# Kinetics of the Aqueous Phase Reactions of Atmospherically Relevant Monoterpene Epoxides

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**ABSTRACT:** Laboratory and field measurements have demonstrated that an isoprene-derived epoxide intermediate (IEPOX) is the origin of a wide range of chemical species found in ambient secondary organic aerosol (SOA). In order to explore the potential relevance of a similar mechanism for the formation of monoterpene-derived SOA, nuclear magnetic resonance techniques were used to study kinetics and reaction products of the aqueous-phase reactions of several monoterpene epoxides:  $\beta$ -pinene oxide, limonene oxide, and limonene dioxide. The present results, combined with a previous study of  $\alpha$ -pinene oxide, indicate that all of these epoxides will react more quickly than IEPOX with aqueous



atmospheric particles, even under low-acidity conditions. As for  $\alpha$ -pinene oxide, the observed products can be mainly rationalized with a hydrolysis mechanism, and no long-lived organosulfate or nitrate species nor species that retain the  $\beta$ -pinene bicyclic carbon backbone are observed. As bicyclic ring-retaining organosulfate and nitrate species have been previously observed in monoterpene-derived SOA, it appears that monoterpene-derived epoxides may not be as versatile as IEPOX in producing a range of SOA species, and other mechanisms are needed to rationalize organosulfate and nitrate formation.

# INTRODUCTION

Biogenic volatile organic compounds (BVOCs) are emitted into the atmosphere in massive quantities, with isoprene and the monoterpenes comprising the largest portion of the roughly 1000 Tg/yr annual emission budget.<sup>1</sup> Once in the atmosphere, BVOCs undergo reactions with oxidants that can ultimately perturb the NO<sub>x</sub> and HO<sub>x</sub> radical cycles that govern the formation of tropospheric ozone, a key atmospheric pollutant.<sup>2</sup> These reactions can also lead to chemical species that serve as precursors for secondary organic aerosol (SOA), which is also known to play a key role in air quality, as well as climate change.<sup>3</sup> In particular, in order for BVOCs to become incorporated into SOA, they must undergo specific types of chemical processing that serve to reduce their volatility.<sup>4</sup>

Because of its paramount importance, the formation mechanisms for isoprene-derived SOA have received intense attention. From a plethora of laboratory and field studies, it is now known that many of the isoprene-derived species found in SOA are ultimately derived from the gas-phase intermediate, isoprene epoxydiol (IEPOX).<sup>5</sup> Because epoxides readily undergo nucleophilic attack by common SOA species, such as water, sulfate, nitrate, and organic nucleophiles,<sup>6</sup> IEPOX serves as a bridge to the formation of the low-volatility polyols, organosulfates, organonitrates, and oligomers that dominate the isoprene-derived species observed in ambient SOA.<sup>7</sup>

There have been a number of studies that have either identified epoxide intermediates formed from the monoterpenes or have identified potential SOA products of such epoxide reactions, or both. For example,  $\alpha$ -pinene oxide, an epoxide formed by O atom insertion across the endocyclic

double bond in  $\alpha$ -pinene, and  $\beta$ -pinene oxide, an epoxide formed by O atom insertion across the exocyclic double bond in  $\beta$ -pinene, have been observed as minor products in gas-phase photooxidation experiments.<sup>8-18</sup> However, despite the relatively large number of studies that have identified either  $\alpha$ - or  $\beta$ pinene oxide as products of pinene oxidation, the conditions under which these products are formed and the quantitative yields of the products remain uncertain. In addition, there have been some laboratory studies of the reactivity of  $\alpha$ -pinene oxide,  $\beta$ -pinene oxide, and limonene oxide (although limonene oxide itself has not been directly detected in an atmospherically relevant reaction system) with SOA-like systems, 11,12,16,19-24 which have suggested that IEPOX-type mechanisms, as well as other monoterpene epoxide-specific mechanisms, are potentially relevant. Field measurements of monoterpene SOA species have also been suggestive of the relevance of IEPOXtype mechanisms.<sup>19,25–28</sup> Additionally, it has been demonstrated that limonene can undergo direct reaction on surfaces characteristic of atmospheric mineral dust, presumably through an epoxide intermediate, which then undergoes hydrolysis to form the low-volatility compound limonene diol.<sup>29</sup> Therefore, it appears that monoterpene epoxides may have atmospheric relevance in a number of different atmospheric aerosol reaction contexts.

In previous work,<sup>23</sup> we reported that  $\alpha$ -pinene oxide reacts very quickly in aqueous solutions, even under low-acidity

Received: September 22, 2017 Revised: November 16, 2017 conditions. Depending on the acid concentration, a number of different products from the reaction of  $\alpha$ -pinene oxide were observed. In contrast to some previous laboratory results, no long-lived organosulfate or organonitrate species were observed, and no species that retain the  $\alpha$ -pinene bicyclic carbon backbone were observed. Instead, the overall product distribution could be explained by various rearrangements of the initial carbocation intermediate formed in the four carbon ring opening of  $\alpha$ -pinene oxide, all of which can be rationalized by the thermodynamically driven relief of the bicyclic ring strain in the  $\alpha$ -pinene carbon backbone.

In this paper, we extend the methods of our previous study of  $\alpha$ -pinene oxide reactivity to other monoterpene epoxides in order to further ascertain the overall potential impact of epoxide intermediates on the formation of monoterpenederived SOA. Specifically, we report measurements of the kinetics and products of the aqueous-phase acid-catalyzed reactions of  $\beta$ -pinene oxide, limonene oxide (an epoxide formed by O atom insertion across the endocyclic double bond in limonene), and limonene diepoxide (a diepoxide formed by an additional O atom insertion across the exocyclic double bond in limonene oxide), using nuclear magnetic resonance (NMR) as the analytic technique. These results are then used to assess the potential impact of these monoterpene epoxides on the particle-phase composition of the atmosphere.

#### EXPERIMENTAL SECTION

β-Pinene Oxide Synthesis. β-Pinene oxide was prepared according to a previously published procedure.<sup>30</sup> To a mixture of 21.25 g (0.16 mol) of β-pinene and 50 g of powdered, anhydrous Na<sub>2</sub>CO<sub>3</sub> in 200 mL of CH<sub>2</sub>Cl<sub>2</sub>, stirred in an ice water bath, 33.5 mL of 39% (0.17 mol) peracetic acid containing 0.3 g of KC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> (all obtained from Sigma-Aldrich) was added dropwise. The mixture was stirred at room temperature until NMR analysis indicated that the β-pinene had been consumed. The solution was vacuum filtered and washed with additional CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed on a rotary evaporator, and the residue was vacuum distilled. The yield was 14.2 g (60%), and NMR analysis indicated >95% purity.

Bulk Aqueous Solution Preparation. To explore the concentration dependence of various atmospherically relevant species on the reaction kinetics and products of the various monoterpene epoxides, bulk aqueous solutions were prepared with varying acid, sulfate, and nitrate concentrations. All experiments were carried out in deuterated solvents, which were necessary for NMR locking purposes. For acid-dependent experiments, deuterated perchloric acid was used (to exclude nucleophilic addition mechanisms other than hydrolysis). For sulfate/nitrate concentration dependence experiments, dilute (0-0.02M) deuterated sulfuric/nitric acid was combined with sodium sulfate/nitrate (0-1 M). These solutions were prepared using commercially available 68 wt % DClO<sub>4</sub> (Sigma-Aldrich), 96-98 wt % D<sub>2</sub>SO<sub>4</sub> (Sigma-Aldrich), 70 wt % DNO<sub>3</sub> (Sigma-Aldrich), 99.9% D<sub>2</sub>O (Cambridge Isotope Laboratories, Inc.), Na<sub>2</sub>SO<sub>4</sub> (Sigma-Aldrich), and NaNO<sub>3</sub> (Sigma-Aldrich). In order to initiate the chemical reaction, the monoterpene epoxide was added to the bulk solution, and the solutions were stirred for at least 1 min to ensure homogeneity before any analysis was performed. The commercially available epoxides used were 97% (+)-cis- and trans-limonene oxide and limonene dioxide (both from Sigma-Aldrich).

**Kinetics Method.** Kinetics measurements of the aqueous phase reactions of monoterpene epoxides were made by collecting sequential <sup>1</sup>H NMR spectra over the course of the experiment and measuring the loss of epoxides. Each measurement was performed in the same manner: 10  $\mu$ L of epoxide was added to a 1 mL aliquot (corresponding to an initial epoxide concentration of about 0.06 M) of the desired aqueous solution, and the solution was stirred in a 20 mL vial. After approximately 1 min of stirring to ensure solution homogeneity, the entire reaction mixture was loaded into an NMR tube, and spectral collection was started. Experiments were performed using a pure  $D_2O$  solution and  $DClO_4$ solutions of differing acidities. A first-order decay rate law was found to fit the epoxide concentration vs time data, and the first-order rate constants were determined for each solution. From the DClO<sub>4</sub> solution data, second-order acid-catalyzed rate constants were also determined.

Chloroform Extraction Method. To identify and quantify all products formed (including phase-partitioned species that have limited water solubility), the product species were extracted from the bulk aqueous reaction mixtures with CDCl<sub>3</sub> (Cambridge Isotope Laboratories, Inc.). A typical solution was prepared by adding about 10 mg of the aqueous soluble internal standard DSS (sodium 2,2-dimethyl-2silapentane-5-sulfonate, Cambridge Isotope Laboratories, Inc.) to a 20 mL vial equipped with a Teflon-coated magnetic stir bar and charged with about 7 mL of a premixed solution containing the inorganic components (as described in the previous section). The reaction was then initiated by micropipetting 100  $\mu$ L of the monoterpene epoxide (corresponding to an initial epoxide concentration of about 0.09 M) into the vial and then stirring the mixture vigorously. Reaction workup began by transferring about a 1 mL aliquot of the aqueous solution into an NMR tube and taking a standard <sup>1</sup>H NMR spectrum (in order to determine the concentrations of the aqueous soluble species). Next, about 6 mL of CDCl<sub>3</sub> was added to the remaining aqueous solution in the vial, and the resulting mixture was stirred for 20 min, after which the aqueous and organic layers (about 6 mL of each) were allowed to separate. Each layer was then micropipetted into two new 20 mL vials. Then, 20.0  $\mu$ L of a second, chloroform-soluble, internal standard (benzene, ACS spectrophotometric grade, ≥99%, Sigma-Aldrich) was micropipetted into the vial containing the organic layer, and the solution was stirred for 2 min. Typically, both <sup>1</sup>H and <sup>13</sup>C NMR spectra were collected for CDCl<sub>3</sub>extracted solutions. NMR analysis of the remaining aqueous layer indicated that the CDCl<sub>3</sub> extraction was not completely efficient for the aqueous soluble species. Therefore, the total product concentrations were determined by adding together the product concentrations determined from the aqueous and CDCl<sub>3</sub> solutions.

**NMR Product Identification and Quantitation Methods.** All NMR spectra were collected on a Varian 400 MHz instrument. In CDCl<sub>3</sub> solutions, <sup>1</sup>H and <sup>13</sup>C chemical shifts were calibrated to the solvent at 7.26 and 77.16 ppm, respectively.<sup>31</sup> In D<sub>2</sub>O solutions, <sup>1</sup>H chemical shifts were calibrated to the solvent at 4.79 ppm. In some cases, DSS was added to D<sub>2</sub>O solutions to provide a <sup>13</sup>C reference at 0.00 ppm.

Some species were identified by comparison to commercially available standards: (+)-*cis*- and *trans*-limonene oxide, limonene dioxide, perillyl alcohol, perillyl aldehyde, myrtenal, and 1*S*,2*S*,4*R*-(+)-limonene 1,2-diol (all obtained from Sigma-Aldrich). However, several other noncommercially available



limonene dioxide

Figure 1. NMR assignments (<sup>1</sup>H referenced to HDO at 4.79 ppm, <sup>13</sup>C referenced to CDCl<sub>3</sub> at 77.16 ppm) for previously unassigned species.

species were identified via previously reported <sup>1</sup>H and <sup>13</sup>C CDCl<sub>3</sub> NMR data:  $\beta$ -pinene oxide,<sup>32</sup> 7-hydroxyterpineol,<sup>33</sup> and dihydrocarvone.<sup>34</sup>

The relative amounts of reaction products were calculated by peak integration of unique nuclei for each species, referenced to the nine methyl protons at 0.00 ppm from DSS, the six protons at 7.34 ppm from benzene, or the six carbon atoms at 128.4 ppm from benzene.

In addition to standard one-dimensional <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy methods, the following correlation NMR spectroscopy methods were also used: <sup>1</sup>H–<sup>1</sup>H correlation spectroscopy (COSY), <sup>13</sup>C distortionless enhancement by polarization transfer (DEPT), <sup>1</sup>H–<sup>13</sup>C heteronuclear single-quantum correlation (HSQC), and <sup>1</sup>H–<sup>13</sup>C heteronuclear multiple bond correlation (HMBC) techniques.<sup>35</sup>

# RESULTS AND DISCUSSION

**NMR Assignments.** While at least partial NMR chemical shift data for all of the reactants and products studied in this work are available in the literature, most of the literature data are not reported as NMR chemical shift *assignments* (the association of individual resonances with specific protons and/ or carbon atoms of the structurally specific chemical species). Because NMR chemical shift assignments are often necessary to sort out the small structural differences that distinguish similar species (especially for isomers), we used extensive correlation NMR spectroscopy experiments to determine <sup>1</sup>H and <sup>13</sup>C assignments for the reactants  $\beta$ -pinene oxide, *cis*- and *trans*-(+)-limonene oxide, and a mixture of four isomers of limonene dioxide as well as the  $\beta$ -pinene oxide reaction products, 7-

hydroxyterpineol and perillyl alcohol. The assignments are given in Figure 1. In the limonene oxide<sup>36,37</sup> and limonene dioxide<sup>38,39</sup> cases, partial assignments were previously reported in the literature, but we believe that all of these previous assignments have errors due to the difficulty in identifying the specific isomers present in the commercially available mixtures. Notably, these previous assignments did not utilize C-H bond correlation NMR spectroscopies (i.e., DEPT, GHSQC, and GHMBC), which we found to be critical in making the specific assignments. In particular, the bond correlation experiments allowed the various individual resonances to be definitively assigned to a single isomer. By analogy to limonene oxide, there should exist a similar cis/trans pair of stereoisomers for limonene dioxide. However, it is unclear exactly how to assign all four of the observed isomers of limonene dioxide to specific isomeric identities. It is possible that the four isomers are due to two sets of cis/trans pairs, in which the pairs are distinguished by two different confirmations made possible by a high barrier to rotation of the exocyclic epoxide group. Because the different isomers were found to have different reaction rate constants, the present kinetics experiments allowed for clear assignment of most <sup>1</sup>H or <sup>13</sup>C peaks to a specific isomer. In many cases, due to the spectral overlap caused by the very similar chemical environments, we were unable to assign the CH<sub>2</sub> units (positions 2, 5, and 6 in Figure 1) in the six-membered rings of some species, and it was not possible to assign any of the nonepoxide <sup>1</sup>H resonances for the limonene diepoxide isomer mixture. However, the assignments were complete enough (in particular, the epoxide proton(s) for each isomeric species was distinguishable) to allow for unambiguous kinetic monitoring of the reaction of each specific isomer epoxide reactant, as well as for the identification of the major reaction products.

**Rate Constant Measurements.** For the reaction of  $\beta$ pinene oxide in  $D_2O_1$  no remaining  $\beta$ -pinene oxide reactant was detected after 5 min of reaction time (the minimum time for sample preparation and the collection of a routine <sup>1</sup>H NMR spectrum). The sensitivity of the NMR detection method for  $\beta$ pinene oxide indicates that about 5% of the initial concentration of  $\beta$ -pinene oxide is the minimum detectable amount. Because 5% remaining reactant corresponds to about three first-order lifetimes, the upper limit on the lifetime of the  $\beta$ -pinene oxide hydrolysis reaction is therefore about 1.7 min, or a lower limit hydrolysis rate constant of about 0.010 s<sup>-1</sup>. In previous work, an identical lower-limit hydrolysis rate constant for  $\alpha$ -pinene oxide was reported.<sup>23</sup> As for  $\alpha$ -pinene oxide, the fact that  $\beta$ -pinene oxide hydrolyzes quickly at neutral pH suggests that water is acting as a general acid catalyst. In this general acid catalysis process, one water molecule acts as the general acid by using one of its acidic hydrogen atoms to form a bond with epoxide oxygen atom (as opposed to a H<sup>+</sup> unit acting in this role in traditional acid catalysis).<sup>40</sup> A second water molecule then acts as the attacking nucleophile on this intermediate water-epoxide species. Ultimately, the original catalytic water molecule is released to the aqueous solution as the final hydrolysis product is formed. It is possible that the use of deuterated solutions (D<sub>2</sub>O specifically in the neutral solution case) in the present study could lead to the observation of different rates of reaction than would be observed for the normal isotope.41

However, it is not straightforward to ascertain whether this effect would lead to slower or faster rates of reaction.

In order to account for both general acid (water) and Bronsted acid-catalyzed processes, the following rate equation was used

$$-\frac{d[epoxide]}{dt} = k_{GA}[H_2O][H_2O][epoxide] + k_{H^+}[H^+][H_2O][epoxide]$$
(1)

where  $k_{\text{GA}}$  is the general acid-catalyzed rate constant and  $k_{\text{H}}^+$  is the Bronsted acid-catalyzed rate constant. Note that water appears twice in the general acid-catalyzed portion of the rate law, once as the catalyst and once as the nucleophile. Because [H<sub>2</sub>O] is constant in the experiments, eq 1 reduces to

$$-\frac{d[\text{epoxide}]}{dt} = k_{\text{GA}}^{"}[\text{epoxide}] + k_{\text{H}^{+}}^{'}[\text{H}^{+}][\text{epoxide}]$$
(2)

where  $k_{GA}'' = k_{GA}[H_2O]^2$  and  $k_{H^+}' = k_{H^+}[H_2O]$ . In the Bronsted acid-dependent experiments,  $[H^+]$  is also a constant, which allows eq 2 to reduce to

$$-\frac{d[epoxide]}{dt} = k''_{GA}[epoxide] + k''_{H^+}[epoxide]$$
$$= k''[epoxide]$$
(3)

where  $k_{H^+}' = k_{H^+}'[H^+]$  and  $k'' = k_{GA}' + k_{H^+}''$ . Equation 3 is firstorder in the epoxide concentration, and the epoxide loss kinetics were analyzed in the framework of this first-order rate law.  $k_{GA}''$  was determined from the first-order loss of epoxide in neutral solutions (the second term in eq 3 is negligible in this case such that  $k'' = k_{GA}''$ ), and k'' values were also determined for several acidic solutions. A plot of the individual k'' values against the appropriate H<sup>+</sup> concentrations yields  $k_{H^+}'$  as the slope and  $k_{GA}''$  as the intercept.

The various isomers of limonene oxide and dioxide were found to react slowly enough in D<sub>2</sub>O to allow NMR monitoring, and their individual first-order general acidcatalyzed hydrolysis rate constants  $(k_{GA}'')$  were determined. In previous literature work aimed at developing processes to separate cis- from trans-limonene oxide, it had been reported that the cis stereoisomer hydrolyzes more quickly than the trans form.<sup>36,37</sup> In general, *cis*-epoxides have been found to hydrolyze faster than *trans*-epoxides,<sup>42</sup> presumably due to the relative stability of the S<sub>N</sub>2-type transition state, which is less sterically hindered for the attacking water nucleophile for the cis isomer. The presently determined rate constants confirm the earlier finding; Table 1 indicates that cis-limonene oxide hydrolyzes almost 200 times faster than trans-limonene oxide. However, it should be noted that cis-limonene oxide was also found to hydrolyze at a rate at least 20 times slower than that of either  $\alpha$ pinene oxide or  $\beta$ -pinene oxide, thus indicating that a large range of hydrolysis rate constants are possible for isomerically

 Table 1. Hydrolysis Rate Constants (and 1 Standard Deviation Error Limits) for Monoterpene Epoxides

species	$k''_{\rm GA}~(10^{-6}~{\rm s}^{-1})$	$k'_{\rm H^+} ({ m M}^{-1} \ { m s}^{-1})$
$\alpha$ -pinene oxide <sup>23</sup>	>10000	
eta-pinene oxide	>10000	
cis-endo-limonene oxide	486 ± 14	$2.88 \pm 0.35$
trans-endo-limonene oxide	$2.534 \pm 0.041$	$1.249 \pm 0.039$
cis-endo-limonene dioxide	$160.3 \pm 9.7$	
trans-endo-limonene dioxide	8.36 ± 0.15	
exo-limonene dioxide	$12.6 \pm 1.0$	

related monoterpene epoxide reactants. Acid-dependent measurements were carried out for *cis*- and *trans*-limonene oxide to determine second-order Bronsted acid-catalyzed rate constants  $(k'_{H^+})$ , the analysis for which is shown in Figure 2. These values are given in Table 1 and indicate that the two stereoisomers have very similar hydrolysis rate constants within the Bronsted acid-catalyzed mechanism.



Figure 2. Limonene oxide hydrolysis kinetics.

For limonene dioxide, it was possible to distinguish between isomers for the endocyclic epoxide proton, and quite different first-order hydrolysis rate constants were determined for these two isomers. Because of the expected cis/trans stereoisomerism in limonene dioxide, the kinetics of the fast-reacting isomer is assumed to follow from the hydrolysis of the cis-endocyclic epoxide ring (as labeled in Table 1), and the kinetics of the slow-reacting isomer is assumed to follow from the hydrolysis of the trans-endocyclic epoxide ring. While the cis-endo and trans-endo rate constants for limonene oxide and limonene dioxide are similar, Table 1 indicates that the presence of the exo-epoxide functionality serves to decrease the reactivity of the cis-endo isomer while increasing the reactivity of the trans-endo isomer. It was not possible to distinguish between isomers for the exocyclic epoxide proton; therefore, a single hydrolysis rate constant is reported and is assumed to follow from the hydrolysis of the exocyclic epoxide ring. Because the transendocylic and exocylic epoxide hydrolysis rate constants are of similar magnitude, the overall hydrolysis of the various isomers of limonene dioxide can produce epoxy diol intermediate species of both types (endocyclic diol and exocyclic epoxide functionality and vice versa) before eventually producing the final tetraol products.<sup>43</sup> To the best of our knowledge, these are the first reported measurements of aqueous-phase reaction rate constants for  $\beta$ -pinene oxide, limonene oxide, and limonene dioxide.

**Reaction Mechanism for**  $\beta$ -Pinene Oxide. In D<sub>2</sub>O solution, the reaction of  $\beta$ -pinene oxide led to two identified and quantified four carbon ring-opened products: the hydrolysis product 7-hydroxyterpineol and the isomerization product perillyl alcohol. The CDCl<sub>3</sub> extraction procedure indicated that neither product was fully water-soluble (and perillyl alcohol was not detectable at all in the aqueous phase). The total relative yields determined were 97% 7-hydroxyterpineol and 3% perillyl alcohol. In 1 M DClO<sub>4</sub> solution, the

relative yields shifted to 94% 7-hydroxyterpineol and 6% perillyl alcohol and a small amount (<10% absolute yield) of unidentified aldehydes. One previous study also found that 7hydroxyterpineol and perillyl alcohol were the major products formed in the Lewis acid-catalyzed reaction of  $\beta$ -pinene oxide,<sup>33</sup> while another study using Lewis acids in a supported liquid catalyst method found perillyl alcohol, myrtenal, and myrtenol as products.<sup>44</sup> In the latter study, water was deliberately excluded from reaction conditions, thus explaining the lack of detection of the hydrolysis product 7-hydroxyterpineol. Authentic samples of myrtenal and myrtenol were used to rule out their formation from  $\beta$ -pinene oxide in the present study. A previous study reported the NMR assignments for the bicyclic ring-retaining 1,7-diol (synthesized via palladiumcatalyzed dihydroxylation of  $\beta$ -pinene).<sup>45</sup> This is the same species that would result if  $\beta$ -pinene oxide underwent a bicyclic ring-retaining hydrolysis reaction. However, there is no evidence in the present NMR data that  $\beta$ -pinene oxide produces this bicyclic ring-retaining diol. In fact, to the best of our knowledge, there appear to be no reports in the synthetic organic chemistry literature that describe the production of the 1,7-diol from the hydrolysis of  $\beta$ -pinene oxide.

In the Na<sub>2</sub>SO<sub>4</sub> solutions, 7-hydroxyterpineol sulfate was observed as a transient species (identified via a characteristic <sup>1</sup>H methyl group resonance at 1.52 ppm vicinal to the sulfate group),<sup>2</sup> hydrolyzing to 7-hydroxyterpineol with a rate constant of about  $5 \times 10^{-4}$  s<sup>-1</sup>. No organonitrate species were detected in the experiments involving NaNO3 solutions. It has been previously reported that the hydrolysis of tertiary organonitrates proceeds much more quickly  $(>100\times)$  than the hydrolysis of tertiary organosulfates like 7-hydroxyterpineol sulfate.<sup>46</sup> With a 7-hydroxyterpineol sulfate hydrolysis lifetime of 33 min, this previously determined organonitrate to organosulfate hydrolysis rate ratio predicts that any 7hydroxyterpineol nitrate that might have formed from the reaction of  $\beta$ -pinene oxide under our solution conditions would undergo hydrolysis in a matter of seconds. A very similar finding was made for the formation and hydrolysis of the analogous  $\alpha$ -pinene oxide reaction product, sobrerol sulfate, and the lack of detection of sobrerol nitrate.<sup>23</sup> Therefore, the lack of detection of 7-hydroxyterpineol nitrate is consistent with the general structure-reactivity relationships that have been previously reported for organosulfate and organonitrate hydrolysis kinetics. A mechanism (depicting both the general acid and Bronsted acid catalyst as "H+" and the nucleophilic addition reactions as S<sub>N</sub>1-type for conceptual clarity) rationalizing the observed  $\beta$ -pinene oxide reaction products is presented in Figure 3. All of these mechanistic features are qualitatively similar to those found for the reactivity of  $\alpha$ -pinene oxide:<sup>23</sup> (1) the products are not fully water-soluble at the reactant concentrations used, (2) a four carbon ring-opened diol is the major product, (3) a four carbon ring-opened unsaturated isomerization product is preferentially formed under higher acid conditions, (4) four ring-opened aldehyde isomerization products are preferentially formed under higher acid conditions, (5) a four carbon ring-opened hydroxy sulfate is quickly hydrolyzed to the major product diol, (6) there is no evidence for the detection of a similar hydroxy nitrate (although formation and fast hydrolysis could not be ruled out), and (7) there is no detection of any bicyclic ring-retaining products of any kind. Previous computational thermodynamics calculations for  $\alpha$ -pinene oxide<sup>23</sup> are consistent with the observed stability of four carbon ring-opened hydrolysis and



Figure 3. Schematic mechanism for the reactions of  $\beta$ -pinene oxide.

isomerization products as compared to bicyclic ring-retaining products and/or organosulfate and nitrate products for  $\beta$ -pinene oxide.

Reaction Mechanism for Limonene Oxide. In D<sub>2</sub>O, the reaction of cis- and trans-limonene oxide led to a single identified hydrolysis product, limonene-1,2-diol. In 1 M DClO<sub>4</sub> solution, the reaction of cis- and trans-limonene oxide led to two identified and quantified six carbon ring-retaining products: 60% yield of the hydrolysis product limonene-1,2-diol and 40% yield of the isomerization product dihydrocarvone. A small amount of an unidentified aldehyde was also observed. The CDCl<sub>3</sub> extraction procedure indicated that neither product was fully water-soluble (and dihydrocarvone was not detectable at all in the aqueous phase). Costa et al. previously reported the formation of these two products (and NMR assignments) from the Lewis acid-catalyzed reaction of limonene oxide. Comparison of the commercially available standard, 1S,2S,4R-(+)-limonene 1,2-diol, to the product spectra confirms that this one specific stereoisomer is formed from the hydrolysis of both cis- and trans-limonene oxide.

A mechanism rationalizing the limonene oxide reaction products is presented in Figure 4. Because limonene oxide contains only a single, relatively stable six-membered ring (as opposed to the presence of an additional highly strained fourmembered ring in both  $\alpha$ - and  $\beta$ -pinene oxide), it is not surprising that the limonene oxide reaction products retain this structural motif.



Figure 4. Schematic mechanism for the reactions of limonene oxide.

**Reaction Mechanism for Limonene Diepoxide.** As mentioned in the NMR Assignments section, commercially available limonene diepoxide is actually a mixture of four isomers. Because the hydrolysis kinetics results indicated that both epoxide rings can open on similar time scales, there are several intermediate species isomers that are also formed, in addition to the final hydrolysis products during reaction in  $D_2O$ . Because of the spectral complexity of this situation, full assignments of the intermediates and final products were not possible. However, the spectra obtained after all epoxide species were observed to react are consistent with the sole production of six carbon ring-retained tetraol isomers.<sup>43</sup> On the basis of the results discussed above, a proposed mechanism for the reaction of limonene dioxide in aqueous solution was constructed and is depicted in Figure 5.

Potential Organosulfate and Nitrate Product Detection for Limonene Epoxide and Diepoxide Reactions. Figure 6 shows <sup>1</sup>H NMR spectra collected during the reaction of limonene diepoxide in solutions with 1.0 M NaClO<sub>4</sub> (top), 1.0 M Na<sub>2</sub>SO<sub>4</sub> (middle), and 1.0 M NaNO<sub>3</sub> (bottom). The 1.0 M NaClO<sub>4</sub> solution was chosen as a reference that produces only hydrolysis and isomerization products because ClO<sub>4</sub><sup>-</sup> is a non-nucleophilic species. Therefore, any difference between the top spectrum and the middle and bottom spectra could indicate the presence of organosulfate and/or nitrate species, respectively. However, the three spectra appear to be nearly identical, which indicates that these experiments do not provide any positive evidence for the formation of organosulfates or nitrates. In addition, because the  $\beta$ -pinene oxide reaction with sulfate was observed to form 7-terpineol sulfate, only to hydrolyze at later times, these solutions were also monitored kinetically. However, no change was observed in these solutions over the same period that corresponded to the hydrolysis of 7terpineol sulfate (about 1 h). Similar conclusions were drawn



Figure 5. Schematic mechanism for the reactions of limonene dioxide.



Figure 6. <sup>1</sup>H NMR spectra of limonene diepoxide in (top, black) 1.0 M NaClO<sub>4</sub>, (middle, blue) 1.0 M Na<sub>2</sub>SO<sub>4</sub>, and (bottom, red) 1.0 M NaNO<sub>3</sub> solution.

from experiments with limonene epoxide and the three 1.0 M solutions. Therefore, the present experiments provide no positive evidence for the formation of organosulfates or nitrates from either limonene epoxide or limonene diepoxide. However, because of the general congestion of these spectra in the region where protons adjacent to sulfate and nitrate groups are typically found (3.5-4.0 ppm),<sup>47</sup> it is possible that organosulfate and/or nitrate species were produced but could not be distinguished from the hydrolysis and isomerization prdoucts.

Atmospheric Implications. The present finding that  $\beta$ pinene oxide has a very short lifetime in neutral aqueous solution suggests that it will react virtually instantaneously on atmospheric aqueous particles to form new particle-phase

species, predominantly the hydrolysis product 7-hydroxyterpineol. More acidic aerosol conditions are predicted to favor the formation of the isomerization product, perillyl alcohol, although even at pH = 0, 7-hydroxyterpineol is predicted to remain the predominant product. 7-Hydroxyterpineol sulfate was observed to form in solutions with elevated sulfate conditions. However, because its neutral hydrolysis lifetime was found to be only 33 min, the present results suggest that 7hydroxyterpineol sulfate is likely to hydrolyze quickly in atmospheric particles. Because no organonitrates of any kind were observed for the reaction of  $\beta$ -pinene oxide, it is also unlikely that 7-hydroxyterpineol nitrate has a significant atmospheric lifetime. These very fast hydrolysis rates stand in contrast to the hydrolysis of the tertiary organosulfates and nitrates formed from IEPOX, which have lifetimes of 460 and 0.67 h, respectively.<sup>6</sup>

The cis and trans isomers of limonene oxide are also predicted to react in neutral solution environments, with lifetimes of 34 min and 4.6 days, respectively. Because typical aerosol lifetimes are estimated to be on the order of 2-10days,<sup>48</sup> even *trans*-limonene oxide is expected to undergo at least partial reaction under neutral aerosol conditions. Under Bronsted acid-catalyzed conditions, the cis and trans isomers react with similar rate constants. While the determination of ambient aerosol pH remains a challenging problem,<sup>49</sup> recent estimates for aerosol acidities in Southern California suggest values of pH = 2-3.<sup>50</sup> For example, at pH = 3, the lifetimes for the cis and trans isomers are calculated to be only 5.8 and 13.3 min, respectively. Therefore, while the general acid-catalyzed reaction rates for cis- and trans-limonene oxide are very different, the Bronsted acid-catalyzed mechanisms more likely to be relevant under atmospheric conditions indicate that both isomers will react with similar, very fast rates to produce mainly the hydrolysis product, limonene 1,2-diol. The limonene dioxide kinetics suggest that the exocyclic limonene monoepoxide (not studied in this work) will probably have similar reactivity to *trans*-limonene oxide. Therefore, all possible limonene epoxides are probably quite reactive under typical atmospheric conditions, producing mainly polyol products. Thus, the hypothesis that limonene epoxide intermediates are a potential explanation for the recent observation of limonene 1,2-diol products in the interaction of limonene with mineral dust is kinetically feasible.<sup>29</sup>

In summary, all monoterpene epoxides studied to date are characterized by facile general acid-catalyzed and even faster Bronsted acid-catalyzed reactions at atmospherically relevant pH values. For comparison, while all of the monoterpene epoxides are predicted to react with lifetimes of less than 15 min at pH = 3, IEPOX has a much longer lifetime of 7.7 h at the same pH.<sup>51</sup> Therefore, from a reactivity standpoint, the monoterpene epoxides seem to be excellent candidates as potential intermediates for monoterpene-derived SOA species. However, these epoxides are much less water-soluble than IEPOX,<sup>23</sup> which could significantly limit their mass transfer in the SOA phase. In addition, Drozd et al. found that that  $\alpha$ pinene oxide reaction was self-limiting due to the formation of a coating of products, which inhibited further uptake of the epoxide.<sup>24</sup> Further, the fact that no long-lived organosulfate or nitrate products have been observed in the aqueous-phase reactions of monoterpene oxides suggests that these species may not lead to the same range of SOA species as the IEPOX intermediate does in the case of isoprene-derived SOA. Indeed, there have been a number of previous reports of long-lived organosulfates and nitrates derived from  $\alpha$ - and  $\beta$ -pinene,<sup>1</sup> including the first reported synthesis of authentic four carbon ring-retaining organosulfate standards derived from  $\alpha$ - and  $\beta$ pinene.<sup>28</sup> Interestingly, these four carbon ring-retaining organosulfates were not synthesized via an epoxide precursor, and it was important that the reactions be carried out under anhydrous conditions. Therefore, it seems that monoterpenederived organosulfates found on SOA are probably produced via a different mechanism than isoprene-derived organosulfates. Specifically, the available evidence suggests that monoterpenederived organosulfates are not produced via epoxide intermediates (unlike isoprene-derived organosulfates) and might require low water content conditions for efficient formation.

# CONCLUSIONS

Three different monoterpene epoxides,  $\beta$ -pinene oxide, limonene oxide, and limonene diepoxide, were found to react very quickly in aqueous solutions representative of typical SOA pH values, with the products of the reactions dominated by hydrolysis mechanisms (i.e., formation of polyol products). No four carbon ring-retaining products were observed for the reactions of  $\alpha$ - or  $\beta$ -pinene oxide, nor were long-lived organosulfate or nitrate products. Therefore, while monoterpene epoxides were shown by the present work to be more reactive than the similar isoprene intermediate IEPOX, it seems that at least some important previously identified monoterpenederived SOA species cannot be explained by the aqueous reactions of monoterpene epoxides on SOA.

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# Notes

The authors declare no competing financial interest.

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