

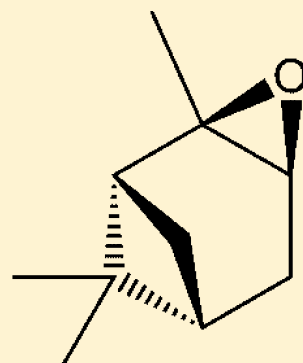
Kinetics and Thermodynamics of Atmospherically Relevant Aqueous Phase Reactions of α -Pinene Oxide

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S Supporting Information

ABSTRACT: Recent work has demonstrated that isoprene-derived epoxide intermediates are responsible for a wide variety of chemical species found in ambient secondary organic aerosol (SOA). Since the second most abundant biogenic hydrocarbon, α -pinene, is also known to form an epoxide intermediate, nuclear magnetic resonance techniques were used to study products, kinetics, and equilibria of the aqueous phase reactions of that epoxide, α -pinene oxide. The present results indicate that α -pinene oxide will react very quickly with aqueous atmospheric particles, even under low acidity conditions. Depending on the acid concentration of the aqueous solutions, a number of new products are observed from the reaction of α -pinene oxide, some of which are expected to partition back to the gas phase. In contrast to some previous results, no long-lived organosulfate or organonitrate species are observed, and no species which retain the α -pinene bicyclic carbon backbone are observed. Rather, the overall product distribution can be explained by various rearrangements of the initial carbocation intermediate formed in the ring opening of α -pinene oxide, all of which can be rationalized by the thermodynamically driven relief of the bicyclic ring strain in the α -pinene carbon backbone.



■ INTRODUCTION

α -Pinene, (2,6,6-trimethylbicyclo[3.1.1]hept-2-ene), is the second most abundant biogenic non-methane hydrocarbon emitted into the atmosphere.¹ Like most-abundant isoprene, α -pinene is emitted by vegetation and is known to contribute to tropospheric ozone production² and the formation of secondary organic aerosol (SOA),³ which are known to be important processes in air pollution and global climate change. Recent laboratory studies of isoprene-derived SOA-phase chemistry^{4–8} and field observations of SOA^{5,9,10} for isoprene-dominated situations has uncovered evidence that many of the individual chemical species observed are the result of the SOA-phase reactions of isoprene epoxydiols (IEPOX), gas phase oxidation products of isoprene.¹¹ In particular, the IEPOX-driven SOA-phase chemistry has been identified as resulting in the formation of a number of species with different functionalities: polyols, aliphatic and cyclic ethers, organosulfates, and organonitrates.⁴ For all of these processes, it has been postulated^{4–7} that the reactions of nucleophiles (electron rich species such as negatively charged inorganic ions and neutral oxygen-containing organic species) with the carbocation intermediates formed as a result of the acid-catalyzed epoxide ring opening are the key to understanding the variety of products formed.

Recently, α -pinene oxide, an epoxide formed by O atom insertion across the endocyclic double bond in α -pinene, has been observed as a minor product in α -pinene gas phase photooxidation environmental chamber experiments.^{12–15} In addition, there have been some laboratory studies of the reactivity of α -pinene oxide with SOA-like systems.^{12,13,16–18} Some of these results have suggested that many of the same

types of chemical reactions might be occurring for α -pinene oxide on SOA as have been identified for IEPOX on SOA,^{16,17} while other results suggest that new types of chemical processes might be important.^{12,13,18} In this paper, we report measurements of the products, kinetics, and equilibria of the aqueous-phase acid-catalyzed reactions of α -pinene oxide, using nuclear magnetic resonance (NMR) as the analytic technique. We also report high level electronic structure calculations intended to elucidate the relative thermodynamic stability of the various products that are observed. These results are then used to predict the impact of α -pinene oxide processing by atmospheric particles on the gas- and particle-phase composition of the atmosphere.

■ EXPERIMENTAL SECTION

Bulk Aqueous Solution Preparation. To explore the concentration dependence of various atmospherically relevant species on the properties of the various α -pinene oxide-derived products, 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 sulfate concentration dependence experiments, dilute (0–0.02 M) deuterated sulfuric acid was combined with sodium sulfate (0–1 M). For nitrate concentration dependence experiments, dilute (0–0.02 M) deuterated nitric acid was combined with sodium nitrate (1–10 M). These solutions were prepared using commercially

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available 96–98 wt % D₂SO₄ (Sigma-Aldrich), 70 wt % DNO₃ (Sigma-Aldrich), 99.9% D₂O (Cambridge Isotope Laboratories, Inc.), Na₂SO₄ (Sigma-Aldrich), and NaNO₃ (Sigma-Aldrich). To initiate the chemical process, either α -pinene oxide (Sigma-Aldrich) was added to the bulk solution or a near-saturated solution of *trans*-sobrerol was acidified, and the solutions were stirred for at least 3 min to ensure homogeneity before any analysis was performed. In some cases, bulk aqueous solutions were directly transferred to NMR tubes to allow for immediate analysis.

Chloroform Extraction Method. To identify and quantify all products formed (including phase-partitioned species which have limited water solubility), the product species were extracted from the bulk aqueous reaction mixtures with deuteriochloroform (CDCl₃). A typical solution was prepared by adding 30.0 mg of the aqueous soluble internal standard DSS (sodium 2,2-dimethyl-2-silapentane-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 μ L of α -pinene oxide 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 ¹H NMR spectrum (in order to determine the concentrations of the aqueous soluble species). Next, about 6 mL of CDCl₃ 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. Next, 20.0 μ L of a second, chloroform-soluble, internal standard (benzene, ACS spectro-photometric grade, \geq 99%, Sigma Aldrich) was micropipetted into the vial containing the organic layer and the solution was stirred for 2 min. Typically, both ¹H and ¹³C NMR spectra were collected for CDCl₃-extracted solutions. ¹H NMR analysis of the remaining aqueous layer indicated that the CDCl₃ extraction was usually about 70% efficient for the aqueous soluble species. Therefore, the total product concentrations were determined by adding together the product concentrations determined from the aqueous and CDCl₃ solutions. A kinetic profile of the reaction mixture was constructed by preparing multiple vials of the reactive solution and performing the workup procedure at different points in time after reaction initiation.

NMR Product Identification and Quantitation. All NMR spectra were collected on a Varian 400 MHz instrument. Some species were identified by comparison to commercially available standards: α -pinene oxide, *trans*-sobrerol (*trans*-*p*-menth-6-ene-2,8-diol), *p*-cymene, and 2,3-pinenediol ((1*S*,2*S*,3*R*,5*S*)-(+)-2,3-pinenediol and (1*R*,2*R*,3*S*,5*R*)-(–)-2,3-pinenediol (all obtained from Sigma Aldrich)). However, several other noncommercially available reaction products were identified via previously reported ¹H and ¹³C CDCl₃ NMR data: *cis*-sobrerol,¹⁹ *trans*-carveol,²⁰ *cis*-carveol,^{21,22} pinol,²³ campholenic aldehyde,²⁰ and fencholenic aldehyde.²⁴

The relative amounts of reaction products were calculated by peak integration of unique nuclei for each species, referenced to the 9 methyl protons at 0.00 ppm from DSS, the 6 protons at 7.34 ppm from benzene, or the 6 carbon atoms at 128.4 ppm from benzene.

Computational Thermodynamics. Geometries (determined at the B3LYP/6-31G(d,p) level) and energies of the relevant α -pinene oxide-derived species were calculated using a modified version of the G2MS compound method (MG2MS)²⁵ a variation on G2 theory.²⁶ The Polarizable Continuum Model (PCM) method²⁷ was used to account for the effects of aqueous solvation on the reactant and product properties. All calculations were carried out with the Gaussian 03 computational suite.²⁸ Each stationary point was confirmed as a potential energy minimum by inspection of the calculated frequencies. The overall energy expression for the MG2MS scheme is defined in eq 1:

$$E_{\text{G2MS}} = E_{\text{CCSD(T)/6-31G(d)}} + E_{\text{MP2/6-311+G(2df,2p)}} - E_{\text{MP2/6-31G(d)}} + \text{HLC} \quad (1)$$

where HLC is an empirically defined correction term with $\text{HLC} = An_{\alpha} + Bn_{\beta}$ where n_{α} and n_{β} are the number of α - and β -electrons, respectively, and the constants A and B are 6.06 and 0.19 mH, respectively (all species investigated were closed shell; therefore, $n_{\alpha} = n_{\beta}$). Our previous MG2MS results for atmospherically relevant systems (including radicals and ions) indicate that the MG2MS calculated thermodynamic properties are typically accurate to within 2.5 kcal mol^{–1} for systems similar to those under study here.²⁹

RESULTS AND DISCUSSION

Product Identification. For the experiments in which α -pinene oxide was simply added to D₂O, four products were identified: the hydrolysis product *trans*-sobrerol and the isomerization products campholenic aldehyde and *trans*- and *cis*-carveol. These species were identified by comparison to either literature NMR data or commercially available standards (as described in the Experimental Section). The ¹H and ¹³C NMR assignments for all species, many of which were determined in both aqueous and CDCl₃ solvents, are tabulated in Table S1 in the Supporting Information. Because no α -pinene oxide reactant could be detected even at the shortest measured reaction times (\sim 5 min), it is estimated that the lifetime of α -pinene oxide in neutral aqueous solution is less than 5 min. As most epoxides require either acid- or base-catalyzed conditions for efficient hydrolysis, we speculate that the hydrolysis of α -pinene oxide occurs with water 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 an H⁺ unit acting in this role in traditional acid catalysis).³⁰ 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 (D₂O 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.³¹ However, it is not straightforward to ascertain whether this effect would lead to slower or faster rates of reaction.

For experiments in which α -pinene oxide was added to acidic solutions (0.01–1.0 M D₂SO₄), two additional products were observed: *cis*-sobrerol and *p*-cymene (an aromatic compound apparently derived from the dehydration of one or more of the other reaction products). See Figure 1 for initial and

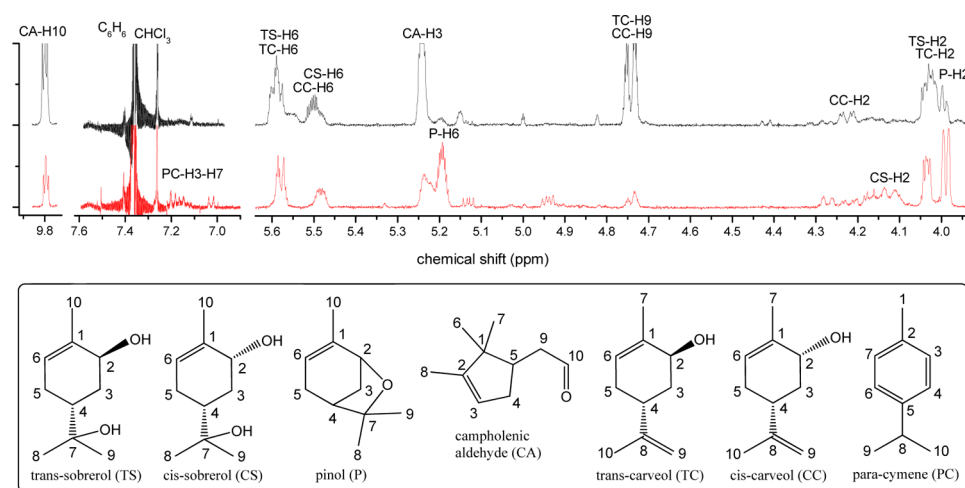


Figure 1. ^1H NMR spectrum from chloroform extract of α -pinene oxide reaction in 1 M D_2SO_4 solution [black trace, initial spectrum collected ($t = 0.5$ h); red trace, equilibrium spectrum collected ($t = 14$ h)].

equilibrium NMR spectra and the structures of identified products. *trans*- and *cis*-Sobrerol were quantified by summing the molar amounts of each species in the post-extraction aqueous and CDCl_3 fractions (these diols were more soluble in the aqueous acidic solutions than the other species and it was not possible to quantitatively extract them into CDCl_3). Because of overlap problems in the CDCl_3 ^1H NMR spectra, ^{13}C NMR was used to individually quantify the amounts of *trans*- and *cis*-sobrerol. In the CDCl_3 fraction, the three carbons near 26 ppm (as shown in Figure 2) were integrated and the

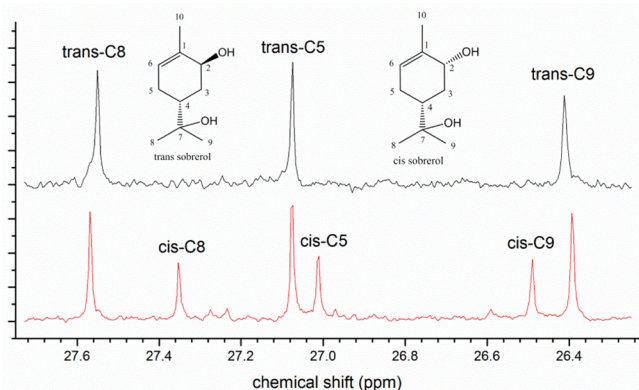


Figure 2. ^{13}C NMR spectrum from chloroform extract of α -pinene oxide reaction in 1 M D_2SO_4 solution [black trace: initial spectrum collected ($t = 0.5$ h); red trace, equilibrium spectrum collected ($t = 14$ h)].

results were averaged and the molar concentration of each species was calculated by reference to the concentration of benzene, as described in the Experimental Section. In the aqueous fraction, the proton geminal to the hydroxyl group near 4 ppm and the vinylic proton in the 5.5 ppm region (as shown in Figure 1) were integrated and the results were averaged and the molar concentration of each species was calculated by reference to the concentration of DSS, as described in the Experimental Section.

All other species were quantified solely via analysis of the post-extraction CDCl_3 layer of the ^1H spectra by reference to the concentration of benzene, as described in the Experimental Section. *cis*-Carveol was identified in the ^{13}C NMR spectra but

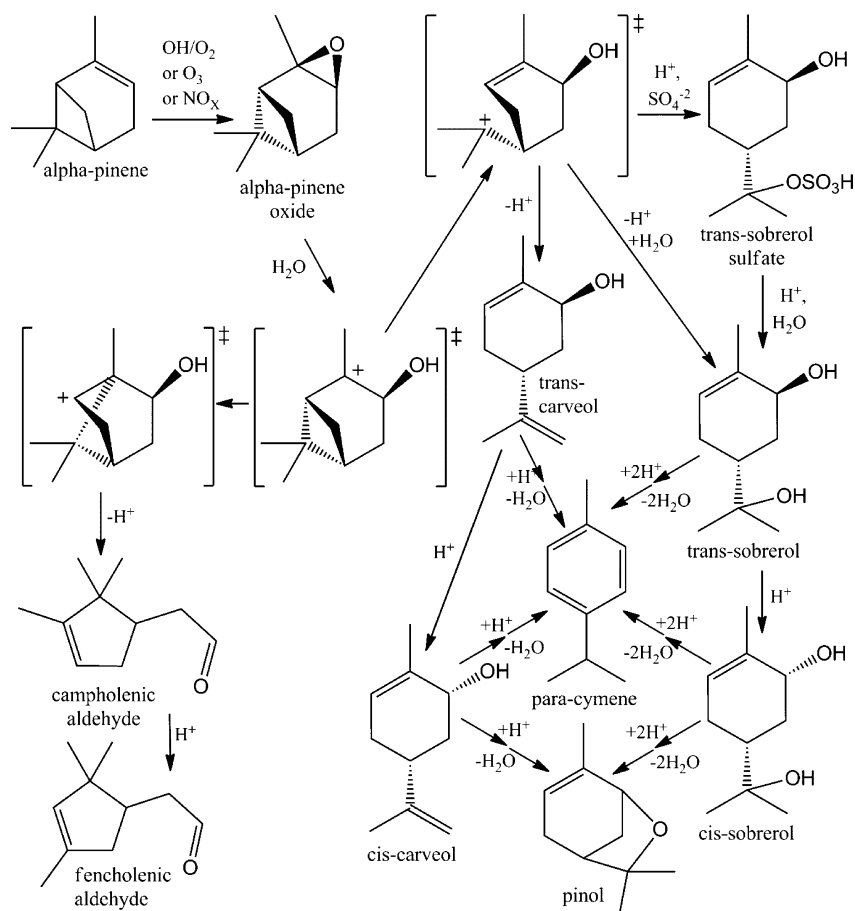
was not quantified due to very low signal strength. Fencholenic aldehyde (a structural isomer of campholenic aldehyde) was tentatively identified in the ^{13}C NMR spectrum of a 1 M D_2SO_4 experiment, but also not quantified. The other species (*trans*-carveol, pinol, campholenic aldehyde, and *p*-cymene) were quantified using the peaks in the ^1H NMR spectra shown in Figure 1. *trans*-Carveol was quantified by its two terminal vinylic protons at 4.73 ppm. Although these peaks overlap with those from *cis*-carveol, the ^{13}C NMR spectra indicate that *cis*-carveol concentrations were very small (in fact, no *cis*-carveol was detected at all in most cases). Campholenic aldehyde was quantified via its aldehyde proton at 9.8 ppm and its vinylic proton at 5.25 ppm. Pinol was quantified via the vinylic proton at 5.20 and the proton geminal to the ether ring at 3.95 ppm. *p*-Cymene was quantified via its two chemically inequivalent aromatic protons near 7.0 ppm. The total molar amounts of the quantified products were always in the range 80–120% of the molar amount of initial α -pinene oxide reactant, thus indicating that the method was successfully quantifying the great majority of the reaction products (and that the calculated product fractions have an associated uncertainty of approximately 20%). For easier further analysis, the molar amounts of each product were converted to a product molar fraction via the total moles of quantified products. Table 1 contains the product fractions for a range of acidic solutions for both initial conditions (usually determined 30 minutes after the reaction was initiated and before acid-catalyzed processes had progressed significantly) and for the same solutions at equilibrium (after acid-catalyzed processes had reached completion).

As an additional test of the sequence of chemical reactions, *trans*-sobrerol was directly added to various acidic solutions. With the notable exception of campholenic aldehyde and *trans*- and *cis*-carveol, the same product species were observed as in the α -pinene oxide acidic solution experiments. Therefore, this experiment indicated that campholenic aldehyde and the carveols are direct (isomerization) products of the reaction of α -pinene oxide, while *cis*-sobrerol, pinol, and *p*-cymene are formed from reactions of *trans*-sobrerol.

The initial values results in Table 1 indicate that the distribution of the direct (isomerization) products also depends on the acid concentration. For example, campholenic aldehyde and carveol are observed to form in higher yields at the highest acid concentration. In previous work, the reactions of α -pinene

Table 1. Initial and Equilibrium Product Molar Fractions as a Function of Acid Concentration

	pure D ₂ O	0.010 M D ₂ SO ₄	0.10 M D ₂ SO ₄	1.0 M D ₂ SO ₄
initial values	<i>t</i> = 0.5 h	<i>t</i> = 0.5 h	<i>t</i> = 0.5 h	<i>t</i> = 0.5 h
C₁₀H₁₈O₂				
<i>trans</i> -sobrerol	0.72	0.81	0.74	0.27
<i>cis</i> -sobrerol	0	0	0.02	0.13
C₁₀H₁₆O				
<i>trans</i> -carveol	0.05	0.04	0.08	0.16
pinol	0	0	0	0.04
campholenic aldehyde	0.23	0.15	0.16	0.41
C₁₀H₁₄				
<i>p</i> -cymene	0	0	0	0
equilibrium values			<i>t</i> = 140 h	<i>t</i> = 14 h
C₁₀H₁₈O₂				
<i>trans</i> -sobrerol			0.43	0.20
<i>cis</i> -sobrerol			0.22	0.09
C₁₀H₁₆O				
<i>trans</i> -carveol			0	0
pinol			0.20	0.34
campholenic aldehyde			0.14	0.35
C₁₀H₁₄				
<i>p</i> -cymene			0.02	0.02

Figure 3. Proposed mechanism for formation of observed species from α -pinene oxide.

oxide were studied in a variety of nonaqueous solvents, and it was found that the yields of the various products depended on both the dielectric constants and basicity of the solvents.²³ Therefore, we surmise that this particular acid concentration effect is due to the fact that the different carbocation intermediates are stabilized to differing degrees in the various acid solutions, rather than due to any direct role for H^+ in the mechanism for the direct products.

Reaction Mechanism. On the basis of the results discussed above, a proposed mechanism for the reaction of α -pinene oxide in acidic solutions was constructed and is depicted in Figure 3. Because the results suggest that campholenic aldehyde, *trans*-carveol, and *trans*-sobrerol are prompt products, we surmise that the carbocation intermediate that results from the general acid catalyzed ring opening of α -pinene oxide is the “parent” of all three species. Figure 3 shows that if this carbocation rearranges to two other, more stable carbocations (species in which the four membered ring strain of the initially formed carbocation has been relieved), all three prompt species can be rationalized, with *trans*-carveol and *trans*-sobrerol resulting from either a rearrangement or a hydration, of one of the carbocations, respectively, and campholenic aldehyde resulting from a rearrangement of the other carbocation. As the other products are not prompt (and need conventional acid catalysis to form efficiently), Figure 3 indicates a set of acid catalyzed reactions that can rationalize the production of *cis*-sobrerol (from *trans*-sobrerol), *cis*-carveol (from *trans*-carveol), pinol (from both *cis*-sobrerol and *cis*-carveol), and *p*-cymene (from the sobrerols and carveols). Some aspects of this mechanism have been previously proposed²³ for the reactions of α -pinene oxide in a variety of nonaqueous solvents.

Full kinetic profiles of the evolving products of the reaction of α -pinene oxide in 0.1 and 1.0 M D_2SO_4 solutions were obtained (the pure D_2O and 0.01 M D_2SO_4 solutions did not reach equilibrium over the course of many months, and therefore only initial product distribution data is presented in Table 1). The experimental data (for the quantifiable products) for the 0.1 M D_2SO_4 system are plotted in Figure 4, with each data point representing the average of two or three separate quantitations. We were able to accurately model the kinetic profiles of each of the four product species according to the simplified mechanism given in Figure 5. In particular, although the explicit mechanism in Figure 3 indicates that *trans*-carveol

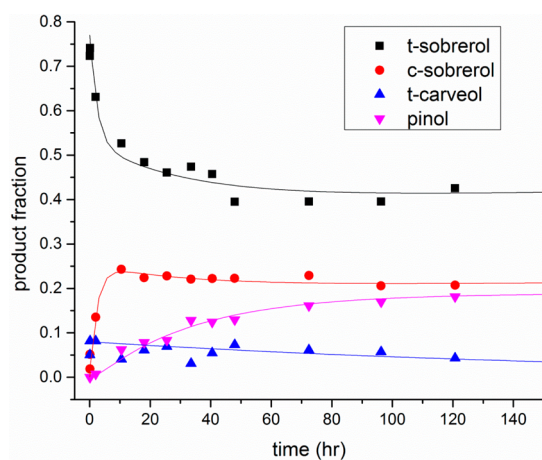


Figure 4. Time dependence of the observed species of α -pinene oxide reaction in 0.1 M D_2SO_4 solution.

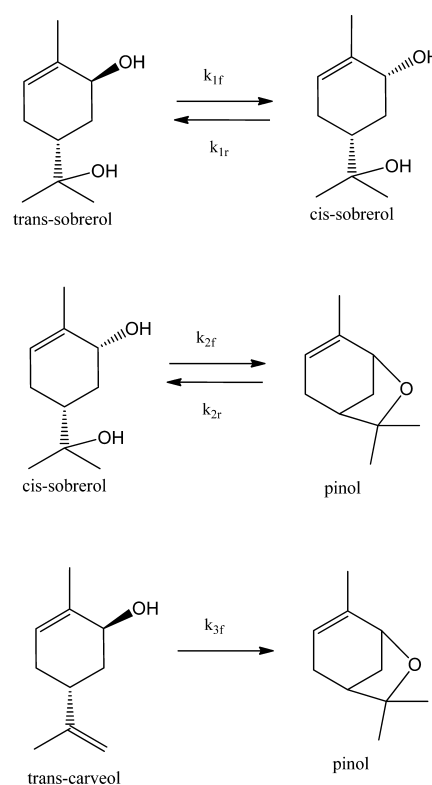


Figure 5. Simplified mechanism for the kinetics analysis of the data presented in Figure 4.

must first isomerize to *cis*-carveol before pinol can be formed via this reaction pathway, we were able to model the kinetic data by including a single *trans*-carveol to pinol reaction step, indicating that the *trans*-carveol to *cis*-carveol isomerization is the rate-limiting step of this subprocess. This assignment of *cis*-carveol as a reactive intermediate is consistent with our finding that *cis*-carveol was only occasionally observed, and in those instances, only in very small concentrations. Kinetecus³² software was used to fit the data to the simplified kinetic model (the calculated product curves are shown as solid lines in Figure 4), and Table 2 reports the pseudo-first order rate

Table 2. Kinetic Parameters Determined from Analysis of 0.1 M D_2SO_4 Reaction System

	k^{1st} for 0.1 M D_2SO_4 run (s^{-1})	lifetime for 0.1 M D_2SO_4 run (h)	k^{2nd} ($M^{-1} s^{-1}$) ^a
k_{1f}	3.8×10^{-5}	7.3	2.9×10^{-4}
k_{1r}	7.4×10^{-5}	3.8	5.7×10^{-4}
k_{2f}	5.7×10^{-6}	49	4.4×10^{-5}
k_{2r}	6.7×10^{-6}	41	5.1×10^{-5}
k_{3f}	1.5×10^{-6}	190	1.2×10^{-5}

^aCalculated assuming $k^{1st} = k^{2nd} [D^+]$ and $[D^+] = 0.13$ M for 0.1 M D_2SO_4 solution.³³

constants (k^{1st}) and lifetimes for the 0.1 M D_2SO_4 system, as well as the second-order-rate constants (k^{2nd}) derived from the calculated D^+ concentrations of the acid solution.³³ We estimate that these rate constants have been determined to an uncertainty of $\pm 50\%$. A similar analysis for the 1.0 M D_2SO_4 system indicated that all processes were acid catalyzed (i.e., each of the pseudo-first order rate constants was found to be

approximately ten times greater than was found for the 0.1 M D_2SO_4 system).

Formation and Reactions of Organosulfates and Organonitrates. For experiments in which α -pinene oxide was added to solutions with fixed acidity (usually 0.02 M D_2SO_4 or DNO_3) and varying sulfate (0–1.0 M Na_2SO_4) or nitrate concentrations (0–10 M $NaNO_3$), only one new species was (briefly) observed, *trans*-sobrerol sulfate. The fact that sulfate can compete with water in the nucleophilic attack on the ring-opened epoxide carbocation intermediate, producing both hydroxy sulfates and diols, respectively, has been observed for many other epoxide systems.^{6,7,31,34,35} A similar process is shown in Figure 3 in which the carbocation intermediate that leads to *trans*-sobrerol can be attacked by sulfate instead of water and form *trans*-sobrerol sulfate. *trans*-sobrerol sulfate was identified via NMR methods in a similar manner to our previous identification of organosulfates derived from simple epoxides,³⁵ as well as those derived from the atmospherically observed isoprene-based epoxides.⁶ Figure 6 shows a 1H NMR

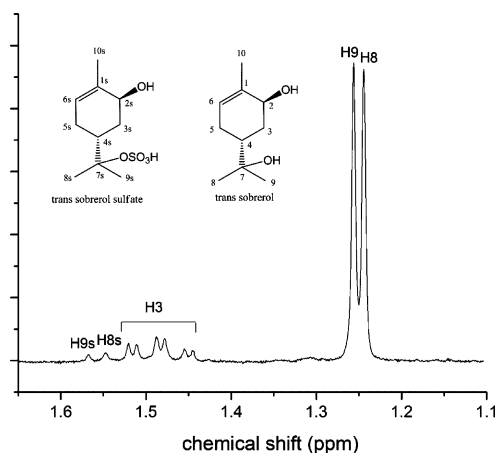


Figure 6. 1H NMR spectrum from reaction of α -pinene oxide reaction in 0.02 M D_2SO_4 /1.0 M Na_2SO_4 solution.

spectrum obtained about five minutes after the initiation of the reaction of α -pinene oxide in a 0.02 M D_2SO_4 /1.0 M Na_2SO_4 solution. Two new peaks at about 1.55 ppm were observed, which were about 0.3 ppm downfield of the H8 and H9 protons of *trans*-sobrerol, as expected for the *trans*-sobrerol sulfate structure (in previous work, we showed that the protons on carbon atoms adjacent to sulfate groups shift about 0.2–0.3 ppm downfield of the same protons that are adjacent to alcohol groups instead³⁵). To confirm that the new peaks were due to an organosulfate, the sulfate content was varied from 0.02 to 1 M (at a constant acid concentration of 0.02 M D_2SO_4). Figure 7 shows that the measured initial *trans*-sobrerol sulfate product fraction had the expected linear dependence on total sulfate concentration, thus confirming the 1.55 ppm peaks were due to an organosulfate.

It was readily apparent that the *trans*-sobrerol sulfate species was a transient species under these conditions, as it was observed to hydrolyze to *trans*-sobrerol quickly. Figure 8 shows the pseudo-first order analysis of the hydrolysis of *trans*-sobrerol sulfate for a 0.02 M D_2SO_4 /1.0 M Na_2SO_4 solution. The analysis resulted in the determination of a hydrolysis reaction lifetime of 27 min. The hydrolysis of *trans*-sobrerol sulfate was investigated at other acid strengths, but was found to be independent of acid concentration between 0 and 0.02 M

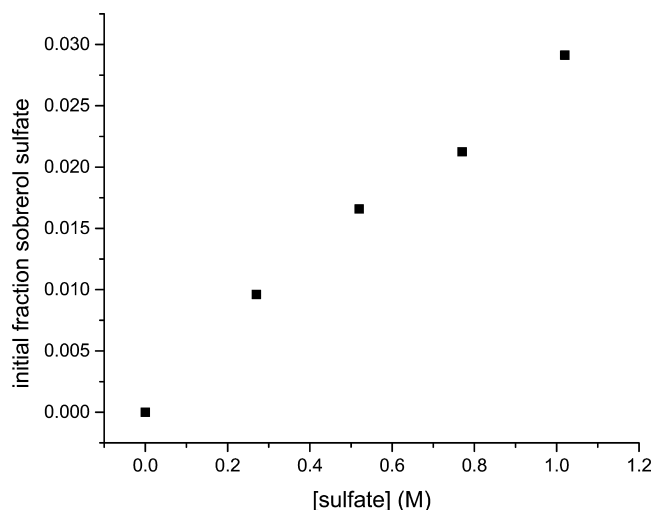


Figure 7. Sulfate dependence of initial *trans*-sobrerol sulfate formation at fixed 0.02 M D_2SO_4 acid concentration.

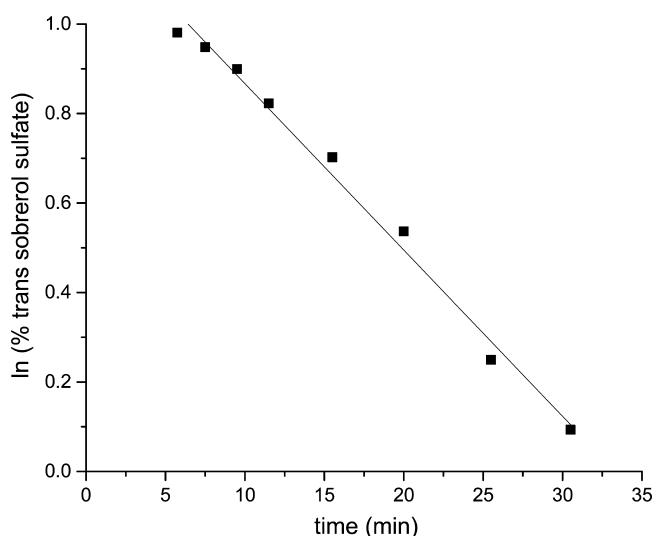


Figure 8. First-order kinetics analysis for the hydrolysis of *trans*-sobrerol sulfate in 0.02 M D_2SO_4 /1.0 M Na_2SO_4 solution.

D_2SO_4 . In previous work, we found that the hydrolysis of similar tertiary organosulfates and organonitrates involves both a neutral (with water perhaps acting as a general acid catalyst) and an acid-catalyzed mechanism.^{6,7} In particular, we noted that neighboring OH groups (as is the case in the isoprene-derived epoxides) slow down the sulfate and nitrate hydrolysis; since *trans* sobrerol sulfate has no neighboring OH groups, it is perhaps not too surprising that *trans*-sobrerol sulfate hydrolyzes quite quickly.

On the other hand, *trans*-sobrerol nitrate was never successfully identified, despite that fact that nitrate concentrations as much as 10 times greater than the sulfate concentrations used to produce *trans*-sobrerol sulfate were used. However, we discovered in our previous work on the hydrolysis of tertiary organosulfates and organonitrates⁷ that organonitrates generally hydrolyze much more quickly than organosulfates (more than 100 times faster). With a *trans*-sobrerol sulfate hydrolysis lifetime of 27 min, this previously determined organonitrate to organosulfate hydrolysis rate ratio predicts that any *trans*-sobrerol nitrate that might have formed from the reaction of α -pinene oxide under our solution

conditions would undergo hydrolysis in a matter of seconds. Therefore, the lack of detection of *trans*-sobrerol nitrate is consistent with the general structure–reactivity relationships that are emerging for the understanding of organosulfate and organonitrate hydrolysis kinetics.

In a similar NMR-based study of the reaction of α -pinene oxide in sulfuric acid,¹⁶ it was reported that diols, hydroxy sulfates, and disulfates which maintained the α -pinene bicyclic carbon backbone (so-called pinane-type species) had been identified. Because these results are at odds with our findings, as well as with previous reports in the natural products literature,^{20,23} we prepared α -pinene oxide/D₂SO₄ solutions identical to those used in the previous study. While we obtained the same ¹H NMR spectrum reported in that work, we contend that the assignments made in the previous work are incorrect. In particular, a comparison our ¹H NMR peak assignments and Figure 4 in the previous work,¹⁶ suggests that the peaks previously assigned as the pinane diol, pinane hydroxy tertiary sulfate, pinane hydroxy secondary sulfate, and pinane disulfate should instead be assigned to pinol, *trans*-sobrerol, *cis*-sobrerol, and *trans*-sobrerol, respectively. In the previous work, the product fractions were quantified as a function of sulfuric acid concentration. Since the acid strength and the sulfate concentration both increase as a function of increasing sulfuric acid concentration, it is not possible to definitively identify organosulfates from such measurements, as other species which require strong acid catalysis will also be enhanced as the sulfuric acid concentrations is increased. Because we investigated all product peaks as a function of sulfate concentration at fixed sulfuric acid concentration, we were able to definitively identify the presence of a single organosulfate, *trans*-sobrerol sulfate, and to also rule out the presence of the organosulfates identified in the previous work. In addition, we compared ¹H NMR spectra of the commercially available pinanediol isomers to the α -pinene oxide/D₂SO₄ reaction system NMR spectra, and did not find evidence for the production of pinanediols from α -pinene oxide. To the best of our knowledge, there appear to be no reports in the synthetic organic chemistry literature that describe the production of anti-pinanediols from the hydrolysis of epoxides of α -pinene. On the other hand, there are previous literature reports that indicate that the commercially available syn-pinane diols are prepared directly from α -pinene via OsO₄-catalysis.³⁶

A previous mass spectrometric-based study of the reactions of α -pinene oxide with sulfuric acid seed aerosols also reported the observation of the campholenic aldehyde and *trans*-carveol species,¹⁷ in agreement with present work. However, that same work also reported the observation of several, apparently long-lived, organosulfates, with the supposition that two of the organosulfates were of the bicyclic ring-retaining pinane-type structures. While we found no experimental evidence for these species in our aqueous solution systems and the computational thermodynamics results suggest that these species are much less stable than many other potential products, the formation of these species under other conditions (such as very high acidity/very low water content) is not contradicted by our results.

Computational Thermodynamics Results. To rationalize the observed product species, we carried out high-level electronic structure calculations in order to estimate the relative stability of various potential products. In particular, the free energies of the various species (in aqueous solution) were calculated relative to the often-dominant product *trans*-sobrerol. These results are presented in Table 3 and in Figure

Table 3. G2MS-Computed Free Energies and EPIWEB-Predicted³⁷ Physical Properties of α -Pinene Oxide Reaction Products in Aqueous Solvent

	G (kcal mol ^{−1}) ^a	vapor pressure ^b (Torr)	H (M atm ^{−1}) ^b	water solubility ^b (g L ^{−1})
C₁₀H₁₈O₂				
<i>trans</i> -sobrerol	0.0 ^a	4.5 × 10 ^{−5}	1.7 × 10 ³	1.7
<i>cis</i> -sobrerol	0.8	4.5 × 10 ^{−5}	1.7 × 10 ³	1.7
pinanediol	15.0	5.5 × 10 ^{−4}	4.8 × 10 ³	2.1
C₁₀H₁₆O				
α -pinene oxide	22.0	1.1	4.4	0.26
<i>trans</i> -carveol	−3.2	0.013	72	0.52
<i>cis</i> -carveol	−3.7	0.013	72	0.52
pinol	−8.1	1.1	4.7	0.20
campholenic aldehyde	−9.3	0.24	3.3	0.11
C₁₀H₁₄				
<i>p</i> -cymene	−45.7	1.5 ^c	0.09 ^c	0.023 ^c
C₁₀H₁₈SO₅				
pinane-1-sulfato-2-ol	18.5	1.1 × 10 ^{−8}	1.4 × 10 ⁹	180
pinane-2-sulfato-1-ol	17.8	1.7 × 10 ^{−8}	1.4 × 10 ⁹	180
<i>trans</i> -sobrerol sulfate	2.0	6.2 × 10 ^{−9}	5.8 × 10 ⁸	70
<i>cis</i> -sobrerol sulfate	2.1	6.2 × 10 ^{−9}	5.8 × 10 ⁸	70
C₁₀H₁₈NO₄				
pinane-1-nitrato-2-ol	18.4			
pinane-2-nitrato-1-ol	14.5			
<i>trans</i> -sobrerol nitrate	0.0			
<i>cis</i> -sobrerol nitrate	2.7			

^aCalculated values from G2MS method (all values relative to *trans*-sobrerol). ^bCalculated values from EPIWEB database.³⁷ ^cCalculated values are not available for species with nitrate groups. ^cExperimental values from EPIWEB database.³⁷

9 (the full computational results used to calculate the free energies are presented in Table S2 in the Supporting Information). The species within a single column in Figure 9 are simply isomers of each other, while species from different columns represent different degrees of hydration or sulfation/nitration. In particular, comparison of species within any of the columns in Figure 9 shows that while the production of pinane-type species (in which the bicyclic α -pinene carbon backbone is conserved) from α -pinene oxide is thermodynamically feasible, these species are much higher in free energy (primarily due to higher enthalpies) than species for which the four membered ring strain has been relieved. Therefore, it appears that the ring strain inherent to the α -pinene bicyclic structure is the thermodynamic driving force responsible for the production of a number of the carbon-backbone rearranged species, a process that has no analogy in the reactions of the previously studied isoprene-derived epoxides. It is also evident from comparison of the three leftmost columns of species in Figure 9, that dehydrated (relative to *trans*-sobrerol) species are

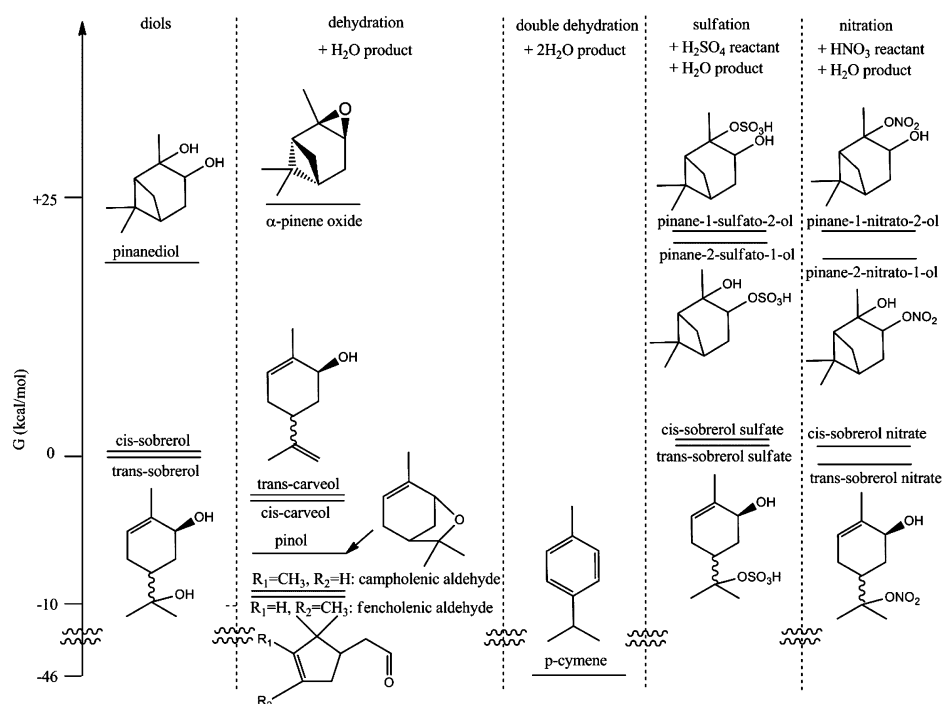


Figure 9. Relative free energies, in aqueous solvent, of α -pinene-oxide-derived species.

thermodynamically favored over hydrated species. This effect may be rationalized by the entropic contribution to the free energies; the liberation of water from the hydrated species leads to higher total entropy for dehydrated species and the free water molecule, which contributes to a lower total free energy for the system. The particular thermodynamic stability of *p*-cymene is further explained by the formation of an aromatic ring system. The thermodynamic calculations also indicate that *trans*- and *cis*-sobrerol have very similar free energies, which was experimentally confirmed by the similar equilibrium fractions of *trans*- and *cis*-sobrerol (see Figure 4).

Atmospheric Implications. The present finding that α -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. The acid dependence studies of the identities and relative yields of the different reaction products suggest that the effective pH of atmospheric particles will likely control the complexity and the kinetics of the overall reaction mechanism. While the direct products, campholenic aldehyde, *trans*-carveol, and *trans*-sobrerol were formed in all solutions studied, the acid strength was found to change the distribution of these direct products, as well as to catalyze the formation of additional species such as *cis*-sobrerol, pinol, and *p*-cymene. The reaction lifetimes listed in Table 2 for a pH \sim 1 solution indicate that the *trans*-sobrerol/*cis*-sobrerol isomerization equilibrium will be established in a matter of hours, while the *cis*-sobrerol/pinol dehydration equilibrium will take about 2 days to be established and the *trans*-carveol to pinol isomerization reaction is characterized by a lifetime of about 1 week. Since most atmospheric particles are estimated to have pH values of 1 or greater,³⁸ these lifetimes most likely represent lower limits for these processes in the ambient atmosphere. Therefore, the less acidic atmospheric particles would be expected to process α -pinene oxide into only campholenic aldehyde, and *trans*-sobrerol for typical particle lifetimes (a few days), while the

more acidic particles would be expected to facilitate some production of *cis*-sobrerol, pinol, and *p*-cymene, with the extent of production of these species very much dependent on the particle pH. *trans*-sobrerol sulfate was observed to form in solutions with elevated sulfate conditions. However, since its neutral hydrolysis lifetime was found to be only 27 min, the present results suggest that *trans*-sobrerol sulfate is not likely an important organosulfate in atmospheric particles. Since no organonitrates of any kind were observed in this study, it is also unlikely that α -pinene oxide-derived organonitrates play a large role in the composition of atmospheric particles.

It is of interest to consider the atmospheric fate of the various reaction products arising from the reactions of α -pinene oxide. In Table 3, vapor pressures, Henry's Law constants, and water solubilities (calculated using the EPIWEB suite of chemical and physical property prediction tools³⁷) were estimated for the various products. The relatively large vapor pressures and small Henry's Law constants for all but the diol species (*trans*- and *cis*-sobrerol) suggest that, barring any other particle phase chemical reactions, campholenic aldehyde, *trans*-carveol, pinol, and *p*-cymene would be expected to partition back to the gas phase. Because of the presence of C=C bonds in campholenic aldehyde, *trans*-carveol and pinol, it is expected that these compounds would undergo fast gas phase oxidation by OH, O₃, and/or NO₃ in the ambient atmosphere, and they would therefore exist only as short-lived species. In previous α -pinene photooxidation environmental chamber experiments (which also detected the presence of α -pinene oxide), *p*-cymene was detected in the gas phase¹⁸ and *trans*-sobrerol was detected as a condensed phase species on the walls of the chamber,¹² findings that are quite consistent with the present proposed mechanism. Therefore, the atmospheric particle processing of α -pinene oxide is predicted to lead to the presence of *trans*- and *cis*-sobrerol (with yields as high as 85% for less acidic conditions) in such particles, and also to the production of new highly reactive gas phase species. Because we were not able

to find any previous studies of the gas phase reactivity of these species, it is difficult to predict the ultimate atmospheric fate of these compounds.

CONCLUSION

The α -pinene photooxidation product, α -pinene oxide, was found to react very quickly in aqueous solutions, with the yields of the various reaction products depending strongly on the acid concentration of the solutions. A full reaction mechanism, as well as a simplified kinetics model, was proposed to rationalize the experimental results. Computational thermodynamics calculations indicate that the relief of ring strain in the bicyclic α -pinene oxide species is a large enthalpic driving force in the formation of the various products, and is the likely reason that no α -pinene bicyclic carbon backbone-containing products were observed. The reaction of α -pinene oxide on atmospheric particles is expected to lead to the presence of *trans*- and *cis*-sorbrol in the atmospheric particles themselves, as well as the production of several new reactive gas phase species.

ASSOCIATED CONTENT

Supporting Information

A table with ^1H and ^{13}C NMR chemical shift information for the many of the relevant species cited in this work and a table containing complete computational thermodynamics results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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