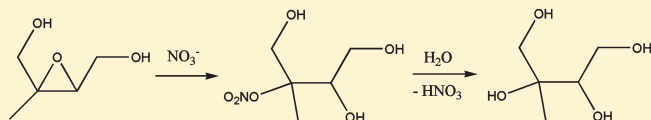ARTICLE

Formation and Stability of Atmospherically Relevant Isoprene-Derived Organosulfates and Organonitrates

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S *Supporting Information*

ABSTRACT: Isoprene is the precursor for number of alcohol, organosulfate, and organonitrate species observed in ambient secondary organic aerosol (SOA). Recent laboratory and field work has suggested that isoprene-derived epoxides may be crucial intermediates that can explain the existence of these compounds in SOA. To confirm this hypothesis, the specific hydroxy epoxides observed in gas phase isoprene photooxidation experiments (as well as several other related species) were synthesized and the bulk phase aqueous reactions of these species in the presence of sulfate and nitrate were studied via nuclear magnetic resonance (NMR) techniques. The results indicate that both primary and tertiary organosulfates and organonitrates are efficiently formed from the potential SOA reactions of isoprene-derived epoxides. However, the tertiary organonitrates are shown to undergo rapid nucleophilic substitution reactions (in which nitrate is substituted for by water or sulfate) over the whole range of SOA pH, while the tertiary organosulfates are found to undergo a much slower acid-dependent hydrolysis reaction. The primary organonitrates and organosulfates under study were found to be stable against nucleophilic substitution reactions, even at low pH. This finding provides a potential explanation for the fact that organosulfates are more commonly detected in ambient SOA than are organonitrates.

INTRODUCTION

Because of the role of secondary organic aerosol (SOA) in the air pollution [1] and climate change [2] issues, the physical and chemical properties of these particles have recently received intense study. Global modeling indicates that isoprene, the dominant nonmethane hydrocarbon emitted into the atmosphere,[3] is the foremost SOA precursor gas.[4] At least seven different chemically distinct compounds containing the isoprene carbon backbone (proposed structures and shorthand names are listed in Figure 1) have now been identified in ambient SOA.[5−11] The existence of these compounds indicates that isoprene can undergo chemical processing, which results in alcohol, sulfate, or nitrate functionalization of the isoprene carbon backbone. While there are known gas phase processes that can lead to alcohol and nitrate functionality for isoprene-derived compounds,[12−15] the presence of isoprene-derived organosulfates has been interpreted as clear evidence for chemical reactions occurring on the SOA particles themselves. Further, recent laboratory [16−18] and field [5,17] work has demonstrated that the hydrolysis of isoprene-derived epoxy diol (the first compound in Figure 1) on SOA is a kinetically facile mechanism for the formation of the most common detected SOA component, 2-methyl tetrol (the third compound in Figure 1). Other laboratory experiments with compounds similar to isoprene have suggested that organosulfates and organonitrates (such as those in Figure 1) are also likely to form from the nucleophilic addition of sulfate and nitrate, respectively, to isoprene-derived epoxydiol on SOA.[19−21] Figure S1 in the Supporting Information shows two potential mechanisms for the formation of nucleophilic addition (where the nucleophile can be H_2O, SO_4^{2-}, or NO_3^-) products from the reactions of epoxides.[22]

In the present study, the two distinct structural isomers (3-methyl-3,4-epoxy-1,2-butanediol and 2-methyl-2,3-epoxy-1,4-butanediol) of isoprene-derived epoxydiol observed by Paulot et al. from the photooxidation of isoprene under atmospherically relevant low NO_x conditions,[17] as well as several other structurally similar hydroxy epoxides are synthesized. Nuclear magnetic resonance (NMR) techniques are then used to study the bulk phase aqueous reactions of these epoxides in the presence of sulfate and/or nitrate in order to determine the structures and stabilities of the products formed. These results allow for a direct estimation of efficiency of the sulfate- and nitrate-forming reactions of isoprene-derived epoxides, as well as new insights on the potential fate of isoprene-derived organosulfates and organonitrates on SOA.

EXPERIMENTAL SECTION

Epoxide Syntheses and Solution Preparation. The syntheses of the epoxides (the six epoxides under study are indicated as the reactants in Figure 2) followed the method described by Cole-Filipiak et al.[16] All experiments were performed using deuterated acid/salt solutions for the purpose of NMR field locking. The acid/salt solutions were custom prepared using commercially available 96−98 wt % D_2SO_4 (Sigma-Aldrich), 70 wt % DNO_3 (Sigma-Aldrich), 99.9% D_2O (Cambridge Isotope Lab, Inc.), Na_2SO_4 (Sigma-Aldrich), and $NaNO_3$
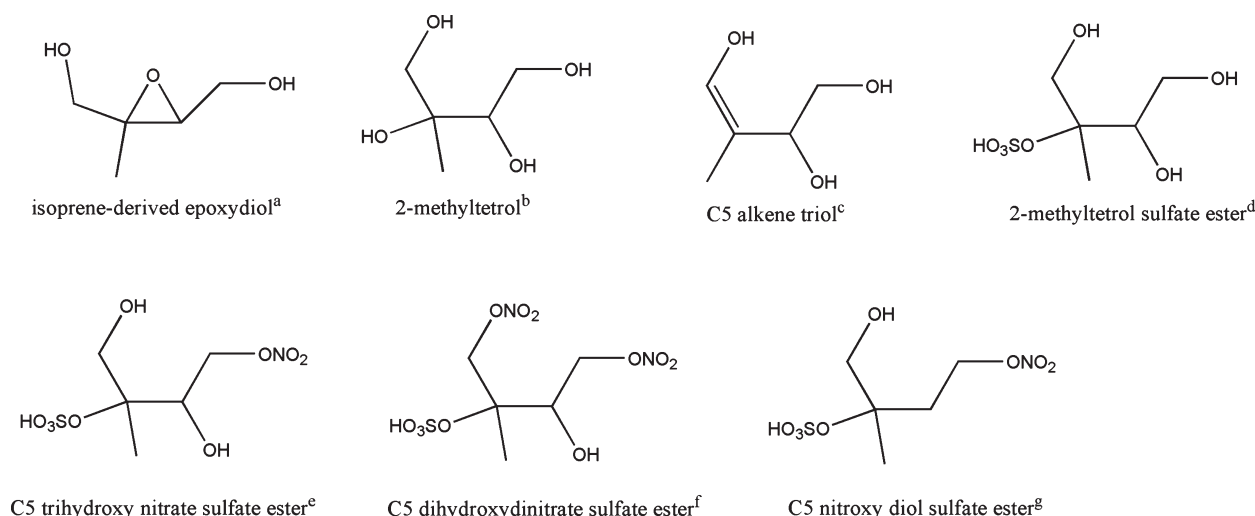
Figure 1. Compounds identified in ambient SOA sharing the same carbon backbone as isoprene (a, ref 5; b, ref 6; c, ref 7; d, refs 8 and 9; e, refs 9 and 10; f, refs 9 and 11, g, ref 11). In most cases, the particular structural isomeric form of these compounds has not been determined.

(Sigma-Aldrich). To each solution, 0.1 wt % sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS, Cambridge Isotope Lab, Inc.) was added as an internal standard.

Organosulfate and Organonitrate Product Measurements. In previous work on the organosulfate product yields for reactions involving simple epoxides, the reaction mixtures were prepared, allowed to react for several epoxide lifetimes (usually between 2 and 24 h), and a single NMR measurement was made to determine the product yields.[20,23] However, because of the discovery of significant reactivity of some of the organosulfate and organonitrate products in the present work, the present product measurements were performed as kinetics experiments. The reaction mixtures were prepared and subjected to NMR analysis as follows. A 2.5 mL aliquot of the desired acid/salt solution (the acid content was varied over a wide range in many of the experiments, while the total nucleophile concentrations were usually held constant at 1 M) was added to a 10 mL beaker and stirred. Next, 25 μL ($\sim$ 0.10 M) of epoxide reactant was added and a timer was started. After approximately 1 min of stirring to ensure solution homogeneity, an aliquot of the reaction mixture was loaded into an NMR tube and NMR spectral collection was started. All ^{1}H NMR spectra were collected on a Varian 400 MHz NMR Spectrometer. The reaction time was recorded as the ending time of each 30 s NMR data collection period. Depending on the rate of reaction for the various species, the solutions were either monitored continuously for a total period of time of about one hour, or were monitored intermittently (daily or weekly) over a total period of time as long as two months. The relative amounts of reactants and products were calculated by peak integration of unique protons for each species, referenced to the 9 methyl protons at 0.00 ppm from DSS.

RESULTS AND DISCUSSION

Identification of Products and Initial Yield Measurements. With the exception of 3,4-epoxy-2-butanol, all of the epoxides under study are based on the isoprene carbon backbone. For the four isoprene-derived epoxides studied with a tertiary carbon center, the nucleophilic addition of either sulfate or nitrate was found to occur solely at the tertiary site. For the one isoprene-

derived epoxide studied with primary and secondary carbon centers, the nucleophilic addition was found to occur solely at the primary site. 3,4-epoxy-2-butanol was also studied to provide a second system with primary-secondary carbon centers; nucleophilic addition was also found to occur solely at the primary site in this system as well. A similar study of organosulfate formation in the reactions of hydroxy butyl epoxides found a similar pattern.[21] The isomer-specific product pathways and initial organosulfate and organonitrate yields (in the presence of 1 M concentrations of each nucelophile) for the reactions of all six epoxides are reported in Figure 2. It should be noted that Figure 2 indicates that both 3-methyl-3,4-epoxy-1,2,-butanediol and 2-methyl-2,3,-epoxy-1,4-butanediol (the two species observed by Paulot et al.[17]) were observed to produce the same nucleophilic addition products. Paralleling previous studies of organosulfate and organonitrate production from the acid-catalyzed reactions of epoxides,[20,21,23] relatively high yields of both organosulfates and organonitrates were observed and higher yields were observed for primary systems as compared to tertiary systems.

Hydrolysis of Tertiary Organonitrate and Organosulfate Products. The tertiary organonitrate products were found to have hydrolysis lifetimes on the time scale of minutes. The NMR spectra revealed no new species, but indicated increasing concentrations of polyol product concurrent with the nitrate loss. The kinetics data for the reaction of 3-methyl-3,4-epoxy-1,2-butanediol in 0.25 M DNO_3/0.75 M $NaNO_3$, for which 2-methyl-2-nitrato-1,3,4-butanetriol is clearly an intermediate product, are shown in Figure 3. Therefore, we surmised that the tertiary organonitrates were undergoing hydrolysis to form polyols and nitric acid

$$RONO_2 + H_2O \rightarrow ROH + HNO_3 \qquad (1)$$

On the other hand, the primary organonitrates were found to be stable against hydrolysis over a two month monitoring period. To ascertain the nature of the hydrolysis mechanism, the experiments were carried out at several different acid concentrations. No acid dependence was observed for solutions ranging from 0.02 to 1.0 M DNO_3. By using appropriate acid concentrations, the epoxide reaction (which leads to organonitrate production) could be made to occur much more quickly than
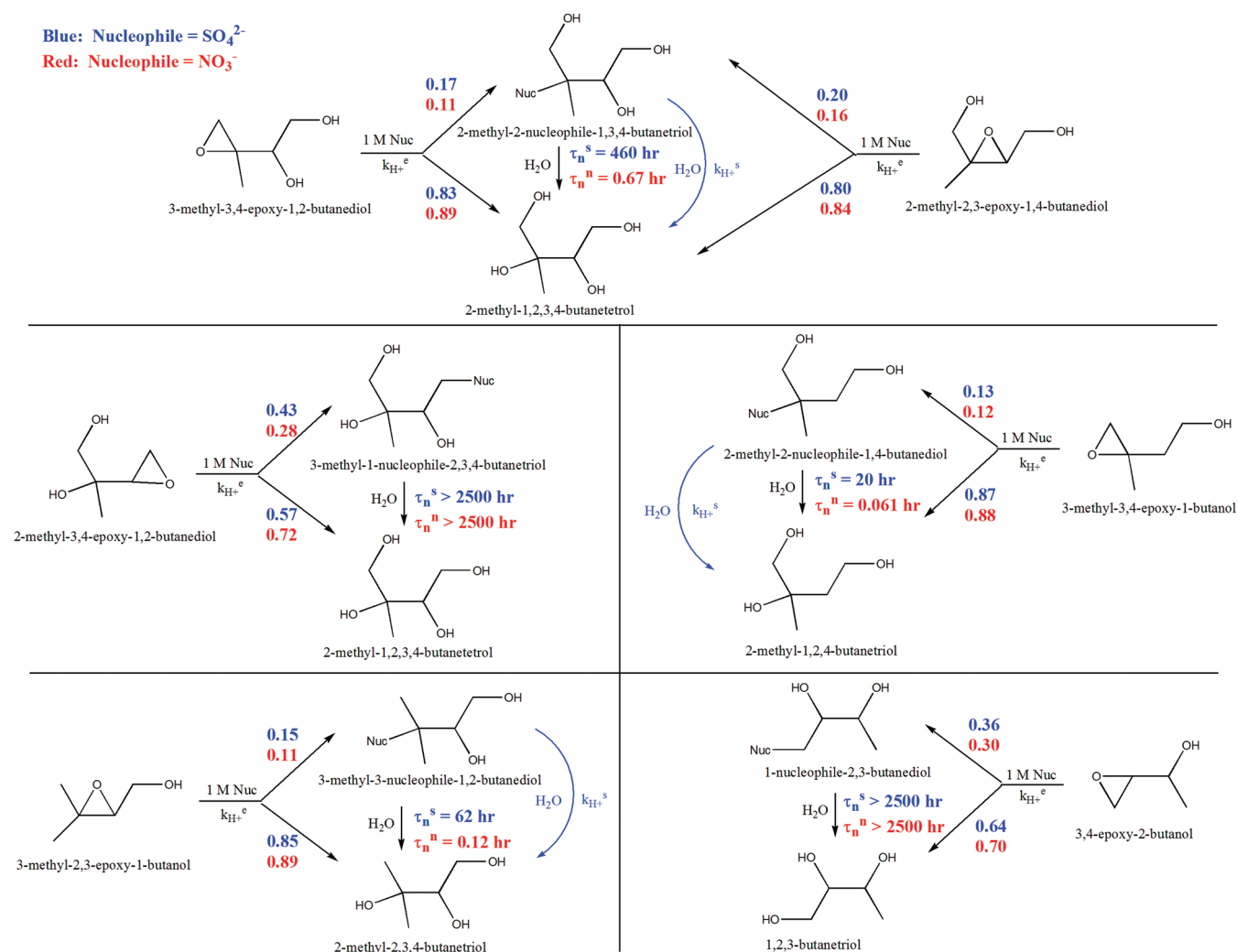
Figure 2. Overall mechanism for the reaction of the six epoxides under study (with the fractional yields determined in the present work indicated) and the hydrolysis pathways (with the neutral mechanism lifetimes determined in the present work indicated) for the nucleophile addition products.
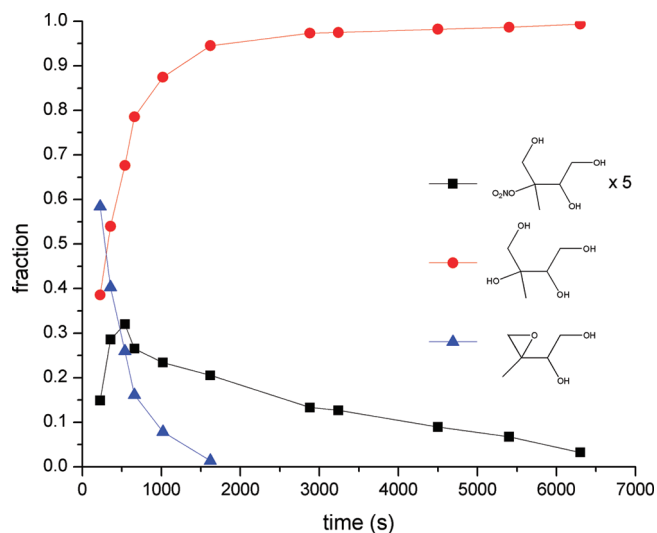

Figure 3. Kinetics data for the reaction of 3-methyl-3,4-epoxy-1,2-butanediol in 0.25 M DNO$_3$/0.75 M NaNO$_3$ solution.

the hydrolysis reaction (which leads to organonitrate loss). In other words, at later times, the production of organonitrates is insignificant and the kinetics data can be analyzed in terms of a simple first order organonitrate loss expression

$$-\frac{d[RONO_2]}{dt} = k_n^n[RONO_2] \qquad (2)$$

where k_n^n is the first-order *neutral* mechanism organo*nitrate* hydrolysis rate constant.

Typically, the first NMR spectrum was collected at about 3 min of reaction time, and the acid concentration was chosen so that the epoxide reaction had a lifetime of about 1 min.

The integrated raw law for eq 2 is

$$-\ln\frac{[RONO_2]}{[RONO_2]_0} = k_n^n t \qquad (3)$$

Figure 2 reports the lifetimes ($\tau_n^n = 1/k_n^n$) for the tertiary organonitrates, as well as lower limit estimates for the lifetimes of the primary organonitrates. Because significant reaction of the tertiary organonitrates had already occurred before the first

NMR spectrum was collected, the integrated rate law was used to extrapolate to the time =0 organonitrate concentration, and the initial organonitrate yields reported in Figure 2 for these species were calculated using this extrapolated value.

While reacting much more slowly than the tertiary organonitrates, the tertiary organosulfate products shown in Figure 2 were also were found to undergo hydrolysis to form polyols and sulfuric acid:

$$ROSO_3H + H_2O \rightarrow ROH + H_2SO_4 \qquad (4)$$

Similar to what was found for the primary organonitrates, the primary organosulfates were found to be stable against hydrolysis over a period of two months. In the case of the hydrolysis of tertiary organosulfates, it was found that a neutral mechanism was operative for acid concentrations less than about 0.1 M, while an acid-catalyzed mechanism was dominant at higher acid concentrations. In order to explore the acid catalysis in more detail, D_2SO_4 concentrations as high as 4 M were used. Due to the use of these highly concentrated solutions, the Aerosol Inorganics Model (AIM)[24] was used to calculate proton activities (a_{H^+} in molal units) for use in the kinetics analysis. Therefore, the tertiary organosulfate hydrolysis kinetics data was analyzed according to a two term rate law

$$-\frac{d[ROSO_3H]}{dt} = k_n^n[ROSO_3H] + k_{H^+}^S\, a_{H^+}\, [ROSO_3H] \quad (5)$$

where k_n^S is the first order *neutral* mechanism organo*sulfate* hydrolysis rate constant and $k_{H^+}^S$ is the second order *acid-dependent* mechanism organo*sulfate* hydrolysis rate constant.

The integrated raw law for eq 5 is

$$-\ln\frac{[ROSO_3H]}{[ROSO_3H]_0} = k_n^S t + a_{H^+}\, k_{H^+}^S\, t \qquad (6)$$

When the acid-dependent term is dominant, the integrated rate law can be written as

$$-\ln\frac{[ROSO_3H]}{[ROSO_3H]_0} = a_{H^+}\, k_{H^+}^S\, t = k_{eff}^S t \qquad (7)$$

where $k_{eff}^S = a_{H^+} + k_{H^+}^S$.

Therefore, a plot of k_{eff}^S versus a_{H^+} yields the value of $k_{H^+}^S$. Formal acid dependent measurements were carried out for 2-methyl-2-sulfato-1,3,4-butanetriol and 2-methyl-2-sulfato-1,4,-butanediol, and $k_{H^+}^S$ was determined be 3.9×10^{-6} m^{-1} s^{-1} and 1.7×10^{-4} m^{-1} s^{-1} (statistical uncertainties in these values are the order of 20%) for the two species, respectively. Figure 2 contains the neutral mechanism lifetimes ($\tau_n^S = 1/k_n^S$) for the tertiary organosulfates, as well as lower limit estimates for the lifetimes of the primary organosulfates. The τ_n^S and τ_n^n values show similar trends across the three tertiary species (i.e., the 2-methyl-2-nucleophile-1,3,4-butanetriol species are the least reactive species for both sulfate and nitrate, and the 2-methyl-2-nucleophile-1,4,-butanetriol species are the most reactive for both sulfate and nitrate). Similar trends were observed by Cole-Filipiak et al.[16] in their determination of the acid-catalyzed epoxide hydrolysis rate constants ($k_{H^+}^e$) for these three tertiary species, thus suggesting that the bond breaking associated with nucleophilic attack (mechanism A-2 for the epoxide reactions) is the rate-limiting step for both the epoxide hydrolysis and nucleophilic hydrolysis substitution pathways.

Previously, our lab investigated the acid-catalyzed mechanism for reaction 4, and its reverse reaction for a number of systems with primary carbon atom centers.[19] In that study, we defined reaction 4 as the "reverse" direction. However, in order to avoid confusion in discussing the present work, we define the fully reversible reaction as follows:

$$ROSO_3H + H_2O \rightleftharpoons ROH + H_2SO_4 \qquad (8)$$

and use this definition to refer to the rate and equilibrium constants determined in our previous work. In the previous work, only very high concentrations of sulfuric acid (65−85 wt %) were used. At 65 wt % D_2SO_4 for the ethylene glycol monosulfate ester/ethylene glycol system ($R = OHCH_2CH_2-$), the effective equilibrium constant ($K'_{eq} = [ROH]_{eq}/[ROSO_3H]_{eq}$) and the lifetime of ethylene glycol monosulfate ester were determined to be 1.1 and 4.8 h, respectively. For comparison, the effective equilibrium constant for the 2-methyl-2-sulfato-1,4,-butanediol/2-methyl-1,2,4-butanetriol system at 40 wt % D_2SO_4 (4 M) was determined in the present work to be >100 (a lower limit determined from the complete loss of detectable amounts of 2-methyl-2-sulfato-1,4,-butanediol) and the lifetime was determined to be 0.12 h. Therefore, it appears that tertiary organosulfates are less thermodynamically stable (relative to the corresponding alcohols) than are primary organosulfates, and that tertiary organosulfates convert much more quickly to alcohols through an acid-catalyzed mechanism. The presence of an acid-catalyzed hydrolysis pathway in the case of the organosulfates (but not in the case of the organonitrates) can be rationalized by differences in the nature of the nucleophilic substitution process. It is well-known that nucleophilic substitution is more facile when the leaving group (the nucleophile undergoing substitution, in this case, sulfate or nitrate) is characterized by low basicity.[25] In the case of the organosulfate products, it is likely that they exist as neutral species ($ROSO_3H$) at low pH and as ionized species ($ROSO_3^-$) at high pH. Figure S2 in the Supporting Information depicts the hypothesis that the differing reactivities of tertiary organonitrates (most reactive, pH-independent) and organosulfates (less reactive, but more reactive at low pH) can be comprehensively rationalized by the relative basicities of the various leaving groups.

Simultaneous Nucleophilic Attack of Sulfate and Nitrate on Epoxides. The observation that tertiary organosulfates and organonitrates are metastable species in aqueous solution indicates that the production of organosulfates and organonitrates from nucleophilic attack on epoxides is a kinetic phenomenon. In other words, the polyol species are the thermodynamically preferred products. Noting the similar initial yield data, it also appears that the nitrate and sulfate nucleophilic attack on the tertiary epoxides is kinetically competitive. In order to directly test whether sulfate and nitrate are in fact competitive nucleophiles, we performed an experiment in which 2-methyl-2,3-epoxy-1,4-butanediol was added to a solution that was 1 M in both sulfate and nitrate. Indeed, both sulfate and nitrate nucleophilic addition products were observed with similar yields, thus confirming that sulfate and nitrate have similar kinetic facility in their reactions with tertiary epoxides.

Nucleophilic Substitution of Nitrate for Sulfate. Because the organonitrates have much shorter lifetimes than the corresponding organosulfates, it is also possible that organonitrates could undergo nucleophilic attack by sulfate to form much more long-lived organosulfate products. In order to test this hypothesis, 2-methyl-2,3-epoxy-1,4-butanediol was reacted in the
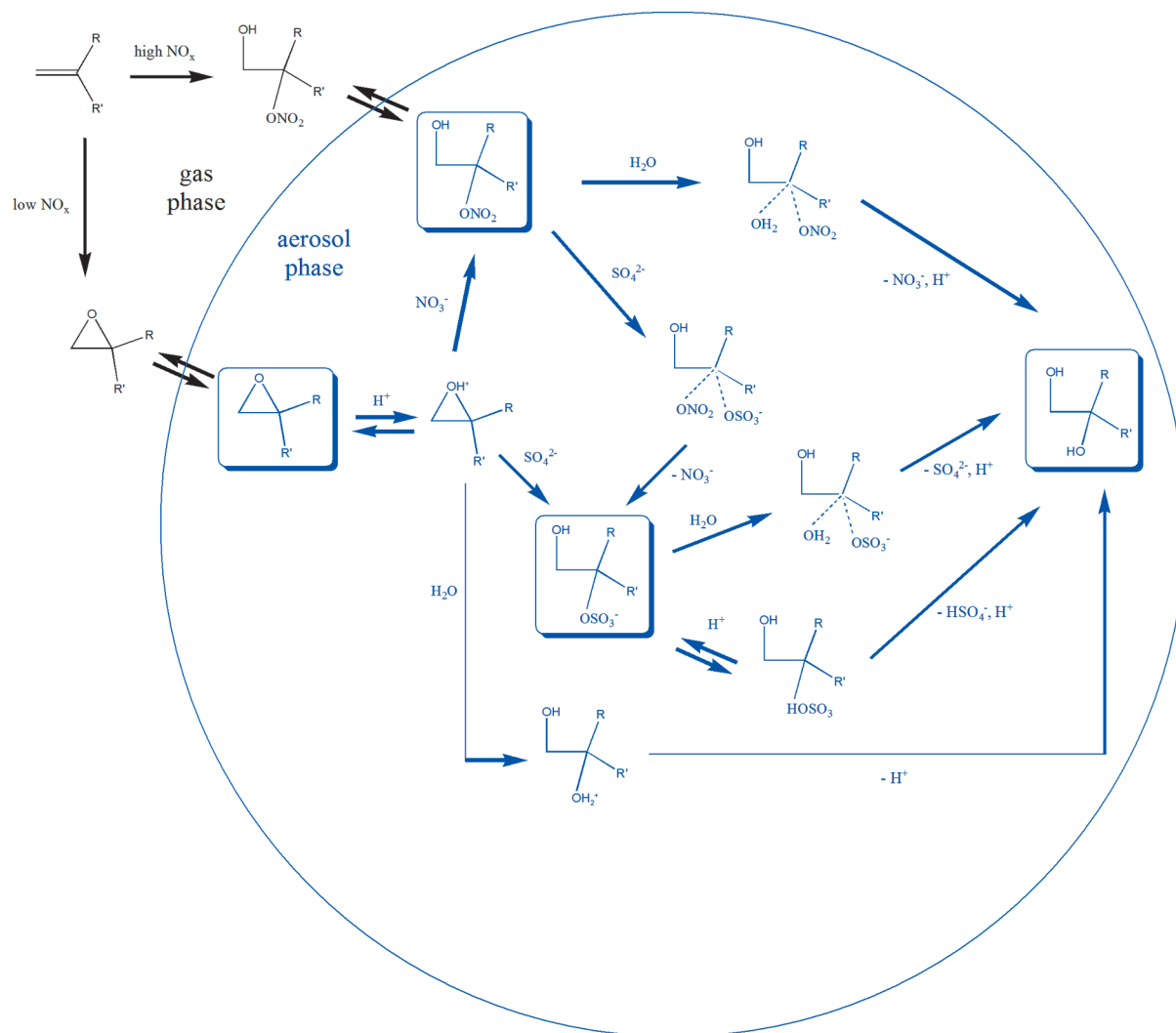
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Figure 4. Proposed pathways for the conversion of tertiary epoxides and organonitrates to organosulfates and polyols on SOA (directly observed stable species are enclosed in boxes).

presence of 1 M nitrate just long enough for all of the epoxide to be consumed, but before the corresponding organonitrate product had time to undergo significant hydrolysis. Then, enough Na_2SO_4 was added to the solution such that sulfate concentration was also 1 M. NMR analysis indicated that some organosulfate product (2-methyl-2-sulfato-1,3,4-butanetriol) product was formed as the organonitrate product (2-methyl-2-sulfato-1,3,4-butanetriol) reacted away. Therefore, in the presence of both sulfate and nitrate, the reaction of tertiary epoxides is expected to lead to organonitrates, organosulfates and polyols during early time periods, with organosulfates and polyols dominating during intermediate time periods, and at long time periods (equilibrium), only polyols are expected to remain.

Atmospheric Implications. In Figure 4, we attempt to summarize the SOA-relevant chemistry for a generic tertiary alkene (for isoprene, R = CH_3 and R′ = $CH = CH_2$). Paulot et al. showed that tertiary epoxides are among the dominant gas phase products in the low NO_x OH-initiated photooxidation of isoprene [17] and Paulot et al. [26] and Lockwood et al. [14] showed that tertiary (hydroxy) organonitrates are among the dominant primary gas phase products in the high NO_x OH-initiated photooxidation of isoprene; therefore, these two species are

depicted in Figure 4 as potential tertiary gaseous isoprene-derived SOA precursors. For isoprene specifically, the potential functionalization of the other two carbon backbone positions is not explicitly depicted in Figure 4. For the epoxide species identified by Paulot et al.,[17] these carbon backbone positions are functionalized by hydroxy groups. It has been noted that these hydroxy groups are likely important in allowing significant partitioning of the epoxide to the SOA phase.[21] By the same token, it is likely that the gas phase hydroxy nitrates of isoprene require additional functionalization in order to efficiently partition to the aerosol phase. For example, if both primary and secondary OH-initiated oxidation of isoprene occurs under high NO_x conditions, a dinitrate diol species would be expected as a product; of course, in this case, only one of the nitrate groups could occur at the tertiary carbon backbone position.

Upon uptake into the aerosol phase, the reactions of the epoxide are represented in Figure 4 according to the A-2 mechanism given in Figure S1 in the Supporting Information. As described above, the mechanism allows for direct polyol, organosulfate, and/or organonitrate formation from the protonated epoxide. The organonitrate can then potentially undergo neutral hydrolysis to the polyol or undergo a nucleophilic
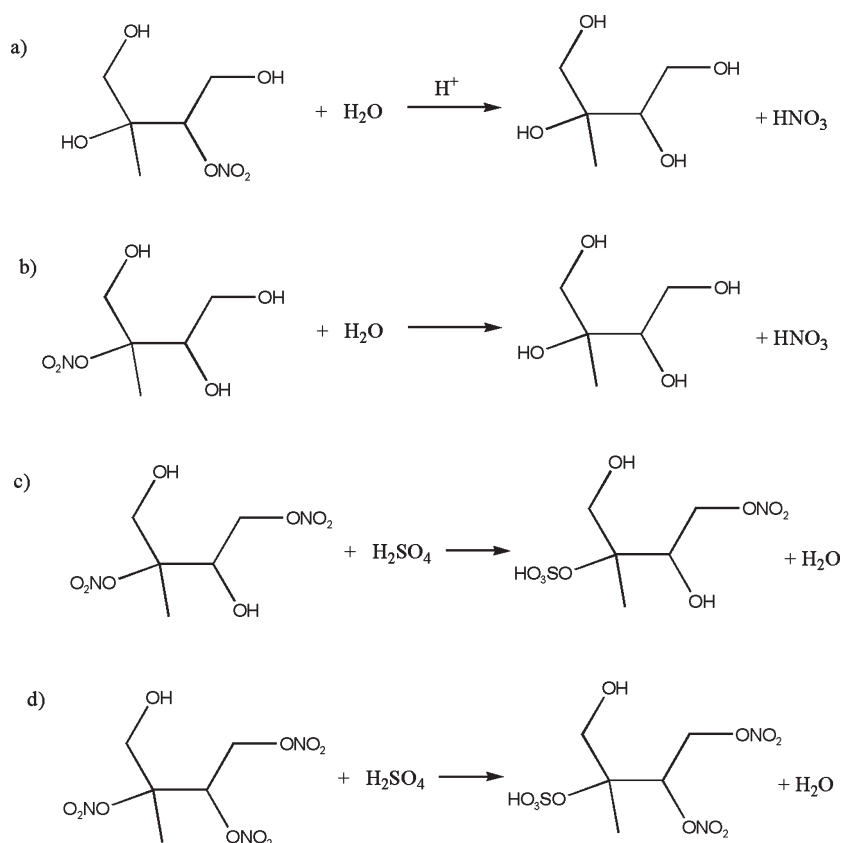
Figure 5. (a) Nitrate hydrolysis pathway proposed by Szmigielski et al.[31] (b) Alternative nitrate hydrolysis pathway to that proposed by Szmigielski et al.. (c) Proposed sulfate nucleophilic substitution pathway for the production of organo mononitrate monosulfate products in SOA. (d) Proposed sulfate nucleophilic substitution pathway for the production of organo dinitrate monosulfate products in SOA.

substitution reaction with sulfate to form an organosulfate. The organosulfate can then potentially undergo either a neutral or acid-catalyzed hydrolysis process to form the polyol. Figure 4 also suggests that a gas phase hydroxy organonitrate can be taken up into the aerosol phase and undergo the same reactions as a hydroxy organonitrate produced in the SOA epoxide reaction.

The actual kinetic parameters for the various processes depicted in Figure 4, coupled with typical SOA acidities and lifetimes, can be used to derive an even simpler picture of potential chemical reactions occurring on ambient SOA. The wet deposition lifetimes for SOA are estimated to be on the order of a few days.[27] Inspection of Figure 2 indicates that all of the tertiary organonitrates have neutral hydrolysis lifetimes that are much shorter than the estimated SOA lifetime; therefore, tertiary organonitrates are not expected to be stable on the time scale of the lifetime of ambient SOA. On the other hand, 2-methyl-2-sulfato-1,3,4-butanetriol, the organosulfate formed from both observed isoprene-derived epoxides, has a very long neutral hydrolysis lifetime of 460 h. 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 ($[H^+_{aerosol}]$) of SOA particles in the Pittsburgh area.[28] In their measurements, the pH of SOA usually ranged from about 4.0 to 1.5, but values as low as 0 were sometimes observed. While a recent study has suggested that the organosulfates themselves may cause errors in this approach,[29] it does provide an approximate range for ambient SOA acidities. Even for a very low pH value of 0 ($a_{H^+} \approx 1$ m), the acid-catalyzed hydrolysis lifetime for

2-methyl-2-sulfato-1,3,4-butanetriol is still a fairly lengthy 60 h. Therefore, the present kinetics data suggests that the tertiary organosulfate formed from the reaction of sulfate with the observed isoprene-derived epoxides will most likely be stable during the lifetime of most ambient SOA. However, other tertiary sulfates (such as those indirectly formed from the organonitrate products of the gas phase oxidation of isoprene oxidation products) may be reactive on SOA, particularly at low pH.

The present kinetic data suggest that tertiary organonitrates, whether they are formed in the gas phase under high NO_x OH-initiated oxidation conditions or on SOA from epoxide reactions, are likely to undergo fast conversion on SOA to tertiary organosulfates and polyols. There have been two recent reports in the literature that are consistent with this hypothesis. Sato reported experiments under dry conditions and in the absence of sulfate in which the SOA formed in the high NO_x OH-initiated photooxidation of isoprene was subjected to liquid chromatography mass spectrometry (LC-MS) analysis.[30] Sato described the identification of mononitrate triol and dinitrate diol species (which are likely to have tertiary nitrate functionality), which were not stable in the aqueous solutions used in the workup for the LC-MS analysis, a result that is consistent with the fast hydrolysis of tertiary organonitrates found in this study. Szmigielski et al. reported experiments in which the products formed in the high NO_x OH-initiated photooxidation of isoprene were allowed to interact with a concentrated sulfuric acid coated-surface.[31] They showed that the total mass collected on the filter was

enhanced in the presence of sulfuric acid and identified 2-methyl-1,2,3,4-butanetetrol (2-methyltetrol) as a major product of the acid-enhanced process. Specifically, they proposed that the acidic surface led to enhanced conversion of organonitrates to polyols. For example, Szmigielski et al. suggested that a potential second generation (i.e., the result of two OH oxidation events) gas phase isoprene product could undergo the reaction shown in Figure 5a on the acidic surface to produce the observed 2-methyl-1,2,3,4-butanetetrol product. However, the present results suggest that such a process need not be acid catalyzed to be quite fast and is much more likely to be efficient for tertiary organonitrates. Therefore, the 2-methyl-1,2,3,4-butanetetrol products observed in the Szmigielski et al. experiments are probably more efficiently formed by the neutral mechanism reaction of tertiary organonitrates as shown in Figure 5b. It is possible that the hydrolysis of primary and secondary organonitrates was also occurring at the very high acid strengths used in the Szmigielski et al. experiments. However, the present kinetics results suggest that such reactions are not likely to occur efficiently on higher pH ambient SOA.

In any case, the demonstrated instability of tertiary organonitrates and their ability to convert to organosulfates and polyols provides a potential explanation for the fact that no mononitrate polyol species have been detected in ambient SOA (see Figure 1). The present results also suggest the possibility that some SOA analytical methods (such as aerosol filter-based sampling occurring in the presence of water and the derivitization approaches often used with GC-MS analysis) may be biased against the observation of such species, and this could also be an explanation for the nonobservation of these species in ambient SOA.

The positive identification of several organo nitrate sulfate species, which have been detected in ambient SOA (see Figure 1) can also be rationalized via the general scheme given in Figure 4. For example, the presence of the organo mononitrate monosulfate species in ambient SOA may be explained by the initial formation of organonitrates consisting of at least one nitrate group at a non tertiary position formed in the gas phase high NO_x OH-initiated oxidation of isoprene (either in the primary or secondary oxidation steps). For example, 2-methyl-2,4-dinitrato-1,3-butanediol can be anticipated as a major product of the gas phase OH-initiated primary and secondary oxidation of isoprene under high NO_x conditions. The present results suggest that if this species partitioned into SOA with high sulfate content, it could undergo reaction shown in Figure 5c to form one of the organo mononitrate monosulfate species detected in ambient SOA shown in Figure 1. The observation of the organo dinitrate monosulfate species in ambient SOA may be explained by a similar logic. The gas phase primary, secondary, and tertiary NO_3-initiated oxidation of isoprene has been shown to produce a trinitrate ol, with one of the nitrate groups likely positioned at the tertiary carbon.[15] Again, upon partitioning into SOA with high sulfate content, such a species could undergo the reaction shown in Figure 5d to produce the organo dinitrate monosulfate species detected in ambient SOA shown in Figure 1.

In conclusion, the present work indicates that tertiary organosulfates and organonitrates are efficiently formed from potential SOA reactions of the two epoxides observed by Paulot et al. in the photooxidation of isoprene under atmospherically relevant low NO_x conditions.[17] However, unlike their primary counterparts, tertiary organonitrates are expected to undergo efficient nucleophilic substitution reactions (in which nitrate is substituted for water or sulfate) on SOA even at neutral pH values.

Similarly, the tertiary organosulfates can also undergo nucleophilic substitution reactions, albeit only at pH values that are lower than that expected for most ambient SOA. Therefore, we predict that tertiary organonitrates (whether they are formed in the gas phase from high NO_x OH-initiated or NO_3-initiated oxidation of isoprene or on SOA from the reactions of epoxides formed in the low NO_x OH-initiated oxidation of isoprene) are likely to undergo fast conversion on SOA to tertiary organosulfates and polyols. This expectation provides a potential explanation for the fact that organosulfates are more commonly detected in ambient SOA than are organonitrates.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Two figures as described in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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