

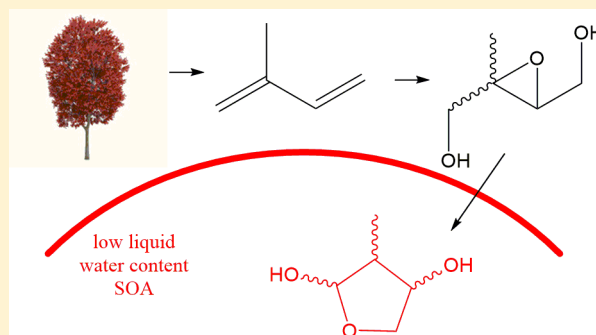
# Assessing the Potential Mechanisms of Isomerization Reactions of Isoprene Epoxydiols on Secondary Organic Aerosol

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## Supporting Information

**ABSTRACT:** Laboratory and field measurements have demonstrated that isoprene epoxydiol (IEPOX) is the base component of a wide range of chemical species found in isoprene-derived secondary organic aerosol (SOA). To address newly raised questions concerning the chemical identities of IEPOX-derived SOA, the results of laboratory experiments carried out in bulk aqueous and organic media and analyzed via nuclear magnetic resonance spectroscopy and computed free energies of possible products are reported. The IEPOX nucleophilic addition product 2-methyltetrol was found to react too slowly in aqueous solution to explain the previous observation of tetrahydrofuran-based species. The IEPOX isomerization reactions in organic media were shown to mainly produce 3-methyltetrahydrofuran-2,4-diols, which were also established by the computational results as one of the most thermodynamically favorable possible IEPOX reaction products. However, these isomerization reactions were found to be relatively slow as compared to nucleophilic addition reactions, indicating that their occurrence on ambient SOA might be limited to low water content situations. No evidence was found for the production of the  $C_5$  alkene triols or 3-methyltetrahydrofuran-3,4-diols previously reported for IEPOX reaction on SOA as analyzed via the gas chromatography/electron ionization-quadrupole mass spectrometry with prior trimethylsilyl derivatization method.



## INTRODUCTION

The chemical content of tropospheric aerosol is often dominated by the presence of organic compounds.<sup>1</sup> This aerosol is a major component of air pollution<sup>2</sup> and plays a significant role in climate change.<sup>3</sup> Much of this organic-laden aerosol is derived from the chemical conversion of volatile organic compounds (VOCs) into less volatile secondary organic aerosol (SOA) components,<sup>4</sup> and the biogenic VOC isoprene is thought to be the gaseous precursor to a large proportion of total global SOA mass.<sup>5</sup> The polyol 2-methyltetrol (2MT) was the first isoprene-derived compound to be definitively identified in ambient SOA,<sup>6</sup> and it has now been established, via both laboratory and field measurements, that an isoprene-derived epoxydiol (IEPOX)<sup>7</sup> oxidation intermediate undergoes nucleophilic addition by water to form 2MT on aqueous SOA.<sup>8–10</sup> It has also been established that organosulfates can be formed by nucleophilic addition of sulfate to IEPOX.<sup>9–11</sup> On the basis of chemical species observed in both laboratory and field studies, it has been further surmised that IEPOX can also undergo nucleophilic addition by 2MT (to form dimers), as well as reactions that can lead to isomers of IEPOX.<sup>10,12,13</sup> However, the specific chemical mechanisms for these processes have yet to be established by laboratory studies.

A proposed reaction scheme<sup>9</sup> for the IEPOX-derived species that were identified in a 2010 field study in Yorkville, GA<sup>10</sup> is given in Figure 1. It is important to note that Figure 1 neglects

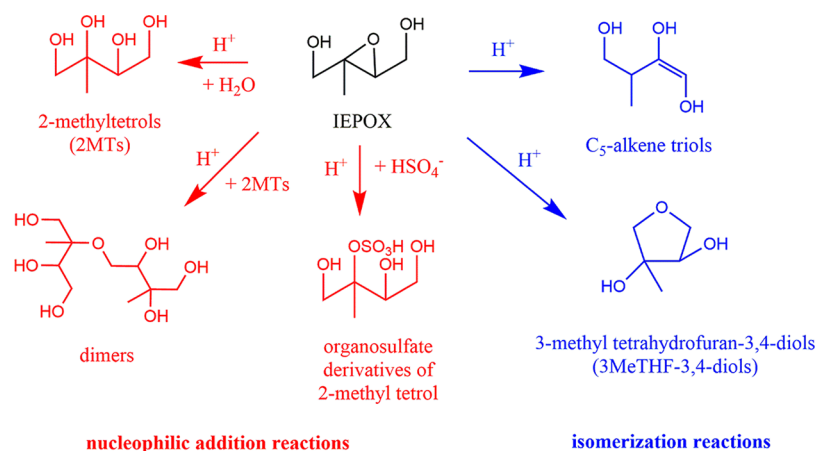
stereoisomerism issues, which can lead to multiple detected species for each of the structural isomers shown. The IEPOX-derived organosulfates were detected using the ultra performance liquid chromatography/electrospray ionization-time-of-flight mass spectrometry method operated in the negative ion mode (UPLC/(−)ESI-TOFMS).<sup>14</sup> The other IEPOX-derived species - 2MTs, dimers, and isomerization products - were detected via the gas chromatography/electron ionization-quadrupole mass spectrometry with prior trimethylsilyl derivatization method (PTMSD/GC/EI-MS).<sup>15</sup> These species cannot be effectively detected with UPLC/(−)ESI-TOFMS due to the poor ionization efficiency of these alcohol functional group-containing compounds.<sup>16</sup> One of the key aspects of the PTMSD/GC/EI-MS method is the expectation that each alcohol functional group in the analyte will be singly derivatized with a trimethylsilyl group (for example, 2MT is characterized by quadruple trimethylsilylation). This allows for the mass spectra to be interpreted in a way that indicates functional group information about a particular signal carrier. The importance of IEPOX-derived products in ambient SOA has also been inferred from the identification of a charge-to-mass carrier at 82 amu ( $C_5H_6O^+$ ) via positive matrix

Received: April 4, 2018

Revised: June 21, 2018

Accepted: June 27, 2018

Published: June 28, 2018



**Figure 1.** Proposed reaction scheme for the formation of IEPOX-derived species detected in 2010 Yorkville, GA field study.<sup>9</sup>

factorization analysis of aerosol mass spectrometer (PMF-AMS) data.<sup>17</sup>

In the 2010 Yorkville, GA study, 2MTs, and C<sub>5</sub> alkene triols were found to be roughly equally abundant.<sup>10</sup> Smaller amounts of 3-methyltetrahydrofuran-3,4-diols (3MeTHF-3,4-diols) and dimers were observed, along with various organosulfates. The 3MeTHF-3,4-diol identification was confirmed by the PTMSD/GC/EI-MS analysis of a synthesized authentic standard, and the establishment of this compound as an IEPOX derivative provided a rationale for the C<sub>5</sub>H<sub>6</sub>O<sup>+</sup> IEPOX tracer identified by PMF-AMS. Authentic standards were not available to confirm the identification of the C<sub>5</sub> alkene triols or of the dimers. However, several recent studies of IEPOX-derived SOA have suggested that it is much less volatile than the mainly monomeric components identified in the Yorkville, GA study would indicate.<sup>18–20</sup> These studies indicate that greater oligomeric component content derived from IEPOX is necessary to rationalize the low volatility SOA observed, and imply that the PTMSD technique may be subject to artifacts, namely that oligomeric species may be degraded to monomeric species under the derivatization conditions.

To help address these potential inconsistencies in the chemical identities of IEPOX-derived SOA, we report laboratory experiments aimed at identifying potential formation pathways for IEPOX isomerization products, with the explicit aim of establishing the IEPOX isomerization reaction mechanisms for formation of the C<sub>5</sub> alkene triols and 3MeTHF-3,4-diols. We also report measurements aimed at establishing the atmospheric feasibility of polyol dehydration cyclization reactions of the 2MTs to form the 3MeTHF-3,4-diols under acidic SOA conditions. Specifically, we use kinetic and thermodynamic techniques applied to 2MT reactions in bulk strongly acidic aqueous media and IEPOX reactions in bulk organic media with the chemical structure-specific nuclear magnetic resonance (NMR) technique as the main experimental analytical approach.

## MATERIALS AND METHODS

**Syntheses.** A sample containing both *trans*- and *cis*- $\beta$ -IEPOX was prepared and characterized using a procedure previously reported in detail by our lab.<sup>21</sup> A sample containing both 2MT diastereomers (2-methylerythritol and 2-methylthreitol) was prepared and characterized via the method described in the [Supporting Information, SI](#).

## Polyol Dehydration Cyclization Solution Preparation.

When possible, the solutions were prepared in DClO<sub>4</sub>/D<sub>2</sub>O to allow locking of the NMR spectrometer. To facilitate relatively quick kinetics monitoring, the polyol loss kinetics were carried out in concentrated deuterated perchloric acid solutions. These solutions were prepared by adding about 50 mg of polyol to 1 mL of concentrated DClO<sub>4</sub> and then stirred to commence the reaction. For the purposes of product identification for the cyclization reactions of the 2MTs, normal isotope concentrated HClO<sub>4</sub> solutions were used instead, due to <sup>13</sup>C NMR spectral complications arising from H-D exchange in concentrated DClO<sub>4</sub> solutions. To provide an internal standard for chemical shift referencing and species quantification, about 10 mg of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was added to each solution. These solutions were prepared using commercially available 99% 1,4-butanediol, >99% meso-erythritol, >98% D-threitol, 68 wt % DClO<sub>4</sub>, 70 wt % HClO<sub>4</sub> (all Sigma-Aldrich), 99.9% D<sub>2</sub>O, and DSS (both Cambridge Isotope Laboratories, Inc.). Authentic samples of >99.9% THF and 95% 1,4-anhydroerythritol (both Sigma-Aldrich) were used to confirm the identify of reaction products.

**IEPOX Isomerization Solution Preparation.** Deuterated dichloromethane (CD<sub>2</sub>Cl<sub>2</sub>) was chosen as the solvent due to its non-nucleophilic nature (to avoid the nucleophilic addition reactions that dominate IEPOX chemistry in aqueous solution) and the fact that it is aprotic, but with relatively high polarity (which afforded better solubility for the various reactants and products than less polar organic solvents). Methanesulfonic acid (MSA) was chosen as the acid catalyst due to its strong nature (pK<sub>a</sub> ≈ −2.6), good solubility in CD<sub>2</sub>Cl<sub>2</sub>, and the weak nucleophilicity of its conjugate base. Dilute MSA solutions were first prepared by sequential dilution of MSA in CD<sub>2</sub>Cl<sub>2</sub> to achieve MSA concentrations between 3 × 10<sup>−3</sup> and 1 × 10<sup>−5</sup> M (to control the rates of reaction for the purposes of NMR monitoring convenience). Next, 10 μL of IEPOX (low concentrations were used to avoid potential dimerization reactions) and about 1.0 mg of DSS or 10 mg benzene (for shift referencing and quantitation purposes) were added to 1 mL of the desired MSA/CD<sub>2</sub>Cl<sub>2</sub> solution and stirred to commence the reaction. In some cases, methanol was also added to the solutions to allow measurements of the competition between the isomerization and the nucleophilic addition pathways. These solutions were prepared using commercially available DSS (Cambridge Isotope Laboratories,

Inc.), >99% MSA, 99.6% CD<sub>2</sub>Cl<sub>2</sub>, >99.9% benzene, and >99.9% methanol (all Sigma-Aldrich).

**NMR Methods.** All samples (about 750  $\mu$ L of the above-described solutions) were loaded into 5 mm NMR tubes, and spectra were collected on a Varian 400 MHz instrument. The <sup>1</sup>H chemical shifts were calibrated to the methyl protons of DSS at 0.00 ppm or the C<sub>6</sub>H<sub>6</sub> protons at 7.33 ppm, and the <sup>13</sup>C chemical shifts were calibrated to the methyl carbons of DSS at 0.00 ppm or the C<sub>6</sub>H<sub>6</sub> carbon nuclei at 130.6 ppm. The relative amounts of species were calculated by peak integration of unique nuclei for each species. For the case of <sup>13</sup>C quantitation, methyl carbon nuclei were used for peak integration in order to ensure that differing relaxation time effects for carbon atoms in different bonding environments did not affect the results. In addition to standard one-dimensional <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy methods, the following correlation NMR spectroscopy methods were also used: <sup>1</sup>H–<sup>1</sup>H Correlation Spectroscopy (COSY), <sup>13</sup>C Distortionless Enhancement by Polarization Transfer (DEPT), <sup>1</sup>H–<sup>13</sup>C Heteronuclear Single-Quantum Correlation (HSQC), and <sup>1</sup>H–<sup>13</sup>C Heteronuclear Multiple Bond Correlation (HMBC)

techniques.<sup>22</sup> This suite of NMR experiments provided information about single- and multiple-bond couplings (Figure S2 diagrams show the different correlation NMR experiments indicate information about the various bond connectivities) that were necessary to confirm assignments for product species and also served to resolve overlapping peaks in the one-dimensional NMR spectra.

**Computational Methods.** Geometries (determined at the B3LYP/6-31G(d,p) level) and energies of the relevant species were calculated using a modified version of the G2MS compound method (MG2MS)<sup>23</sup> a variation on G2 theory.<sup>24</sup> The Polarizable Continuum Model (PCM) method<sup>25</sup> was used to account for the effects of solvation on the reactant and product properties. Calculations for all species were carried out for H<sub>2</sub>O solvent, and some species for CH<sub>2</sub>Cl<sub>2</sub>. All calculations were carried out with the Gaussian 03 and 09 computational suites.<sup>26</sup> Each stationary point was confirmed as a potential energy minimum by inspection of the calculated frequencies. The overall energy expression for the MG2MS scheme is defined in eq 1:

$$E_{\text{G2MS}} = E_{\text{CCSD(T)}/6-31\text{G(d)}} + E_{\text{MP2}/6-311+\text{G(2df,2p)}} - E_{\text{MP2}/6-31\text{G(d)}} + \text{HLC} \quad (1)$$

where HLC is an empirically defined correction term with  $\text{HLC} = An_{\alpha} + Bn_{\beta}$  where  $n_{\alpha}$  and  $n_{\beta}$  are the number of  $\alpha$ - and  $\beta$ -electrons, respectively, and the constants  $A$  and  $B$  are 6.06 and 0.19 mH, respectively (all species investigated were closed shell; therefore  $n_{\alpha} = n_{\beta}$ ). Our previous MG2MS results for atmospherically relevant systems (including radicals and ions) indicate that the MG2MS calculated thermodynamic properties are typically accurate to within 10 kJ mol<sup>−1</sup> for systems similar to those under study here.<sup>27</sup>

## RESULTS AND DISCUSSION

**Polyol Dehydration Cyclization Experiments.** To explore the structural effects on the kinetics of polyol dehydration cyclization reactions, five different 1,4-polyols (all of which cyclize into THF derivatives) were studied. Each of the polyols was found to follow a first order rate law. Figure S3 shows the first order kinetics analysis for the reaction of the two 2MT diastereomers in 60 wt % DClO<sub>4</sub>. Table S1 contains the lifetimes (determined to a precision of about 5%) for each of the examined polyols in 70 wt % DClO<sub>4</sub> solutions, as well as additional data for the 2MT species in 60 wt % DClO<sub>4</sub>. The lifetimes indicate that additional hydroxyl groups at the 2 and 3 position slow down the cyclization of the butanetetraols relative to 1,4-butanediol by about a factor of 15. D-Threitol was found to react slightly faster than meso-erythritol, presumably due to easier rotation of the threitol backbone into the structure necessary for the cyclization reaction. This effect was more pronounced for the cases of 2-methylthreitol and 2-methylerythritol (presumably due to the presence of the bulky methyl group at the 2 position), which had lifetimes that differed by about a factor of 3. However, both 2MTs were found to have significantly shorter lifetimes than even 1,4-butanediol in 70 wt % DClO<sub>4</sub>. This effect is likely explained by the role of the tertiary carbon center in stabilizing carbocation intermediate(s) in the acid-catalyzed cyclization mechanism. In 60 wt % DClO<sub>4</sub> solutions, both 2MT diastereomers were found to react about 60 times more slowly than in 70 wt % DClO<sub>4</sub> solutions. The excess acidity framework of Cox and

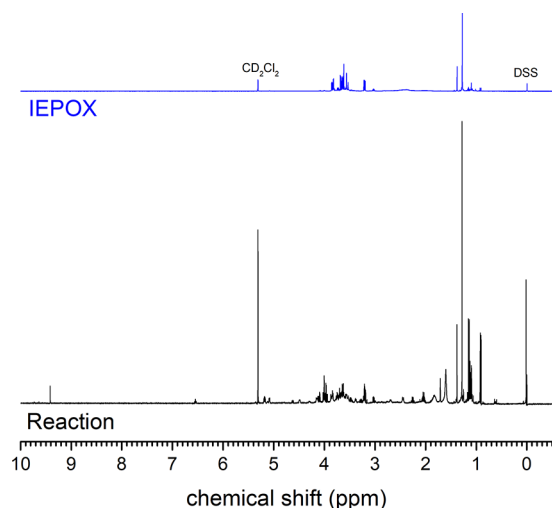
Yates<sup>28</sup> predicts an effective D<sup>+</sup> activity factor ratio of about 75 for the two strong acid solutions, which is in good agreement with experimentally determined lifetime factor.

The reaction of 1,4-butanediol exclusively produced THF and the reaction of meso-erythritol exclusively produced 1,4-anhydroerythritol (both confirmed by comparison to authentic standards). The reaction of the 2MTs in the strong acid solutions produced a dark solution that eventually became heterogeneous in nature due to the production of dark solid particles. However, this phenomenon did not interfere with the monitoring of the aqueous phase reaction and it was possible to confirm the aqueous phase products as the *cis*- and *trans*-3MeTHF-3,4-diols previously synthesized (via strong acid-catalyzed and high temperature reaction of the 2MTs) and characterized by NMR.<sup>10,29</sup> The formation of THF species from the cyclization of 1,4-polyols is a well-known acid-catalyzed process,<sup>30</sup> and the mechanism for the formation of the 3MeTHF-3,4-diols is given in Figure S4.

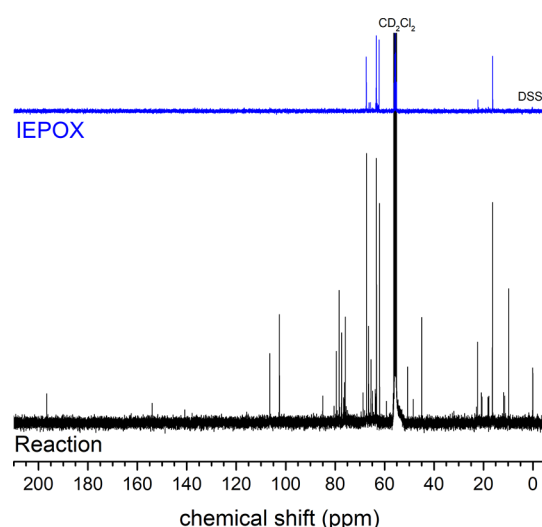
**IEPOX Isomerization Experiments.** Representative one-dimensional <sup>1</sup>H and <sup>13</sup>C NMR spectra for the IEPOX reactant and the MSA-catalyzed reaction of IEPOX (which had a 4:1 *trans*/*cis* ratio) in CD<sub>2</sub>Cl<sub>2</sub> are given in Figures 2 and 3, respectively. While there are clearly new species evident in the region for protons that are geminal to hydroxyl groups (3.0–4.0 ppm) and for methyl group protons (0.9–1.5 ppm) regions of the <sup>1</sup>H NMR spectrum, the presence of peaks in the 9.5 ppm range specifically indicate the formation of aldehyde products. The <sup>13</sup>C NMR spectrum also shows evidence for aldehydic carbon nuclei around 200 ppm. However, the intensities in the <sup>13</sup>C NMR spectrum clearly show that the major products of the IEPOX reaction produce new peaks in the 105 and 45 ppm regions (as well as the 60–80 ppm carbon nuclei geminal to hydroxyl groups region and the 10–25 ppm methyl regions), which are quite distinct from the IEPOX resonances, and with higher signal strength than the aldehyde resonances.

On the basis of the previous IEPOX studies using PTMSD/GC/EI-MS techniques,<sup>10</sup> the present nucleophile-free exper-





**Figure 2.**  $^1\text{H}$  NMR spectrum of the IEPOX reactant (top) and the IEPOX/MSA reaction (bottom) in  $\text{CD}_2\text{Cl}_2$  solvent in the presence of DSS.



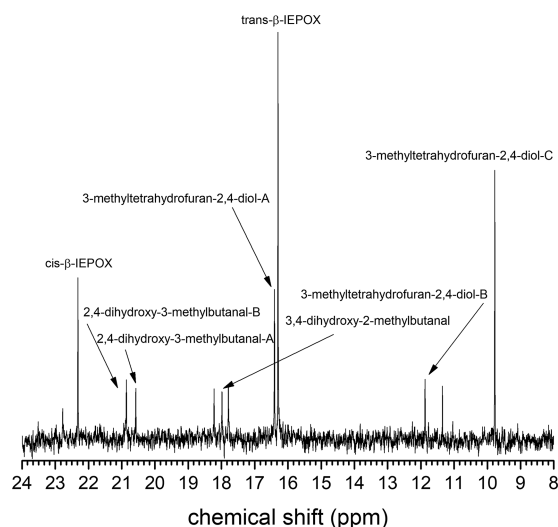
**Figure 3.**  $^{13}\text{C}$  NMR spectrum of the IEPOX reactant (top) and the IEPOX/MSA reaction (bottom) in  $\text{CD}_2\text{Cl}_2$  solvent in the presence of DSS.

imental conditions would be expected to lead to the two identified IEPOX isomerization product types,  $\text{C}_5$  alkene triols and 3MeTHF-3,4-diols. Because this earlier work had also synthesized the 3MeTHF-3,4-diols and characterized them with  $^1\text{H}$  and  $^{13}\text{C}$  NMR, it was a relatively simple matter to confirm whether these compounds were responsible for the signals observed in the present experiment (as was successfully done in the 2MT polyol dehydration cyclization experiments described in the previous section). While the resonances attributed to aldehydic species are obviously not a match for the  $\text{C}_5$  alkene triols nor the 3MeTHF-3,4-diols, the major product resonances near 105 and 45 ppm are also not consistent with the 3MeTHF-3,4-diols spectra. To the best of our knowledge, the  $\text{C}_5$  alkene triols have never been isolated or characterized via NMR techniques. However, it is unlikely that these species would lead to the specific resonances observed near 105 and 45 ppm either. Terminal olefinic carbon nuclei typically have chemical shifts around 115 ppm,<sup>31</sup> which conceivably could be the source of the 105 ppm resonances

in the present experiment. However, any of the possible  $\text{C}_5$  alkene triols would also have an internal olefinic carbon nucleus—these nuclei have chemical shifts more typically in the 125–140 ppm range. The other nonmethyl carbon nuclei in the  $\text{C}_5$  alkene triols are of the type in which hydroxyl groups are geminal. In this case, typical  $^{13}\text{C}$  chemical shifts for such aliphatic hydroxyl-bonded carbon nuclei are usually found in the 60–80 ppm range; the observed peaks at 45 ppm are not consistent with this carbon nucleus type. Therefore, under the present conditions, IEPOX reactions do not appear to produce significant amounts of either the  $\text{C}_5$  alkene triols nor the 3MeTHF-3,4-diols.

Correlation NMR spectroscopy methods, which are capable of identifying single and multiple H–H, C–H, and C–C bond couplings, were used to systematically construct the specific molecular origins of the IEPOX product signals (Figure S5). Figures S6–S9 include information illustrating how HMQC, HMBC, and COSY experiments were used to identify and assign one particular major product of the IEPOX reaction: 3-methyltetrahydrofuran-2,4-diol (3MeTHF-2,4-diol) diastereomer A (the alphabetical labels simply represent the order in which the diastereomers were identified, and do not imply any information about their actual structures). Briefly, the single bond HMQC experiments allowed for particular protons to be associated with the carbon nuclei to which they are bonded, and the multi bond HMBC experiments allowed for the determination of which carbon nuclei are bonded to each other (through their common proton couplings). The COSY experiment established that the H2 proton was adjacent to an alcohol proton. This information is sufficient to definitively determine the structure of this particular species. While this particular molecular structure is a close isomeric relative of the 3MeTHF-3,4-diols identified by Lin et al.,<sup>10</sup> the NMR resonances are quite different due to the fact that the hydroxyl groups are not adjacent in the 3MeTHF-2,4-diols. Two other diastereomers (labeled B and C) of 3MeTHF-2,4-diol were identified in a similar manner as were the structures of the aldehydic species: two diastereomers (labeled A and B) of 2,4-dihydroxy-3-methylbutanal and a single diastereomer of 3,4-dihydroxy-2-methylbutanal.  $^1\text{H}$  and  $^{13}\text{C}$  assignments for all identified species are given in Figure S5. An annotated  $^{13}\text{C}$  spectrum of the methyl region is given in Figure 4. These identified product peaks were integrated, and absolute product yields were determined from the amount of IEPOX consumed. The absolute yields reported in Table 1 (which are characterized by a precision of about 10%) indicate that about 72% of the reacted IEPOX has been identified among the various products, and that the three 3MeTHF-2,4-diol diastereomer products are derived from a little more than 50% of the reacted IEPOX.

**IEPOX Isomerization–Nucleophilic Addition Competition Experiments.** Previous work aimed at identifying the products of IEPOX reaction in bulk aqueous solution did not identify any isomerization products.<sup>8,11</sup> This is likely because the high concentration of water (or the presence of strong nucleophiles such as sulfate and nitrate) leads to reaction rates for nucleophilic addition that exceed that for isomerization. To estimate the relative rates of these two processes, IEPOX reactions under the isomerization reaction conditions described above were carried out in the presence of low concentrations of the relatively weak nucleophile, methanol. Water itself could not be used as the competing nucleophile because of its poor solubility in  $\text{CD}_2\text{Cl}_2$ . In one such



**Figure 4.** Annotated  $^{13}\text{C}$  methyl region for the IEPOX/MSA reaction system.

**Table 1.** Absolute Product Yields from IEPOX/MSA/ $\text{CD}_2\text{Cl}_2$  Reaction System

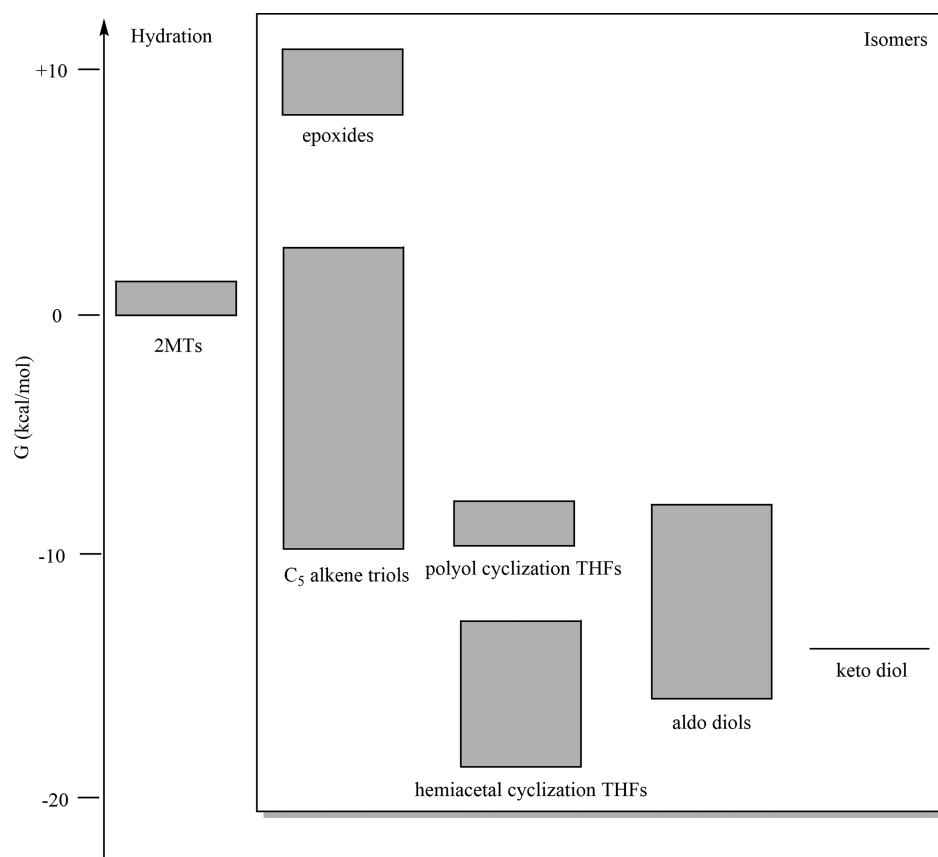
Structure	Name	Product Yield (%)
	2,4-dihydroxy-3-methylbutanal - A	5.2
	2,4-dihydroxy-3-methylbutanal - B	9.3
	3,4-dihydroxy-2-methylbutanal	6.6
	3-methyltetrahydrofuran-2,4-diol - A	18.8
	3-methyltetrahydrofuran-2,4-diol - B	6.8
	3-methyltetrahydrofuran-2,4-diol - C	24.9

experiment, the methanol concentration was 1.2 M, and the yield of the methanol nucleophilic addition product was approximately equal to the total yield of isomerization products. In a separate experiment, it was determined that the nucleophilic strength of methanol in its reaction with IEPOX is 0.69 relative to water. Therefore, had the experiment been run with 1.2 M  $\text{H}_2\text{O}$ , the water nucleophilic addition reaction rate would have been about 1.5 $\times$  that of the isomerization reactions. For IEPOX reactions run in aqueous solution (water formal concentration of about 55 M), the calculated result is that nucleophilic addition reaction product concentrations should be more than 60 $\times$  greater than isomerization reaction product concentrations. This estimate is consistent with the previous nonobservation of isomerization products under aqueous conditions.<sup>8,11</sup>

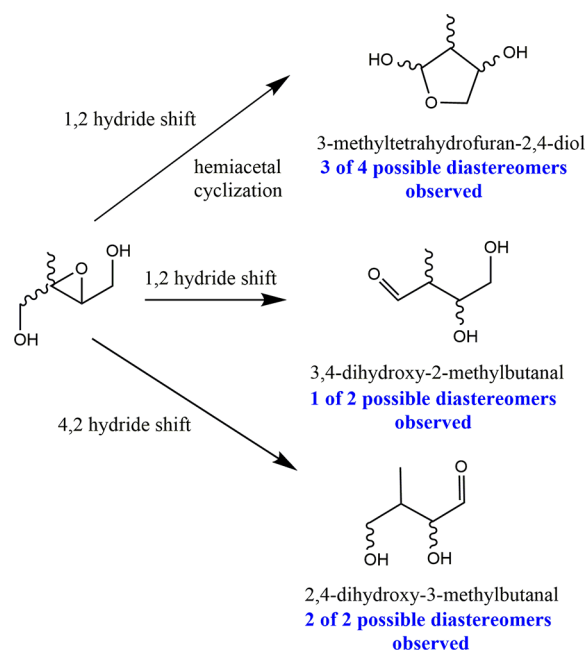
**Computational Free Energies.** To assist with the construction of a mechanism to explain the observed products, the free energies of a variety of  $\text{C}_5\text{H}_{10}\text{O}_3$  isomers were computed in water solvent using the G2MS method. For the  $\text{C}_5$  alkene triols, all possible isomers were systematically

considered. The aldo diol and keto diol structures were derived from the tautomeric form of the relevant  $\text{C}_5$  alkene triols. The “polyol cyclization THFs” are the THF derivatives observed in the 2MT polyol dehydration cyclization experiments and are the IEPOX isomerization species identified by Lin et al.<sup>10</sup> The “hemiacetal cyclization THFs” are the THF derivatives that could possibly form from the aldo diols via the well-known hemiacetal reaction.<sup>32</sup> The free energy scale was referenced to the hydrolysis reaction of *trans*- $\beta$ -IEPOX to form 2-methylerythritol, which was defined as having a free energy of reaction of zero. The free energies of select members of each structural class were also calculated in  $\text{CH}_2\text{Cl}_2$  solvent, and it was found that the free energies differed by an average of about 1  $\text{kcal mol}^{-1}$ , and these differences did not lead to significant changes in the relative free energies of the possible isomerization species. Table S2 lists the specific structural isomers considered and their free energies, with the isomers organized by structure type and in ascending free energy order for the water solvent calculations. The ranges of free energy for the different structural types are depicted in Figure 5. Interestingly, all considered isomers are predicted to be able to form spontaneously from IEPOX under standard conditions, and most of these isomers are thermodynamically more stable than the 2MTs. However, the present experimental polyol kinetics results indicate that relatively high activation barriers likely separate the 2MTs from these more thermodynamically stable species. While the  $\text{C}_5$  alkene triols are generally the least thermodynamically favorable structure type, they are nonetheless thermodynamically feasible IEPOX isomerization products. However, the aldo diols and keto diol, which are tautomers of several of the  $\text{C}_5$  alkene triols, are generally the more thermodynamically stable open chain form. And, most relevant for explaining the present experimentally observed major products of IEPOX isomerization, the hemiacetal cyclization THF species are the most thermodynamically stable structures of all.

**Proposed IEPOX Isomerization Mechanism.** It was noted that the one of the experimentally identified aldo diols (3,4-dihydroxy-2-methylbutanal) is a related species, via the hemiacetal mechanism, to the major product 3MeTHF-2,4-diols. The only other experimentally identified product is another aldo diol, 2,4-dihydroxy-3-methylbutanal. A proposed reaction scheme to rationalize all experimentally observed IEPOX isomerization products is given in Figure 6. In particular, a 1,2-hydride shift reaction is invoked to account for the formation of 3,4-dihydroxy-2-methylbutanal and the 3MeTHF-2,4-diols via hemiacetal cyclization. Figure 7 shows the proposed acid-catalyzed mechanism, in which a common intermediate can branch into both the observed aldo diol and the THF products. Because the available kinetic data indicate that the 3,4-dihydroxy-2-methylbutanal to 3MeTHF-2,4-diols ratio stays constant at all times, this mechanism seems more likely than one in which 3,4-dihydroxy-2-methylbutanal is an actual precursor species to the 3MeTHF-2,4-diols. The other experimentally observed aldo diol, 2,4-dihydroxy-3-methylbutanal, is rationalized via a 4,2-hydride shift reaction. There are probably several other unidentified IEPOX isomerization reaction products formed via similar mechanisms (including the fourth possible unidentified 3MeTHF-2,4-diol diastereomer and the second possible unidentified 2,4-dihydroxy-3-methylbutanal diastereomer, as well as THF-type species related to this aldo diol) in smaller yields, which could comprise some of the 28% of “missing” reacted IEPOX.



**Figure 5.** Schematic diagram of computed free energies (see Table S2 for specific values).



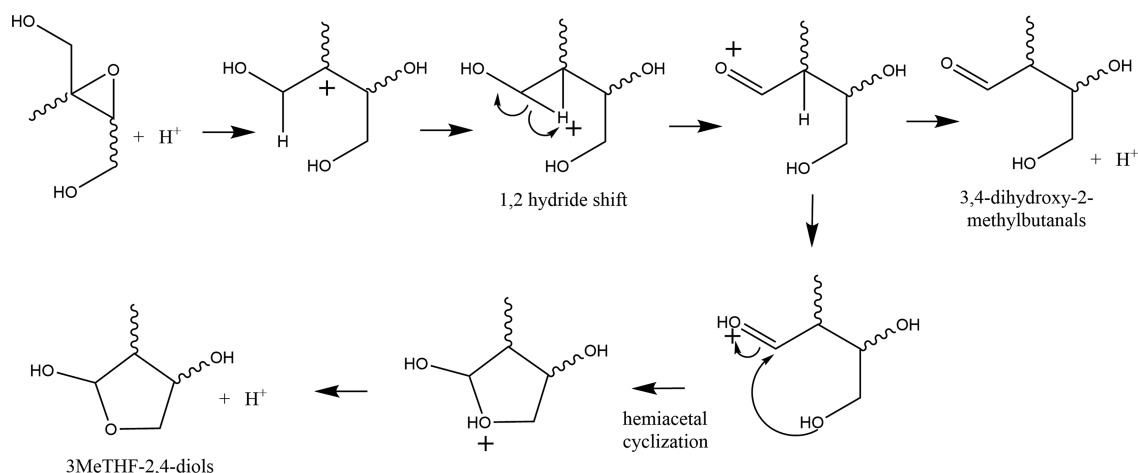
**Figure 6.** IEPOX isomerization reaction scheme.

**Atmospheric Implications.** The atmospheric feasibility of 2MT polyol dehydration cyclization reactions to form THF-type products was estimated using the excess acidity framework,<sup>28</sup> which allows for an extrapolation of the high acidity rate constants determined in the present work to the less acidic conditions more representative of SOA. While SOA

pH remains a difficult to determine quantity,<sup>33,34</sup> it is unlikely that most ambient SOA has an effective pH of less than zero. The excess acidity method extrapolation of the cyclization rate constants to pH = 0 yields lifetimes of 121 yr and 408 yr for 2-methylthreitol and 2-methylerythritol, respectively, with higher pH extrapolations leading to even longer calculated lifetimes. Therefore, the 2MTs are not expected to undergo such cyclization reactions on feasible time scales in aqueous SOA under atmospheric conditions.

The observed IEPOX isomerization reactions were also found to be relatively slow compared to nucleophilic addition reactions. For SOA with high levels of nucleophiles such as water, sulfate, nitrate and carboxylates, it seems unlikely that IEPOX isomerization reactions could compete effectively with nucleophilic addition reactions. Therefore, the 2010 observation at Yorkville, GA that about half of the total IEPOX-derived species were derived from IEPOX isomerization reactions<sup>10</sup> could be interpreted as indicating that the IEPOX processing happened under low water content conditions specifically, and low nucleophile content conditions more generally.

The observed bulk phase IEPOX isomerization reaction products in the present work are at odds with the IEPOX isomerization reaction products observed in previous studies of laboratory-generated and field-sampled IEPOX SOA analyzed via the PTMSD/GC/EI-MS technique. One possible explanation for the discrepancy is the possibility that different IEPOX reaction mechanisms are operating in the present reaction conditions as compared to the previous SOA experiments, especially for the SOA cases in which highly nonideal solution conditions may be present. It is important to note that the



**Figure 7.** IEPOX isomerization mechanism to produce 3,4-dihydroxy-2-methylbutanals and 3MeTHF-2,4-diols.

3MeTHF-3,4-diols standards previously synthesized and characterized via NMR by Lin et al. were prepared via the 2MTs and not IEPOX itself.<sup>10</sup> Therefore, this aspect of the previous work does not contradict the results of the present study. The present postulated mechanism for the formation of the observed bulk phase IEPOX isomerization products is compelling in two ways. First, it predicts the production of some of the most thermodynamically stable species uncovered in the computational aspect of the present work, while the species identified in the previous work are generally less thermodynamically stable. Second, the mechanism employs relatively well-known organic chemistry transformations (hydride shifts and hemiacetal cyclization), which suggest qualitative kinetic feasibility for the pathways to the product species observed. Another possibility for the discrepancy between the identified products in the present work and the previous work is the recent supposition that the PTMSD/GC/EI-MS technique may lead to more extensive chemical transformations than the expected simple silylation reaction at the site of the alcohol groups in the analytes. In particular, several recently reported experiments show that the IEPOX-derived fraction of SOA is significantly less volatile than any of the previously identified species, suggesting that the observed derivatization products are possibly derivatization condition-driven decomposition products of oligomeric species.<sup>18–20</sup> It also might be possible that the derivatization conditions, which use elevated temperatures and catalysts, could also facilitate transformations of monomeric constituents. For example, it is conceivable that the aldo diols identified in the present work could be triply silylated rather than doubly silylated due to reactivity at the carbonyl group and thus be the origin of the  $C_5$  alkene triols identified by PTMSD/GC/EI-MS. However, it seems less likely that the derivatization conditions could enable a conversion from the thermodynamically more stable 3MeTHF-2,4-diols to the less stable 3MeTHF-3,4-diols (unless the silylated derivatives have reversed relative free energies). More speculatively, it might be possible that the derivatization conditions serve to dramatically increase the rate of polyol dehydration cyclization reactions and could facilitate the conversion of the 2MTs to the 3MeTHF-3,4-diols. In any case, the present findings imply that IEPOX isomerization reactions will not be competitive in nucleophile-rich SOA environments and the inconsistencies between the present bulk organic phase NMR-identified products and the SOA

PTMSD/GC/EI-MS-identified products of IEPOX reaction raise questions about the required conditions for the atmospheric relevance of these processes. It is probable that new analytical methods for SOA analysis will be needed to resolve these discrepancies. The likely kinetic dominance of nucleophilic addition reactions under typical atmospheric conditions is consistent with the assertion that oligomeric components may dominate IEPOX-derived SOA,<sup>18–20</sup> assuming that the oligomer-forming nucleophilic addition reactions of the 2MTs to IEPOX are able to compete effectively with other monomer-forming reactions such as nucleophilic addition of water and sulfate. In conclusion, the potential lack of atmospheric relevance for IEPOX isomerization reactions is an important issue to resolve as a number of SOA modeling techniques now incorporate explicit IEPOX reaction mechanisms in their chemical reaction modules.<sup>35–38</sup>

## ■ ASSOCIATED CONTENT

### § Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b01780.

Synthesis and characterization of reactants used in the work, data and proposed mechanism for the polyol dehydration cyclization reactions,  $^1H$  and  $^{13}C$  NMR spectra and assignments for the various species identified in the work, representative correlation NMR spectra, and computational free energies for  $C_5H_{10}O_3$  and  $C_5H_{12}O_4$  isomers (PDF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This material is based on work supported by the National Science Foundation under Grant Nos. 1153861, 1427949, and 1559319.



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