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Authors

Abellar, Karizza A
Cope, James D
Nguyen, Tran B

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Second-Order Kinetic Rate Coefficients for the Aqueous-Phase Hydroxyl Radical (OH) Oxidation of Isoprene-Derived Secondary Organic Aerosol Compounds at 298 K

Karizza A. Abellar, James D. Cope, and Tran B. Nguyen*

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ABSTRACT: The hydroxyl radical (OH) oxidation of the most abundant nonmethane volatile organic compound emitted to the atmosphere, isoprene (C_5H_8), produces a number of chemical species that partition to the condensed phase via gas-particle partitioning or form condensed-phase compounds via multiphase/heterogeneous chemistry to generate secondary organic aerosols (SOA). The SOA species in aerosol water or cloud/fog droplets may oxidize further via aqueous reaction with OH radicals, among other fates. Rate coefficients for compounds in isoprene's photochemical cascade are well constrained in the gas phase; however, a gap of information exists for the aqueous OH rate coefficients of the condensed-phased products, precluding the atmospheric modeling of the oxidative fate of isoprene-derived SOA. This work investigated the OH-initiated oxidation kinetic rate coefficients (k_{OH}) for six major SOA compounds formed from the high-NO and low-NO channels of isoprene's atmospheric oxidation and one analog, most of which were synthesized and purified for study: (k_1) 2-methyltetrol [MT: 1.14 ($\pm$0.17) $\times$ 10^9 M^{-1} s^{-1}], (k_2) 2-methyl-1,2,3-trihydroxy-4-sulfate [MT-4-S: 1.52 ($\pm$0.25) $\times$ 10^9 M^{-1} s^{-1}], (k_3) 2-methyl-1,2-dihydroxy-3-sulfate [MD-3-S: 0.56 ($\pm$0.15) $\times$ 10^9 M^{-1} s^{-1}], (k_4) 2-methyl-1,2-dihydroxy-but-3-ene [MDE: 4.35 ($\pm$1.16) $\times$ 10^9 M^{-1} s^{-1}], (k_5) 2-methyl-2,3-dihydroxy-1,4-dinitrate [MD-1,4-DN: 0.24 ($\pm$0.04) $\times$ 10^9 M^{-1} s^{-1}], (k_6) 2-methyl-1,2,4-trihydroxy-3-nitrate [MT-3-N: 1.12 ($\pm$0.15) $\times$ 10^9 M^{-1} s^{-1}], and (k_7) 2-methylglyceric acid [MGA: pH 2:1.41 ($\pm$0.49) $\times$ 10^9 M^{-1} s^{-1}; pH 5:0.97 ($\pm$0.42) $\times$ 10^9 M^{-1} s^{-1}]. The second-order rate coefficients are determined against the known k_{OH} of erythritol in pure water. The decays of each reagent were measured with nuclear magnetic resonance (NMR) and high-performance liquid chromatography-high resolution mass spectrometry (HPLC-HRMS). The aqueous photooxidation fates of isoprene-derived SOA compounds are substantial and may impact the SOA budget when implemented into global models.
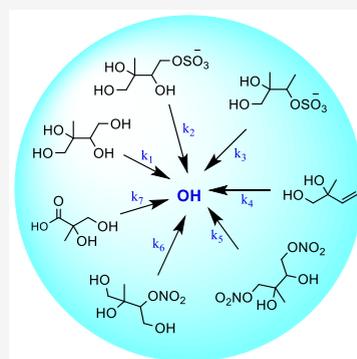
KEYWORDS: aqueous photooxidation, OH radical oxidation, isoprene derived compounds, methyltetrol, organosulfate, organonitrate

1. INTRODUCTION

Isoprene (C_5H_8) is the single most abundant nonmethane hydrocarbon emitted into the atmosphere, dwarfing the emissions of monoterpenes and anthropogenic chemicals combined.[1] Recently, the gas phase chemistry of isoprene and its major oxidation products, which occur primarily through the oxidation with hydroxyl (OH) radicals, was reviewed with a remarkable level of detail (ref 2 and references therein). While the initial reactions in the gas-phase chemistry of isoprene may be relatively well-constrained, Wennberg and coauthors indicated that it is not possible to accurately represent the condensed-phase fates of isoprene reaction products at this time, due in large part to the fact that condensed phase mechanisms and reaction rates are not well understood. Missing oxidative sink channels of isoprene's oxidation products in the condensed phase will add significant uncertainty to the accurate simulation of atmospheric composition and climate feedbacks, due the impacts on aerosol organic nitrogen (which are NO$_x$ sinks or reservoirs) and secondary organic aerosol (SOA) mass, size, and composition (including hygroscopic and surface-active species such as organosulfates or acids that can affect cloud nucleation).

In this work, we focus on select species that are known or suspected to be major components of isoprene SOA (Scheme 1). The low-NO photooxidation channel of isoprene produces the stable reaction intermediates, the isoprene epoxydiols (IEPOX). IEPOX partitions to the aqueous phase and then undergoes nucleophilic addition with water to form the 2-methyltetrols (**MT**), or with sulfate ions to form the 2-methyltrihydroxysulfates (**MTS**). The sulfate group is thought to primarily exist in the tertiary position.[3] For the compounds

Scheme 1. Hydroxyl Radical (OH) Initiated Oxidation of Isoprene, Highlighting Select Routes and the Major Isomers of Key Products That May Exist in the Condensed Phase[a]

[a]Blue arrows indicate aqueous or multiphase reactions in liquid water. Compounds in boxes, or their isomers, are studied in this work. Acronyms are discussed in the text.

with multiple structural isomers in this work, we will denote the position of the heteroatom of interest in the skeleton of isoprene; i.e., the isomer of MTS with a tertiary sulfate (2-methyl-1,3,4-trihydroxy-2-sulfate) will be referred to as MT-2-S while an isomer with a primary position will be MT-1-S or MT-4-S. MT and MTS are found abundantly in SOA sampled over the vast isoprene-rich areas of the world, and both are used as tracers for isoprene SOA from the low-NO channel.[4−8] Individually, MT can comprise 5−9%[9−11] and MTS can comprise 9−13%[4,12] of all organic carbon from fine particulate matter in mixed biogenic-anthropogenic areas. 2-Methylglyceric acid (**MGA**), an isoprene SOA tracer from the high-NO$_2$ channel, is also found in significant concentrations in ambient aerosol from isoprene.[13,14] The high-NO$_2$ photooxidation of isoprene's first-generation product methacrolein produces methacryloyl peroxynitrate (MPAN), which further reacts with OH to form a reactive intermediate hydroxymethyl methyl-α-lactone (HMML), which ring opens to MGA in the presence of water.[15,16] There are also sulfated versions of MGA not studied here, produced when HMML is ring-opened with sulfate ions, which are quite important in the atmosphere during pollution episodes.[12] The isoprene 2-methyl dihydroxy dinitrates (MDDN) can be formed from the second-generation alkyl nitrate channel of isoprene, although its branching ratio from the first-generation isoprene hydroxynitrates (ISOPN) is uncertain and is estimated with an upper bound of 30%.[17] The most abundant isomer is thought to have the nitrates in the tertiary and secondary position, i.e., 2-methyl-1,4-dihydroxy-2,3-dinitrate (MD-2,3-DN), because the thermodynamically preferred alkyl radicals will be produced in higher abundance after the OH addition to double bonds. The ISOPN with the nitrate group in the tertiary position can quickly hydrolyze[18−21] to 2-methyl-1,2-dihydroxy-but-3-ene (**MDE**). The MDDNs may also hydrolyze to the methyl trihydroxy

mononitrates (**MTN**); the most prevalent example will be MD-2,3-DN hydrolyzing at the tertiary position to a 2-methyl-1,2,4-trihydroxy-3-nitrate (MT-3-N).

Kinetic rate coefficients for many condensed-phase products of isoprene are yet unknown due to the challenges of obtaining pure standards for these compounds, which typically need to be custom synthesized. The recent synthetic availability of ISOPN[17] and IEPOX[22] open doors for investigating compounds that require them as precursors. In addition, significant analytical challenges arise when customizing the separation/detection methods of isoprene's condensed-phase products to their abundant and diverse polar functional groups and usual lack of chromophores. In this work, we synthesized, purified, and developed analytical methods and obtained room-temperature kinetic rate coefficients for the compounds highlighted in Scheme 1. We performed competitive rate experiments and determined the unknown bimolecular OH rate coefficients (k_{OH}) against that of the polyol erythritol ($C_4H_{10}O_4$, $k_{OH} = 1.9$ (± 0.2) $\times 10^9$ M^{-1} s^{-1}).[23]

2. METHODS

Materials and Synthesis. Acetonitrile (MeCN; ≥ 99%), bromine, CDCl$_3$ (99.8 atom %D), 3-chloroperbenzoic acid (≤77%; m-CPBA), cyclohexane (≥99%), erythritol (99%), ethyl acetate (≥99.5%), hexane, CHCl$_3$, 50 wt % hydrogen peroxide (H$_2$O$_2$) in water, isoprene (99%), sulfuric acid (H$_2$SO$_4$; 99.999%), 2-methyl-2-vinyloxirane (95%), trifluoro-acetic acid (99%), Bu$_4$NHSO$_4$ (97%), KMnO$_4$ (99%), and xylitol (≥99%) were obtained from Sigma-Aldrich. α-Methylglyceric acid (M311505) was purchased from Toronto Research Chemicals (TRC), Inc. All were used without further purification. Compounds were dissolved and diluted using ultrapure H$_2$O from a Milli-Q purification system (Millipore Sigma, 18 MΩ). δ-IEPOX (erythro- and threo-2-(oxiran-2-yl)

propane-1,2-diol) was synthesized according to the literature.[24] 2-Methyltetrol (MT), 2-methyl-1,2-dihydroxy-but-3-ene (MDE), and 2-methyl-1,2,3-trihydroxy-4-sulfate (MT-4-S) were synthesized and purified according to the literature;[25] their nuclear magnetic resonance (NMR) spectra matched previously reported data. Organosulfates were purified for use over an ion-exchange column (Dowex 50WX4, 50−100 mesh). Details for the syntheses of 2-methyl-2,3-dihydroxy-1,4-dinitrate and the 2-methyl-1,2,4-trihydroxy-3-nitrate are described below, as they have not been reported elsewhere. All synthesized chemicals used in this work had purities >95% as determined by ^{1}H NMR. The manufacturer-reported purity of MGA was ∼98%.

Synthesis of 1,4-Dibromo-2-methylbut-2-ene (Dibromoalkene). Isoprene (9.9 mL, 0.1 mmol) was cooled in CHCl$_3$ to 0 °C under an inert atmosphere; to this was added bromine (6.8 g, 0.1 mL) dropwise with stirring. After the addition, the solution was slightly orange. Stirring at 0 °C and monitoring by TLC proceeded until isoprene was completely consumed. The solution was concentrated and isolated via column chromatography using 1:1 hexane to CDCl$_3$, obtaining dibromoalkene as a yellow oil (15.1 g, 67%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.91 (m, 1H) 3.96 (s, 4H) 1.86 (s, 3H).

Synthesis of 2-Methylbut-2-ene-1,4-dinitrate (Dinitroalkene). Dibromoalkene (2.3 g, 0.013 mol) was added dropwise to a stirred solution of AgNO$_3$ (5.2 g, 0.03 mol) in MeCN (10 mL) in the dark at 0 °C and left to stir for 48 h. Solution was filtered over Celite (Acros Organics) to remove AgBr and concentrated. Dinitroalkene was purified via column chromatography using hexane/ethyl acetate (9:1), obtaining dinitroalkene as a clear oil (1.4 g, 66%). ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.71 (t, 1H, J = 7 Hz), 5.00 (m, 2H) 4.86 (s, 2H), 1.85 (s, 3H).

Synthesis of 2-Methyl-2,3-dihydroxy-1,4-dinitrate (MD-1,4-DN). Dinitroalkene (1.4 g, 7 mmol) was added to a 85:15 solution of acetone/water (16 mL) and cooled 0 °C. To this was added ground KMnO$_4$ (1.15g, 7 mmol) portionwise over the course of 1 h with stirring. The reaction was then stirred for 1 h, and the MnO$_2$ was filtered off. The brown solution was concentrated leaving a brown oil. After concentration, CHCl$_3$ (10 mL) was added, the brown precipitate was removed, and the solution was concentrated giving a clear oil which was used without further purification. ^{1}H NMR (400 MHz, D$_2$O): δ 4.86 (dd, 1H, J = 12 Hz, 3 Hz), 4.61 (s, 2H), 4.59 (m, 1H), 3.97 (dd, 1H, J = 8 Hz, 3 Hz), 1.33 (s, 3H).

Synthesis of 2-Methyl-1,2,4-trihydroxy-3-nitrate (MT-3-N). (E)-2-Methyl-1,4-dihydroxybut-2-ene was synthesized as previously described.[26] A solution of (E)-2-methyl-1,4-dihydroxybut-2-ene in CHCl$_3$ (0.2 mL, 1.96 mmol) was cooled to 0 °C under an inert atmosphere, and to this was added bromine (0.31 mL, 2 mmol) dropwise with stirring. After the addition, the solution was slightly orange; stirring at 0 °C and monitoring by TLC proceeded until the precursor was completely consumed. The solution was concentrated and isolated via column chromatography using a 1:1 hexane to CDCl$_3$. This was added dropwise to a stirred solution of AgNO$_3$ (0.26 g, 1.6 mmol) in MeCN (10 mL) in the dark at 0 °C under an inert atmosphere and left to stir for 48 h. The solution was filtered over Celite (Acros Organics) to remove AgBr and concentrated under vacuum leaving a yellow oil (0.121 g, 64%). It is assumed that the species obtained is a mixture of dinitrate and mononitrate. Complete hydrolysis of

the dinitrate to the mononitrate occurred upon storage in water at room temperature, as confirmed by HPLC-HRMS and NMR. ^{1}H NMR (400 MHz, CDCl3): δ 3.49 (m, 2H), 3.09 (dt, 1H), 2.87−2.75 (m, 2H), 1.10 (s, 3H).

Experiments and Analyses. Aqueous photooxidation of the organic compounds of interest was carried out in an enclosed photochemistry chamber lined with UV-reflective aluminum (Anomet Inc.) and a broadband UV-B lamp (Figure S1).[27] A relative rate technique[27] was used, wherein the second-order rate coefficients for the compound of interest with respect to oxidation by the OH radical was determined against a reference compound with a known rate coefficient in the same reaction. The reference compound selected for study was erythritol (C$_4$H$_{10}$O$_4$), with a reported rate constant of 1.9 × 10^9 M^{-1} s^{-1}.[23]

$$\text{OH} + \text{compound of interest} \rightarrow \text{products} \tag{1}$$

$$\text{OH} + \text{erythritol} \rightarrow \text{products} \tag{2}$$
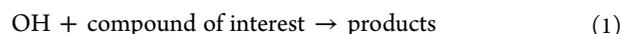
Rate coefficients for the reactions were obtained as follows:

$$\ln\left(\frac{[\text{compound of interest}]_0}{[\text{compound of interest}]_t}\right) = \frac{k_1}{k_2} \ln\left(\frac{[\text{erythritol}]_0}{[\text{erythritol}]_t}\right)$$

where [compound of interest]$_0$ and [erythritol]$_0$ are the respective chromatographic or spectroscopic peak areas for those species at time zero, [compound of interest]$_t$ and [erythritol]$_t$ are the peak area at time t, and k_1 and k_2 are the bimolecular rate coefficients for reactions 1 and 2, respectively. A plot of ln([erythritol]$_0$/[erythritol]$_t$) and ln([compound of interest]$_0$/[compound of interest]$_t$) generates a linear plot in the positive quadrant, where k_1/k_2 is the slope of the line. Direct photolysis and dark H$_2$O$_2$ rates were measured for compounds under investigation to be negligible, often not observable, under the conditions of this study. Thus, direct photolysis and dark H$_2$O$_2$ oxidation are not expected to contribute to the OH rate coefficients reported here.

Prior to irradiation, a 5 mL solution of 1.0 mM erythritol and 1.0 mM compound of interest in milli-Q water was prepared. OH radicals were generated by irradiating 20 mM H$_2$O$_2$ with the UV-B lamp. For the pH-dependent study of MGA, a few drops of H$_2$SO$_4$ were added to the solution until the desired pH was achieved. All other determinations were performed at pH 5−7. The aqueous solution was transferred to a 3.5 mL capped quartz cuvette with a stopper (Thor Laboratories). This was placed in the photochemistry chamber to irradiate for 2 h. A 500 μL aliquot of the solution was collected at t = 0, 15, 30, 45, 60, and 120 min for analysis using a microliter pipet (Eppendorf). Prior to instrumental analysis, xylitol (0.762 mM) was added to the solution as an internal reference standard for erythritol.

With the exception of MDE, all compounds were analyzed using an Agilent 1100 high performance liquid chromatography (HPLC) coupled to a linear-trap-quadrupole Orbitrap (LTQ-Orbitrap) mass spectrometer (Thermo Corp., Waltham MA) operating at a mass resolving power of 60 000 m/Δm at m/z 400. Xcalibur 2.0 software was used for analysis of chromatograms and mass spectra. Separations of MT, MD-1,4-DN, MT-3-N, erythritol, and xylitol were performed using a Shodex Asahipak NH2P-40 2D column (2 mm × 150 mm, 4 μm, 100 Å) using a method recently reported elsewhere.[28] An Agilent Poroshell InfinityLab EC-C18 (2.1 mm × 100 mm, 2.7 μm, 120 Å) column was used to separate MD-3-S and MT-4-S

Scheme 2. Synthesis of IEPOX and the Ring Open Products from 2-Methyl-2-vinyloxirane
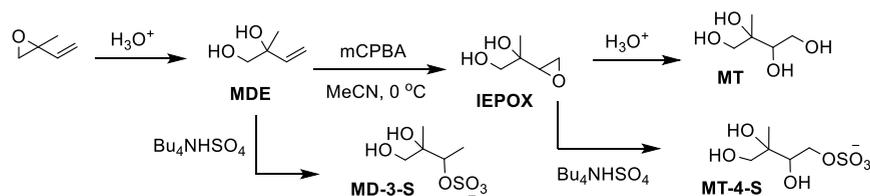
Scheme 3. Synthesis of MTN and MDDN from Isoprene
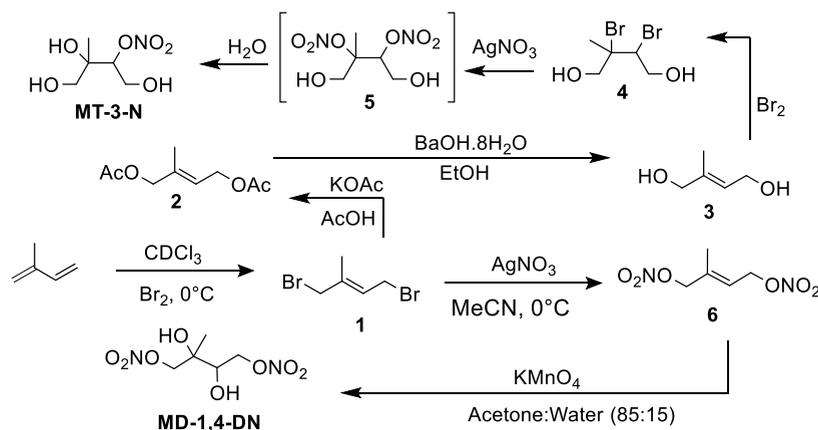
using an isocratic method with a flow rate of 0.270 mL/min, and a mobile phase (60:40) consisting of 0.05% ammonium formate in water (v/v) and acetonitrile. Separation of MGA was adapted from the HPLC-ACPI-MS method of Liu et al.[29] using the same column; the run time was reduced to 3 min as MGA appeared at ~2 min.

NMR was used to quantify the decay of the erythritol and MDE, given the distinct proton environments of the alkene. Due to the lower sensitivity of NMR analysis, 100 mM of both species polyol was mixed with 1 M H_2O_2 in order to increase the analytical signal. Reactions for NMR analyses were performed by directly irradiating the sample within a 5 mm quartz NMR tube rated for 500 MHz. ^1H spectra were collected on a 400 MHz Bruker instrument (400 MHz Bruker Avance III HD Nanobay Spectrometer) using an autosampler and analyzed using TOPSPIN. Cyclohexane in $CDCl_3$ (0.8 vol %) was used as an internal standard. The internal standard mixture was loaded into a glass capillary, flame-sealed, and dropped into an NMR tube containing the reaction mixture. The solution was irradiated and analyzed at $t = 0$, 30, 60, and 90 min.

■ RESULTS AND DISCUSSION

Syntheses. The major isomers of organonitrates and organosulfates species formed in the atmosphere generally have the N or S group in the tertiary position (Scheme 1). However, these tertiary $RONO_2$ and $ROSO_3^-$ also have shorter hydrolysis lifetimes compared to their primary or secondary counterparts.[30] Thus, we determine the OH rate coefficients for isomers of isoprene-derived organosulfates and organonitrates that are stable in aqueous solutions, which are more feasible to synthesize and purify, and for which the photochemical fate is likely more competitive compared to hydrolysis. For this investigation, primary and secondary organonitrates and organosulfates were synthesized using modified procedures from those previously reported (Scheme

2),[31] as well as from original procedures (Scheme 3). The ring opening of the 2-methyl-2-vinyloxirane forms MDE, which was both used for experiments and further converted into the δ1-IEPOX using mCPBA. From the δ1-IEPOX, MT and MT-4-S can be generated by controlled ring opening using different reagents.[25] During the synthesis of MT-4-S, 2-methyl-1,2-dihydroxy-3-sulfate anion (MD-3-S) was obtained as a byproduct from the reaction, via the addition of the sulfate to the alkenyl group of MDE, and was purified for experiments. The NMR appeared to show a mixture of isomers after purification; however, the secondary sulfate was the dominant isomer.

The syntheses of 2-methyl-1,2,4-trihydroxy-3-nitrate (MT-3-N) and 2-methyl-2,3-dihydroxy-1,4-dinitrate (MD-1,4-DN) are multistep processes that were developed as part of this work (Scheme 3). The secondary trihydroxy mononitrate MT-3-N is the prevalent isomer expected in the atmosphere after MDDN hydrolysis, and may be the main organic nitrogen species that is converted from MDDNs in environmental water such as aqueous aerosols. The primary MD-1,4-DN was investigated over the more prominent MD-2,3-DN isomer (5 in Scheme 3, which was also synthesized but cannot be stored) due to its stability. Starting with isoprene, the 1,4 dibromo species 1 can be generated from the reaction with bromine at 0 °C. 1 is then acetylated to 2, and hydrolyzed to 3, which is then brominated to a dihydroxy dibromide 4. Nitration with $AgNO_3$ in cold acetonitrile affords the unstable 2-methyl-1,4-dihydroxy 2,3-dinitrate (MD-2,3-DN) 5 from isoprene that is then hydrolyzed to MT-3-N, which is the only species observed analytically. The same 1,4-dibromo species 1 can be converted into a dinitro compound 6 via the addition of $AgNO_3$, and the resultant AgBr can be filtered off. From this compound, the MD-1,4,-DN can then be produced using 1 equiv of $KMnO_4$.

Kinetic Experiments. From the synthesized compounds, rate coefficients ratios with erythritol were determined over a

1−3 h period using HPLC or NMR. Figure 1 shows representative mass peaks and chromatograms of the erythritol
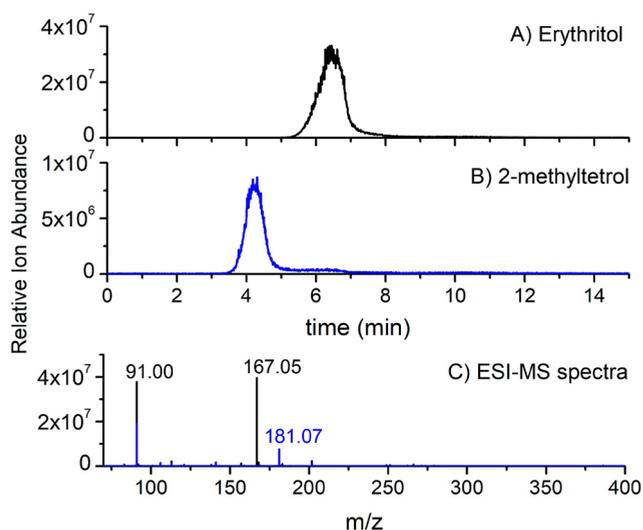
Figure 1. Representative data for the relative rate determinations of 2-methyltetrol oxidation in reference to erythritol. Chromatographic peaks of (A) erythritol and (B) 2-methyltetrol are obtained on the same column, shown with their corresponding (C) electrospray ionization mass spectrometry spectra of the M+HCOO⁻ ions that are overlaid for the purpose of presentation.

and 2-methyltetrol (MT) as observed in the HPLC-HRMS. The quasimolecular ions of erythritol (m/z 167.05) and MT (m/z 181.07) can be observed as their clusters with the formate ion present in the eluent solution. Erythritol and MT have similar structures and, thus, a common in-source fragment at m/z 91, which is assigned to the deprotonated glycerol ($C_3H_7O_3^-$). Figure 2 shows a representative NMR spectrum of erythritol and MDE. The doublet of doublets at 5.88 ppm of the alkene group on MDE and the doublet for the two secondary sites of erythritol at 3.70 ppm (Figure 2, asterisk) were used for quantification due to minimal spectral interference. The evolution of the NMR spectra throughout the experiment is shown in Figure S2.
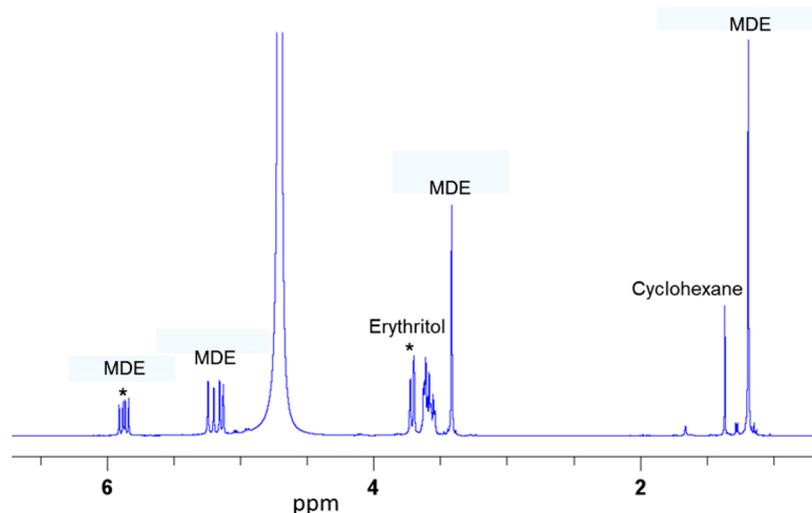
From the first-order decay of erythritol using its known k_{OH}, OH steady-state concentrations used for experiments were calculated to be within the range $(0.6-1.2) \times 10^{-13}$ M, which is comparable to modeled aqueous OH in atmospheric water droplets and aerosols.[23] Ratios of k_1/k_2 for the different compounds are shown in Figure 3, as averages from 2 to 4 repeated trials, depending on the availability of synthesized reagents. Table 1 shows the k_{OH} values for the compounds under study after applying the known rate coefficient of erythritol to the rate ratios in Figure 3. It was found that the additional methyl group of MT decreases the OH oxidation rate by ~40% compared to erythritol (Figure 3A). This could be due to the substitution of a secondary carbon (R−(HO)HC−R) H-abstraction site for a primary carbon at the methyl group R−(HO)(CH₃)C−R. The aqueous OH photo-oxidation rate coefficient of MT from this work (1.14×10^9 M⁻¹ s⁻¹) is of similar scale, but is slightly slower, compared to its precursor IEPOX (1.4×10^9 M⁻¹ s⁻¹).[32] All of the studied compounds have lower k_{OH} compared to erythritol, with the exception of MDE due to its double bond. OH addition to double bonds is known to be rapid compared to abstraction; thus, the results are qualitatively consistent with expectations. However, the enhancement of k_{OH} for MDE by a factor of 2 over erythritol is not as significant as expected for some alkenes, compared to the nearly diffusion limited rates of methacrolein or divinylethers.[33] It is possible the two OH groups on MDE, in their specific positions, may slow down the reaction considerably compared to other alkenes, although further comparison is challenging due to the lack of aqueous k_{OH} data for analogous compounds, including the isoprene alkenyl hydroxyhydroperoxide (ISOPOOH).

MGA is the only acid under study; thus, its k_{OH} was investigated at two atmospherically relevant pH values. The pK_a of MGA is not known, though often it is assumed to be similar to that of glyceric acid (~3.5).[16,25] Thus, at a pH of 5 that is relevant to cloudwater, MGA may primarily be in its dissociated form. When at pH 2 that is relevant to sulfate aerosols, MGA may primarily be neutral. We found the OH rates of MGA to be fairly similar to MT, and not significantly different at the two pH values under study. The rate of oxidation is possibly faster at the lower pH. This result is not

Figure 2. Representative NMR spectrum for the relative rate studies of 2-methyl-1,2-dihydroxy-but-3-ene (MDE) oxidation in reference to erythritol. Peaks used for quantification are denoted with an asterisk.
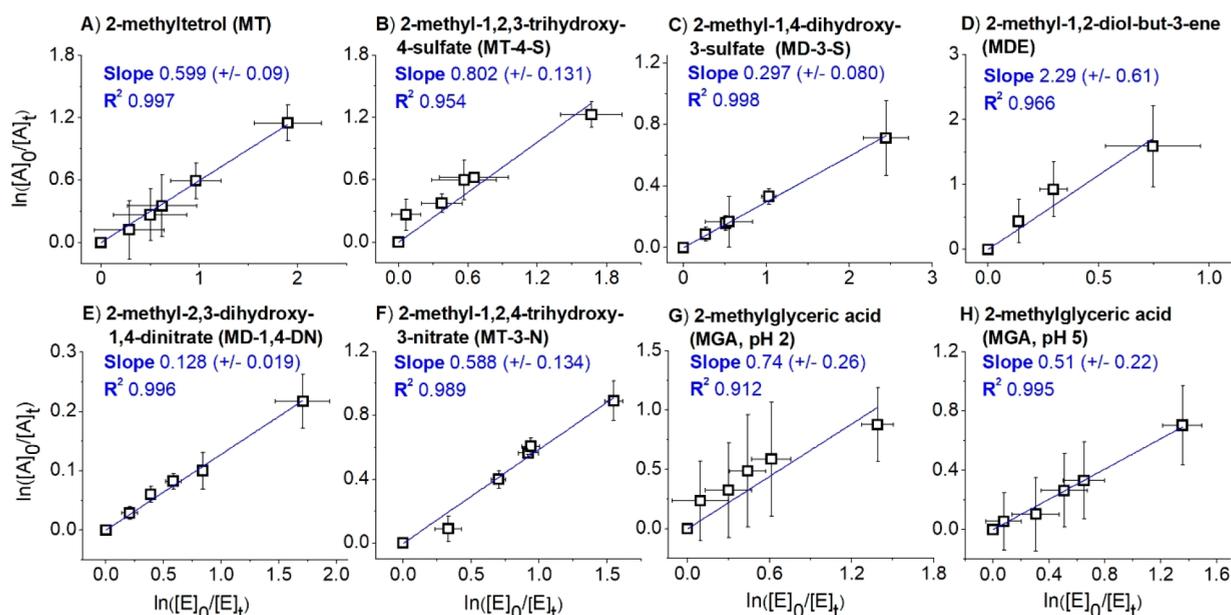
Figure 3. Relative rate determinations for the compounds of interest ("A") against reference compound erythritol ("E"). Linear least-squares fits assume a y-intercept of zero. Errors in the x and y direction are experimentally determined $1 - \sigma$ values from multiple trials. Chemical structures are shown in Table 1.

Table 1. Measured Second-Order k_{OH} Values, SOA Channel Denoted from Isoprene

Compound	Abbrev.	Isomer studied	k_{OH} $(M^{-1} s^{-1})^{a}$ at 298 K	SOA channel
2-methyltetrol	MT		$1.14 \ (\pm 0.17) \times 10^9$	Low NO
2-methyl-1,2,3-trihydroxy-4-sulfate	MT-4-S		$1.52 \ (\pm 0.25) \times 10^9$	Low NO
2-methyl-1,2-dihydroxy-3-sulfate	MD-3-S		$0.56 \ (\pm 0.15) \times 10^9$	---
2-methyl-1,2-dihydroxy-but-3-ene	MDE		$4.35 \ (\pm 1.16) \times 10^9$	High NO
2-methyl-2,3-dihydroxy-1,4-dinitrate	MD-1,4-DN		$0.24 \ (\pm 0.04) \times 10^9$	High NO
2-methyl-1,2,4-trihydroxy-3-nitrate	MT-3-N		$1.12 \ (\pm 0.15) \times 10^9$	High NO
2-methylglyceric acid	MGA		**pH 2** $1.41 \ (\pm 0.49) \times 10^9$ **pH 5** $0.97 \ (\pm 0.42) \times 10^9$	High NO$_2$

^{a}Measured against reference compound erythritol (1.9×10^9 M^{-1} s^{-1}).

consistent with those of smaller acids; e.g., formate and acetate oxidize faster with OH than their neutral counterparts.[34] It is possible that the multiple functional groups of MGA, larger size, and/or the tertiary carbon alpha to the COOH may slow down the CO$_2$ loss from its carboxylate—this is consistent with the observation that the k_{OH} enhancement of acetate/acetic acid is a factor of 7 while for formate/formic acid it is a

factor of 34.[34] It is also possible that the dissociation equilibrium of MGA is (a) not similar to glyceric acid as previously assumed or (b) different in complex mixtures compared to pure water,[35] which may cause MGA to be in the neutral form at both solution pH values under study. It should be noted that the MGA experiment produced the highest uncertainty in the series for reasons unknown. Thus, it is also

entirely possible the true pH trend of MGA's oxidation rate coefficient cannot be observed within the uncertainties of our experiments.

Given that the pK_a's of the isoprene organosulfates are estimated to be negative,[36] these organosulfates will likely exist in aerosol water as anions. The sodiated ions were synthesized in this work. The isoprene-derived MT-4-S had a faster rate coefficient with OH compared to MT. This rate coefficient ($\sim 1.5 \times 10^9$ M^{-1} s^{-1}) should be quite competitive with hydrolysis, as the hydrolysis lifetime of the tertiary isoprene organosulfate is estimated to be 60−460 h depending on pH.[21] Assuming an [OH]$_{ss}$ of 1×10^{-14} M in atmospheric aerosol water or aqueous droplets,[23] the lifetime of isoprene sulfates is ~ 18 h if the tertiary organosulfate can be assumed to have the same k_{OH} as the primary.

In reality, the tertiary MT-2-S (2-methyl-1,3,4-trihydroxy-2-sulfate) will likely have a different k_{OH} value compared to primary MT-4-S (2-methyl-1,2,3-trihydroxy-4-sulfate). However, the exact difference in reactivity for multifunctional compounds with the same number and type of C−H bonds, but where the functional groups exchange positions, is unclear. For example, multifunctional phenols where the functional groups (e.g., methoxy, hydroxyl, methyl) exchange positions but the C−H bonds are the same have k_{OH} values that vary by less than a factor of 2,[37−40] although these aromatic systems may not be directly applicable to the aliphatic MTS. Different series of aliphatic alkanediols[41] or carbonyl nitrates[42] where the heteroatom groups change position, while at the same time altering the number of H attached to primary, secondary, or tertiary carbons, can change k_{OH} by a factor of 3. Even if the k_{OH} for MT-2-S was 3 times slower than that for MT-4-S, aqueous oxidation will be expected to win against hydrolysis under many typical conditions[23] of deliquesced particles and aqueous droplets in the atmosphere. The MD-3-S with one fewer hydroxyl group, and a sulfate group in a secondary position, was observed to be a third as fast as MT-4-S. There are not enough data points here for a true discussion of structure−activity; thus, we defer this discussion for future work. We aim to develop new synthetic routes to other organosulfate compounds for future study, including the tertiary MTS.

The oxidation of the primary MDDN is the slowest out of the compounds under study; however, its oxidation rate is not negligible. The oxidative fates of the major isomer MD-2,3-DN are not expected to be competitive with hydrolysis,[18,19] even if OH rate coefficients are enhanced by an order of magnitude compared to those determined here. The hydrolysis of MD-2,3-DN will generate the 2-methyl-1,2,4-trihydroxy-3-nitrate (MT-3-N) as the major isomer, for which oxidation will be a much more relevant fate. The oxidation of MT-3-N is considerably fast, of a similar scale compared to MT. Correspondingly, the aqueous OH life time of MTN is approximately 24 h at [OH] $\sim 1 \times 10^{-14}$ M in atmospheric aerosol water or aqueous droplets,[23] which should be highly competitive with the estimated hydrolysis lifetimes for secondary organonitrates under near neutral (>5000 h) conditions. Highly acidic (50% D$_2$SO$_4$, pH[43] ~ -4) conditions can reduce the hydrolysis lifetime of secondary organonitrates to ~ 2 h,[21] but negative pH environments are not expected in the atmosphere. The kinetic experiments in this work were performed at neutral pH and, thus, should not suffer from hydrolysis interference. On sulfate-based particles with a pH of 2, the lower pH is accompanied by higher average [OH]$_{ss}$ for

urban and remote deliquesced aerosol particles,[23] which suggest that oxidation will likely be an important fate for the MT-3-N on aerosols. It is not clear if the OH oxidation of MTNs will produce inorganic nitrate, analogously to the hydrolysis, which will provide a sink for atmospheric NO$_x$ and act as a precursor to reactive oxygen species[44] that can further speed up the oxidation. This may be a worthy topic for future research. The minor isomers of MDDN, such as MD-1,4-DN and MD-1,3-DN that do not hydrolyze quickly, may accumulate on aerosols. Thus, their removal by OH will be competitive with other fates. Thus, the aqueous oxidation reactions of all isoprene-derived condensed-phase compounds studied here may be important for atmospheric modeling on aqueous aerosols and fog/cloud droplets.

Impacts. Isoprene-derived compounds are known to be major SOA constituents; however, they tend to be treated as photochemically inert in the aqueous phase in atmospheric models due to a lack of data, an assumption that is not supported by the results in this work. Often, the only way isoprene-derived SOA compounds are removed in models is through deposition of the particle with a lifetime on the order of days.[45] We report several new bimolecular OH rate coefficients for major isoprene-derived compounds such as the 2-methyltetrols (MT), 2-methylglyceric acid (MGA), and various isomers of C$_5$ hydroxylated organosulfates and organonitrates. These rate coefficients will outcompete particle deposition in models under daytime conditions. It is also clear that aqueous OH oxidation will be a competitive sink for the isoprene-derived organosulfates against hydrolysis, likely winning in many scenarios. The three OH functional groups on this molecule slow down its hydrolysis compared to other tertiary organosulfates,[20] and yet we found its k_{OH} is reasonably high. For the organonitrates and dinitrates, hydrolysis will win for the tertiary isomers. However, the mononitrate hydrolysis products of dinitrates (MDDNs) such as MT-3-N will have a major oxidative fate, and minor isomers of MDDNs may build up concentrations due to their aqueous stability and be removed by OH or other radicals. Recent updates to global models have shown that current SOA formation mechanisms tend to overestimate isoprene-derived SOA, likely due to underestimating chemical losses of isoprene-derived SOA constituents.[45−47] Incorporations of OH sink terms for the isoprene-derived compounds studied here may help reconcile these SOA budgets with respect to field observations.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.1c04606.

> Emission photon flux spectrum of the lamps used in this work; nuclear magnetic resonance spectra for the MDE vs erythritol experiment at four time intervals (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Tran B. Nguyen − *Department of Environmental Toxicology, University of California—Davis, Davis, California 95616, United States;* ⓞ orcid.org/0000-0001-9206-4359; Email: tbn@ucdavis.edu

Authors

Karizza A. Abellar − *Department of Chemistry, University of California—Davis, Davis, California 95616, United States*

James D. Cope − *Department of Environmental Toxicology, University of California—Davis, Davis, California 95616, United States*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.est.1c04606

Notes

The authors declare no competing financial interest.

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