

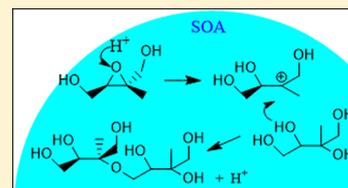
Assessing Potential Oligomerization Reaction Mechanisms of Isoprene Epoxydiols on Secondary Organic Aerosol

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Supporting Information

ABSTRACT: Extensive studies of secondary organic aerosol (SOA) formation have identified isoprene epoxydiol (IEPOX) intermediates as key species in the formation of isoprene-derived SOA. Recent work has suggested that isoprene-derived dimers and oligomers may constitute a significant fraction of SOA, but a mechanism for the formation of such abundant SOA components has yet to be established. The potential for dimer formation from the nucleophilic addition of 2-methyltetrol to *trans*- β -IEPOX was assessed through a series of model epoxide–nucleophile experiments using nuclear magnetic resonance (NMR) spectroscopy. These experiments helped establish a rigorous understanding of structural, stereochemical, and NMR chemical shift trends, which were used along with nucleophilic strength calculations to interpret the results of the *trans*- β -IEPOX + 2-methyltetrol reaction and evaluate its relevance in the atmosphere. A preference for less sterically hindered nucleophiles was observed in all model systems. In all addition products, a significant increase in NMR chemical shift was observed directly adjacent to the epoxide–nucleophile linkage, with smaller decreases in chemical shift at all other sites. A partial NMR assignment of a single *trans*- β -IEPOX + 2-methyltetrol nucleophilic addition product was obtained, but nucleophilic strength calculations suggest that 2-methyltetrol is a poor nucleophile. Therefore, this reaction is unlikely to significantly contribute to dimer and oligomer formation on SOA. Nevertheless, the structural and stereochemical considerations, NMR assignments, and NMR chemical shift trends reported here will prove useful in future attempts to synthesize dimer and oligomer analytical standards.



INTRODUCTION

A significant portion of the atmosphere's particulate matter consists of secondary organic aerosol (SOA),¹ which has been implicated in human respiratory and cardiovascular disease,² visibility loss,³ and climate modification.⁴ Isoprene, a hydrocarbon released from broad-leaf trees in substantial quantities, is thought to contribute significantly to SOA formation and growth.^{5,6} Extensive studies of SOA formation have identified isoprene epoxydiols (IEPOX)⁷ as key intermediates in the formation of isoprene-derived SOA (*i*SOA). Subsequent laboratory and field studies have rationalized the formation of previously observed *i*SOA components such as 2-methyltetrols (2MT), organosulfates, and organonitrates through acid-catalyzed, condensed-phase, nucleophilic addition reactions of IEPOX on SOA.^{7–14} More recent work has suggested that isoprene-derived dimers and higher-order oligomers may constitute a substantial fraction of *i*SOA.^{15–17} Due to their low estimated volatility, these dimers and higher-order oligomers may have profound effects on aerosol properties, including aerosol particle viscosity and the rates of diffusion and evaporative processes.¹⁸ Additionally, the potentially substantial concentration of these species could have important implications for regional and global aerosol models.^{15,19,20}

While the presence and influence of oligomer-influenced *i*SOA has been identified in a number of previous studies, the molecular speciation remains poorly understood. Using gas chromatography/electron ionization-quadrupole mass spec-

trometry (GC/EI-MS) with a prior trimethylsilyl derivatization workup as the detection method, Surratt et al. observed the formation of C₁₀H₂₂O₇ dimers during isoprene oxidation chamber studies under low-NO_x conditions.²¹ In the same study, the authors discovered similar compounds present in ambient *i*SOA that had been previously collected in the Amazonian rainforest but found that the mass fraction of these compounds comprised less than 1% of the total IEPOX-derived set of quantified compounds. In 2012, Lin et al. quantified these dimers in ambient aerosol and demonstrated correlations between their formation and IEPOX uptake in a series of chamber experiments.¹⁰ On the other hand, *i*SOA volatility studies have suggested that a significantly larger fraction (>80%) of IEPOX-derived SOA is comprised of lower volatility species (such as dimeric and oligomeric components) and have suggested that the trimethylsilyl derivatization process may cause decomposition of oligomers and produce artificially high estimates of monomeric components.^{15,16} Indeed, the newly developed hydrophilic interaction liquid chromatography (HILIC)/electrospray ionization (ESI)-high resolution (HR)-quadrupole time-of-flight mass spectrometry (QTOFMS) method has revealed that the GC/EI-MS technique does lead to the degradation of certain IEPOX-

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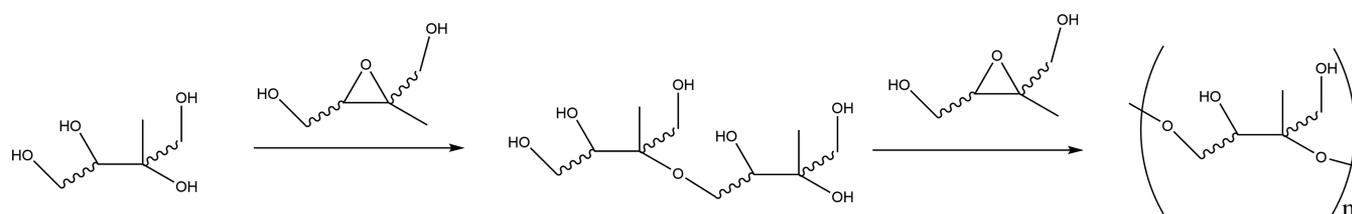
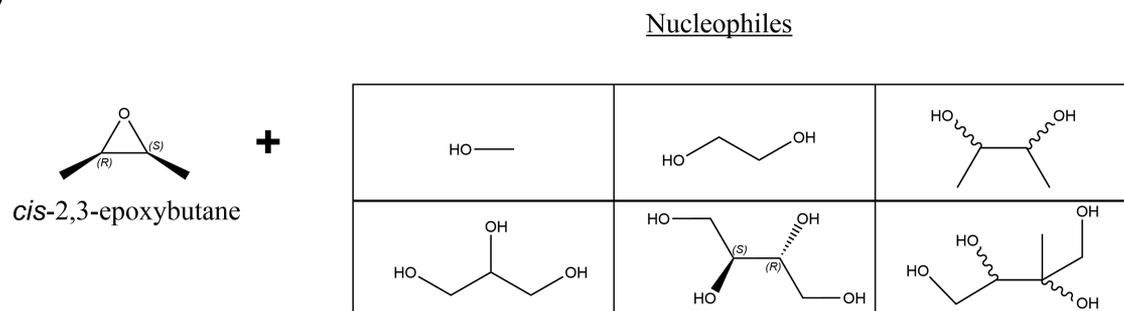
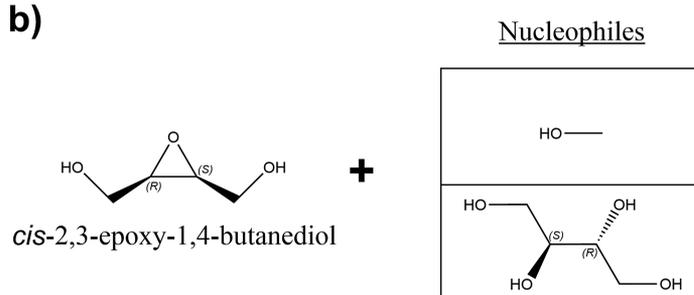


Figure 1. Proposed schematic for acid-catalyzed IEPOX + 2MT dimer and higher-order oligomer formation.

a)



b)



c)

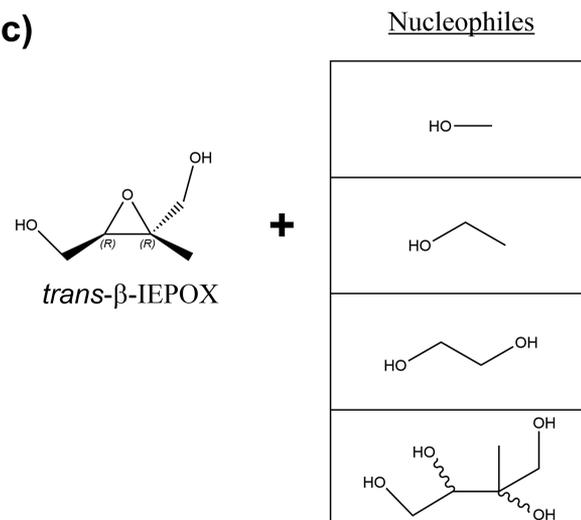


Figure 2. Systems studied: (a) *cis*-2,3-epoxybutane + nucleophile; (b) *cis*-2,3-epoxy-1,4-butanediol + nucleophile; (c) *trans*- β -IEPOX + nucleophile.

derived species,²² which further suggests that past molecular speciation efforts to quantify oligomers may have underestimated their atmospheric abundance. In addition, the lack of available analytical standards for potential *i*SOA molecular components such as oligomers has hindered the effort to develop techniques that can better identify and quantify the molecular composition of *i*SOA. Therefore, synthesis and characterization procedures for such standards are also needed.

It has been previously suggested that the observed $C_{10}H_{22}O_7$ dimers may arise from nucleophilic addition of 2MT to IEPOX.¹⁰ Subsequent reaction of such species with IEPOX can also serve to explain the presence of higher-order oligomers. A schematic of this proposed oligomerization process is given in Figure 1.

In the present study, we assess the potential for the atmospherically dominant IEPOX isomer, *trans*- β -IEPOX,²³ to undergo nucleophilic addition by 2MT to form the aforementioned $C_{10}H_{22}O_7$ dimer species in bulk aqueous

solution using nuclear magnetic resonance (NMR) as the primary analytical technique. The bulk solution method allows for careful control over reactant and catalysts species, as well as their concentrations, and the NMR method can be used to determine isomer specific structures and relative concentrations for product species.²⁴ While these strengths of the bulk solution method are more difficult to achieve for direct aerosol studies, both atmospheric chamber and flow tube studies of aerosols can more accurately incorporate the gas–particle dynamics present in the actual atmosphere, as well as such situations as solution nonideality.^{25–27}

Due to the potential number of structural and stereochemical isomers that might be formed in the *trans*- β -IEPOX + 2MT nucleophilic addition reaction, as well as the inherent chemical shift overlap challenges that arise when using NMR to characterize dimers, a series of simpler epoxide–nucleophile systems were first considered. These model systems of increasing complexity were studied in order to methodically

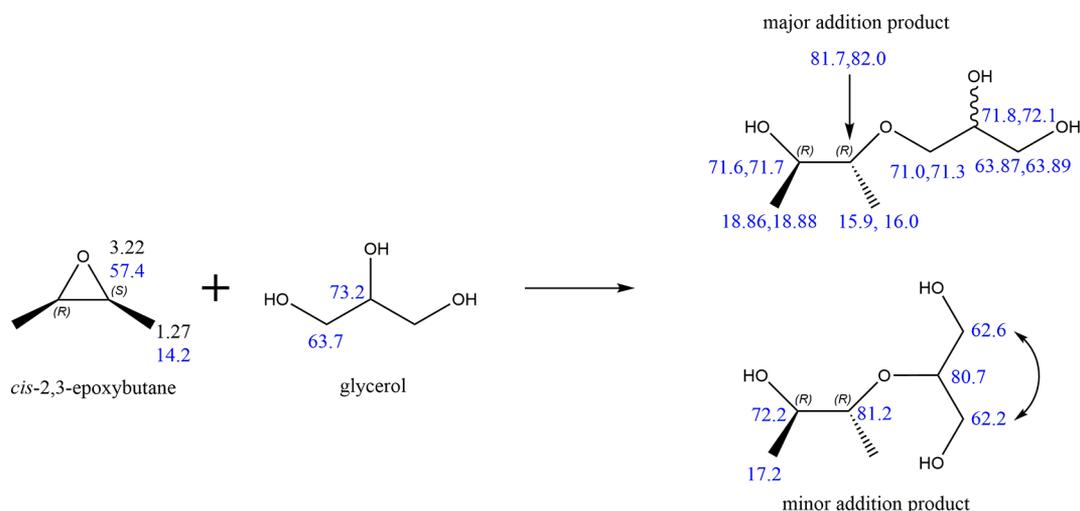


Figure 3. *cis*-2,3-Epoxybutane + glycerol reaction ^1H NMR (black) and ^{13}C NMR (blue) assignments in D_2O . ^1H NMR is referenced to HDO at 4.79 ppm, and ^{13}C NMR is referenced to a secondary calibration of *racemic* (RR/SS) 2,3-butanediol at 18.98 ppm (primary calibration is to *meso*-erythritol at 63.8 ppm). Two assignments are listed for the major structural isomer, as there are two diastereomers present due to a stereocenter at the glycerol C-2 position. The *cis*-2,3-epoxybutane assignments correspond to a separate dilute solution of epoxide in D_2O calibrated to 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS) at 0.0 ppm, as described in the [Supporting Information](#). The double-headed arrow indicates that it could not be determined whether the specified assignment or an exchanged assignment is correct.

establish structural, stereochemical, and ^{13}C NMR chemical shift trends that would allow the prediction and ultimately the assignment of the NMR spectrum for the atmospherically relevant *trans*- β -IEPOX + 2MT system. The nucleophilic addition reaction of *cis*-2,3-epoxybutane with a variety of different nucleophiles was chosen for study because it is the most structurally simple, stereospecific four-carbon epoxide that is commercially available. Similar experiments were conducted with the symmetric epoxide *cis*-2,3-epoxy-1,4-butanediol, which differs structurally from *trans*- β -IEPOX by only a methyl group. Finally, the reactions between *trans*- β -IEPOX and various nucleophiles of increasing complexity (culminating with 2MT) were investigated. The full set of systems studied are given in [Figure 2](#).

Nucleophilic strength calculations were also performed in order to predict the atmospheric conditions under which 2MT addition to *trans*- β -IEPOX might be efficient and serve as a route to the formation of oligomeric *i*SOA.

MATERIALS AND METHODS

Syntheses. A sample containing *cis*-2,3-epoxy-1,4-butanediol, a sample containing both 2MT diastereomers (1.5:1 ratio of 2-methylthreitol to 2-methylerythritol), and samples containing both *trans*- β -IEPOX and varying amounts of a minor *cis*- β -IEPOX impurity were each prepared and characterized according to separate procedures previously reported by our lab.^{8,24,28} The NMR-determined purities of both isomer mixtures with respect to other components were >95%.

Bulk Solution Preparation. All reactions were run in bulk solutions, the specific compositions of which were designed to favor nucleophilic addition to epoxides (as opposed to epoxide–epoxide reactions) and are detailed for each system in the [Supporting Information](#). Briefly, most reactions totaled 750 μL in volume, were performed with excess (at least 10-fold) nucleophile concentrations, and contained epoxide and trifluoroacetic acid catalyst concentrations of approximately 0.1–1.5 and 0.05 M, respectively. Solutions were prepared at

room temperature (20 $^\circ\text{C}$) and were then stirred overnight before being transferred to a 5 mm NMR tube for analysis. In some cases, in order to increase product yield, systems were run “neat,” whereby reactants were combined and stirred without solvent for 24 h before being added to an equal volume of NMR solvent for analysis. When reactant solubilities prevented successful neat preparation, reactions were run in deuterated nucleophile solvents if available.

Experiments were performed using commercially available chemicals obtained from Sigma-Aldrich (*cis*-2,3-epoxybutane, 97%; trifluoroacetic acid, $\geq 99.0\%$; dichloromethane- d_2 , $>99.00\%$; *meso*-erythritol, $>99\%$; ethylene glycol, 99.8%; glycerol, $\geq 99\%$), Cambridge Isotope Laboratories, Inc. (deuterium oxide, 99.5%; methanol- d_4 , 99.5%; ethanol- d_6 , 99%), and Tokyo Chemical Industry Co. (2,3-butanediol, $>97.0\%$).

NMR Methods. NMR spectra were collected on a Varian 400 MHz instrument using built-in pulse sequences, except in cases where an increased number of scans was necessary to enhance signal-to-noise. Spectra were calibrated to a variety of standards (often solvent peaks), which are specified for each system in the [Supporting Information](#). In addition to traditional 1-dimensional ^1H NMR and ^{13}C NMR spectra, the complexity of many systems required the use of 2-dimensional NMR techniques, including distortionless enhancement by polarization transfer (DEPT), ^1H – ^{13}C heteronuclear single quantum coherence spectroscopy (HSQC), and ^1H – ^{13}C heteronuclear multiple bond coherence spectroscopy (HMBC).²⁹ These experiments provided information about bond connectivity through single and multiple bond correlations. An increased number of scans and smaller increments were also used when necessary in 2-dimensional experiments to increase signal-to-noise and resolution, respectively.

RESULTS AND DISCUSSION

NMR Assignments for Model Systems. NMR assignments for each of the model systems listed in [Figure 2](#) are

reported in the Supporting Information. Assignments were primarily made using ^{13}C NMR, as ^1H NMR spectra were frequently uninterpretable as a result of extensive chemical shift overlap between nucleophilic addition products and nucleophile reactants. Additional structural interpretation was achieved using ^{13}C DEPT, while HSQC and HMBC were only used in some cases to confirm assignments, as ^1H NMR overlap complicated these spectra as well. The following paragraph describes the detailed assignment process for the *cis*-2,3-epoxybutane + glycerol system, which contains information about structural preferences and stereoisomerism considerations that are representative of those observed in all systems.

NMR assignments for the reactants and the nucleophilic addition products for the *cis*-2,3-epoxybutane + glycerol system are given in Figure 3, and a labeled ^{13}C NMR spectrum of the products in D_2O solvent is shown in Figure 4. As noted

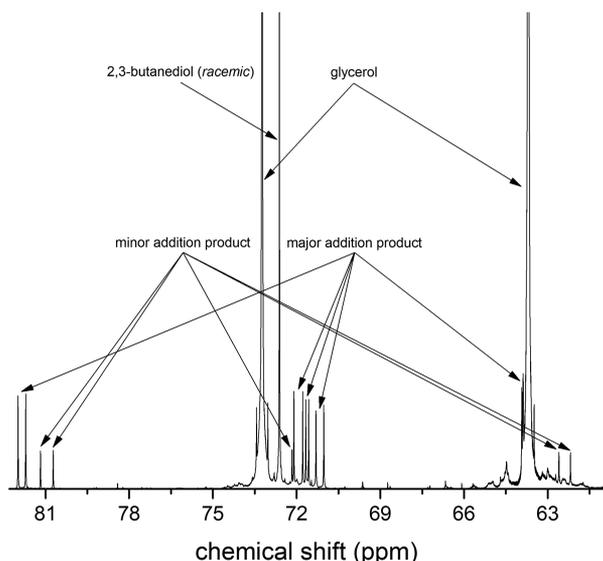


Figure 4. ^{13}C NMR spectrum of *cis*-2,3-epoxybutane + glycerol reaction in D_2O . In addition to glycerol and *cis*-2,3-epoxybutane + glycerol addition products, *racemic* 2,3-butanediol formed from the nucleophilic addition of water (introduced to the system via dilute TFA) to *cis*-2,3-epoxybutane was also observed. The ratio of the major primary addition product to that of the minor secondary addition product was about 5:1.

previously, the presence of multiple nucleophilic hydroxy groups and epoxide attack sites creates the potential for complex structural isomerism. In this case, *cis*-2,3-epoxybutane contains only one nucleophilic attack site, but the two types of nucleophilic hydroxy groups (1° and 2°) on glycerol can lead to two possible structural isomers of the addition product. Indeed, two structural isomers were observed: a major product corresponding to 1° addition and a minor product corresponding to 2° addition. The clear preference for 1° hydroxy attack over 2° was observed for all systems with polyol nucleophiles and is consistent with steric arguments that predict a decrease in nucleophilicity for more hindered nucleophilic sites.

Because *cis*-2,3-epoxybutane is a stereospecific isomer (RS configuration) and acid-catalyzed nucleophilic addition is known to lead to an inversion of configuration,³⁰ any nucleophilic addition product must have a single configuration, RR (or equivalently SS), on the epoxide side of the product. However, for systems in which there are one or more

stereocenters on the nucleophile side of the addition product, multiple NMR-observable diastereomers may be observed for a given structural isomer. In this particular case, the stereocenter created at the C-2 carbon on the glycerol side of the 1° glycerol addition product results in two observed diastereomers, while 2° glycerol addition does not lead to the formation of a new stereocenter on the glycerol side of the 2° glycerol addition product.

Chemical Shift Trends for Model Systems. In order to help interpret NMR spectra of the complex *trans*- β -IEPOX + 2MT reaction, trends in ^{13}C NMR chemical shift from model systems were established by calculating the difference in chemical shift between the carbon nuclei of nucleophilic addition products (which are each composed of a “nucleophile unit” and a “ring-opened epoxide unit”) and those of related species that closely resemble these nucleophile and ring-opened epoxide units. For the portion of the addition product derived from the nucleophile reactant, the chemical shift difference was calculated relative to the original nucleophile itself. For the remainder of the addition product derived from the epoxide, the difference in chemical shift was calculated relative to the epoxide’s hydrolysis product (formed from nucleophilic addition of water). For example, the chemical shift differences for the nucleophilic addition product of the reaction of methanol with *cis*-2,3-epoxybutane were calculated by using the chemical shift values for the nucleophilic addition product (given in Figure S1) and subtracting the chemical shift value for methanol (also given in Figure S1) from the appropriate value in the addition product and subtracting the chemical shift values for *racemic* 2,3-butanediol (given in Figure S3) from the appropriate values in the addition product, yielding the final chemical shift differences for the addition product (given in Figure S11). The average ^{13}C NMR chemical shift differences (and one standard deviation error limits) compiled from the *cis*-2,3-epoxybutane- and *trans*- β -IEPOX-based model systems for general 1° nucleophile addition are given in Figure 5. The *trans*- β -IEPOX general product is drawn with a 3° epoxide-side linkage in Figure 5, as

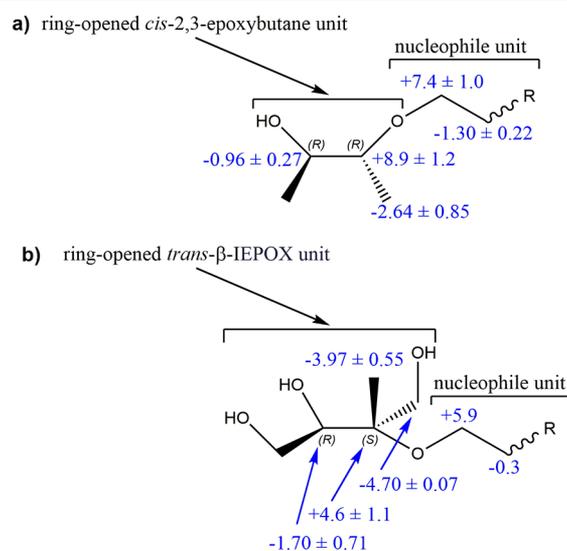


Figure 5. Average differences (and one standard deviation precision) in ^{13}C NMR chemical shift (ppm) for (a) *cis*-2,3-epoxybutane + nucleophile model systems and (b) *trans*- β -IEPOX + nucleophile model systems.

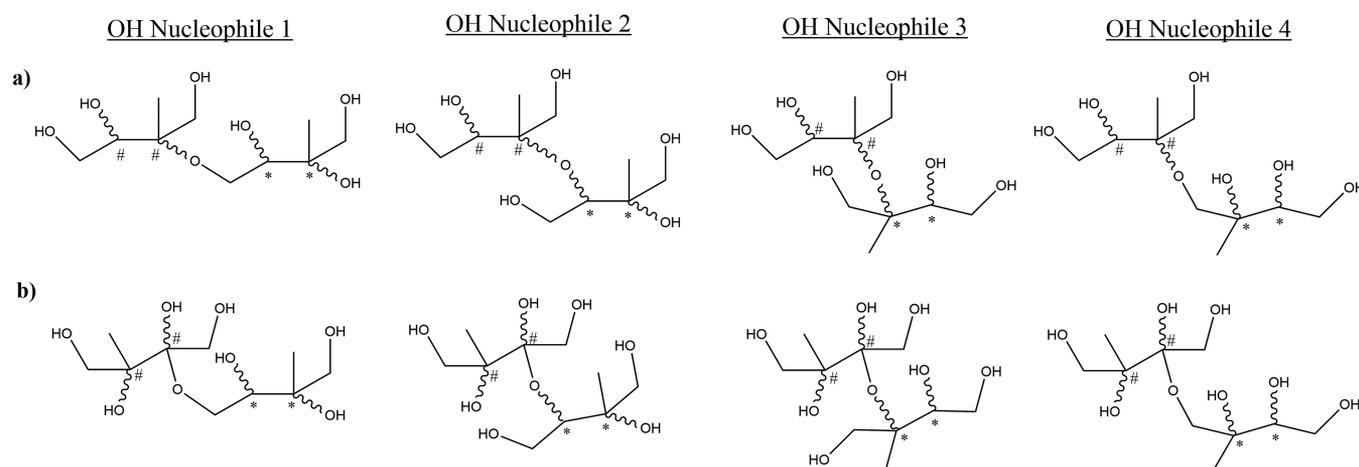


Figure 6. Possible structural isomers ((a) depicts tertiary addition to IEPOX, and (b) depicts secondary addition to IEPOX) and stereocenters (# indicates IEPOX-derived stereocenter, and * indicates 2MT-derived stereocenter) in *trans*- β -IEPOX + 2MT addition products.

trans- β -IEPOX was observed to undergo nucleophilic addition exclusively at its 3° site in all model systems. This regioselectivity suggests the potential importance of an A-1-type nucleophilic addition mechanism (similar to the S_N1 nucleophilic substitution mechanism), as discussed in a previous study of *trans*- β -IEPOX reactivity.³¹ However, that same study also suggests that the mechanism may also possess some A-2 character (similar to S_N2 nucleophilic substitution), which would lead to accentuated nucleophile steric effects. The actual chemical shift differences for each individual model system are reported in the [Supporting Information](#). Because the nucleophile (reacted in excess) and the hydrolysis product (water was often present in systems as a competing nucleophile, and hydrolysis products themselves were often the nucleophile of interest) were present postreaction in every case, these chemical shift differences represent differences calculated within a single solvent system. Therefore, the spread of chemical shift differences (as represented by the standard deviation from the average) is due to actual chemical shift differences in the different nucleophilic addition products and is not influenced by solvent-induced chemical shift changes. As the precision data in [Figure 5](#) indicates, the chemical shift differences were reliably reproduced for a number of different nucleophile addition products, thus demonstrating the efficacy of this analysis approach.

In all model systems, significant increases in ¹³C NMR chemical shift were observed at the carbon atoms on both sides of the ether linkage of the addition products. This deshielding effect is consistent with substituent trends that indicate that ether groups are somewhat less electron donating than hydroxy groups.³⁰ Most other carbon nuclei in the addition products decreased in chemical shift, with larger decreases observed for nuclei closer to the linkage. *trans*- β -IEPOX systems exhibited smaller chemical shift increases directly adjacent to the ether linkage and larger decreases away from the linkage than *cis*-2,3-epoxybutane and *cis*-2,3-epoxy-1,4-butanediol model systems, which is likely reflective of the chemical shift trends depending on the exact nature of the carbon substitution situation. The chemical shift differences presented in [Figure 5](#) may aid in the assignment of nucleophilic addition products in future synthesis efforts, as they provide a method for generating predicted nucleophile addition product ¹³C NMR spectra for *trans*- β -IEPOX-related species. This method is demonstrated

for the potentially atmospherically relevant *trans*- β -IEPOX + 2MT reaction in the following sections.

***trans*- β -IEPOX + 2MT Reaction System Solubility Issues.** The experimental design of the *trans*- β -IEPOX + 2MT reaction system was restricted by reactant and product solubilities. The previously described high-yielding “neat” preparation could not be performed due to the inability of TFA and/or *trans*- β -IEPOX to dissolve in 2-MT. Additionally, limited solubility of 2MT in water (on the order of a few hundred mg/mL) was observed, with improved solubility in methanol. Therefore, the *trans*- β -IEPOX + 2MT reaction was run in CD₃OD (deuterated for NMR locking purposes), and thus, a competing *trans*- β -IEPOX + CD₃OD nucleophilic addition pathway was also observed. Such limited solubilities of 2MT and 2MT-containing products will likely need to be considered in future efforts to synthesize species that may serve as standards for analytical identification of isoprene-derived oligomers.

***trans*- β -IEPOX + 2MT Reaction System Isomer Considerations.** While the *cis*-2,3-epoxybutane + glycerol nucleophilic addition products illustrated the basic structural and stereoisomer complexities that are possible in epoxide + polyol reactions, the much more complex *trans*- β -IEPOX + 2MT system required a more systematic approach to the isomerism issue. For example, the presence of multiple hydroxy groups on 2MT and multiple nucleophilic attack sites on *trans*- β -IEPOX creates the potential for a variety of addition product structural isomers. The four nucleophilic hydroxy groups (“OH Nucleophile 1”, “OH Nucleophile 2”, etc.) on 2MT may act as nucleophiles at either of the asymmetric attack sites (i.e., secondary and tertiary sites) on the IEPOX ring, making for a total of eight possible structural isomers, which are given in [Figure 6](#). The total number of possible stereoisomers for a given structural isomer is 2^{*n*}, where *n* is the number of stereocenters in a given structural isomer. Each of the eight structural isomers has a total of four stereocenters (indicated by a hashtag or asterisk in [Figure 6](#)), which can lead to as many as 16 stereoisomers per structural isomer. However, most stereoisomers occur as enantiomeric pairs, and the two members of the pair are not distinguishable by NMR methods. Nonetheless, as many as 64 (8 structural × 8 diastereomers per structural isomer) NMR-distinguishable nucleophilic addition isomers are possible in the *trans*- β -IEPOX + 2MT reaction

system. However, because stereospecific *trans*- β -IEPOX was used in the experiments and acid-catalyzed epoxide ring opening always leads to an inversion of configuration, the two hashtag-labeled stereocenters in Figure 6 must have opposite configurations (RS or SR; the RS configuration is depicted in all structures).³² Due to this constraint, these two stereocenters serve to act as single stereocenter with respect to the configuration of the rest of the nucleophilic addition product. Because a stereochemically pure sample of 2MT was not available, the asterisk-labeled stereocenters have no such constraint. Therefore, due to the presence of three effective stereocenters, each structural isomer has a total of up to eight stereoisomers possible or up to four possible NMR-distinguishable diastereomers. Fortunately, the number of structural isomers to be considered is also fewer than the theoretical maximum of eight. Previous studies have shown an exclusive preference for attack at the tertiary carbon atom of IEPOX by such large nucleophiles as HSO_4^- and NO_3^- ,²⁸ and the model IEPOX + alcohol systems in the present study were also characterized by exclusive tertiary attack. Therefore, it seems reasonable to expect that only tertiary IEPOX-linked nucleophilic addition products are possible for the *trans*- β -IEPOX + 2MT reaction, thus excluding the bottom row of structural isomers in Figure 6 from consideration. The epoxide + polyol model systems in the present study also indicated that less sterically hindered nucleophilic groups form a larger proportion of nucleophilic addition products. Therefore, while none of the structural isomers in listed in the top row of Figure 6 can be completely eliminated from consideration on this basis, it is reasonable to surmise that the primary 2MT-linked nucleophilic addition products are most likely to form and the tertiary 2MT-linked products are least likely to form.

***trans*- β -IEPOX + 2MT Addition Product NMR Spectrum Prediction and Assignment.** In order to interpret the ^{13}C NMR spectrum, chemical shift predictions were first made on the basis of the chemical shift differences observed for the IEPOX + alcohol model systems (Figure 5b). These expected changes in chemical shift for the expected major addition product resulting from primary OH attack at the tertiary *trans*- β -IEPOX site are shown in Figure 7a, which are then used in conjunction with the absolute chemical shifts of 2MT to calculate the actual predicted ^{13}C NMR chemical shifts as shown in Figure 7b.

As discussed above, solubility issues required the use of methanol solvent for the *trans*- β -IEPOX + 2MT reaction. Because the majority of *trans*- β -IEPOX underwent nucleophilic addition with the more abundant, less sterically hindered CD_3OD nucleophile, relatively small amounts of *trans*- β -IEPOX + 2MT addition product were observed. Figure 8 shows the NMR assignments for the reactants and the partially identified addition product for the *trans*- β -IEPOX + 2MT reaction. Most notably, the formation of four tertiary (as confirmed by DEPT experiments) carbon peaks was observed in the 79–81 ppm region of the ^{13}C NMR reaction spectrum, which is consistent with the prediction of the formation of four diastereomers for each structural isomer. The large chemical shift of these signals confirms that this structural isomer must be the result of 2MT nucleophilic attack at the 3° *trans*- β -IEPOX site, as expected. While the DEPT data and chemical shift predictions seem to rule out a structural isomer formed by 2MT using its secondary hydroxy group as a nucleophile, this analysis cannot conclusively identify which of the two primary hydroxy nucleophilic site addition products was formed.

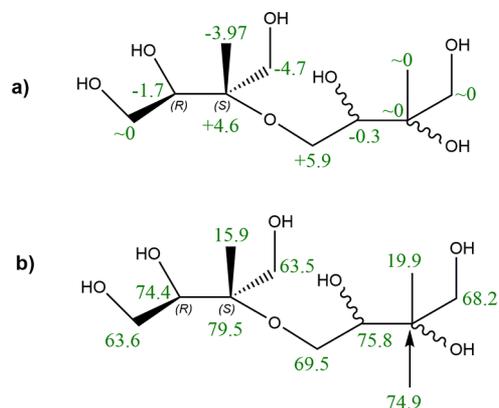


Figure 7. (a) Predicted changes in ^{13}C NMR chemical shift (ppm) for the expected major *trans*- β -IEPOX + 2MT addition product. (b) Predicted ^{13}C NMR shifts for the expected major *trans*- β -IEPOX + 2MT addition product (calculated from ^{13}C NMR chemical shift differences in (a) and 2-methylerythritol ^{13}C NMR shifts reported in Figure 8).

Therefore, while Figures 7 and 8 depict the least structurally hindered of the two primary hydroxy group linked addition products, it is possible that the other primary linked structural isomer is the one that has been observed. Most likely, both structural isomers were formed with similar yields, but we were only able to identify one of them amid the extremely congested spectrum. Several other ^{13}C resonances from this *trans*- β -IEPOX + 2MT addition product could be assigned that were consistent with the chemical shift predictions in Figure 7 and their associated uncertainties (given in Figure 5).

Nucleophilic Strength Calculations. Nucleophilic competition is ultimately the primary kinetic factor that determines which ring-opened *trans*- β -IEPOX products are formed in SOA reactions. Therefore, in order to assess the atmospheric relevance of a particular nucleophilic addition pathway, it is crucial to evaluate the intrinsic strength of the nucleophile involved, in addition to its relative concentration. The nucleophilic strength of a nucleophile (nucleophile 1) relative to a different, competing nucleophile (nucleophile 2) also present in a given system can be determined from the initial nucleophile mole fractions (X) and final nucleophilic addition product mole fractions (Y) via eq 1:

$$\frac{\text{nucleophile 1 strength}}{\text{nucleophile 2 strength}} = \frac{(Y_{\text{nuc1}}/X_{\text{nuc1}})}{(Y_{\text{nuc2}}/X_{\text{nuc2}})} \quad (1)$$

By defining the nucleophilic strength of water as 1 (nucleophile 2), the nucleophilic strengths of the various alcohols (nucleophile 1) used in this study were determined relative to water for each epoxide–nucleophile system. The results of these calculations are reported (with an estimated relative uncertainty of 15%) in Table 1. X values were determined from volume and mass measurements, while Y values were determined from ^{13}C NMR integration. In order to allow straightforward comparisons between systems of different isomeric complexity, the yields from all diastereomeric products from a particular structural isomer were summed in the determination of the Y values. Because the presence of a competing water nucleophile was needed for nucleophilic strength calculations, not all of the epoxide–nucleophile systems could be evaluated. However, some experiments (*cis*-2,3-epoxybutane + methanol, *cis*-2,3-epoxybutane + glycerol, and *trans*- β -IEPOX + methanol) were repeated with water

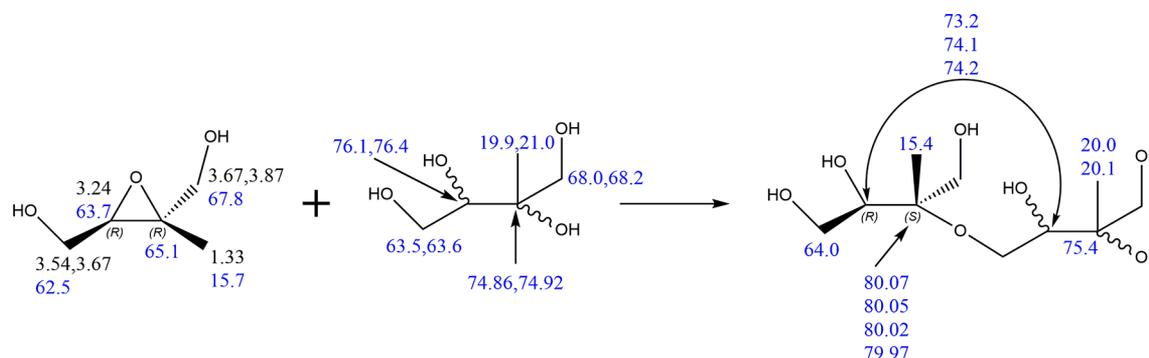


Figure 8. ^1H NMR (black, referenced to CHD_2OD at 3.31 ppm) and ^{13}C NMR (blue, referenced to CHD_2OD at 49.00 ppm) assignments and addition product ^{13}C NMR assignment for the *trans*- β -IEPOX + 2MT reaction in CD_3OD solvent. As indicated in the Supporting Information, *trans*- β -IEPOX assignments represent a separate dilute solution of epoxide in D_2O calibrated to DSS at 0.0 ppm.

Table 1. Relative Nucleophilic Strength Determinations for Each of the Epoxide–Nucleophile Systems

reaction	nucleophile	relative nucleophilicity
1° Addition by Methanol		
<i>cis</i> -2,3-epoxybutane + methanol	methanol	1.2
<i>cis</i> -2,3-epoxy-1,4-butanediol + methanol	methanol	1.2
<i>trans</i> - β -IEPOX + methanol	methanol	0.72
1° Addition by Polyols		
<i>cis</i> -2,3-epoxybutane + glycerol	glycerol 1° OH	0.57
<i>cis</i> -2,3-epoxybutane + <i>meso</i> -erythritol	<i>meso</i> -erythritol 1° OH	0.51
<i>trans</i> - β -IEPOX + ethylene glycol	ethylene glycol 1° OH	0.41
<i>trans</i> - β -IEPOX + 2MT	2-methyltetrol 1° OH	0.36
2° Addition by Polyols		
<i>cis</i> -2,3-epoxybutane + glycerol	glycerol 2° OH	0.11
<i>cis</i> -2,3-epoxybutane + <i>meso</i> -erythritol	<i>meso</i> -erythritol 2° OH	0.10

present. Nucleophilic strengths for *cis*-2,3-epoxybutane + 2,3-butanediol, 2,3-epoxybutane + 2MT, and *cis*-2,3-epoxy-1,4-butanediol + *meso*-erythritol systems could not be determined because of ^{13}C NMR integration complications.

The trends in relative nucleophilic strength observed in Table 1 can largely be rationalized by steric arguments: nucleophilicity decreases in strength with increasing steric complexity of both the alcohol and epoxide, and 1° alcohol nucleophilic addition is clearly preferred over 2° alcohol addition. The observed factor of 5 decrease in nucleophilic strength for 2° glycerol and *meso*-erythritol addition as compared to 1° addition suggests that 2° addition for 2MT will be similarly suppressed, which is consistent with the lack of identification of a secondary addition product from the *trans*- β -IEPOX + 2MT reaction. Nucleophilic strength calculations were generally in good agreement with a previous determination of methanol nucleophilicity, in which the relative nucleophilic strength of methanol with methacrylic acid epoxide was reported to be similar to water.³³ Previous studies of atmospherically relevant nucleophiles have also reported relative nucleophilic strengths of on the order of 10 for sulfate and nitrates,¹¹ on order of 100 for halides,³⁴ and on the order of 1000 for amines.³⁵ While ambient nucleophile concentration and SOA acidity must also be considered to assess the overall SOA reactivity of atmospherically relevant nucleophiles with epoxides, the relative nucleophilic strengths of the alcohols presented in Table 1 are clearly quite poor, similar to or less

than water. Most significantly, the relative nucleophilic strength of the bulky 2MT nucleophile reacting with *trans*- β -IEPOX was found to be the lowest for any *trans*- β -IEPOX nucleophilic addition product studied to date.

Atmospheric Implications. The poor nucleophilicity of 2MT suggests that the formation of the observed $\text{C}_{10}\text{H}_{22}\text{O}_7$ dimers and higher-order oligomers in IEPOX-derived SOA are only likely to be a result of *trans*- β -IEPOX + 2MT reaction for situations in which other atmospherically abundant nucleophiles are at low concentrations. Since this would seem to be a rather rare SOA composition situation, *trans*- β -IEPOX + 2MT nucleophile addition reactions are not likely to help rationalize the recent studies that have suggested that the majority of IEPOX-derived SOA is comprised of lower volatility dimeric and oligomeric components. While it is possible that the solution nonideality of atmospheric aerosols may lead to different relative nucleophilicities than those determined in the present work, our previous studies on the relative nucleophilicities of inorganic ions as a function of ionic strength did not reveal a strong effect.³⁴ Ultimately, further bulk solution and aerosol-specific mechanistic studies will likely be needed to help clarify the chemical reactions that can lead to the formation of dimers and oligomers in *i*SOA.

While the kinetics of the *trans*- β -IEPOX + 2MT reaction appears to be insufficient to rationalize extensive oligomerization in IEPOX-derived SOA, the chemical shift trends and assignments presented here may aid in future attempts to synthesize analytical standards, which are needed to confirm the molecular constituents of *i*SOA. Such standard preparation efforts will likely also need to consider the many structural and stereoisomer complications of oligomer formation uncovered by the present work.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b05247.

Bulk solution conditions, NMR assignments, and ^{13}C NMR chemical shift differences for each of the nucleophile + epoxide systems (PDF)

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Notes

The authors declare no competing financial interest.

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