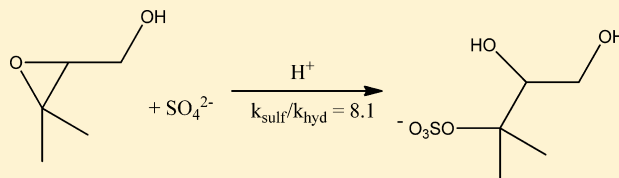


# Organosulfate and Nitrate Formation and Reactivity from Epoxides Derived from 2-Methyl-3-buten-2-ol

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**ABSTRACT:** Recent work has suggested that 2-methyl-3-buten-2-ol (MBO)-derived epoxide intermediates are responsible for some of the molecular species commonly found in ambient secondary organic aerosol (SOA). Nuclear magnetic resonance techniques were used to study the reaction kinetics and products of two potential MBO-derived epoxides under acidic solution conditions in the presence of sulfate and nitrate nucleophiles. These epoxides were found to undergo reasonably fast acid-catalyzed reaction at typical SOA acidities and to produce a variety of organosulfate and nitrate species. This finding supports a previous supposition that 3-methylbutane-1,2,3-triol and at least some of the MBO-derived organosulfates previously detected on SOA are formed from the reactions of these epoxides. In general, the particular MBO-derived organosulfates and nitrates produced from MBO-derived epoxides and their respective stability toward hydrolysis were similar to those found for isoprene-derived epoxides; the nucleophilic reactions were observed to be quite regioselective, and the tertiary addition product species were found to hydrolyze on atmospherically relevant time scales.



## INTRODUCTION

Biogenic volatile organic compounds (BVOCs) are known to form secondary organic aerosol (SOA), which is a critical component in air quality and global climate change models.<sup>1</sup> Recent studies have shown that the abundant BVOC, 2-methyl-3-buten-2-ol (MBO), is capable of forming SOA, which has been found to consist of several major components: 3-methylbutane-1,2,3-triol (also known as 2,3-dihydroxyisopentanol, DHIP) and organosulfates.<sup>2–5</sup> By analogy to isoprene, where both laboratory studies of isoprene-derived SOA-phase chemistry<sup>6–10</sup> and field observations of SOA<sup>7,11,12</sup> for isoprene-dominated situations have uncovered evidence that many of the individual chemical species observed are the result of the SOA-phase reactions of isoprene epoxydiols (IEPOX),<sup>13</sup> it has been proposed that MBO-derived SOA formation may also be driven by the formation of epoxide intermediates.<sup>4</sup> Zhang et al. have proposed an epoxide-forming mechanism<sup>4</sup> for the OH-initiated oxidation of MBO, which is given in Figure 1.

For the SOA processes involving epoxide intermediates, it has been postulated<sup>16–9</sup> that the reactions of nucleophiles (electron rich species such as negatively charged inorganic ions and neutral oxygen-containing species) with the carbocation intermediates formed as a result of acid-catalyzed epoxide ring opening are the key to understanding the variety of products formed. In a recent study, Zhang et al. synthetically prepared one of the potential MBO-derived epoxide intermediates (3,3-dimethyloxiran-2-yl)methanol (MBO 2,3-epoxide) and carried out atmospheric chamber aerosol uptake studies.<sup>4</sup> It was demonstrated that MBO 2,3-epoxide was effectively taken up by acidic aerosol (but not by neutral aerosol), and DHIP and three isomeric organomonosulfate products were characterized. The latter result is unexpected, as at most two organomonosulfate products are expected from nucleophilic attack on the two epoxide carbon

atoms in MBO 2,3-epoxide. Further, previous studies of nucleophilic reactions for IEPOX compounds have suggested that these reactions can be highly regioselective such that only one isomer product (from preferred nucleophilic attack on only one of the two epoxide carbon atoms) is often observed.<sup>8</sup> Ambient SOA samples were also analyzed in the Zhang et al. study, and DHIP and the same three organosulfate isomers were also observed.<sup>4</sup> Therefore, it is of interest to directly establish the kinetic feasibility of the MBO-derived epoxide reactions under typical SOA acidities and to determine the isomer-specific products formed from the MBO-derived epoxides.

In this paper, we report measurements of the reaction kinetics of the aqueous-phase acid-catalyzed reactions of both MBO 2,3-epoxide and 2-(oxiran-2-yl)propan-2-ol (MBO 3,4-epoxide) in the presence of both sulfate and nitrate nucleophiles using nuclear magnetic resonance (NMR) as the analytic technique. We report fully isomer-specific NMR assignments of the various products that are observed, in addition to information on the kinetic stability of these products. These results are then used to determine kinetic schemes for the reactions of MBO-derived epoxides and their reaction products so that the atmospheric relevance of these reactions can be directly addressed.

## EXPERIMENTAL SECTION

**Synthesis of (3,3-Dimethyloxiran-2-yl)methanol (MBO 2,3-Epoxide).** The preparation of MBO 2,3-epoxide was based on a recently published procedure.<sup>4</sup> MBO 2,3-epoxide was

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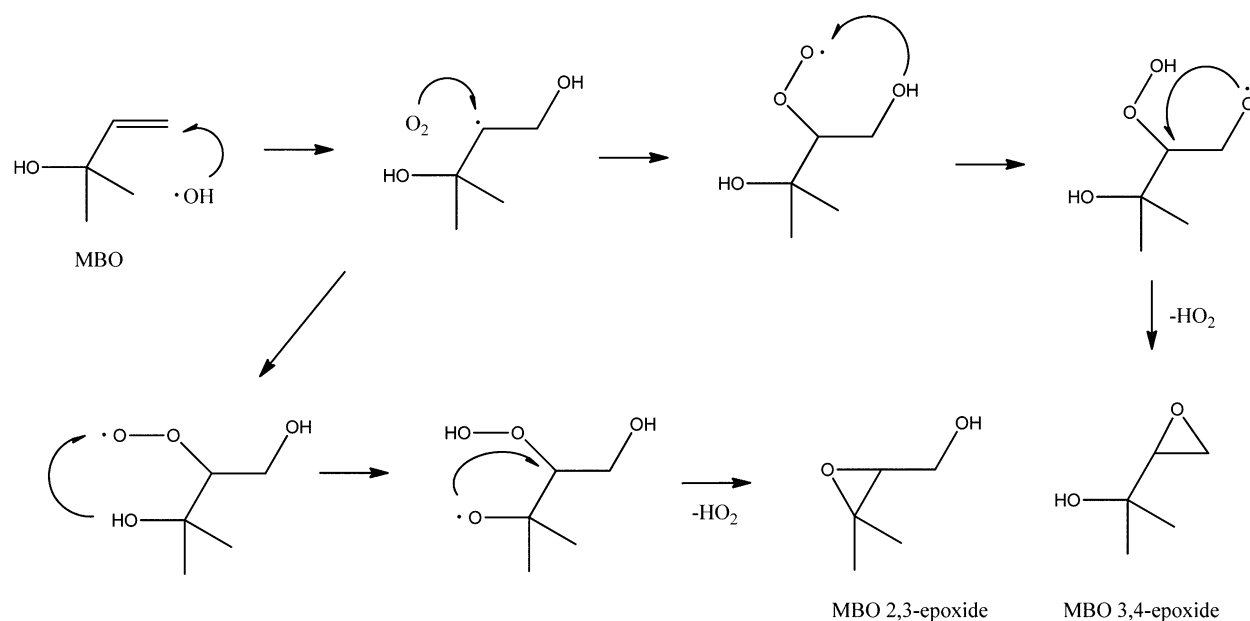


Figure 1. Proposed epoxide formation mechanism from MBO.<sup>4</sup>

prepared by slowly adding 11.7 g (52 mmol) of *m*-chloroperbenzoic acid (mCPBA, 77%, Sigma-Aldrich) to a mixture consisting of 4.5 g (52 mmol) of 3-methyl-2-buten-1-ol and 60 mL of acetonitrile and then stirring at room temperature for 1 week. The solution was filtered after being cooled to  $-20$  °C, and the acetonitrile was removed under reduced pressure at 25 °C. The residue was purified by flash chromatography (6 in. column, SiO<sub>2</sub>, 2:1 hexanes/diethyl ether mobile phase) to give the final MBO 2,3-epoxide product. The purity of the final product was confirmed by comparing the <sup>1</sup>H NMR spectrum to previously reported spectra.<sup>4,14</sup>

**Synthesis of 2-(Oxiran-2-yl)propan-2-ol (MBO 3,4-Epoxide).** MBO 3,4-epoxide was prepared by slowly adding 11.8 g (53 mmol) of mCPBA to a mixture consisting of 4.5 g of MBO and 60 mL of acetonitrile and then stirring at room temperature for 1 week. The solution was filtered after being cooled to  $-20$  °C, and the acetonitrile was removed under reduced pressure at 25 °C. The residue was purified by flash chromatography (10 in. column, SiO<sub>2</sub>, 3:1 hexanes/diethyl ether followed by 2:1 hexanes/diethyl ether followed by pure diethyl ether mobile phases) to give the purified MBO 3,4-epoxide. The purity of the final product was confirmed by comparing the <sup>1</sup>H NMR spectrum to a previously reported spectrum.<sup>15</sup>

**Synthesis of 3-Methylbutane-1,2,3-triol (2,3-Dihydroxyisopentanol, DHIP).** DHIP was prepared by adding 1.0 mL of MBO 2,3-epoxide to 25 mL of 0.05 M HClO<sub>4</sub> and stirring the mixture for 10 min. The HClO<sub>4</sub> was neutralized by adding 1.0 M NaOH until the pH of the solution reached 7.0. The water was removed under reduced pressure at 40 °C. The triol was identified and its purity confirmed via <sup>1</sup>H, <sup>13</sup>C, and HMQC<sup>16</sup> NMR spectroscopy.

**Bulk Aqueous Solution Preparation.** Bulk aqueous solutions were prepared with varying acid, sulfate, and nitrate concentrations. All experiments were carried out in deuterated solvents, which were necessary for NMR locking purposes. These solutions were prepared using commercially available 96–98 wt % D<sub>2</sub>SO<sub>4</sub> (Sigma-Aldrich), 70 wt % DNO<sub>3</sub> (Sigma-Aldrich), 99.9% D<sub>2</sub>O (Cambridge Isotope Laboratories, Inc.), Na<sub>2</sub>SO<sub>4</sub> (Sigma-Aldrich), and NaNO<sub>3</sub> (Sigma-Aldrich). To

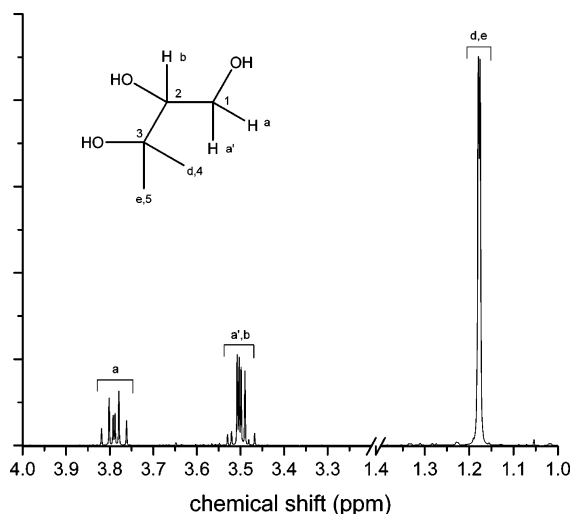
initiate the chemical process, the epoxides were added to the solutions and stirred for 1–3 min to ensure solution homogeneity before they were transferred to an NMR tube for subsequent analysis.

**NMR Product Identification and Quantitation.** All NMR spectra were collected on a Varian 400 MHz instrument. The <sup>1</sup>H chemical shifts were calibrated relative to HDO (4.79 ppm) and the <sup>13</sup>C chemical shifts were calibrated relative to the methyl groups (0.0 ppm) of 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS). The relative amounts of reaction reactants and products were calculated by peak integration of unique protons for each species.

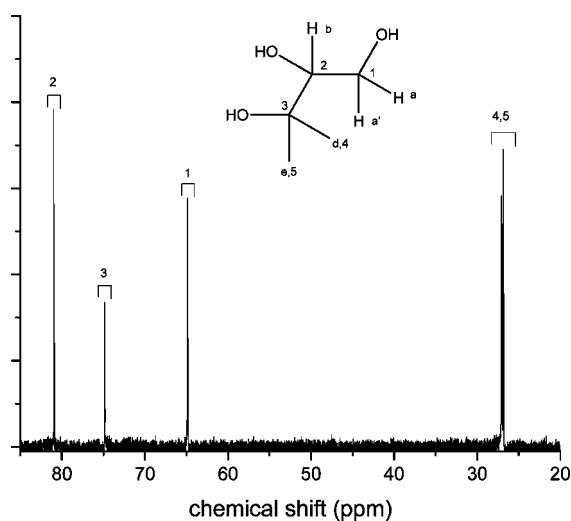
## RESULTS AND DISCUSSION

**DHIP NMR Assignment.** Previous NMR-based investigations of organosulfate and nitrate species were aided by the existence of systematic <sup>1</sup>H chemical shift differences between polyol species and species in which one or more of the alcohol groups were replaced by a nitrate or sulfate functional group. Therefore, a full nuclei-specific assignment of the NMR spectra of the DHIP anticipated product of the hydrolysis of both MBO epoxides, was carried out as a prelude to the NMR identification of MBO-derived sulfates and nitrates. Figures 2, 3, and 4 contain the <sup>1</sup>H, <sup>13</sup>C, and HMQC NMR spectra for DHIP, along with the nuclei-specific assignments. Though the <sup>13</sup>C spectrum was straightforward to interpret, the HMQC spectrum was very important in making the <sup>1</sup>H assignments, as this spectrum clearly shows coincidental identical chemical shift values for protons a' and b, and chemical inequivalence of protons a and a'.

**Product Identification of the Nucleophilic Reactions of Sulfate and Nitrate with MBO 2,3-Epoxide.** A partial <sup>1</sup>H NMR assignment was previously performed in our lab, which ascertained that the reactions of both sulfate and nitrate with MBO 2,3-epoxide lead to a single species, the tertiary nucleophilic addition product.<sup>8</sup> Because of the specific interest in determining the total number of organosulfate isomers that can form from MBO in the present work, a new complete <sup>1</sup>H NMR assignment was performed and the outcome of this analysis is given in Figure 5. As expected for the tertiary sulfate



**Figure 2.**  $^1\text{H}$  NMR spectrum of DHIP in  $\text{D}_2\text{O}$  (calibrated relative to HDO at 4.79 ppm).



**Figure 3.**  $^{13}\text{C}$  NMR spectrum of DHIP in  $\text{D}_2\text{O}$  (calibrated relative to DSS at 0.0 ppm).

addition product, the methyl group protons on the carbon atoms adjacent to the sulfate group (d-st and e-st) are shifted by about 0.3 ppm from the corresponding polyol protons (d and e), matching the systematic adjacent sulfate shift observed for other previously studied sulfate species.<sup>17,18</sup> The other tertiary sulfate addition product protons have very similar, but still resolvably different, chemical shifts to the corresponding polyol protons due to the less proximate location of the sulfate functional group to these protons. As there are no other features in the  $^1\text{H}$  NMR spectrum, the present analysis confirms the previous conclusion that the tertiary sulfate addition product is the sole product (any undetected products are estimated to be present at less than 1% of the concentration of total products measured) of the MBO 2,3-epoxide + sulfate reaction.

A similar analysis of the  $^1\text{H}$  NMR spectrum for the reaction of MBO 2,3-epoxide with nitrate also led to the conclusion that a tertiary nitrate addition product is the regioselective product. The actual nucleophilic addition mechanism operating in this case may be either a  $\text{S}_{\text{N}}-1$ - or  $\text{S}_{\text{N}}-2$ -type mechanism (the idealized sequential and concerted mechanisms, respectively) or a mechanism that is better described as being intermediate

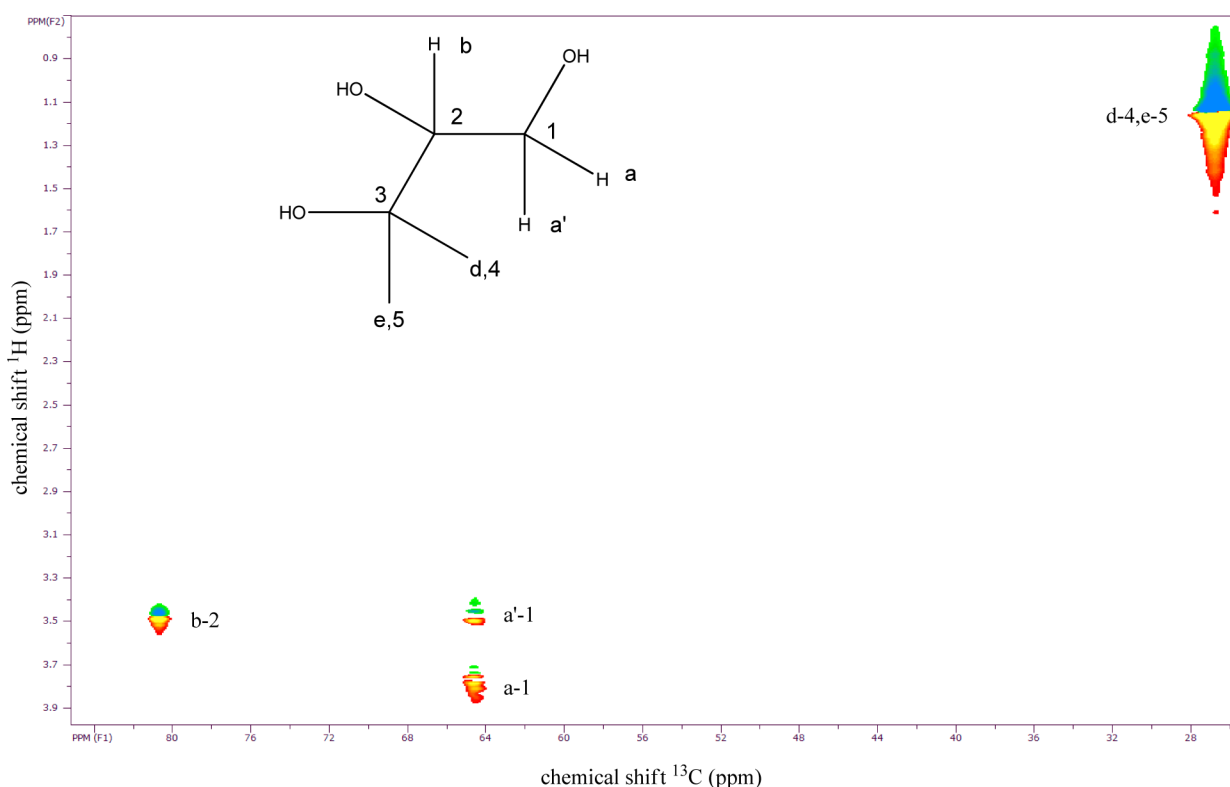
between these textbook cases.<sup>19–21</sup> The fact that the tertiary addition product was observed to be the sole product lends some support to the existence of a mechanism with partial  $\text{S}_{\text{N}}-1$ -type character, as this pathway is predicated on the stability of a tertiary carbocation intermediate that is the result of an initial acid-catalyzed ring opening step.

The relative integrations of the isomer specific peaks were used to determine organosulfate and nitrate yields for experiments carried out at 0.25 M  $\text{D}_2\text{SO}_4/0.75$  M  $\text{Na}_2\text{SO}_4$  or 0.25 M  $\text{MDNO}_3/0.75$  M  $\text{DNO}_3$ , respectively. These yields can be converted to a nucleophilic strength scale that is relative to the corresponding hydrolysis reaction ( $k_{\text{sulf}}/k_{\text{hydr}}$  or  $k_{\text{nit}}/k_{\text{hydr}}$ ),

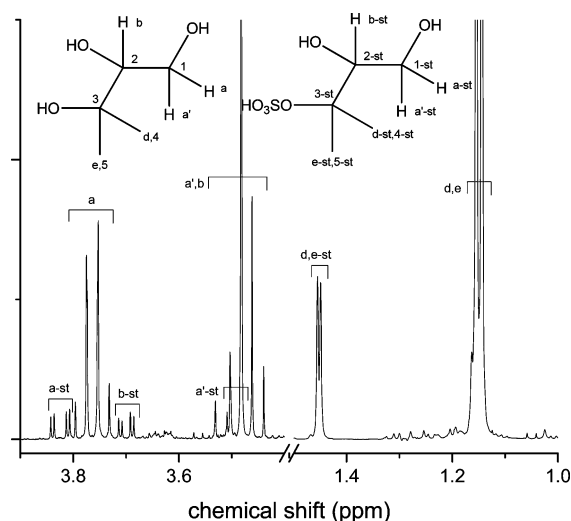
$$\frac{\text{ion nucleophilic strength}}{\text{water nucleophilic strength}} = \frac{k_{\text{ion}}}{k_{\text{hydr}}} = \frac{(Y_{\text{ion product}}/X_{\text{ion}})}{(Y_{\text{hydrolysis product}}/X_{\text{H}_2\text{O}})} \quad (1)$$

where  $Y$  is the relevant product mole fraction as measured via NMR quantitation methods at the end of the reaction and  $X$  is the relevant reactant nucleophile mole fraction as determined from the initial solution composition. Because the nitrate formed from MBO 2,3-epoxide was unstable with respect to hydrolysis (which is discussed in detail in a subsequent section) on the time scale of the initial NMR measurement, the  $Y$  value for this case was estimated from the first order loss equation for this species by extrapolating to time zero of the reaction. For the sulfate solutions, the extended aerosol inorganics model (E-AIM) was used to calculate the ion concentrations.<sup>22</sup> The nucleophilic strength ratios for sulfate and nitrate relative to water for MBO 2,3-epoxide are given in Table 1 and are compared to those determined for similar isoprene-derived epoxides.<sup>8</sup> As expected, the nucleophilic strengths scale according to the charge of the attacking nucleophile:  $\text{SO}_4^{2-} > \text{NO}_3^- > \text{H}_2\text{O}$ . It may be seen that the nucleophile strengths of both sulfate and nitrate (relative to water) are somewhat less for MBO 2,3-epoxide than for the structurally similar IEPOX-4.

**Product Identification of the Nucleophilic Reactions of Sulfate with MBO 3,4-Epoxyde.** The  $^1\text{H}$  NMR spectrum showing the products of the reaction of MBO 3,4-epoxyde with sulfate given in Figure 6. As expected for the primary sulfate addition product, the protons on the carbon atom directly bonded to the sulfate group (a-sp and a'-sp) are shifted by about 0.5 ppm from the corresponding polyol protons (a and a'), matching the systematic directly bonded sulfate shift observed for other previously studied sulfate species.<sup>17,18</sup> Additionally, the proton on the carbon atom adjacent to the sulfate group (b-sp) are shifted by about 0.3 ppm from the corresponding polyol proton (b), matching the previously cited systematic adjacent sulfate shift observed for other previously studied sulfate species. The other primary sulfate addition product protons (d-sp and e-sp) are resolved but have a smaller chemical shift relative to the polyol protons (d and e) due to the less proximate location of the sulfate functional group to these protons. As there are no other features in the  $^1\text{H}$  NMR spectrum, the present analysis indicates that the primary sulfate addition product is the sole product (any undetected products are estimated to be present at less than 1% of the concentration of total products measured) of the MBO 3,4-epoxyde + sulfate reaction. For nucleophilic reactions with primary and secondary substituted carbon atoms,  $\text{S}_{\text{N}}-2$ -type mechanisms are expected.<sup>19</sup> In this concerted mechanism, the steric hindrance encountered by the attacking nucleophile is often predictive of the trends observed in relative nucleophilic strength. Because sulfate is expected to experience higher steric hindrance in nucleophilic attack at the secondary position



**Figure 4.** HMQC NMR spectrum of DHIP in  $D_2O$  (calibrated relative to HDO at 4.79 ( $^1H$ ) and DSS at 0.0 ppm ( $^{13}C$ )).



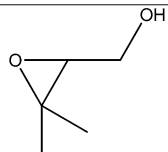
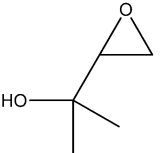
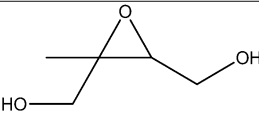
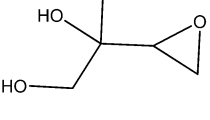
**Figure 5.**  $^1H$  NMR spectrum of products formed from the reaction of MBO 2,3-epoxide in 1 M sulfate solution (calibrated relative to HDO at 4.79 ppm).

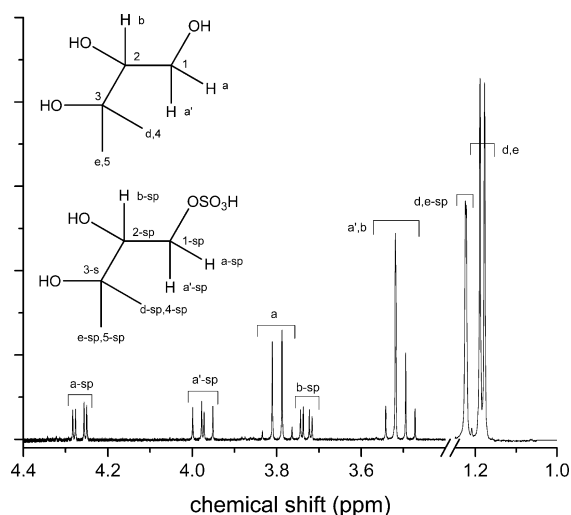
(relative to the primary position) in MBO 3,4-epoxide, a  $S_{N-2}$ -type mechanism is capable of explaining the experimental observation of a sole primary addition product. The relative integrations of the isomer specific peaks were used to determine the primary sulfate addition product yields and thus the nucleophilic strength ratio for sulfate addition relative to water (given in Table 1). As was observed for isoprene-derived epoxides,<sup>8</sup> the sulfate nucleophilic strength ratio for primary addition was observed to be greater than that for tertiary addition for the MBO-derived epoxides.

**Product Identification of the Nucleophilic Reactions of Nitrate with MBO 3,4-Epoxyde.** The  $^1H$  NMR spectrum

showing the products of the reaction of MBO 3,4-epoxide with nitrate given in Figure 7. As expected for the primary nitrate addition product, the protons on the carbon atom directly bonded to the nitrate group (a-np and a'-np) are shifted by about 1.0 ppm from the corresponding polyol protons (a and a'), matching the systematic directly bonded nitrate shift observed for other previously studied nitrate species.<sup>17,18</sup> Additionally, the proton on the carbon atom adjacent to the nitrate group (b-np) is shifted by about 0.3 ppm from the corresponding polyol proton (b), matching the previously cited systematic adjacent nitrate shift observed for other previously studied nitrate species. The other primary nitrate addition product protons (d-np and e-np) are resolved but have a smaller chemical shift relative to the polyol protons (d and e) due to the less proximate location of the nitrate functional group to these protons. In contrast to the MBO 3,4-epoxide + sulfate reaction results, the NMR spectrum also indicates the presence of the secondary nitrate addition product. In particular, the 1.0 ppm shift of the secondary proton on the nitrate addition product (b-ns) from the polyol secondary proton (b) indicates the specific location of the nitrate group for this isomer. The fact that both primary (major) and secondary (minor) nitrate addition products are formed in the reaction of MBO 3,4-epoxide + nitrate indicates the existence of a more complex  $S_{N-2}$ -type mechanism for this reaction. Presumably, the smaller size of the nitrate nucleophile (relative to sulfate) lessens the importance of steric hindrance in the preferred position of nucleophilic attack on MBO 3,4-epoxide, such a secondary addition pathway becomes competitive with the primary addition pathway with the result that the overall nucleophilic addition of nitrate is not strictly regioselective. The relative integrations of the isomer specific peaks were used to determine primary and secondary nitrate addition product yields and thus the nucleophilic strength ratios for nitrate addition relative to water (given in Table 1). As was observed for isoprene-derived

Table 1. Nucleophilic Strength Ratios for MBO- and Isoprene-Derived Epoxides

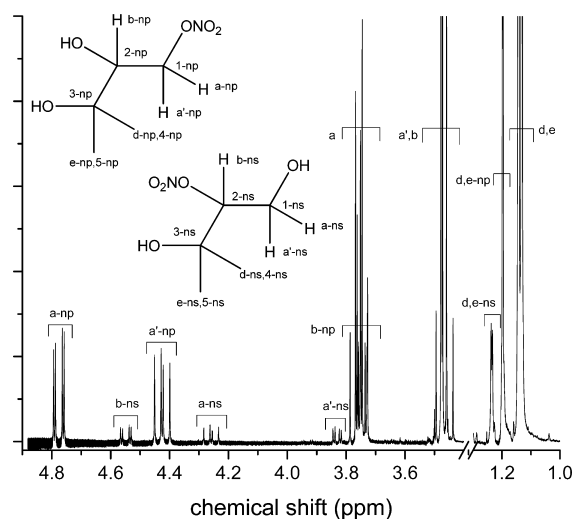
Parent hydrocarbon	Epoxide reactant	$k_{\text{sulf}}/k_{\text{hydr}}$	$k_{\text{nit}}/k_{\text{hydr}}$
MBO (present work)	 MBO 2,3-epoxide	8.1 (tertiary)	4.7 (tertiary)
	 MBO 3,4-epoxide	30 (primary)	9.3 (primary) 2.7 (secondary)
Isoprene <sup>8</sup>	 IEPOX-4	21 (tertiary)	10 (tertiary)
	 IEPOX-1	67 (primary)	21 (primary)



**Figure 6.**  $^1\text{H}$  NMR spectrum of products formed from the reaction of MBO 3,4-epoxide in 1 M sulfate solution (calibrated relative to HDO at 4.79 ppm).

epoxides, the nitrate nucleophilic strength ratio for primary addition was observed to be greater than that for tertiary addition for the MBO-derived epoxides. However, no secondary nitrate addition product was observed in the previous study of isoprene-derived epoxides.<sup>8</sup>

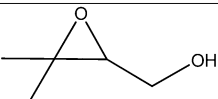
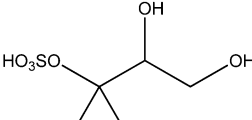
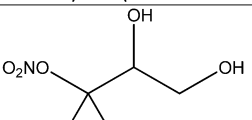
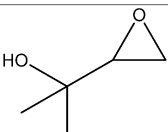
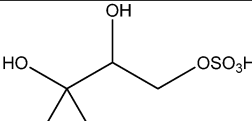
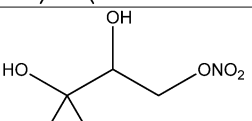
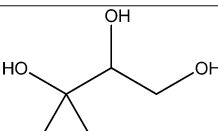
**Hydrolysis Kinetics for MBO 2,3- and 3,4-Epoxide.** The acid-catalyzed hydrolysis rate constants for the MBO epoxides were determined via a pseudo-first-order approach (the MBO epoxide first-order loss rate constants were determined as a function of acid catalyst concentration). The acid-catalyzed second-order rate constants are given in Table 2. The present



**Figure 7.**  $^1\text{H}$  NMR spectrum of products formed from the reaction of MBO 3,4-epoxide in 1 M nitrate solution (calibrated relative to HDO at 4.79 ppm).

MBO 2,3-epoxide hydrolysis rate constant is in good agreement with a previous measurement ( $0.41$  vs  $0.48\text{ M}^{-1}\text{ s}^{-1}$ ),<sup>10</sup> and the newly determined 3,4-MBO epoxide hydrolysis rate constant was well predicted by a previously constructed epoxide structure–reactivity model ( $0.0044$  vs  $0.0045\text{ M}^{-1}\text{ s}^{-1}$ ).<sup>10</sup> The MBO 2,3-epoxide hydrolysis rate constant is much larger than the MBO 3,4-epoxide hydrolysis rate constant, presumably due to the involvement of the much more favorable tertiary carbocation intermediate that is a key species in the MBO 2,3-epoxide hydrolysis mechanism.

Table 2. Experimentally Determined Rate Constants (with 1 $\sigma$  Statistical Error Given)

Species	$k_{H^+}$ ( $M^{-1} s^{-1}$ )	$k_{hydro}^{neutral}$ ( $s^{-1}$ )	$k_{sulfate\ esterif}^{75\ wt\ \% D_2SO_4}$ ( $s^{-1}$ )
	$4.075 \pm 0.0035 \times 10^{-1}$		
		$4.42 \pm 0.20 \times 10^{-6}$	
		$2.10 \pm 0.14 \times 10^{-3}$	
	$4.36 \pm 0.13 \times 10^{-3}$		
		$< 2 \times 10^{-7}$	
		$< 2 \times 10^{-7}$	
			$1.792 \pm 0.047 \times 10^{-4}$

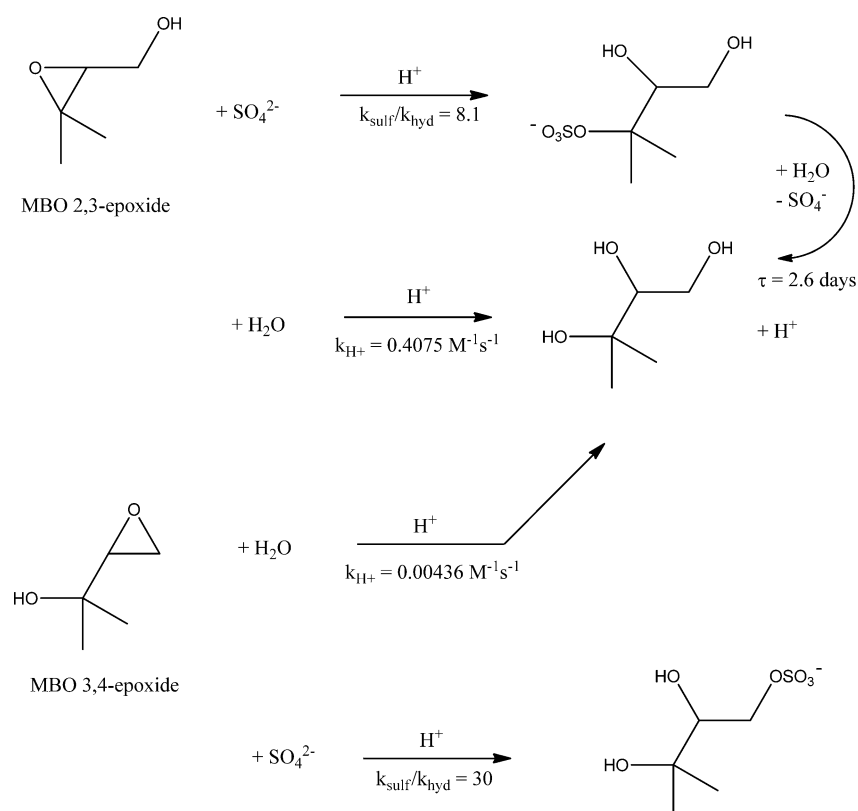
**Hydrolysis Kinetics for MBO-Derived Organosulfate and Nitrates.** In previous work, it was determined that tertiary organosulfates and nitrates are capable of kinetically facile hydrolysis under typical acidities, whereas primary and secondary organosulfates are stable against hydrolysis at even higher than atmospherically relevant acid concentrations.<sup>8,9</sup> To determine whether hydrolysis might also be an atmospherically relevant fate for MBO-derived organosulfates and nitrates, the reaction solutions used to study the formation of organosulfates and nitrates from MBO were monitored for extended time periods (beyond the point at which the epoxide reactions have gone to completion) to look for evidence of hydrolysis processes. As was found in the earlier work on isoprene-derived epoxides,<sup>8</sup> both the tertiary MBO-derived organosulfate and nitrate species were found to undergo an acid-independent hydrolysis process, whereas no detectable hydrolysis was detected over a 1 week time scale at any acid concentration for the primary organosulfate and nitrate species. The first-order neutral hydrolysis rate constants for the tertiary species are given in Table 2 (as are upper limit rate constant estimates for the primary species). As was found previously for isoprene-derived organosulfates and nitrates,<sup>8</sup> the tertiary nitrate species was found to hydrolyze much faster than the corresponding tertiary sulfate species. The fact that none of the other product species was observed to hydrolyze over a 1

week monitoring period is also consistent with previous studies of isoprene-derived organosulfates and nitrates.

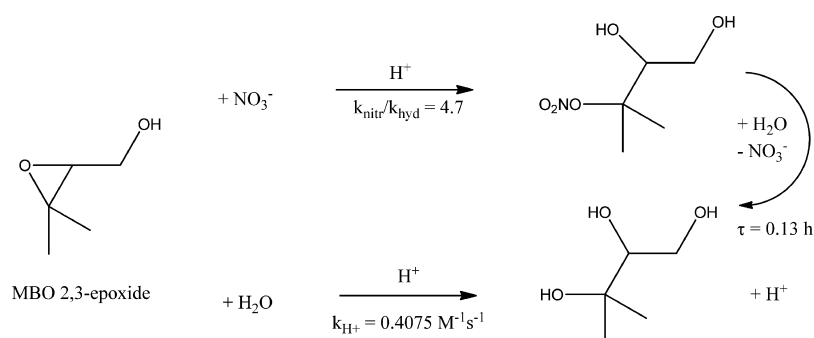
**Aqueous-Phase Mechanisms.** On the basis of the product identification study for the reactions of MBO-derived epoxides in aqueous sulfate and nitrate solutions and the MBO epoxide and MBO-derived organosulfate and nitrate hydrolysis kinetics measurements, kinetics schemes for these reactions were developed. The kinetics schemes for the reactions of aqueous sulfate solutions with MBO-derived epoxides are given in Figure 8, and kinetics schemes for the reactions of aqueous nitrate solutions with MBO 2,3-epoxide and MBO 3,4-epoxide are given in Figures 9 and 10, respectively.

**Sulfate Esterification Kinetics of DHIP.** To investigate the potential relevance of sulfate esterification reactions as a source of MBO-derived organosulfates, the sulfate esterification rate constant for DHIP was determined via a pseudo-first-order approach (the DHIP first-order loss rate constants was measured at a fixed sulfuric acid composition, 75 wt %  $D_2SO_4$ ). This particular acid composition was chosen for study because it was used in a previous kinetic study of sulfate esterification reactions for various alcohol reactants.<sup>23</sup> The first-order rate constant for the sulfate esterification of DHIP in 75 wt %  $D_2SO_4$  is reported in Table 2.

**Atmospheric Implications.** Zhang et al. have used measurements of the concentrations of the ionic components



**Figure 8.** Kinetics schematic for reactions of MBO-derived epoxides in aqueous sulfate solutions.

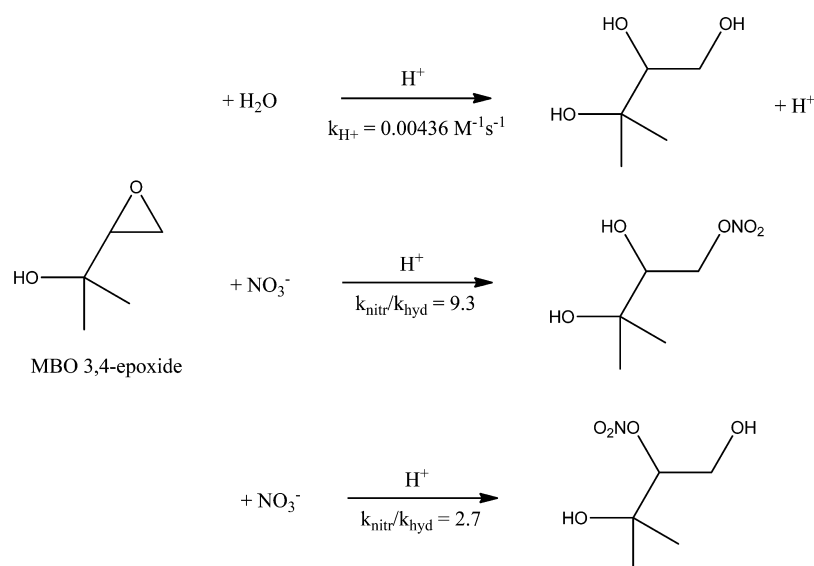


**Figure 9.** Kinetics schematic for reactions of MBO 2,3-epoxide in aqueous nitrate solutions.

of the aerosols (such as sulfate, nitrate, chloride, and ammonium) to estimate the acidity ( $[\text{H}^+_{\text{aerosol}}]$ ) of SOA particles in the Pittsburgh area.<sup>24</sup> In their measurements, the pH of SOA usually ranged from about 4.0 to 1.5, but values as low as 0 were sometimes observed. The aqueous-phase hydrolysis reactions of MBO 2,3-epoxide are predicted to occur on an atmospherically relevant time scale ( $\tau = 6.8 \text{ h}$ ) even at  $\text{pH} = 4.0$ , whereas more acidic conditions ( $\text{pH} = 2$ ) are necessary for MBO 3,4-epoxide to react on the same 6.8 h time scale. Therefore, the present results confirm that both MBO-derived epoxides react quickly enough under typical aerosol acidities to serve as precursors for the MBO-related products observed on ambient aerosols (DHIP and organosulfates).<sup>4</sup>

Although the sulfate and nitrate relative nucleophilic strengths for attack on MBO-derived epoxides were found to be somewhat less than for the isoprene-derived epoxides<sup>8</sup> (see Table 1 for comparison), their large nucleophilic strengths relative to water indicate that the MBO epoxides are potential precursors for organosulfates and nitrates on ambient aerosol. However, the

present work suggests that the two likely MBO-derived epoxides are expected to produce only two organosulfate isomers as initial products (the tertiary and primary sulfate addition product species as shown in Figure 8), whereas all three organonitrate isomers were observed as initial products (the tertiary nitrate addition product forms from MBO 2,3-epoxide as shown in Figure 9 and the primary and secondary organonitrate addition products form from MBO 3,4-epoxide as shown Figure 10). On the one hand, the tertiary organosulfate hydrolysis was found to occur on a time scale ( $\tau = 2.6 \text{ days}$ ) similar to SOA lifetimes; therefore, the tertiary organosulfate species is likely “metastable” under atmospheric conditions. On the other hand, the tertiary organonitrate hydrolysis was found to be so fast ( $\tau = 0.13 \text{ h}$ ) that this species may not be expected to exist in significant concentrations on SOA under atmospheric conditions. The primary organosulfate and primary and secondary organonitrate species are expected to be stable against hydrolysis ( $\tau > 58 \text{ days}$ ) over atmospherically relevant time scales.



**Figure 10.** Kinetics schematic for reactions of MBO 3,4-epoxide in aqueous nitrate solutions.

As noted in the Introduction, Zhang et al. have detected the presence of three distinct MBO-derived organosulfate isomers in both atmospheric chamber experiments using MBO 2,3-epoxide and in ambient SOA samples.<sup>4</sup> Because the present work determined that only one organosulfate isomer was formed in the aqueous sulfate reaction with MBO 2,3-epoxide, it seems likely that there are other sources of MBO-derived organosulfates in both the previous laboratory and ambient SOA measurements. In the case of ambient SOA, it is likely that MBO 3,4-epoxide is also a precursor to at least some of the three detected organosulfates. However, the present work has determined that the aqueous sulfate reaction with the MBO 3,4-epoxide only produces one additional organosulfate isomer, the primary addition product. Therefore, to explain the presence of three distinct MBO-derived organosulfate isomers observed in ambient SOA seems to require an additional mechanism. For example, the Zhang et al. experiments were performed with very low water content; it is possible that such different effective solution conditions in the aerosol particles could favor the formation of the secondary sulfate addition product. Although radical-initiated processes in the aerosol phase<sup>25</sup> could potentially lead to the formation of different organosulfate isomers than are formed from the acid-catalyzed epoxide mechanism presently under study, the fact that Zhang et al. observed the same number of isomers in their dark atmospheric chamber SOA experiments as in their analysis of ambient SOA samples<sup>4</sup> suggests that such processes are not the key to understanding this discrepancy.

Although the epoxide reactions with sulfate were found to be quite regiospecific (only one of two possible isomers was observed from each of the reactions of MBO 2,3- and 3,4-epoxide), sulfate esterification reactions of DHIP are likely to be much less regiospecific and up to three monosulfate isomers may be produced. However, a previous study of the kinetics of sulfate esterification reactions of alcohols with aqueous sulfate solutions indicated that these reactions are likely to be too slow to effectively form organosulfates under typical atmospheric conditions (in particular, typical SOA acidities appear to be much too low for this acid-catalyzed process to be relevant).<sup>23</sup> The value of the sulfate esterification rate constant in 75 wt % sulfuric acid for DHIP in the present work ( $1.8 \times 10^{-4} \text{ s}^{-1}$ ) was

found to be slightly less than the rate constants determined for the sulfate esterification reactions of similar polyols at 75 wt % sulfuric acid: ethylene glycol ( $7.3 \times 10^{-4} \text{ s}^{-1}$ ) and butane-1,2,3,4-tetraol ( $7.2 \times 10^{-4}$ ).<sup>23</sup> Therefore, the sulfate esterification mechanism does not appear to be a kinetically feasible route to the formation of additional MBO-derived organosulfate isomers in the ambient atmosphere.

## CONCLUSION

Two potential MBO-derived epoxides, MBO 2,3- and 3,4-epoxide, were found to undergo reasonably fast acid-catalyzed reaction at typical SOA acidities and to produce a variety of organosulfate and nitrate species. This finding supports the previous supposition<sup>4</sup> that DHIP and at least some of the MBO-derived organosulfates previously detected on SOA<sup>3,5</sup> are likely the products of the reactions of these epoxides. In general, the particular MBO-derived organosulfate and nitrates produced from MBO-derived epoxides and their respective stability toward hydrolysis was similar to that found for isoprene-derived epoxides in that the nucleophilic reactions were observed to be quite regiospecific and the tertiary species were found to hydrolyze on atmospherically relevant time scales.<sup>8</sup> However, this regiospecificity for the MBO-derived epoxide reactions with aqueous sulfate solutions seems to suggest that these reactions alone cannot rationalize the three distinct MBO-derived organosulfate isomers detected on atmospheric chamber-generated and ambient SOA.

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### Notes

The authors declare no competing financial interest.

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