

Kinetics of the Hydrolysis of Atmospherically Relevant Isoprene-Derived Hydroxy Epoxides

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Isoprene (the most abundant nonmethane hydrocarbon emitted into the atmosphere) is known to undergo oxidation to 2-methyl-1,2,3,4-butanetetraol, a hydrophilic compound present in secondary organic aerosol (SOA) in the atmosphere. Recent laboratory work has shown that gas phase hydroxy epoxides are produced in the low NO_x photooxidation of isoprene and that these epoxides are likely to undergo efficient acid-catalyzed hydrolysis on SOA to 2-methyl-1,2,3,4-butanetetraol at typical SOA acidities. In order to confirm this hypothesis, the specific hydroxy epoxides observed in the isoprene photooxidation experiment (as well as several other related species) were synthesized, and the hydrolysis kinetics of all species were studied via nuclear magnetic resonance (NMR) techniques. It was determined that the isoprene-derived hydroxy epoxides should undergo efficient hydrolysis under atmospheric conditions, particular on lower pH SOA. An empirical structure–reactivity model was constructed that parametrized the hydrolysis rate constants according to the carbon substitution pattern on the epoxide ring and number of neighboring hydroxy functional groups. Compared to the previously studied similar nonfunctionalized epoxides, the presence of a hydroxy group at the α position to the epoxy group was found to reduce the hydrolysis rate constant by a factor of 20, and the presence of a hydroxy group at the beta position to the epoxy group was found to reduce the hydrolysis rate constant by a factor of 6.

Introduction

Because secondary organic aerosol (SOA) is known to play a critical role in issues such as air pollution (1) and climate change (2), there continues to be intense interest in the formation mechanisms for these particles. Isoprene, the dominant non-methane hydrocarbon emitted into the atmosphere (3), has only recently been implicated in SOA formation. In 2004, Claeys et al. identified 2-methyl-1,2,3,4-butanetetraol in SOA found in air samples from the Amazon and inferred that it must be an oxidation product of isoprene (4). Several laboratory and field studies have now confirmed that 2-methyl-1,2,3,4-butanetetraol (and several other species with alcohol and sulfate functionality) is produced in the photooxidation of isoprene (5–10). Based on this work, global modeling now suggests that isoprene is the single largest source of SOA (11).

However, the mechanism by which isoprene is converted into multifunctional species such as 2-methyl-1,2,3,4-bu-

tanetetraol remains uncertain. Previously, Minerath et al. investigated the potential role of epoxides as a key intermediate in the formation of polyols from a variety of small alkenes (12) and found the reactions to be kinetically feasible under atmospheric conditions. In the most recent work (13), Minerath et al. investigated the acid-catalyzed hydrolysis of isoprene-derived monoepoxides and mono- and diepoxides derived from 1,3-butadiene (a well-known reaction in which an epoxide ring is replaced by two hydroxy groups (14), as depicted in Figure 1). Despite the wide range of hydrolysis rate constants observed for the various species, the acid-catalyzed hydrolysis pathway was postulated to be a kinetically feasible mechanism for the formation of the isoprene-derived species commonly observed in SOA. However, a specific gas phase formation mechanism for such isoprene epoxides had not yet been identified. Filling this gap, Paulot et al. identified two dihydroxy epoxides (3-methyl-3,4-epoxy-1,2-butanediol and 2-methyl-2,3-epoxy-1,4-butanediol) produced from the photooxidation of isoprene in an environmental chamber under low NO_x conditions (15). In subsequent work, it was shown that these species were more rapidly taken up into seed particles under acidic conditions (16). Recently, isoprene-derived hydroxy epoxides, polyols, and sulfates have been observed to coexist in ambient SOA sampled in the southeastern United States (17), thus providing direct evidence for the atmospheric relevance of the proposed epoxide hydrolysis mechanism.

In the present study, the two dihydroxy epoxide species observed by Paulot et al. as well as two other possible isoprene epoxides (2-methyl-1,2,3,4-diepoxybutane and 2-methyl-3,4-epoxy-1,2-butanediol) are synthesized, and their acid-catalyzed hydrolysis rate constants are determined via nuclear magnetic resonance (NMR) techniques. These results allow for an estimation of the kinetic feasibility of the hydrolysis reactions of the species observed by Paulot et al. on SOA (15). Several other 4- and 5-carbon hydroxy epoxides are also synthesized and kinetically investigated in order to better rationalize the structural effects of epoxide carbon substitution and the number and position of neighboring hydroxy groups on the hydrolysis rate constant observed in the isoprene-derived epoxides. Based on this more extensive hydrolysis rate constant data set, an empirical structure–reactivity model is developed for the general prediction of hydrolysis rate constants for hydroxy epoxides. In addition to providing a parametrization of the present results for the isoprene-derived epoxides, the model should also be useful in predicting the rate of hydrolysis for other epoxides potentially formed (such as those formed from monoterpenes (18–21)) in the atmosphere.

Experimental Section

Synthesis of (\pm)-2-Methyl-1,2,3,4-diepoxybutane. The synthesis of (\pm)-2-methyl-1,2,3,4-diepoxybutane followed a hybrid method based on the procedures of Wistuba et al. (22) and Chiappe et al. (23) Approximately 300 mL of CH_2Cl_2 was distilled into a 500 mL round-bottom flask, and 28.05 g of meta-chloroperoxybenzoic acid (mCPBA, Sigma-Aldrich) was added. To this solution was added at once 6.2 mL of isoprene,

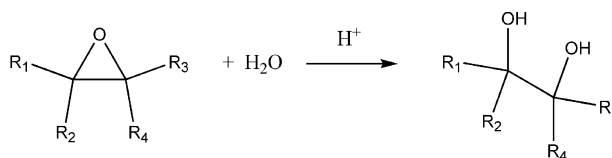


FIGURE 1. Acid-catalyzed hydrolysis of epoxides.

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and the solution was swirled and capped. The reaction was let sit for one week at room temperature and then stored at 4 °C for at least 4 h. The solution was then gravity filtered to remove any insoluble products. A 2 molar excess of KF (22.08 g) was dried in vacuo at 120 °C for 2 h and added to the filtrate, and the mixture was vigorously stirred. After 1 h, this solution was again gravity filtered, and a majority of the solvent was removed under reduced pressure at room temperature. Vacuum distillation of the remaining solution at 300 mTorr yielded approximately 2 g of (±)-2-methyl-1,2,3,4-diepoxybutane (the presence of the two diastereometric forms of 2-methyl-1,2,3,4-diepoxybutane was most easily ascertained by the presence of two methyl group singlets in the NMR spectrum). As was the case for all syntheses, ¹H NMR was used to confirm the product identities and to assess the purity of the product. ¹H NMR spectra for all of the isoprene-derived epoxides (and the hydrolysis product of all of these epoxides, 2-methyl-1,2,3,4-butanetetraol) are given in the Supporting Information.

Synthesis of (±)-2-Methyl-3,4-epoxy-1,2-butanediol. The synthesis of (±)-2-methyl-3,4-epoxy-1,2-butanediol required the preparation of 2-methyl-3-butene-1,2-diol, which was produced according to the method of Ruppert and Becker (24). Five mL of commercially available 95% 2-methyl-2-vinyloxirane (Sigma-Aldrich), used without further purification, was added to a 125 mL Erlenmeyer flask containing 25 mL of room temperature H₂O with stirring. After several minutes, the solution was heated to 80 °C on a heating mantle for 1 h. The reaction was then saturated with NaCl and washed twice with 100 mL portions of diethyl ether. The ethereal layer was then dried for at least 1 h over Na₂SO₄ (approximately 5 g) in a 250 mL Erlenmeyer flask and gravity filtered, and the solvent was removed under reduced pressure. Vacuum distillation of the remaining product at 54 °C and 1 Torr yielded approximately 4 g of 2-methyl-3-butene-1,2-diol. Epoxidation of 2-methyl-3-butene-1,2-diol was carried out according to the procedure outlined above for the synthesis of (±)-2-methyl-1,2,3,4-diepoxybutane, with equimolar mCPBA (because there is only one epoxide ring forming in this synthesis), yielding approximately 2 g of (±)-2-methyl-3,4-epoxy-1,2-butanediol.

Synthesis of (±)-3-Methyl-3,4-epoxy-1,2-butanediol. The synthesis of (±)-3-methyl-3,4-epoxy-1,2-butanediol required the preparation of 3-methyl-1,2-epoxy-3-butene, which was produced according to the Harwood et al. (25). To 300 mL of freshly distilled CH₂Cl₂ were placed 30 g of powdered NaOH and 25.8 g of trimethyl sulfonium methyl sulfate (Oakwood Products, Inc.) in a 500 mL round-bottom flask. The solution was vigorously stirred, while 100 μL of methacrolein (Sigma-Aldrich) was added via digital pipet every 3 min over the course of 5 h for a total 10 mL of methacrolein added. The reaction was then stored overnight at 4 °C. 100 mL of H₂O was added, and the resulting organic phase was separated, washed with an additional 100 mL of water, separated again, and then dried for at least 1 h over MgSO₄. A majority of the solvent was removed under reduced pressure yielding approximately 5 g of 3-methyl-1,2-epoxy-3-butene. The 3-methyl-1,2-epoxy-3-butene/CH₂Cl₂ mixture was added to 50 mL of 0.002 M H₂SO₄ in a 125 mL Erlenmeyer flask and stirred at room temperature for several minutes. The solution was then heated to 80 °C with a heating mantle for 1 h and then distilled in vacuo, yielding approximately 3 g of 3-methyl-3-butene-1,2-diol (24). Epoxidation of the diol was performed according to the procedure outlined in the synthesis of (±)-2-methyl-1,2,3,4-diepoxybutane, again scaled appropriately to form one epoxide ring, yielding approximately 2 g of (±)-3-methyl-3,4-epoxy-1,2-butanediol.

Synthesis of (±)-2-Methyl-2,3-epoxy-1,4-butanediol. The synthesis of (±)-2-methyl-2-butene-1,4-diol was based on the three step procedure of Shepard and Johnson (26).

49.4 g of Br₂ was added to 75 mL of CHCl₃ at 0 °C in a 50 mL Erlenmeyer flask. Separately, 20.84 g of isoprene was added to 30 mL of CHCl₃ in a 250 mL round-bottom flask in a bath of diethyl ether and dry ice. The bromine solution was added dropwise to the isoprene solution over 1.5 h with a Pasteur pipet, while the temperature of the isoprene solution was maintained below -25 °C. Five g of NaHSO₄ was added, and the solution was mixed thoroughly until an orange to yellow color change was observed. Two vacuum distillations were performed yielding approximately 30 g of 2-methyl-1,4-dibromo-2-butene. 7.47 g of potassium acetate was powdered and transferred to a 250 mL round-bottom flask. Approximately 30 mL of glacial acetic acid was added. 7.32 g of the dibromo species was weighed out and added to the acetic acid solution. The open flask was then placed in a 100 °C oil bath with stirring for 18 h. After this time, the reaction was poured into 100 mL of H₂O in a 500 mL separatory funnel. Three diethyl ether washes (totaling approximately 400 mL) of the combined aqueous and organic layers were performed. The ethereal layer was separated, and the solvent was removed under reduced pressure, resulting in approximately 5 g of 2-methyl-1,4-diacetate-2-butene-1,4-diol. To 50 mL of 95% ethanol in a 100 mL round-bottom flask, 31.01 g of Ba(OH)₂•8H₂O was added, and the solution was placed in a 70 °C oil bath with reflux condenser. The diacetate species was then added to the ethanol solution with stirring, and the reaction proceeded for 5 h. After cooling, the solution was vacuum filtered, and the precipitate was washed with ethanol for a combined liquid volume of 400 mL. The ethanol was then removed under reduced pressure. Vacuum distillation of the remaining product yielded 1.9 g of 2-methyl-2-butene-1,4-diol. This diol species was then added to approximately 150 mL of dry CH₂Cl₂ in a 250 mL round-bottom flask. 3.21 g of mCPBA was added, and the solution was capped, swirled, and let sit for one week at room temperature. 2.19 g of KF was then dried under vacuum at 120 °C and added to the reaction with stirring for one hour. Upon filtration of the reaction, it was noted that the product was extremely viscous and was being trapped by the filter. Additional CH₂Cl₂ was used to wash the filtrate and bring the product back into solution. The solvent was removed under reduced pressure, yielding about 1 g of (±)-2-methyl-2,3-epoxy-1,4-butanediol.

Synthesis of Other Hydroxy Epoxides. The other hydroxy epoxides investigated in this work were prepared starting from commercially obtained hydroxy alkenes and following the epoxidation procedure outlined in the synthesis of (±)-2-methyl-1,2,3,4-diepoxybutane, again scaled appropriately for one epoxide ring formation.

Epoxide Hydrolysis Kinetics Measurements. All ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were collected on a Varian 400 MHz NMR spectrometer. Spectra were analyzed using SpinWorks 3.1. Kinetic experiments were performed using deuterated acid solutions for the purpose of locking. These acid solutions were custom prepared using commercially available 96–98 wt % D₂SO₄ (Sigma-Aldrich) and 99.9% D₂O (Cambridge Isotope Lab, Inc.). To each acid solution, 0.1 wt % sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS, Cambridge Isotope Lab, Inc.) was added as an internal standard.

Kinetic measurements were made by collecting sequential ¹H NMR spectra over the course of 1 h with approximately 2 min elapsing between the ends of each collection. For each experiment, an acid concentration was chosen to yield a significant amount of product during the hour of data collection. In a 25 mL Erlenmeyer flask, a 5 mL aliquot of the desired acid was stirred. To this, 50 μL of epoxide was added and a timer started. After 3 min of stirring, a sample was loaded into an NMR tube, and spectral collection was started. The reaction time was recorded at the end of each collection. Relative amounts of reactant and product were calculated

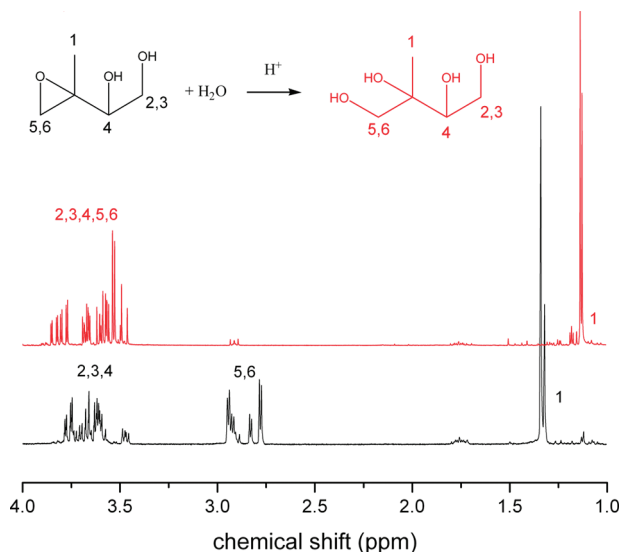


FIGURE 2. Reactant (black structure and spectrum) and product (red structure and spectrum) NMR spectra for the hydrolysis of 3-methyl-3,4-epoxy-1,2-butanediol to 2-methyl-1,2,3,4-butanetetraol.

by appropriate peak integration referenced to the 9 methyl protons at 0.00 ppm from DSS. For example, Figure 2 shows the reactant and product NMR spectra for the hydrolysis of 3-methyl-3,4-epoxy-1,2-butanediol.

Results and Discussion

Determination of Hydrolysis Rate Constants. The acid-catalyzed hydrolysis of epoxides is known to be first order in both the epoxide and proton concentrations (27, 28)

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

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

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

The second order hydrolysis rate constants (k) were calculated from the first order rate constants (k') and the proton concentration was calculated from the Aerosol Inorganics Model (AIM) (29) for each solution via eq 3 and are reported in Table 1. Based on run to run variability, we estimate that the rate constants are characterized by a precision of approximately 20%. In our earlier work on simple (without hydroxy functionalization) isoprene-derived epoxides, we surmised that, in the absence of significant effects from the hydroxy groups, the hydrolysis rate constants for the two species observed by Paulot et al., 3-methyl-3,4-epoxy-1,2-butanediol and 2-methyl-2,3-epoxy-1,4-butanediol (15), should have hydrolysis rate constants similar to that of 2-methyl-1,2-epoxypropane ($8.7 \text{ M}^{-1} \text{ s}^{-1}$) and 2-methyl-2,3-epoxybutane ($9.0 \text{ M}^{-1} \text{ s}^{-1}$), respectively (12). It is clear from the data in Table 1 that the neighboring hydroxy groups significantly depress the hydrolysis rate constant values as compared to otherwise structurally similar nonhydroxy functionalized epoxides. Since the hydrolysis rate constant for 2-methyl-1,2,3,4-diepoxybutane was also determined to

be significantly smaller than the value for the structurally similar 2-methyl-1,2-epoxypropane species, it appears that neighboring epoxide rings also serve to depress the hydrolysis rate constant values (as was also noted in our earlier study of 1,2,3,4-diepoxybutane) (13).

Estimate of SOA Lifetime for Isoprene-Derived Epoxides. 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 (30). Zhang et al. then used the thermodynamic model of Clegg et al. (31) 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. From these estimates of SOA pH, the lifetimes of the hydrolysis reactions for the isoprene-derived epoxides were calculated using the following equation

$$\tau = [H^+]^{-1}k^{-1} \quad (4)$$

where $[H^+]$ is the assumed SOA acid concentration. The calculated hydrolysis lifetimes for the isoprene derived epoxides on SOA are given in Table 2. As the data in Table 2 demonstrate, the hydrolysis reactions at low aerosol pH have lifetimes well within the estimated wet deposition lifetime for SOA of a few days (32). Therefore, while the actual hydrolysis rate constants are significantly lower for the two epoxides observed by Paulot et al. (15) than was expected based on the hydrolysis rate constants for the structurally similar nonhydroxy functionalized epoxy alkanes, the hydrolysis reactions for these species are nonetheless expected to be kinetically efficient on SOA at lower pH values.

Empirical Structure Reactivity Model for the Hydrolysis Rate Constants. While it is well-known that the carbon substitution pattern of the epoxide ring has a dramatic effect on the hydrolysis rate constant (14), the present work makes it clear that neighboring hydroxy groups can also have a dramatic effect on the rate constant, reducing the rate of the hydrolysis reaction by up to 3 orders of magnitude. To better understand the relationship between rate constant and neighboring hydroxyl groups, a variety of 4- and 5-carbon hydroxy epoxides were synthesized and their hydrolysis rate constants measured.

Each epoxide was assigned a simple carbon substitution number (CSN) according to the relative reactivity of the epoxide ring based on the S_N1 -type mechanism of the hydrolysis reaction. For example, the epoxide ring in 1,2-epoxyethane (ethylene oxide) has two primary substituted carbon atoms (referred to as 1° - 1°) and is known to be the least reactive simple aliphatic epoxide (14). For the purposes of the empirical model, this least reactive epoxide is assigned a CSN of 1. The next least reactive aliphatic epoxide is a primary-secondary (1° - 2°) substituted system; this epoxide is assigned a CSN of 2 and so on up to a CSN of 6 for a tertiary-tertiary (3° - 3°) substituted system. The assigned CSN for each species is given in Table 1.

In addition, the effect of neighboring hydroxy groups on the hydrolysis rate constants was parametrized by simply counting the number of neighboring hydroxy groups. This number was straightforwardly assigned by counting the total number of α - or β -hydroxy groups (relative to the nearest epoxide carbon), referred to as HN_α and HN_β , respectively. The assigned HN_α and HN_β values for each species are also given in Table 1.

In addition to the species given in Table 1, the hydrolysis rate constant data (all with $HN_\alpha = HN_\beta = 0$ and the CSN value in parentheses) for 1,2-epoxyethane (CSN = 1), 1,2-epoxypropane (CSN = 2) (33), 1,2-epoxybutane (CSN = 2), *trans*-2,3-epoxybutane (CSN = 3), 2-methyl-1,2-epoxypropane (CSN = 4), 2-methyl-2,3-epoxybutane (CSN = 5), and

TABLE 1. Experimental Hydrolysis Rate Constants and Empirical Model Parameters for the Epoxides Studied in the Present Work

Name	Structure	k_{exp} ($\text{M}^{-1}\text{s}^{-1}$)	CSN	HN_{α}	HN_{β}	k_{model} ($\text{M}^{-1}\text{s}^{-1}$)
2-methyl-1,2,3,4-diepoxybutane		0.035 ^a				
2-methyl-3,4-epoxy-1,2-butanediol		0.0015	2	1	1	0.0071
3-methyl-3,4-epoxy-1,2-butanediol ^b		0.0079	4	1	1	0.013
2-methyl-2,3-epoxy-1,4-butanediol ^b		0.036	5	1	1	0.052
2,3-epoxy-1,4-butanediol		0.0014	3	1	1	0.0030
3-methyl-2,3-epoxy-1-butanol		0.48	5	1	0	0.33
3-methyl-3,4-epoxy-1-butanol		0.37	4	0	1	0.26
3,4-epoxy-1-butanol		0.015	2	0	1	0.015
3,4-epoxy-2-butanol		0.0043	2	1	0	0.0045

^a Hydrolysis rate constant for the opening of the 1,2 epoxide ring. ^b Observed by Paulot et al. (15).

TABLE 2. Estimated SOA Lifetimes of Isoprene-Derived Epoxides

Name	Structure	Lifetime at pH=1.5 (days)	Lifetime at pH=4.0(days)
2-methyl-1,2,3,4-diepoxybutane		0.01 ^a	3.3 ^a
2-methyl-3,4-epoxy-1,2-butanediol		0.24	77
3-methyl-3,4-epoxy-1,2-butanediol ^b		0.05	15
2-methyl-2,3-epoxy-1,4-butanediol ^b		0.01	3.2

^a Lifetime based on hydrolysis rate constant for the opening of the 1,2 epoxide ring. ^b Observed by Paulot et al. (15).

2,3-dimethyl-2,3-epoxybutane (CSN = 6) (12) as well as 3,4-epoxy-1,2-butanediol (CSN = 2, HN_{α} = 1, HN_{β} = 1) (13) were included in the model fitting process. 2-Methyl-1,2,3,4-diepoxybutane was not included in the model fitting process, since the 3,4 epoxide ring exerts a different functional group effect on the hydrolysis rate constant for the 1,2 epoxide ring hydrolysis than do hydroxy groups. It was found that the

$\log_{10}k$ values for the epoxides in the model set varied linearly with CSN and both HN values. Since CSN, HN_{α} , and HN_{β} are very crude proxies for variations in the transition state energies as a function of structural differences in the various species, it is remarkable that reasonably linear behavior is observed. Figure 3 shows that the dependence of the hydrolysis rate constant on CSN and HN is approximately

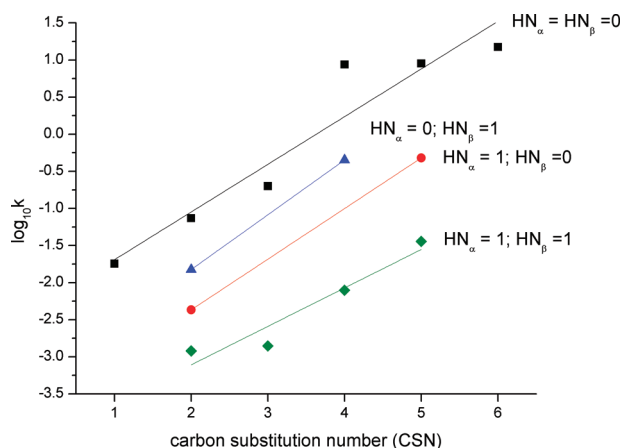


FIGURE 3. Carbon substitution number dependence of the hydrolysis rate constants for different neighboring hydroxy group situations.

separable (similar CSN-dependent slopes are obtained at different fixed HN values, as depicted in Figure 3). Therefore, multiple linear regression techniques were used to determine the following simple three parameter empirical model for the hydrolysis rate constants of epoxides

$$\log_{10} k = 0.622 \cdot \text{CSN} - 1.32 \cdot \text{HN}_{\alpha} - 0.797 \cdot \text{HN}_{\beta} - 2.27 \quad (5)$$

Table 1 includes all hydrolysis rate constants measured in the present study as well as their CSN, HN_{α} , HN_{β} , and model-predicted hydrolysis rate constants. As will be discussed below, the presence of the electronegative oxygen atom (whether in the functional form of an additional epoxide ring or a hydroxy group) seems to be the key structural feature that causes the hydrolysis rate constants to be depressed compared to the values expected if no functional groups are present. On average, the model-predicted values agree with the experimental values to within 50%. The regression equation indicates that the presence of a α -hydroxy group depresses the hydrolysis rate constant by roughly a factor of 20, while the presence of a β -hydroxy group depresses the hydrolysis rate constant by roughly a factor of 6.

As discussed above, the CSN and HN parameters in the empirical model are likely proxies for changing transition state energies as a function of structural differences in the various species. The CSN dependence has been previously rationalized as being due to the increasing stability of the carbocation intermediate as the carbon substitution on the epoxide ring is increased (14). Since both neighboring epoxide rings and hydroxy groups were found to depress the hydrolysis rate constant, it appears that the presence of electronegative oxygen atoms reduces the stability of the transition state, likely by drawing away electron density from the reactive epoxide oxygen atom. This is reflected in the experimental data, in which a α -hydroxy group has a more pronounced effect upon the rate constant than a β -hydroxy group, as the σ bond based effect is expected to decrease with decreasing proximity (and is why γ -hydroxy groups are not considered in this study). In previous work, Pritchard and Long observed a similar effect for 1,2-epoxypropane (propylene oxide): both hydroxy and chloro substitution at the α -position served to depress the hydrolysis rate constant by 1 to 2 orders of magnitude (27).

In conclusion, we have carried out the synthesis of the two dihydroxy epoxide species observed by Paulot et al. (15) as well as two other possible isoprene epoxides and have made measurements of their acid-catalyzed hydrolysis rate constants via nuclear magnetic resonance (NMR) techniques. These kinetics results indicate that, despite the fact that the

hydroxy groups serve to depress the hydrolysis rate constants as compared to simple nonfunctionalized epoxides (12, 13), the dihydroxy epoxide species observed by Paulot et al. can nonetheless undergo efficient hydrolysis on SOA, particularly at the lower end of the pH values typically found in the atmosphere (30). The recent observation that ambient SOA can contain both hydroxy epoxides and their corresponding hydrolysis products (17) seems to confirm the present result that the hydrolysis lifetimes are on the order of the SOA lifetimes for moderate SOA pH values. Using the present results and the hydrolysis rate constants from a larger family of epoxides (including newly measured hydrolysis rate constants for several other C_4 and C_5 hydroxy epoxides), an empirical structure reactivity model has been developed, which is parametrized according to the carbon substitution pattern on the epoxide ring and the number of neighboring hydroxy groups. Since the model predicts the hydrolysis rate constants at a reasonable level of accuracy for the experimentally measured set of epoxides considered in the present study, we expect that the model will be useful for predicting hydrolysis rate constants for other atmospherically relevant epoxides (such as those formed in the oxidation of monoterpene (19–21)).

Acknowledgments

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Supporting Information Available

^1H NMR spectra for all of the isoprene-derived epoxides (and the hydrolysis product of all of these epoxides, 2-methyl-1,2,3,4-butanetetraol) (Figures S1–S5). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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