>
<td>60.5</td>
<td>22.1</td>
<td>PILS Filter</td>
<td>IC HILIC/ESI-HR-QTOFMS</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SEMS</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2-MTSs</td>
<td>O₃ + UV</td>
<td>63.0</td>
<td>22.4</td>
<td>PILS Filter</td>
<td>IC HILIC/ESI-HR-QTOFMS</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SEMS</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2-MTSs + Acidified AS</td>
<td>O₃ + UV</td>
<td>64.3</td>
<td>21.4</td>
<td>Filter SEMS</td>
<td>IC HILIC/ESI-HR-QTOFMS</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>IEPOX SOA</td>
<td>O₃ + UV</td>
<td>58.2</td>
<td>21.4</td>
<td>Filter SEMS</td>
<td>IC HILIC/ESI-HR-QTOFMS</td>
</tr>
</tbody>
</table>

<sup>a</sup> AS = ammonium sulfate.

<sup>b</sup> ’OH exposure ranges from $8.51 \times 10^{11}$ to $2 \times 10^{12}$ molecule cm$^{-3}$ s.
Table S2. Organosulfates identified from heterogeneous \(^*\)OH oxidation of 2-MTSs (O:C = 1.4).

<table>
<thead>
<tr>
<th>No</th>
<th>Formula</th>
<th>[M-H](^-) Mass</th>
<th>Structure</th>
<th>O:C</th>
<th>Retention Time (min)</th>
<th>Mass Error (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Theoretical Mass</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>C(_5)H(_9)O(_7)S(^-)</td>
<td>213.0074</td>
<td>(\text{O}_3\text{SO}_2\text{OH}) (a)</td>
<td>1.4</td>
<td>1.75, 1.99, 2.31, 3.07, 3.66</td>
<td>-0.54, -1.41, -1.23, -3.31, -0.24</td>
</tr>
<tr>
<td>2</td>
<td>C(_5)H(_7)O(_7)S(^-)</td>
<td>210.9918</td>
<td>(\text{O}_3\text{SO}_2\text{OH}) (a)</td>
<td>1.4</td>
<td>1.02, 1.22, 1.41</td>
<td>0.99, -0.73, -0.79</td>
</tr>
<tr>
<td>3</td>
<td>C(_5)H(_11)O(_8)S(^-)</td>
<td>231.0180</td>
<td>(\text{HO}_3\text{SO}_3\text{OH}) (a)</td>
<td>1.6</td>
<td>5.84</td>
<td>0.43</td>
</tr>
<tr>
<td>4</td>
<td>C(_5)H(_9)O(_8)S(^-)</td>
<td>229.0024</td>
<td>(\text{HO}_3\text{SO}_3\text{OH}) (a)</td>
<td>1.6</td>
<td>2.28, 3.17, 3.75</td>
<td>-0.74, -1.81, -2.63</td>
</tr>
<tr>
<td>5</td>
<td>C(_5)H(_7)O(_8)S(^-)</td>
<td>226.9867</td>
<td>(\text{O}_3\text{SO}_2\text{OH}) (a)</td>
<td>1.6</td>
<td>1.12, 1.66</td>
<td>-4.50, -1.32</td>
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<tr>
<td>6</td>
<td>C(_4)H(_9)O(_7)S(^-)</td>
<td>198.9918</td>
<td>(\text{HO}_3\text{SO}_3\text{OH}) (a)</td>
<td>1.6</td>
<td>23.4</td>
<td>0.76</td>
</tr>
<tr>
<td>7</td>
<td>C(_3)H(_7)O(_6)S(^-)</td>
<td>170.9969</td>
<td>(\text{HO}_3\text{SO}_3\text{OH}) (a)</td>
<td>2.0</td>
<td>4.36, 6.52</td>
<td>-1.13, -0.14</td>
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<tr>
<td>8</td>
<td>C(_3)H(_9)O(_6)S(^-)</td>
<td>168.9812</td>
<td>(\text{O}_3\text{SO}_2\text{OH}) (a)</td>
<td>2.0</td>
<td>2.14, 6.52</td>
<td>-0.24, -2.2</td>
</tr>
<tr>
<td>9</td>
<td>C(_3)H(_7)O(_7)S(^-)</td>
<td>184.9761</td>
<td>(\text{HO}_3\text{SO}_3\text{OH}) (a)</td>
<td>2.3</td>
<td>24.43</td>
<td>2.75</td>
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<tr>
<td>10</td>
<td>C(_2)H(_3)O(_6)S(^-)</td>
<td>154.9656</td>
<td>(\text{O}_3\text{SO}_2\text{OH}) (a)</td>
<td>3</td>
<td>22.58</td>
<td>-3.22</td>
</tr>
<tr>
<td>11</td>
<td>C(_2)H(_3)O(_5)S(^-)</td>
<td>138.9707</td>
<td>(\text{O}_3\text{SO}_2\text{OH}) (a)</td>
<td>2.5</td>
<td>0.99, 5.65</td>
<td>2.88, 0.6</td>
</tr>
</tbody>
</table>

\(a\)More isomers are available.
Figure S1. Experimental setup for exposing particulate 2-MTSs to various levels of ‘OH exposure.
Figure S2. HILIC/ESI-HR-QTOFMS extracted ion chromatograms (EICs) of the most abundant OS ions: m/z 231 \((\text{C}_5\text{H}_{11}\text{O}_8\text{S}^-)\), 229 \((\text{C}_5\text{H}_{9}\text{O}_8\text{S}^-)\), 213 \((\text{C}_5\text{H}_{9}\text{O}_7\text{S}^-)\), and 211 \((\text{C}_5\text{H}_{7}\text{O}_7\text{S}^-)\) formed through the heterogeneous \(\cdot\text{OH}\) oxidation of 2-MTS aerosol in the laboratory using an aerosolized 2-MTS standard (1st row) and an 2-MTS standard spiked with sulfuric acid (2nd row) and trans-\(\beta\)-IEPOX SOA generated in an indoor smog chamber (3rd row). The signals were normalized to the maximum signal of the parent 2-MTSs detected by HILIC/ESI-HR-QTOFMS at m/z 215 for the same sample.
Figure S3. HILIC/ESI-HR-QTOFMS EICs of other OS ions: m/z 227 (C₅H₇O₈S⁻), 171 (C₃H₇O₆S⁻), 169 (C₃H₅O₆S⁻), 185 (C₃H₅O₆S⁻), 155 (C₂H₃O₆S⁻) and 139 (C₂H₃O₅S⁻) formed through (A) the heterogeneous OH oxidation of 2-MTS aerosols equivalent to ~16 photochemical days in the laboratory, and detected in PM₂.₅ samples collected from (B) Look Rock, USA, (C) Manaus, Brazil, (D) Galápagos, Ecuador. The signals were normalized to the maximum peak height in EIC of each ion in each sample.
Figure S4. HILIC/ESI-HR-QTOFMS EICs for 2-MTSs observed at m/z 215 in aerosol samples collected from heterogeneous OH oxidation experiments in the laboratory using aerosolized 2-MTSs standard (1st row) and aerosolized 2-MTSs standard spiked with sulfuric acid (2nd row) and trans-β-IEPOX SOA generated in indoor smog chamber (3rd row).
Figure S5. HILIC/ESI-HR-QTOFMS peak areas of major OS products formed from the heterogeneous OH oxidation of 2-MTS aerosols normalized by the peak areas of the 2-MTS precursors (m/z 215) for field and laboratory samples. The laboratory samples with maximum OH exposure levels (2 × 10^{12} molecule cm^{-3}s, equivalent to ~15 days with OH concentration of 1.5 × 10^6 molecule cm^{-3}) were shown here. Note that the results are semi-quantitative since the differences in response factors for different OSs were not considered. This is because not all authentic standards are available for those OSs.
Figure S6. Ion Chromatograms (RT = 4-6 min) before and after heterogeneous oxidation of 2-MTSs shown in gray and orange trace, respectively. Retention time of peaks corresponding to glycolate and formate was confirmed by authentic standards.
Figure S7. HILIC/ESI-HR-QTOFMS EICs of ions observed at m/z 199 (C₈H₇O₇S⁻) for A(1) 10 ppm 2-MG-OS standard synthesized in house following a published method and B(1) laboratory samples from heterogeneous •OH oxidation of 2-MTS aerosols. Their corresponding MS² spectra (A(2) and B(2)) confirm that the major fragment ions at m/z 97 (HSO₄⁻)) and m/z 119 (deprotonated 2-MG) are consistent with the literature.
Figure S8. AFM (A) height and (B) phase images, as well as (C) SEM image collected for non-aged 2-MTS aerosols atomized into the OFR. These images show that the aerosol is homogeneously-mixed aqueous aerosol particles. See Section S8 for sample collection and microscopy analysis by AFM and SEM.
Scheme 1. Proposed reaction pathways following H-abstraction by $\cdot$OH at the secondary carbon C1. Solid black boxes indicate products that were observed by HILIC/ESI-HR-QTOFMS. Solid red boxes indicate products that were observed by IC. Molecules greyed out are reaction intermediates that should be present in their corresponding hemiacetals or lactones.

R1: Russell
R2: Bennett and Summers
R3: $\beta$-scission of alkoxy radical
Scheme 2. Proposed reaction pathways following H-abstraction by 'OH at the primary carbon C2. Solid black boxes indicate products that were observed by HILIC/ESI-HR-QTOFMS. Solid red boxes indicate products that were observed by IC. Molecules greyed out are reaction intermediates that should be present in their corresponding hemiacetals or lactones.

R1: Russell
R2: Bennett and Summers
R3: β-scission of alkoxy radical
Scheme 3. Proposed Reaction Pathways following H-abstraction by ·OH at the secondary carbon C3. Solid boxes indicate products that were observed by HILIC/ESI-HR-QTOFMS. Solid red boxes indicate products that were observed by IC. Molecules greyed out are reaction intermediates that should be present as their corresponding hemiacetals or lactones.

R1: Russell
R2: Bennett and Summers
R3: β-scission of alkoxy radical
Scheme 4. Proposed reaction pathways following H-abstraction by OH at the secondary carbon C4. Solid black boxes indicate products that were observed by HILIC/ESI-HR-QTOFMS. Solid red boxes indicate products that were observed by IC. Molecules greyed out are reaction intermediates that should be present in their corresponding hemiacetals or lactones.

R1: Russell
R2: Bennett and Summers
R3: β-scission of alkoxy radical
Scheme 5. Proposed reaction pathway that leads to the formation of $\text{C}_3\text{H}_5\text{O}_6\text{S}^-$ ($m/z$ 169). Solid boxes indicate these products were observed by HILIC/ESI-HR-QTOFMS. Dotted boxes indicate proposed products that were not detected. Molecule greyed out is geminal diol that should be present in aldehyde form.

Scheme 6. Proposed reaction pathway that leads to the formation of $\text{C}_5\text{H}_7\text{O}_8\text{S}^-$ ($m/z$ 227) via the Bennett-Summers reaction of the $\text{RO}_2^*$ corresponding to the cyclic $m/z$ 213 hemiacetals. Solid boxes indicate these products were observed by HILIC/ESI-HR-QTOFMS.
Scheme 7. Proposed reaction pathway that leads to the formation of $\text{C}_2\text{H}_3\text{O}_5\text{S}^-$ ($m/z$ 139), $\text{C}_2\text{H}_3\text{O}_6\text{S}^-$ ($m/z$ 155) and $\text{C}_3\text{H}_5\text{O}_7\text{S}^-$ ($m/z$ 185) from $\text{R}^\bullet$. Solid boxes indicate these products were observed by HILIC/ESI-HR-QTOFMS.

From Scheme 2

$$
\begin{align*}
\text{HO} & \quad \text{HO} \\
\text{OSO}_3^- & \quad \text{OSO}_3^- \\
\text{OH} & \quad \text{OH} \\
\text{C}_2\text{H}_3\text{O}_5\text{S}^- & \quad \text{C}_2\text{H}_3\text{O}_5\text{S}^- \\
\text{m/z 139} & \quad \text{m/z 139} \\
\text{1,2-H Shift} & \\
\text{HO} & \quad \text{HO} \\
\text{OSO}_3^- & \quad \text{OSO}_3^- \\
\text{OH} & \quad \text{OH} \\
\text{C}_2\text{H}_3\text{O}_5\text{S}^- & \quad \text{C}_2\text{H}_3\text{O}_5\text{S}^- \\
\text{m/z 139} & \quad \text{m/z 139} \\
\end{align*}
$$
References


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