

Kinetics of the Reactions of Isoprene-Derived Epoxides in Model Tropospheric Aerosol Solutions

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Polyols and organic sulfates have recently been identified in the secondary organic aerosol (SOA) formed in the photooxidation of isoprene in both the laboratory and under ambient atmospheric conditions. Nuclear magnetic resonance methods were used to monitor the bulk reaction kinetics of acid-catalyzed hydrolysis reactions for isoprene- and 1,3-butadiene-derived epoxides in order to determine the rates for such reactions in aerosols under the previously studied laboratory conditions and under ambient atmospheric conditions. The measured rate constants were found to vary over 7 orders of magnitude. For the fast case of the hydrolysis of 1,2-epoxyisoprene, the lifetime at neutral pH was found to be only 3 min. On the other hand, for the relatively slow reaction of 1,2-epoxy-3,4-hydroxybutane, the lifetime at the most acidic conditions commonly observed in tropospheric aerosols (pH 1.5) was found to be 7.7 h, a value that is still less than the several day lifetime of tropospheric aerosols. Therefore, the present results suggest that, despite a wide range in reactivities, several possible reactions of isoprene-derived epoxides should be kinetically efficient on atmospheric SOA. The reactions were also studied with the elevated sulfate concentrations that are often characteristic of tropospheric aerosols, and sulfate products were identified for all species except 1,2-epoxyisoprene. Other nucleophiles that may be present in aerosols (nitrate, chloride, bromide, and iodide) were also investigated, and it was found that nitrate and sulfate have similar nucleophilic strength, while the halides are much stronger nucleophiles in their reactions with epoxides. Therefore, aerosols which contain significant concentrations of these species may be expected to readily form species similar to those already identified for the reactions of epoxides with sulfate.

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). Because isoprene is the dominant nonmethane hydrocarbon present in the atmosphere (3), there has been extensive investigation of the chemical processes that lead to SOA from isoprene (4–10). Specifically, polyols (particularly 2-methyl-1,2,3,4-tetrahydroxybutane) and polyol monosulfates have been identified as key species in the SOA formed from isoprene at locations in the southeastern United States (7, 11), and K-puszt, Hungary

(12). However, the gas- and particle-phase mechanisms that explain the formation of these species remain in question.

In previous work in our lab, we investigated two potential routes by which such sulfate products could be formed via particle-phase chemical reactions. Alcohols are known to form in the gas phase from the self-reaction of peroxy radicals under low NO_x conditions (4). Therefore, one potential route to sulfate products is the reaction of alcohols with sulfuric acid. However, Minerath et al. showed that at the acid conditions typical of lower tropospheric aerosols (pH 1.5–4.0) (13) these reactions are not kinetically efficient enough to explain the observation of sulfates in ambient SOA (14). A second sulfate-forming mechanism was suggested by Iinuma et al. (15), who have recently confirmed that the epoxides known to form in the oxidation of biogenic monoterpenes react efficiently with sulfuric acid to form hydroxy sulfates (16), in addition to the usual diol products formed from the acid-catalyzed hydrolysis of epoxides (17). Epoxides are known to form from the reaction of $\text{O}(^3\text{P})$ with isoprene (18) at nearly 80% yield, and epoxide yields on the order of about 2–3% have been observed in the atmospheric pressure ozonolysis of isoprene (19, 20). Recently, the laboratory studies of Paulot et al. have shown that high yields of epoxides are observed in the OH-initiated oxidation of isoprene (21). The net effect of these oxidation processes is the replacement of one or both of the double bonds in isoprene with epoxide rings (Figure 1a shows potential mono and diepoxides formed from isoprene

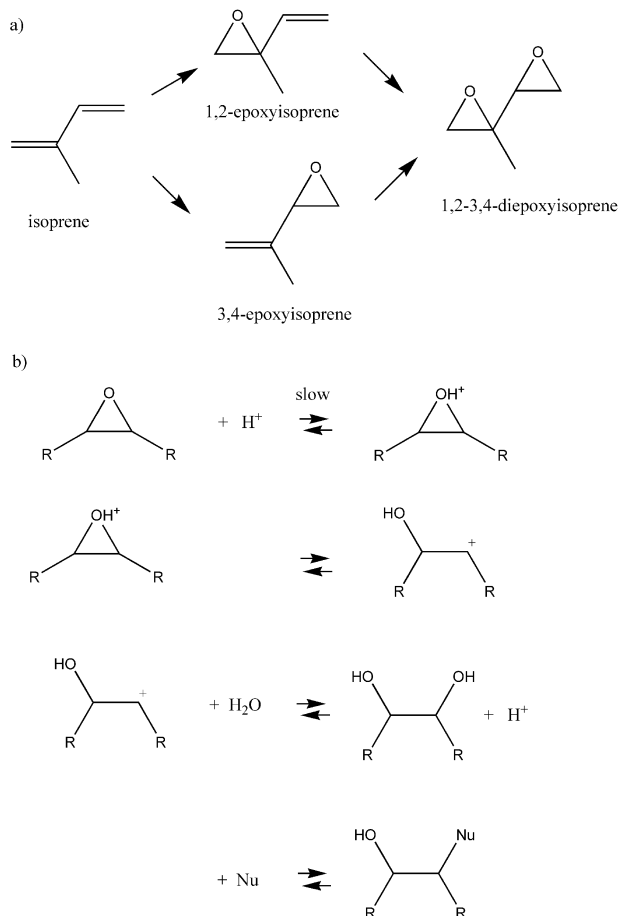


FIGURE 1. (a) Potential isoprene epoxides. (b) Proposed acid-catalyzed nucleophilic addition to epoxides mechanism.

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oxidation). In this second sulfate-forming mechanism (shown in Figure 1b), the acid-catalyzed ring-opening of the epoxide is the rate-limiting step in the overall process, and water and sulfate (indicated as a generic nucleophile in Figure 1) act as competing nucleophiles in the fast steps that lead to the final diol and hydroxy sulfate products. In a second study, our lab showed the hydrolysis of epoxides formed from simple alkenes is expected to be very kinetically efficient at typical SOA pH levels, and at elevated sulfate levels, both diol and hydroxy sulfate species were observed as major products of the reactions of these epoxides (22). We postulated that similar reactions for epoxides derived from isoprene would also be kinetically efficient on SOA and would be capable of forming both the polyol and sulfate products observed in ambient SOA.

In the present study, the acid-catalyzed reactions of isoprene- and 1,3-butadiene-derived epoxides are investigated. While the two monoepoxides expected to form from the primary oxidation of isoprene, 1,2-epoxyisoprene and 3,4-epoxyisoprene, are directly studied, the isoprene diepoxide species potentially formed from a two step oxidation process was not available for study. Therefore, 1,2–3,4-diepoxylbutane (a diepoxide derived from 1,3-butadiene) is used as a surrogate for isoprene diepoxide. We also studied 3,4-epoxy-1-butene, as it is determined to have similar reaction properties to 3,4-epoxyisoprene, but is commercially available and possesses a simpler NMR spectrum than 3,4-epoxyisoprene. Hydrolysis rate constant and product yield (as function of sulfate concentration) measurements for the epoxide reactions are performed using nuclear magnetic resonance (NMR) techniques. The reaction products of potentially atmospherically relevant nucleophiles (nitrate, chloride, bromide, and iodide) are also quantified. Based on these mechanistic and kinetic parameters, the potential for polyol and hydroxy nucleophile formation from the reaction of isoprene-derived epoxides with tropospheric aerosols is evaluated.

Experimental Section

^1H NMR methods were used for the epoxide loss kinetics measurements and to identify and quantify products. ^{13}C , COSY, and HMQC (23) NMR methods were occasionally employed to confirm product identifications. In some cases, inverse gated decoupling ^{13}C experiments (23) (which allow quantification of ^{13}C signals) were performed. All experiments used deuterated acid solutions for NMR locking purposes, and chemical shifts were to be referenced to the upfield methyl proton resonance (defined as 0 ppm) of 2,2-dimethyl-2-silapentane-5-sulfonic acid (DSS).

The experiments were performed with epoxides used as obtained from Sigma-Aldrich, with the exception of 3,4-epoxyisoprene: 3,4-epoxy-1-butene (butadiene monoxide, 98%), 1,2–3,4-diepoxylbutane (butadiene diepoxide, 97%), and 1,2-epoxyisoprene (methyl vinyl oxirane, 95%). We synthesized 3,4-epoxyisoprene according to a previously reported procedure (24).

For the hydrolysis kinetics measurements, solutions were prepared by adding a small volume (usually 25–50 μL) of the reactant epoxide to 5 mL of a $\text{D}_2\text{SO}_4/\text{D}_2\text{O}$ solution. For the product analysis experiments, differing amounts of nucleophile-containing salts were dissolved in the 5 mL $\text{D}_2\text{SO}_4/\text{D}_2\text{O}$ solutions before the epoxide was added. The sulfuric acid solutions were prepared by diluting commercially obtained 96 wt % D_2SO_4 with D_2O (Sigma-Aldrich). DSS was also added to each solution (at 0.1 wt % concentration) to allow chemical shift referencing and as an internal standard. 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,

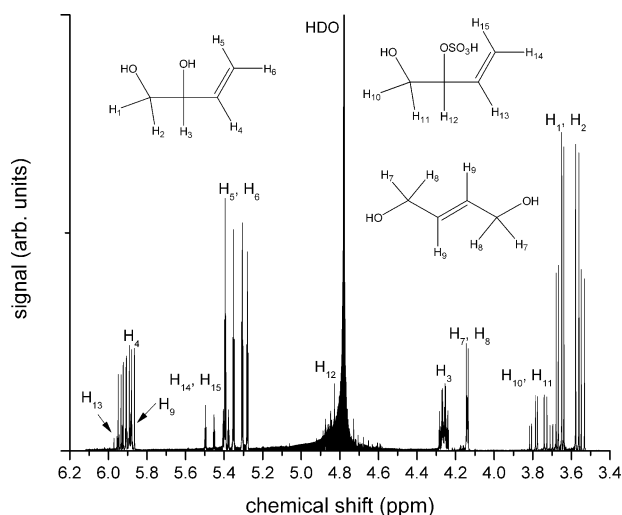


FIGURE 2. ^1H NMR spectrum collected at the end of the reaction of 3,4-epoxy-1-butene in 0.02 M $\text{D}_2\text{SO}_4/1.0$ M $\text{Na}_2\text{SO}_4/\text{D}_2\text{O}$.

and the progress of the reaction was monitored with a 400 MHz NMR spectrometer at a constant temperature of 297 ± 1 K with 2 min time resolution. For the product analysis experiments, solutions were stored for 24 h (to allow them 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 product 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. In the cases where inverse gated decoupling ^{13}C experiments were used for product quantification, a similar analysis was used for the chemically unique carbon atoms.

Results and Discussion

Identification of Reaction Products. Figure 2 shows an NMR spectrum, with assignments indicated, collected at the end of the reaction of 3,4-epoxy-1-butene 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. For the unsaturated epoxides, 1,4-addition products are possible due to allylic rearrangement of the carbocation intermediate (17). By reference to standard spectra for 3,4-dihydroxy-1-butene and 1,4-dihydroxy-2-butene, it is clear that both products are present in the spectrum shown in Figure 2. However, we did not observe similar allylic rearrangement products for 1,2-epoxyisoprene or 3,4-epoxyisoprene, which is likely due to the special stability of the tertiary carbocation intermediates in those cases. The proton bonded to the carbon atom which was *adjacent* to the carbon atom with differing functional groups (alcohol or other functional group that was the result of nucleophilic attack by a species other than water) was used to identify and quantify the various products. For example, Figure 2 shows that protons 1 and 2 for the 3,4-dihydroxy species can be clearly resolved from protons 10 and 11 for 1-sulfato-2-hydroxy species formed in the reaction of 3,4-epoxy-1-butene in the presence of the high levels of the sulfate nucleophile. The spectra for the other nucleophiles are very similar; however, they can be distinguished by the relative chemical shift difference ($\Delta\delta$) between the multiplet for protons 1 and 2 and the multiplet for protons 10 and 11: $\Delta\delta(\text{SO}_4^{2-}) = 0.18$ ppm, $\Delta\delta(\text{NO}_3^-) = 0.24$ ppm, $\Delta\delta(\text{Cl}^-) = 0.17$ ppm, $\Delta\delta(\text{Br}^-) = 0.28$ ppm, $\Delta\delta(\text{I}^-) = 0.23$ ppm or 0.46 ppm

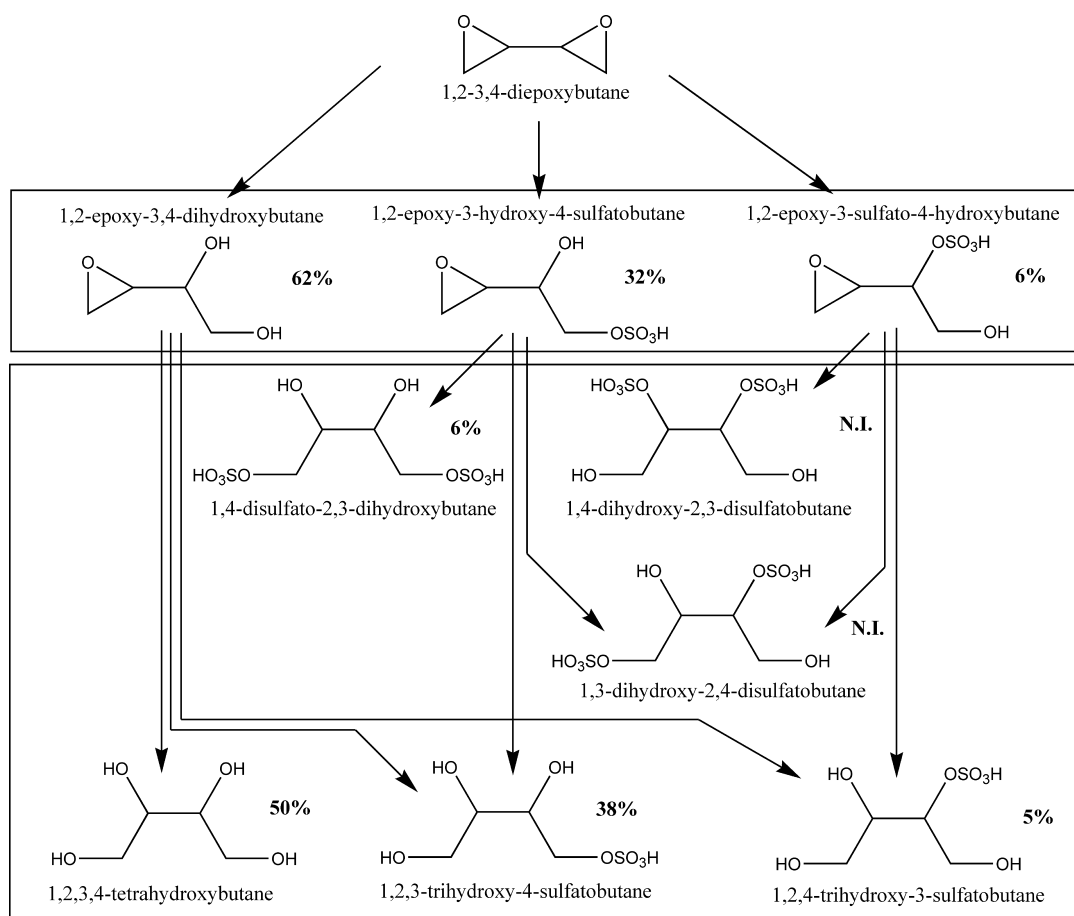


FIGURE 3. Mechanism for the reaction of 1,2–3,4-diepoxybutane. The product yields for each of the two ring-opening epoxide reactions are given in bold type as determined from a high sulfate experiment (0.4 M D₂SO₄/1.0 M Na₂SO₄/D₂O) or are indicated as not identified (N.I.).

(primary addition product). Therefore, this general assignment and quantification scheme was used for all systems.

For the reaction of 1,2,3,4-diepoxybutane in the presence of sulfate, two epoxide ring-opening processes are possible (as outlined in Figure 3). Using the proton bonded to the secondary epoxide carbon in the monoepoxide product formed in the first ring-opening step, it was again possible to identify and quantify the specific functionality of the products formed in the first ring-opening step. For example, this proton for 1,2–3,4-diepoxybutane has a chemical shift of 3.07 ppm, the proton for 1,2-epoxy-3,4-dihydroxybutane has a chemical shift of 3.17 ppm, the proton for 1,2-epoxy-3-hydroxy-4-sulfatobutane has a chemical shift of 3.24 ppm, and the proton for 1,2-epoxy-3-sulfato-4-hydroxybutane has a chemical shift of 3.31 ppm. For the second ring-opening step, the situation is more complicated, as there are three reactants (the latter three species listed above) that can lead to six possible observed products. Two diastereomers of 1,2,3,4-tetrahydroxybutane were identified as products by comparison to standards, while three (1,2,3-trihydroxy-4-sulfatobutane, 1,2,4-trihydroxy-3-sulfatobutane, 1,4-disulfato-2,3-dihydroxybutane) of the five other possible product species were identified by the associating the characteristic ¹H and ¹³C chemical shift values that indicate sulfate functionality with particular carbon chain positions. As will be explained in the Nucleophile Product Analysis section, it is believed that the two unassigned possible products (1,4-dihydroxy-2,3-disulfatobutane and 1,3-dihydroxy-2,4-disulfatobutane) were not identified because they were present in very low concentrations.

Hydrolysis Rate Constant Analysis. The acid-catalyzed hydrolysis of epoxides is known to be first order in both the epoxide and proton concentrations (25, 26).

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

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

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

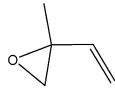
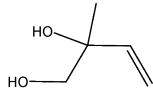
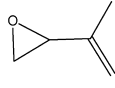
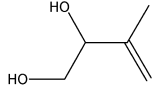
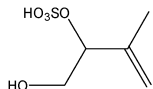
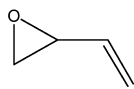
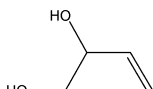
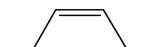
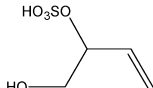
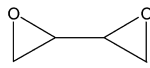
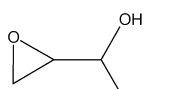
where

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

The second order hydrolysis rate constants (*k*) were calculated from the first order rate constants (*k'*) and the proton concentration calculated from the aerosol inorganics model (AIM) (27) for each solution via eq 3 and are reported in Table 1. The rate constant for the hydrolysis of 1,2-epoxy-3,4-dihydroxybutane, the major product of the hydrolysis of 1,2–3,4-diepoxybutane, was determined by direct fitting of the time dependent concentration data for both species (assuming a simple sequential A → B → C mechanism) using a numerical kinetics solver (28).

Our previous work on the hydrolysis of epoxides formed from simple alkenes indicated that the stabilization of the

TABLE 1. Monoepoxide Hydrolysis Rate Constants and Product Yields for 1 M Na₂SO₄/0.2 M D₂SO₄/D₂O Solutions

reactant	k (M ⁻¹ s ⁻¹)	observed products	product %
1,2-epoxy isoprene 	56000	3,4-dihydroxy-3-methyl-1-butene 	>99
3,4-epoxy isoprene 	5.6	3,4-dihydroxy-2-methyl-1-butene  4-hydroxy-2-methyl-3-sulfato-1-butene 	85 15
3,4-epoxy-1-butene 	3.1	3,4-dihydroxy-1-butene  1,4-dihydroxy-2-butene  4-hydroxy-3-sulfato-1-butene 	73 14 13
1,2-3,4-diepoxybutane 	0.0013	see Figure 3	
1,2-epoxy-3,4-dihydroxybutane 	0.0012	see Figure 3	

carbocation intermediate (stability trend: primary < secondary < tertiary) was directly correlated to the value of the hydrolysis rate constant observed for different epoxides (22, 26). In the present work, this pattern was also observed. In the case of the hydrolysis rate constants for 1,2-3,4-diepoxybutane and 1,2-epoxy-3,4-dihydroxybutane (which are both primary-secondary epoxides), relatively small constants were determined, as was the case for our earlier measurement of the hydrolysis rate constant for 1,2-epoxybutane. However, 3,4-epoxy-1-butene and 3,4-epoxyisoprene (which are also both primary-secondary epoxides) were found to have relatively large hydrolysis rate constants (similar to the values we previously determined for tertiary monoepoxides derived from simple alkenes). Since the major difference between the two pairs of compounds is the presence of a double bond in the dialkene-derived monoepoxides, it is apparent that the allylic stabilization of the carbocation in the dialkene-derived monoepoxides is responsible for the much larger

hydrolysis rate constants observed for 3,4-epoxy-1-butene and 3,4-epoxyisoprene. For the case of 1,2-epoxyisoprene (a primary-tertiary epoxide), an extremely large hydrolysis rate constant was measured (1,2-epoxy isoprene has a lifetime of 3 min at neutral pH). In this case, the combination of a tertiary carbocation and allylic stabilization apparently confers a high degree of reactivity on 1,2-epoxyisoprene.

Nucleophile Product Analysis. In order to investigate the possibility of the formation of nucleophile products (other than polyols), experiments were carried out in solutions created by adding differing amounts of nucleophile-containing salts to a 0.2 M D₂SO₄/D₂O solution. The AIM model indicates that over the range of the salt concentrations used, the D⁺ concentrations are effectively buffered at values ranging from 0.1 and 0.3 M for the different salts, while the calculated nucleophile concentrations are similar to the formal salt concentrations (for example, the AIM model predicts that a 0.2 M D₂SO₄/1 M Na₂SO₄ solution has a D⁺

concentration of 0.12 M and a SO_4^{2-} concentration of 0.92 M and a 0.2 M D_2SO_4 /1 M NaNO_3 solution has a D^+ concentration of 0.276 M and a NO_3^- concentration of 1.0 M).

The maximum sulfate (1.0 M Na_2SO_4 , 0.92 M SO_4^{2-}) product yields for the monoepoxides are given in Table 1. Strictly speaking, the reported values are relative products yields; however, the NMR spectra indicate quantitative consumption of the reactant epoxides in all cases and negligible signals from unidentified products. Therefore, the absolute yields for these reactions are expected to be very similar to the reported relative yields. Similar to our findings for the epoxides derived from simple alkenes (22), the primary-secondary monoepoxides produced significant yields (13–15%) of sulfate products. However, it was also observed that the products were solely the result of sulfate attack at the secondary carbon site; in our previous work on primary-secondary epoxides formed from simple alkenes, we found that sulfate attack was equally probable at the primary and secondary carbon atoms. It is likely that subtle differences in the relative stabilities of the primary and secondary carbocation intermediates are responsible for this result. Interestingly, no sulfate products were observed for 1,2-epoxyisoprene, the epoxide with the largest hydrolysis rate constant. We postulate that large hydrolysis rate constants are correlated with lower sulfate yields, an effect that was apparent (but less dramatic) in our earlier study of epoxides derived from simple alkenes. However, it is worth noting that other tertiary epoxides, such as those studied previously by our lab (22) and by Iinuma et al. (16) have been shown to produce sulfate products.

The corresponding maximum sulfate product yields for the reaction products of 1,2–3,4-diepoxybutane are given in Figure 3. The first epoxide ring-opening step in the reaction of 1,2–3,4-diepoxybutane was found to produce high yields of monoepoxide hydroxy sulfates (38%), with a preference for sulfate attack at the primary carbon atom of the epoxide. 1,2,3,4-tetrahydroxybutane and sulfates (including 6% disulfate) were equally represented in the final product distribution. In order to rationalize the final product distribution, all three monoepoxides formed in the first ring-opening step must yield about 20% sulfate products in the second ring-opening step. Therefore, although both the first and second epoxide ring-opening hydrolysis rate constants were found to be similar (0.0013 and $0.0012 \text{ M}^{-1} \text{ s}^{-1}$, respectively), the second epoxide ring-opening reactions produced a somewhat lower percentage of sulfates than in the first epoxide ring-opening reaction. If these product branching ratios are used to predict the product yields of the other expected, but unidentified, final products (1,4-dihydroxy-2,3-disulfatobutane and 1,3-dihydroxy-2,4-disulfatobutane), both species are calculated to be present at 1% yield or less, thus providing an explanation for the difficulty in confirming the presence of these species.

Since aerosol solutions can be highly nonideal (owing to their high concentrations of ions), it is important to assess whether the presence of different counterions can effect the relative nucleophilic strength of water and sulfate in the reactions of epoxides. For example, highly acidic sulfate aerosols will have protons as the dominant counterion, while more neutral sulfate aerosols will have large concentrations of ammonium ion. Metal ions are also known to be present in aerosols (29). Figure 4 shows the results of product experiments for 3,4-epoxy-1-butene conducted with different sulfate salts. In order to allow a direct comparison, the sulfate product yields are plotted according to the sulfate activity for each solution (the activities were explicitly calculated from the AIM model for Na_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$, which had quite similar values, and the Na_2SO_4 values were used as estimates for K_2SO_4 and MgSO_4). It is clear that the identity

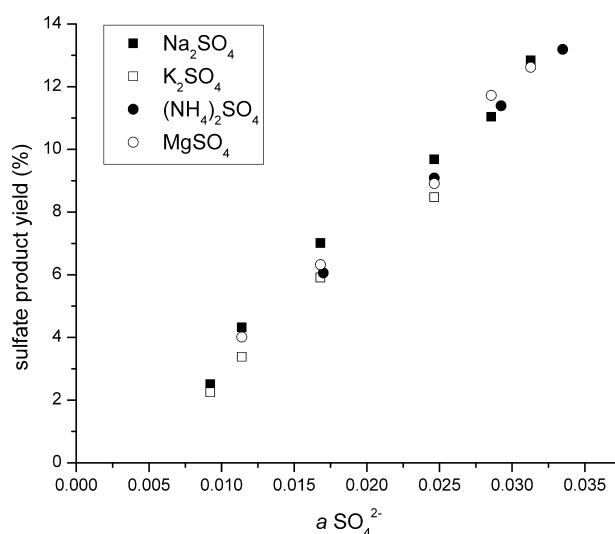


FIGURE 4. Counter ion sulfate product yield dependence for 3,4-epoxy-1-butene.

TABLE 2. Nucleophile Activities^a and 3,4-Epoxy-1-Butene Nucleophile Addition Product Yields^b for Various Sodium Salt Concentrations in 0.2 M $\text{D}_2\text{SO}_4/\text{D}_2\text{O}$ Solutions

		0.25 M	0.50 M	0.75 M	1.0 M	2.0 M
Na_2SO_4	$a\text{SO}_4^{2-}$	0.0168	0.0246	0.0286	0.0313	
	yield (%)	7	10	11	13	
NaNO_3	$a\text{NO}_3^-$	0.161	0.307		0.574	1.06
	yield (%)	5	8		13	17
NaCl	$a\text{Cl}^-$	0.175	0.348		0.706	1.53
	yield (%)	12	22		32	44
NaBr	$a\text{Br}^-$	0.183	0.348		0.687	1.46
	yield (%)	24	35		52	56
NaI	$a\text{I}^-$	0.186	0.362		0.736	1.65
	3-iodo-4-hydroxy yield (%)	17	26		19	6
	3-hydroxy-4-iodo yield (%)	31	39		62	82
	total iodide yield (%)	48	55		81	88

^a Activities calculated from $a = \gamma c$. Activity coefficients (γ) for sulfate, nitrate, and chloride from AIM model (27) and bromide activities from ref 35. ^b The 3-nucleophile-4-hydroxy isomer was exclusively observed for all systems except NaI , and the balances of the total product yield were 3,4- and 1,4-dihydroxy-1-butenes.

of the counterion has no effect on the sulfate product yields over this range of sulfate activities.

Tropospheric aerosols also contain a number of other negative ions that might act as nucleophiles in epoxide reactions. Nitrates are a common constituent of aerosols (30), and the halides (chloride, bromide, and iodide) are often significant components of marine aerosols (31). Previous work on the relative nucleophilic strength of these species in the reactions of 1,2-epoxyethane (32) established the following relative nucleophilic strength ordering (based on the formal concentrations of the relevant species): $\text{H}_2\text{O} < \text{NO}_3^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$. Table 2 reports the results for the nucleophile product yields for the reaction of 3,4-epoxy-1-butene with the sodium salts of sulfate, nitrate, chloride, bromide, and iodide. From these results, it is apparent that sulfate and nitrate have similar nucleophilic strengths for the same formal concentration strength (for example, 1.0 M solutions of Na_2SO_4 and NaNO_3 both lead to 13% nucleophile addition product). It is also apparent that the previously

determined relative nucleophilic strengths of the halide ions for reactions of 1,2-epoxyethane are also appropriate for the reactions of halide ions with 3,4-epoxy-1-butene. Therefore, on a formal concentration basis, the halides are significantly better nucleophiles than sulfate or nitrate. Since 1,2-epoxyisoprene did not form any sulfate products, we also carried out reactions of this epoxide in the presence of the stronger halide nucleophiles to see whether any products other than the dihydroxy species were formed. Interestingly, only dihydroxy products were formed, even in the presence of high concentrations of iodide. In any case, aerosols with significant concentrations of nitrate and, particularly, halide ions, would be expected to facilitate epoxide reactions similar to those observed for sulfate.

Potential Significance to Ambient and Laboratory Secondary Organic Aerosol Observations of Polyols and Sulfates Derived from Isoprene. 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. In the measurement of ambient SOA, the chemical complexity of the particles does not allow for a direct comparison to our laboratory studies in which sulfuric acid content is controlled in the 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 ($[H^+]_{\text{aerosol}}$) of SOA particles in the Pittsburgh area (13). Zhang et al. then used the thermodynamic model of Clegg et al. (33) 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.

For the potential monoepoxides formed from the primary oxidation of isoprene, the present results are easily interpreted. At pH 1.5 ($[H^+] = 3 \times 10^{-2}$ M), the lifetimes for 1,2-epoxyisoprene and 3,4-epoxyisoprene are 600 μ s and 6 s, respectively. At pH 4.0 ($[H^+] = 1 \times 10^{-4}$ M), the lifetimes for 1,2-epoxyisoprene and 3,4-epoxyisoprene are 180 ms and 30 min, respectively. Since the wet deposition lifetime of SOA is on the order of a few days (34), it appears that, even at mildly acidic conditions, both isoprene monoepoxides will react quickly on SOA. The sulfate product studies indicate that the reaction of 1,2-epoxyisoprene in the presence of 1 M SO_4^{2-} exclusively leads to 1,2-dihydroxyisoprene, while the reaction of 3,4-epoxyisoprene yields 15% 4-hydroxy-2-methyl-3-sulfato-1-butene.

Since the potential diepoxide oxidation product of isoprene was not directly studied (and it is of obvious interest since the observed isoprene SOA products are often tetrafunctional), it is necessary to use a combination of the results for the various epoxides in order to estimate the reaction parameters for isoprene diepoxide. The results for 1,2-3,4-diepoxylbutane suggest that the kinetics of diepoxides can be approximated as two separate monoepoxide reactions, each with their own rate constants and sulfate branching ratios. For example, the relatively small rate constant for the first epoxide ring-opening of 1,2-3,4-diepoxylbutane is similar to the small rate constant previously measured for 1,2-epoxylbutane (22). The sulfate branching ratio of this step (38%) is also similar to that observed for 1,2-epoxylbutane (27%). In addition, the rate constant for the second epoxide ring-opening is almost the same as in the first step, indicating that the second epoxide ring-opening reaction is little affected by presence of the two neighboring hydroxy groups. Nonetheless, the sulfate branching ratio for the second epoxide ring-opening reaction (20%) is somewhat smaller than is observed in the first step. Because of the special reactivity of tertiary epoxides, the presence of the methyl group in the case of 1,2-3,4-diepoxylisoprene will lead to a significantly

reaction sequence than was observed for the 1,2-3,4-diepoxylbutane. However, because the 1,2-3,4-diepoxylbutane results indicate that the two epoxide ring-opening processes can be approximately treated separately, the reactions of 1,2-3,4-diepoxylisoprene can be approximated as the sequential reaction at the 1,2-epoxy functionality, which would be expected to be similar to 2-methyl-2,3-epoxylbutane (which has a pH 1.5 lifetime of 12 s and a pH 4.0 lifetime of 58 min and produces 11% sulfate at 1 M SO_4^{2-}) (22) followed by the reaction at the 3,4-epoxy functionality, which would be expected to be similar to 1,2-epoxy-3,4-dihydroxylbutane (which has a pH 1.5 lifetime of 7.7 h and a pH 4.0 lifetime of 38 days and produces 20% sulfate at 1 M SO_4^{2-}). In summary, particularly for SOA particles with pH values of about 2 or less, it is expected that isoprene diepoxide would have time to form tetrafunctional products, with a significant fraction of them with sulfate functionality, during the average several day lifetime of an SOA particle.

Paulot et al. recently reported high yields of 2,3-epoxy-1,4-dihydroxylisoprene and 1,2-epoxy-3,4-dihydroxylisoprene in the OH-initiated oxidation of isoprene; these products were rationalized as the result of secondary OH-initiated oxidation of hydroxy peroxides produced in the primary OH-initiated oxidation of isoprene (21). Since both of these monoepoxides have tertiary functionality, but are not capable of allylic stabilization (unlike the isoprene monoepoxides investigated in this work), it is expected that both of these species would have reactivities similar to 2-methyl-2,3-epoxylbutane (relatively large hydrolysis rate constants and significant sulfate-forming ability), and would therefore be expected to efficiently form tetrafunctional compounds on typical SOA particles.

In the laboratory studies of Surratt et al. (8), isoprene SOA was studied using seed sulfuric acid aerosols at 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, it is clear that sufficient acid and sulfate (both the H^+ and sulfate concentrations were in excess of 6 M) were present and that plenty of time was available for the polyol and hydroxy sulfate products to have formed by the proposed mechanism.

In summary, the present results suggest that the SOA reactivity of potential epoxides formed in the atmospheric oxidation of isoprene is sufficient to explain the existence of the isoprene-derived polyols and sulfates observed in ambient and laboratory SOA. In addition, the experiments confirming the possible nucleophilic reactive role of nitrate, chloride, bromide, and iodide species found in aerosols suggests that epoxides might be a source of organic hydroxy nitrates and halides in SOA.

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