

## Article

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# Assessing the Potential for Diol and Hydroxy Sulfate Ester Formation from the Reaction of Epoxides in Tropospheric Aerosols

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Polyols and sulfate esters have recently been identified in the secondary organic aerosol (SOA) formed in the photooxidation of biogenic hydrocarbons both in the laboratory and under ambient atmospheric conditions. In the present study, the potential role of the reactions of epoxides in SOA to form diols and hydroxy sulfate esters is explored. Nuclear magnetic resonance methods were used to monitor the bulk reaction kinetics of the epoxide hydrolysis reactions for a number of simple epoxides. The experiments were carried out at various acid concentrations in order to confirm the acid-catalysis rate order and to determine the second-order rate constants for such reactions in aerosols under the previously studied laboratory conditions and under ambient atmospheric conditions. The measured rate constants depended systematically on the carbon substitution nature of the epoxide ring, with the tertiary epoxides characterized by the largest rate constants. The hydroxy sulfate yield was observed to depend linearly on the total sulfate concentration, with yields as high as 30% observed at high sulfate concentrations. Due to the large values of the observed rate constants, these reactions are expected to be efficient even for mostly neutralized tropospheric SOA, let alone the much more acidic SOA particles previously studied in laboratory experiments. Therefore, the epoxide hydrolysis mechanism appears to be a kinetically feasible route to the formation of the diols and hydroxy sulfate esters observed in the SOA resulting from the photooxidation of biogenic hydrocarbons.

## Introduction

It is well-known that secondary organic aerosol (SOA) is a key player in the atmospheric issues of air pollution (1) and global climate change (2). Recently, there has been extensive investigation of potential particle-phase processes that could be responsible for the enhanced SOA yields observed from the photochemical oxidation of various volatile organic compounds (VOCs). In particular, the role of acid-catalyzed chemical reactions as a route by which volatile compounds are converted to less volatile ones has been extensively investigated (3–14).

Organic sulfate ester products have been detected in laboratory investigations of the SOA formed from sulfuric acid seed particles and the products formed during the

photochemical oxidation of the biogenic compounds isoprene (5, 6),  $\alpha$ - and  $\beta$ -pinene (5, 7, 8), and limonene (9) in the presence of sulfuric acid seed particles. Nitrooxy sulfate esters products have also been detected in the  $\text{NO}_3$ -initiated photochemical oxidation of biogenic compounds (15, 16). Sulfate ester products have been identified in the interaction of glyoxal and pinonaldehyde with sulfuric acid aerosols (8, 17) and in the interaction of the isoprene photooxidation product glyoxal with ammonium sulfate aerosols (15, 18).

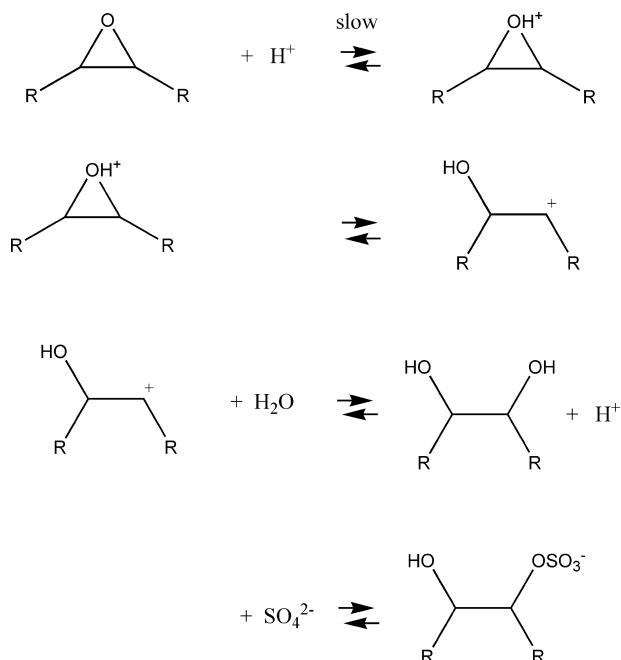
Sulfate ester products are particularly interesting potential SOA constituents, as they are likely to be nonvolatile and may be considered as “terminal” SOA compounds. Sulfate ester products arising from isoprene and  $\alpha$ - and  $\beta$ -pinene oxidation processes, as well as from oxidation products of primary plant material containing unsaturated fatty acid moieties and plant leaf volatiles, have also been identified in ambient SOA in the southeastern United States (5, 15); Bavaria, Germany (7); and K-puszt, Hungary (18). Recent measurements suggest that the contribution of sulfate esters to the total ambient aerosol mass might be high as 30% in some locations (15, 19), and their presence in rainwater (20) suggests that the sulfate esters play a potentially important role in wet deposition and cloud activation processes.

In previous work in our laboratory, we investigated the potential role of the reactions of alcohols with sulfuric acid aerosols as a route by which sulfate esters could be formed (21). Earlier work had indicated that sulfate esters are the exclusive product of the reaction of alcohols and sulfuric acid, although it appeared that very high sulfuric acid concentrations were needed to shift the equilibrium to favor sulfate ester products and to make the process kinetically efficient (22). While upper tropospheric aerosols are often composed of highly concentrated sulfuric acid, recent aerosol mass spectrometry (AMS) measurements of SOA in Pittsburgh, PA have indicated that partial neutralization of sulfuric acid by ammonia leads to aerosols with pH values that typically lie in the range from 1.5 to 4.0 (23). If these AMS-estimated acidity conditions are typical of lower tropospheric aerosols, our kinetics measurements indicated that the reactions between alcohols and sulfuric acid are unlikely to be kinetically efficient enough to explain the observation of sulfate esters in ambient SOA.

An alternative sulfate ester-forming mechanism was suggested by Iinuma et al., who proposed that the epoxides known to form in the oxidation of monoterpenes could react with sulfuric acid to form hydroxy sulfate esters (7). Since it is well-known that epoxides are rapidly hydrolyzed under mildly acidic conditions (24), it is possible that hydroxy sulfate esters could form under conditions in which sulfate can compete with  $\text{H}_2\text{O}$  for the role of the nucleophile in the traditional epoxide hydrolysis mechanism (shown in Figure 1). While this particular reaction has apparently not been previously investigated, the acid-catalyzed formation of hydroxy nitrate esters has been observed in the hydrolysis of epoxides in the presence of excess  $\text{NO}_3^-$  ions (25). The diol-forming pathway is also potentially atmospherically significant, as recent work on the SOA formed in the photooxidation of isoprene has invoked epoxide hydrolysis processes to explain the observation of polyols in the particle phase (26).

Epoxides have been observed as gas phase oxidation products in laboratory studies of the reaction of alkenes with various atmospheric oxidants. In all cases, the net effect of the oxidation is the addition of an oxygen atom across the double bond in the alkene. Epoxides are the major product of the reaction of alkenes with  $\text{O}(^1\text{P})$ ; for example, the reaction

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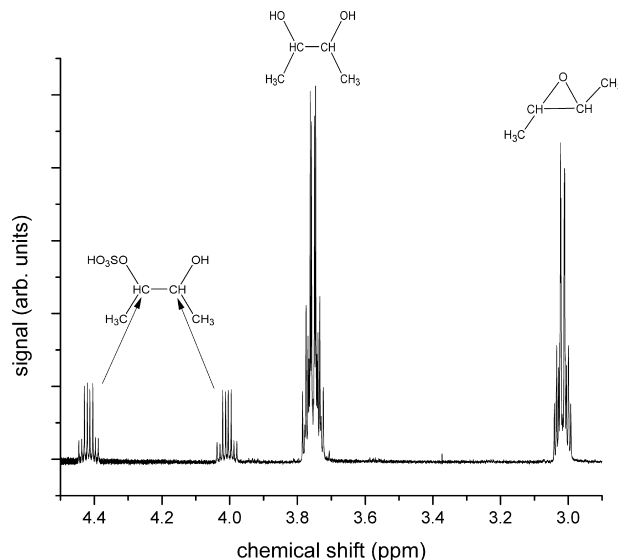
**FIGURE 1.** Proposed acid-catalyzed hydrolysis and hydroxy sulfate ester-forming mechanism.

of  $\text{O}(\text{P})$  with isoprene (27) and  $\alpha$ -pinene (28) follows an epoxide-producing pathway at nearly 80% yield. Epoxides have been observed as a minor product in the oxidation of variety of alkenes by ozone (28–34) and nitrate radical (35–39). For example, epoxide yields on the order of about 2–3% have been observed in the atmospheric pressure ozonolysis of isoprene (29, 30), 1,3-butadiene (29, 31), and  $\alpha$ -pinene (28, 32, 34). In the case of the  $\text{NO}_3$ -initiated production of epoxides, the product yields were found to vary substantially with pressure (35, 36), with yields as high as 15% reported for the  $\alpha$ -pinene system (38). Epoxides have also been observed in the OH-initiated oxidation of toluene (40, 41). The epoxidation of alkenes also has the effect of converting a water-insoluble species into a water-soluble one. For example, 1-butene has a water solubility of 0.02% by mass, while the epoxide of 1-butene has a water solubility of 9% by mass (42). Therefore, it is expected that aerosol epoxide concentrations will be limited by the rates of the gas uptake process, which will be largely determined by the gas phase epoxide concentration levels.

In the present study, the acid-catalyzed reactions of epoxides that are the potential products of the oxidation of several atmospherically abundant alkenes are investigated. Product yield and hydrolysis rate constant measurements for the epoxide reactions are performed using nuclear magnetic resonance (NMR) techniques. The nature of the acid catalysis and the effect of sulfate content on the observed hydroxy sulfate ester yields are investigated. On the basis of these mechanistic and kinetic parameters, the potential for diol and hydroxy sulfate ester formation from the reaction of epoxides in tropospheric aerosols is evaluated.

## Experimental Section

The experiments were performed with epoxides used as obtained from Sigma-Aldrich: 1,2-epoxybutane (99%), *trans*-2,3-epoxybutane (96%), 2-methyl-1,2-epoxypropane (97%), 2-methyl-2,3-epoxybutane (97%), and 2,3-dimethyl-2,3-epoxybutane (99%). For the hydrolysis kinetics measurements, solutions were prepared by adding a small volume (usually 25  $\mu\text{L}$ ) of the reactant epoxide (used as received from the vendor) to 5 mL of a  $\text{D}_2\text{SO}_4/\text{D}_2\text{O}$  solution (due to the solvent locking requirements of  $^1\text{H}$  NMR techniques, the experiments



**FIGURE 2.**  $^1\text{H}$  NMR spectrum collected during the reaction of *trans*-2,3-epoxybutane in 0.02 M  $\text{D}_2\text{SO}_4/1.0$  M  $\text{Na}_2\text{SO}_4/\text{D}_2\text{O}$ . All resonances are due to the internal hydrogen atoms in the reactant epoxide and in the product diol and hydroxy sulfate ester. The terminal methyl group proton resonances for the three species are located upfield at around 1.5 ppm (not shown).

were performed in  $\text{D}_2\text{SO}_4/\text{D}_2\text{O}$  solutions). Since these reactions are acid-catalyzed, there exists a possibility that the results obtained with the  $\text{D}_2\text{SO}_4/\text{D}_2\text{O}$  system would be different than those obtained with a  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  system. However, our previous study of this effect in the acid-catalyzed sulfate esterification of alcohols indicated little difference in the kinetics results for the two systems (21). For the product analysis experiments, differing amounts of  $\text{Na}_2\text{SO}_4$  were dissolved in the 5 mL of  $\text{D}_2\text{SO}_4/\text{D}_2\text{O}$  solutions before the epoxide was added. The sulfuric acid solutions were prepared by diluting commercially obtained 96 wt %  $\text{D}_2\text{SO}_4$  with  $\text{D}_2\text{O}$  (Sigma-Aldrich). Some experiments were also performed in similarly prepared  $\text{DCl}/\text{D}_2\text{O}$  solutions. After addition of all reactants, the solutions were vigorously mixed for 3 min. For the hydrolysis kinetics experiments, some of the solution was transferred to a 5 mm NMR tube, and the progress of the reaction was monitored with a 400 MHz NMR spectrometer at a constant temperature of  $297 \pm 1$  K. Although each NMR spectrum took only about 30 s to collect, the automated procedure that preceded the collection of each spectrum limited the time resolution of the data collection to about 2 min. For the product analysis experiments, the solution was stored for 24 h (to allow it to reach equilibrium) before the NMR analysis was performed. The relative epoxide concentrations (used for the hydrolysis kinetics analysis) were determined from integrations of the NMR signal from one set of chemically unique protons from each NMR spectrum in the time series. The relative diol and sulfate ester concentrations (used for the product analysis) were determined from integrations of the NMR signal arising from one set of chemically unique protons for each species, with the integration values normalized according to the number of protons contributing to each signal.

## Results and Discussion

**Identification of Reaction Products.** Figure 2 shows an NMR spectrum collected during the reaction of *trans*-2,3-epoxybutane in a 0.02 M  $\text{D}_2\text{SO}_4/1.0$  M  $\text{Na}_2\text{SO}_4/\text{D}_2\text{O}$  solution. The aerosol inorganics model (AIM) (43) was used to calculate the concentrations of all species for both the  $\text{D}_2\text{SO}_4/\text{D}_2\text{O}$  and  $\text{D}_2\text{SO}_4/\text{Na}_2\text{SO}_4/\text{D}_2\text{O}$  solutions. For this particular solution,

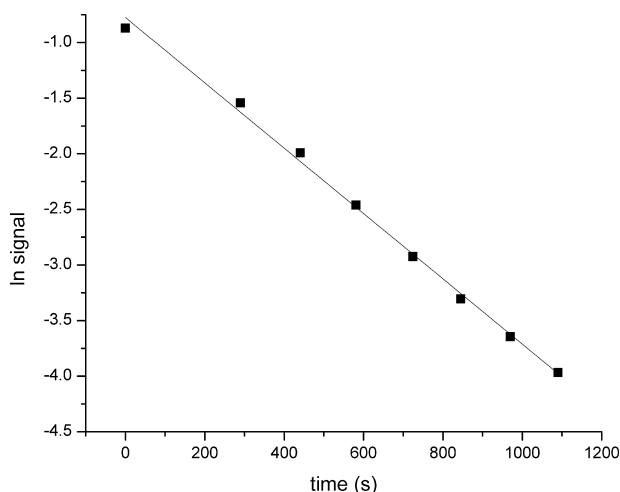


FIGURE 3. First-order kinetics analysis for the hydrolysis of *trans*-2,3-epoxybutane in 0.01 M D<sub>2</sub>SO<sub>4</sub>/D<sub>2</sub>O.

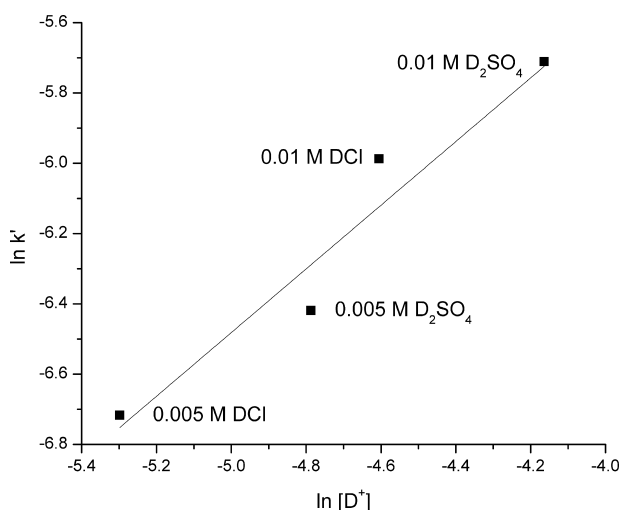


FIGURE 4. Acid-catalysis rate order analysis for the hydrolysis of *trans*-2,3-epoxybutane.

the relevant concentrations are  $[D^+] = 0.011$  M,  $[DSO_4^-] = 0.029$  M, and  $[SO_4^{2-}] = 0.991$  M. The chemically equivalent internal protons in *trans*-2,3-epoxybutane are observed at 3.0 ppm (all chemical shifts were internally referenced to HDO), and the chemically equivalent internal protons in the diol product, 2,3-butanediol, are observed at 3.75 ppm (as confirmed by comparison to a commercially obtained sample of 2,3-butanediol). In our previous study of the reaction of alcohols with sulfuric acid, we studied the reaction of the diol ethylene glycol to form hydroxy monosulfate esters (21). In that work, we noted that the chemically inequivalent protons in hydroxy monosulfate esters were easily identified by their chemical shift relative to the chemically equivalent protons of the diol. In the present case, the proton attached to the hydroxy-functionalized carbon atom appears slightly downfield of the diol protons at 4.0 ppm, while the proton attached to the sulfate ester functionalized carbon atom appears at the more significantly downfield position of 4.4 ppm. These assignments are supported by earlier NMR work on biochemical molecules containing hydroxy sulfate moieties (44, 45); in these previous studies it was also reported that the substitution of a sulfate group for an alcohol group leads to a shift of about 0.6 ppm downfield for the proton attached to the sulfate ester-functionalized carbon atom and a shift of about 0.2 ppm downfield for the proton attached to the adjacent carbon atom.

For all epoxide systems in which  $[SO_4^{2-}] < 0.05$  M, diol products were the only products observed, and no epoxide reactant was detected at long times. Some experiments were performed with similarly dilute DCl/D<sub>2</sub>O solutions, and again, only diol products were observed. Because our detection limit is about 1% of the initial epoxide concentration, the lower limit on the equilibrium constant for the hydrolysis reaction is 100. Hydroxy sulfate esters were observed as products when  $[SO_4^{2-}] \geq 0.05$  M. To the best of our knowledge, this is the first observation of hydroxy sulfate ester products from reactions involving epoxides. For the asymmetric epoxides 1,2-epoxybutane, 2-methyl-1,2-epoxypropane, and 2-methyl-2,3-epoxybutane, two different hydroxy sulfate ester products are possible: an isomer in which the hydroxy group is attached to the more substituted carbon atom and an isomer in which the sulfate ester group is attached to the more substituted carbon atom. These isomers are easily identified using the relative chemical shift values (the largest downfield shift from the diol signal indicates the sulfate ester-functionalized carbon site). Since it is well-known that the acid-catalyzed hydrolysis of epoxides proceeds via a carbocation intermediate (24), it is expected that sulfate nucleophilic attack would be favored at the more substituted carbon atom. Indeed, for 2-methyl-1,2-epoxypropane and 2-methyl-2,3-epoxybutane systems, the favored isomer is the only one observed. However, for the 1,2-epoxybutane system, both isomers are observed in about equal abundance. This result is likely explained by the unusual stability of the tertiary carbocations formed in the reaction of 2-methyl-1,2-epoxypropane and 2-methyl-2,3-epoxybutane.

**Kinetics Analysis.** The acid-catalyzed hydrolysis of epoxides is known to be first-order in both the epoxide and proton concentrations (46, 47).

$$\frac{-d[\text{epoxide}]}{dt} = k[\text{epoxide}][D^+] \quad (1)$$

For a single experiment with a particular  $D^+$  concentration (which remains constant during the reaction because it is a catalyst), the rate equation reduces to the simple first-order case

$$\frac{-d[\text{epoxide}]}{dt} = k'[\text{epoxide}] \quad (2)$$

where

$$k' = k[D^+] \quad (3)$$

Figure 3 shows the first-order kinetics plot resulting from an experiment in which the loss of *trans*-2,3-epoxybutane in 0.01 M D<sub>2</sub>SO<sub>4</sub>/D<sub>2</sub>O ( $[D^+] = 0.015$  M,  $[DSO_4^-] = 0.006$  M, and  $[SO_4^{2-}] = 0.004$  M) was monitored. For the case of the hydrolysis of *trans*-2,3-epoxybutane, a formal proton rate order analysis was performed to confirm the first-order nature of the process. In this case, eq 3 is expressed more generally as

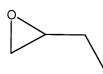
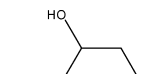
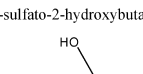
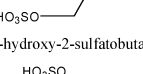
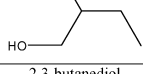
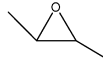
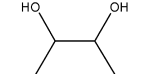
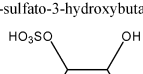
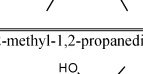

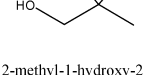
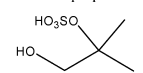
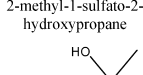
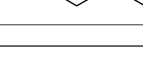
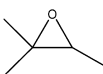
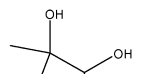
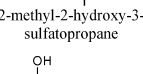
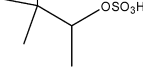
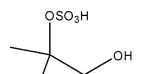
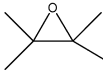
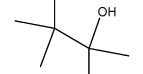
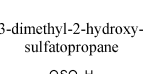

$$k' = k[D^+]^n \quad (4)$$

or, in linear form,

$$\log k' = \log k + n \log [D^+] \quad (5)$$

Therefore, a plot of the logarithm of  $k'$  values from experiments such as those depicted in Figure 3 versus the logarithm of the  $D^+$  concentration yields the proton rate order,  $n$ , as the slope. Additionally, in order to confirm that the other ions present have no effect on the acid-catalyzed hydrolysis kinetics, the proton rate order analysis was performed using both D<sub>2</sub>SO<sub>4</sub>/D<sub>2</sub>O and DCl/D<sub>2</sub>O solutions, with the  $D^+$  concentrations calculated for the D<sub>2</sub>SO<sub>4</sub>/D<sub>2</sub>O solutions from the AIM model. Figure 4 shows a formal proton

TABLE 1. Hydrolysis Rate Constants and Product Yields

reactant	acid-catalyzed hydrolysis rate constant ( $M^{-1} s^{-1}$ )	potential products	product yields in 0.02 M $D_2SO_4$ /1 M $Na_2SO_4$ (%)
1,2-epoxybutane 	0.074	1,2-butanediol  1-sulfato-2-hydroxybutane  1-hydroxy-2-sulfatobutane  14 	73  13  14
trans-2,3-epoxybutane 	0.20	2,3-butanediol  2-sulfato-3-hydroxybutane  11 	89  11
2-methyl-1,2-epoxypropane 	8.7	2-methyl-1,2-propanediol  86 2-methyl-1-hydroxy-2-sulfatopropane  14 2-methyl-1-sulfato-2-hydroxypropane  <1 	86  14  <1
2-methyl-2,3-epoxybutane 	9.0	2-methyl-2,3-butanediol  89 2-methyl-2-hydroxy-3-sulfatopropane  <1 2-methyl-2-sulfato-3-hydroxybutane  11 	89  <1  11
2,3-dimethyl-2,3-epoxybutane 	15	2,3-dimethyl-2,3-butanediol  93 2,3-dimethyl-2-hydroxy-3-sulfatopropane  7 	93  7

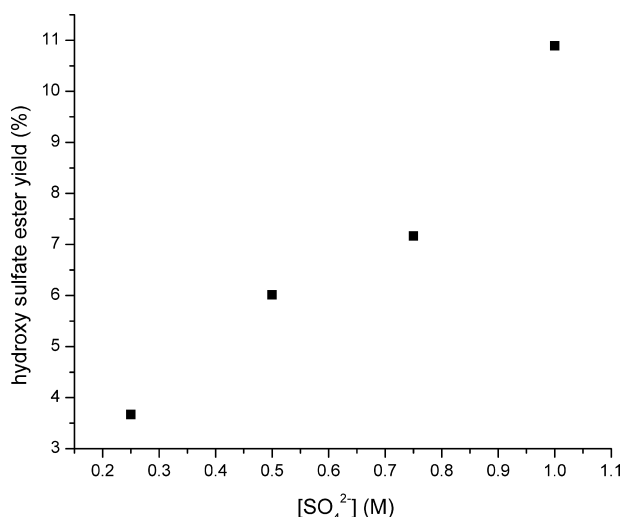
rate order analysis for *trans*-2,3-epoxybutane in which four different solutions were used. The rate order determined from this plot was 0.92, thus confirming the first-order nature of the acid-catalyzed hydrolysis. The consistency of the results indicates that the hydrolysis kinetics are not affected by the presence of other ions for these relatively dilute conditions.

The second-order hydrolysis rate constants ( $k$ ) were calculated from the first-order rate constants ( $k'$ ) and the proton concentration calculated from the AIM model for each solution via eq 3. These second-order rate constants for each of the epoxide systems are given in Table 1. Each of the individual rate constants reported is the average of at least three independent experiments and is characterized by a one standard deviation statistical error of about 5%. In a separate experiment, both the epoxide loss and diol and hydroxy sulfate ester production kinetics data were collected for a 0.02 M  $D_2SO_4$ /1.0 M  $Na_2SO_4$ / $D_2O$  solution (this solution has nearly the same  $D^+$  concentration,  $[D^+] = 0.011$  M, as the 0.01 M  $DCl$ / $D_2O$  solution used in the proton rate order experiments). The overall epoxide loss rate constant determined from this experiment was similar to the hydrolysis rate constant determined for the 0.01 M  $DCl$ / $D_2O$  experiment. This result indicates that the overall epoxide loss is rate-

limited by the acid catalysis step and that the presence of high sulfate concentrations has no discernible effect on the epoxide loss kinetics. Further, the diol and hydroxy sulfate products were found to be prompt products of the epoxide loss process. Therefore, while the water and sulfate nucleophilic addition steps shown in Figure 1 must be kinetically competitive with each other in order to explain the presence of both diol and hydroxy sulfate ester products, each step must occur much more quickly than the acid-catalysis step.

Previous work has indicated that the stabilization of the carbocation intermediate is directly correlated to the value of the hydrolysis rate constant observed for different epoxides (46, 47). In the present work, three of the epoxides contain at least one tertiary carbon on the epoxide ring: 2-methyl-1,2-epoxypropane, 2-methyl-2,3-epoxybutane, and 2,3-dimethyl-2,3-epoxybutane. All three of these epoxides were found to have extremely large hydrolysis rate constants, with 2,3-dimethyl-2,3-epoxybutane, the species with two tertiary carbons on its epoxide ring, having the largest of all of the rate constants. *trans*-2,3-Epoxybutane contains two secondary carbons on its epoxide ring; it was found to have a much smaller hydrolysis rate constant. Finally, 1,2-epoxybutane, with one secondary and one primary carbon on its epoxide





**FIGURE 5.** Dependence of the hydroxy sulfate ester yield for the reaction of *trans*-2,3-epoxybutane in 0.02 M D<sub>2</sub>SO<sub>4</sub>/D<sub>2</sub>O as a function of total sulfate.

ring, was found to have the smallest hydrolysis rate constant of the epoxides investigated in the present study. Therefore, the values of the hydrolysis rate constants are easily understood by the substitution nature of the epoxide ring carbon atoms in the reactant epoxides.

The hydrolysis rate constants for the perchlorate-catalyzed hydrolysis reactions of *trans*-2,3-epoxybutane and 2-methyl-1,2-epoxypropane have been previously measured using dilatometric methods. The presently determined hydrolysis rate constant for *trans*-2,3-epoxybutane ( $0.20 \text{ M}^{-1} \text{ s}^{-1}$ ) compares well to the previously determined value ( $0.32 \text{ M}^{-1} \text{ s}^{-1}$ ) (46), as does the presently determined hydrolysis rate constant for 2-methyl-1,2-epoxypropane ( $8.7 \text{ M}^{-1} \text{ s}^{-1}$ ) to the previously determined value ( $7.3 \text{ M}^{-1} \text{ s}^{-1}$ ) (47).

**Sulfate-Dependence Product Analysis.** In order to investigate the possibility of the formation of hydroxy sulfate ester products under higher sulfate concentrations than used in the hydrolysis kinetics studies ( $\leq 0.02 \text{ M SO}_4^{2-}$ ), product studies were carried out in solutions created by adding differing amounts of Na<sub>2</sub>SO<sub>4</sub> (to create Na<sub>2</sub>SO<sub>4</sub> concentrations between 0.25 and 1.0 M) to a 0.02 M D<sub>2</sub>SO<sub>4</sub>/D<sub>2</sub>O solution. The AIM model indicates that, over the range of the Na<sub>2</sub>SO<sub>4</sub> concentrations used, the D<sup>+</sup> and DSO<sub>4</sub><sup>-</sup> concentrations are effectively buffered at values of about 0.01 and 0.03 M, respectively, while the SO<sub>4</sub><sup>2-</sup> concentrations are virtually identical to the Na<sub>2</sub>SO<sub>4</sub> concentrations. Therefore, the range of SO<sub>4</sub><sup>2-</sup> concentrations used in these experiments varied from about 0.25 to 1 M. Figure 5 shows the results of such a study for *trans*-2,3-epoxybutane in 0.02 M D<sub>2</sub>SO<sub>4</sub>/D<sub>2</sub>O. It is apparent that hydroxy sulfate ester yields systematically increased up to the maximum SO<sub>4</sub><sup>2-</sup> concentration used (the maximum solubility of Na<sub>2</sub>SO<sub>4</sub> in water is about 1 M). Similar SO<sub>4</sub><sup>2-</sup>-dependence studies were carried out for all epoxide systems, with the result that hydroxy sulfate ester yields increased up to the 1 M maximum SO<sub>4</sub><sup>2-</sup> concentration limit in all cases. The maximum hydroxy sulfate ester yields observed for each epoxide system are listed in Table 1. Although there have been no previous studies on hydroxy sulfate ester formation from epoxides, the formation of hydroxy nitrate esters from epoxides has been reported. Similar to the present result for added sulfate, it was found that the hydroxy nitrate ester yield from the acid-catalyzed hydrolysis of epoxides increased linearly with added nitrate (25).

As discussed in the Identification of Reaction Products section for the asymmetric epoxides, epoxides with a tertiary carbon were observed to exclusively produce hydroxy sulfate

ester isomers with the sulfate functionality attached to the tertiary carbon atom. However, the product yield values reported in Table 1 seem to indicate that the substitution nature of the epoxide carbon atoms also has an effect on the overall hydroxy sulfate ester yield. For example, the two epoxides with a primary carbon atom, 1,2-epoxybutane and 2-methyl-1,2-epoxypropane, were observed to have the largest overall sulfate ester yield, while the epoxide with two tertiary carbons, 2,3-dimethyl-2,3-epoxybutane, was observed to have the smallest overall sulfate ester yield. Because the sulfate ion is much larger than water, we postulate that nucleophilic attack by sulfate ion is sterically hindered in the highly substituted epoxides.

**Potential Significance to Laboratory and Ambient Secondary Organic Aerosol Observations of Diols and Hydroxy Sulfate Esters.** Because the SOA formed in laboratory experiments and under atmospheric conditions is physically and chemically complex and the bulk solutions investigated in this work are quite simple, the extrapolation of the present results to SOA systems is necessarily approximate. Specifically, the present work is expected to be most relevant to SOA with an aqueous phase that is acidic with a high sulfate concentration. In the isoprene and  $\alpha$ -pinene SOA laboratory experiments of Surratt et al. (5, 6), a relative humidity of 30%, which corresponds to an equivalent sulfuric acid content of 52.5 wt % at 298 K, and total reaction times of between 30 min and 24 h were utilized. In these experiments, both the H<sup>+</sup> and sulfate concentrations were in excess of 6 M. For the slowest epoxide hydrolysis case (1,2-epoxybutane) under these conditions, an epoxide lifetime of 2.3 s is calculated, and the hydroxy sulfate ester yield would obviously be predicted to be significant at these very high sulfate levels. In the  $\beta$ -pinene and limonene SOA laboratory experiments of Iinuma et al. (7, 9), a relative humidity of about 50%, which corresponds to a sulfuric acid content of about 43 wt % at 298 K, and a total reaction time of 2.5 h were utilized. Again, both the acid and sulfate content (both concentrations are in excess of 5 M) of the aerosols in this experiment are more than sufficient to quickly form hydroxy sulfate esters via the proposed epoxide hydrolysis mechanism. Therefore, it appears that the proposed epoxide hydrolysis mechanism is kinetically consistent with the laboratory sulfate ester SOA findings.

In the measurement of ambient SOA, the chemical complexity of the particles does not allow for a direct comparison to the laboratory studies in which sulfuric acid content is controlled in the seed aerosol particles or bulk solutions. However, Zhang et al. have used measurements of the concentrations of the ionic components 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 (23). Zhang et al. then used the thermodynamic model of Clegg et al. (48) to calculate an average pH value for the SOA sampled. In their measurements, the pH of SOA usually ranged from about 4.0 to 1.5, but values as low as 0.0 were sometimes observed. Zhang et al. also determined that sulfate makes up about half of the mass of the aerosols sampled in Pittsburgh. Therefore, ambient sulfate levels in SOA are very high, and it is likely that any aqueous component of SOA will have very high sulfate concentrations.

For the slowest epoxide hydrolysis case (1,2-epoxybutane) at pH = 1.5 ( $[\text{H}^+] = 3 \times 10^{-2} \text{ M}$ ), a lifetime of 450 s is calculated. Therefore, for SOA at pH = 1.5, it appears that the epoxide reaction will likely be very efficient for the broad range of epoxides that are potentially formed in the atmosphere. At pH = 4.0 ( $[\text{H}^+] = 1 \times 10^{-4} \text{ M}$ ), for the slowest epoxide reaction case (1,2-epoxybutane), a lifetime of 37 h is calculated. For the fastest epoxide reaction case (2,3-dimethyl-2,3-epoxybutane), a lifetime of 35 min is calculated at pH = 4.0. Since the wet deposition lifetime of SOA is on

the order of a few days (49), it appears that at even higher pH conditions, most epoxides will have time to react on SOAs (particularly those with tertiary carbon atoms).

Although the present results are directly applicable to epoxides formed from the atmospheric oxidation of the alkenes 1-butene, 2-butene, 2-methylpropene, 2-methyl-2-butene, and 2,3-dimethyl-2-butene, the laboratory and ambient SOA studies have focused on the chemistry arising from the products of the atmospheric oxidation of biogenic hydrocarbons. While direct studies of the epoxide chemistry of this class of compounds are currently underway in our laboratory, it is possible to use the present results to predict the overall reaction kinetics and hydroxy sulfate ester yields of epoxides formed from biogenic hydrocarbons. In the case of epoxides formed in the atmospheric oxidation of isoprene, both possible epoxide isomers contain primary carbon atoms and would be expected to form a high yield of hydroxy sulfate esters. However, the epoxide isomer with a tertiary carbon would be expected to react faster overall. The epoxide resulting from the atmospheric oxidation of  $\beta$ -pinene contains a primary and a tertiary carbon atom. This epoxide would be expected to both react very quickly and to form a relatively high yields of hydroxy sulfate esters. The epoxide resulting from the atmospheric oxidation of  $\alpha$ -pinene contains a secondary and a tertiary carbon atom. This epoxide would be expected to react quickly but to less efficiently form hydroxy sulfate esters. In the atmospheric oxidation of limonene, there are two possible epoxide isomers; however, the exocyclic epoxide isomer, with primary and tertiary carbon atoms, would be expected to hydrolyze more quickly and to form more hydroxy sulfate ester product than the endocyclic epoxide isomer. In any case, the present results suggest that the SOA reactivity of epoxides formed in the atmospheric oxidation of biogenic compounds should be similar to epoxides studied in the present work and, therefore, should be considered as potential precursors for the sulfate esters and polyols observed in laboratory and ambient SOA.

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