Chapter 3

Evidence for Organosulfates in Secondary Organic Aerosol*

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3.1 Abstract

Recent work has shown that particle-phase reactions contribute to the formation of secondary organic aerosol (SOA), with enhancements of SOA yields in the presence of acidic seed aerosol. In this study, the chemical composition of SOA from the photooxidations of α-pinene and isoprene, in the presence or absence of sulfate seed aerosol, is investigated through a series of controlled chamber experiments in two separate laboratories. By using electrospray ionization – mass spectrometry, sulfate esters in SOA produced in laboratory photooxidation experiments are identified for the first time. Sulfate esters are found to account for a larger fraction of the SOA mass when the acidity of seed aerosol is increased, a result consistent with aerosol acidity increasing SOA formation. Many of the isoprene and α-pinene sulfate esters identified in these chamber experiments are also found in ambient aerosol collected at several locations in the southeastern U.S. It is likely that this pathway is important for other biogenic terpenes, and may be important in the formation of humic-like substances (HULIS) in ambient aerosol.

3.2 Introduction

Particle-phase reactions are now understood to play an important role in secondary organic aerosol (SOA) formation (*1*). Particle-phase oligomerization leads to the formation of high-molecular-weight (MW) species (*2*−*4*); suggested oligomerization reactions include the reactive uptake of volatile aldehydes or ketones via peroxyhemiacetal formation (*5*, *6*), hydration, hemiacetal/acetal formation, and aldol condensation (*7*, *8*). Esterification in isoprene photooxidation (*9*, *10*) has also been reported in SOA formation. The role of these reactions remains in some doubt as some of the proposed reactions (e.g. hemiacetal/acetal formation and aldol condensation) are not thermodynamically favorable at ambient conditions (*11*, *12*).

Laboratory chamber studies have demonstrated that the presence of acidic seed aerosol enhances the SOA yields observed from the oxidation of various volatile organic compounds (VOCs), such as α-pinene (*2*, *3*, *13, 14*), isoprene (*8*, *14*, *15*), and several model cycloalkenes (*2*) over those with a less acidic seed aerosol. Despite recent advances in understanding particle-phase SOA chemistry, the role of particle-phase acidity in enhancing SOA formation remains essentially unexplained. Recent studies have presented mass spectrometric evidence that the reactive uptake of glyoxal and pinonaldehyde (principal gas-phase oxidation products from aromatics and α-pinene, respectively) on acidic aerosol involves organosulfate formation (sulfate esters or derivatives; for simplicity, we will use hereafter the term sulfate esters to also denote sulfate derivatives; i.e. sulfate derivatives formed from a carbonyl compound) (*16*−*18*). In addition, several field studies have reported sulfate ester signatures in aerosol collected on filters using Fourier transform infrared spectroscopy (*19, 20*) and electrospray ionization (ESI) – mass spectrometry (MS) (*21, 22*). Nevertheless, the importance of organosulfate formation to SOA remains unclear. Traditional analytical methods, such as gas chromatography/mass spectrometry (GC/MS) with prior derivatization, may not be well suited for identifying organosulfates. It is likely that single derivatization protocols, such as trimethylsilylation, GC injection and column temperatures could cause the degradation or misinterpretation of such species (*23*). On the other hand, ESI-MS has been shown as an effective method for the detection and quantification of organosulfate species (*24*, *25*).

In the present study ESI-MS is used to detect and structurally elucidate sulfate esters in SOA formed from the photooxidations of isoprene and α-pinene under differing combinations of NO_x levels and seed aerosol acidities. As a result, the formation of sulfate esters may be a major contributor to the observed enhancement in SOA yields in the presence of acidic aerosol.

3.3 Experimental Section

3.3.1 Isoprene Chamber Experiments

A summary of experimental conditions for all isoprene photooxidation experiments can be found in Table 3.1. Isoprene photooxidation experiments were conducted in Caltech's dual indoor 28 m^3 Teflon chambers (*26*, *27*) and in EPA's fixed volume 14.5 m^3 indoor chamber (*15*). The temperatures, aerosol size distributions, and relative humidities, as well as the O_3, nitric oxide (NO), NO_x concentrations were continuously measured in both facilities. The isoprene concentrations in both facilities were monitored by GC with flame ionization detection. The Caltech experiments were conducted in the static mode (i.e. batch reactor) whereas the EPA experiments were conducted in the dynamic mode (i.e. continuous stirred tank reactor) with the exception of EPA-326 which was a static mode experiment. Hydroxyl radical (OH) precursors (H_2O_2 or HONO) were employed in the Caltech experiments (*28*, *29*). For all Caltech low-NO_x experiments, only H_2O_2 was added, resulting in NO_x concentrations < 1 ppb. Caltech high-NO_x experiments either used H_2O_2 and an initial amount of NO (~ 800 ppb), or with HONO and NO_x as a side product. In the Caltech experiments, three initial inorganic seed aerosol conditions were used: (1) the absence of aerosol where SOA formation was initiated by nucleation; (2) ammonium sulfate (AS) aerosol; and (3) acidified ammonium sulfate (AAS) aerosol. Concentrations of the aqueous solutions that were introduced into the chambers by atomization are shown in Table 3.1. The initial seed aerosol concentrations that resulted ranged from ~ 19 − 24 μg/m^3. Teflon filters (PALL Life Sciences, 47-mm diameter, 1.0-μm pore size, Teflo filters) were collected for offline chemical analysis from the Caltech experiments at the point at which the aerosol volume reached its maximum value, as determined by the differential mobility analyzer (DMA). All experiments were carried out at relative humidities (RHs) < 9 %.

In the dynamic experiments in the EPA chamber, reactants such as NO, SO_2 and isoprene were continuously added from high-pressure cylinders to the reaction chamber through a mixing manifold. The steady-state nature of chamber operation allows for filter sampling for extended periods for determining the composition of the resultant SOA. Once steady state conditions were attained (~ 24 h), samples for determining the composition of the SOA were collected on glass fiber filters preceded by a carbon strip denuder. Two sets of EPA experiments were conducted. In the first set, the following aerosol conditions were used: AS, AAS, and sulfuric acid, with each of the aqueous solutions atomized into the chamber by atomization. The initial aerosol concentrations were 0.1, 30.0 and 30.0 μg/m^3, for EPA-299 Stage 1, EPA-299 Stage 2, and EPA-299 Stage 3, respectively. For the second set of EPA experiments, EPA-199 Stage 1 and EPA-199 Stage 2, acidic aerosol was generated by adding 60 and 200 ppb of SO_2, respectively to the reactant mixture. All EPA experiments were conducted at a relative humidity of ~ 30%. Results from both EPA experiments (i.e. SOA yields, gas-phase products, trends, etc.) will be discussed in more detail in forthcoming publications; evidence for organosulfates is the focus here.

3.3.2 α-Pinene Chamber Experiments

All α-pinene experiments were conducted in the EPA dynamic chamber (*15*). Conditions for each experiment are listed in Table 3.2. The EPA experiments consisted of one α-pinene/NO_x irradiation experiment along with a series of experiments where mixtures of hydrocarbons containing α-pinene were irradiated in the presence of NO_x. For some of these experiments, SO_2 was added to the chamber to generate acidity in the aerosol. The same collection protocol was used here as that employed in the EPA isoprene experiments.

3.3.3 Ambient Aerosol Collection

Ambient aerosol was collected from the Southeastern Aerosol Research and Characterization Study (SEARCH) network and analyzed for sulfate esters. This network comprises of four urban-rural (or urban-suburban) site pairs at locations across the southeast U.S. and was initiated in mid-1998 to carry out systematic measurements of temporal and spatial variability of PM, in particular $PM_{2.5}$, gases relevant to secondary O_3 formation, and surface meteorology (*22*). Twenty-four hour composite quartz filters were taken on four days at four different sites during June 2004: Birmingham, AL (BHM – urban site), Centerville, AL (CTR – rural site outside of BHM), Jefferson Street (JST, near downtown Atlanta, GA), and Pensacola, FL (PS – marine influenced urban site). Details of these sites (terrain, vegetation, transportation and industrial sources), sample collection and handling procedures, and specific aerosol and gas-phase measurements obtained are given elsewhere (*22*, *30*).

3.3.4 Filter Extraction and Chemical Analyses

Detailed extraction procedures for Teflon and quartz filters are described elsewhere (*9*, *22*). Glass-fiber filters were extracted in the same manner as Teflon filters (*9*), except resultant extracts were filtered through a PALL Life Sciences Acrodisc CR 25 mm syringe filter (PTFE membrane, 0.2 μm pore size) to remove filter fibers. All sample extracts were analyzed by a Hewlett-Packard 1100 Series HPLC instrument, coupled with a quadrupole mass spectrometer, and by direct infusion onto a ThermoElectron LCQ ion trap mass spectrometer (ITMS), both equipped with an ESI source operated in the negative (−) ionization mode. Details of the operating conditions for these instruments are described elsewhere (*9*). Briefly, all samples were analyzed on the LC/MS instrument in the full scan mode and upfront collision-induced dissociation (CID) mode of analysis. Comparison of the resulting mass spectra produced from these two modes of analyses on the LC/MS instrument allows for some structural information to be obtained on the detected SOA components. Samples were also analyzed on the ThermoElectron LCQ ITMS instrument to confirm these results, and in some cases, provide further structural elucidation. Sulfate standards of sodium propyl sulfate (City Chemical, 98% purity), sodium lauryl sulfate (City Chemical, 98% purity), and 1-butyl-3-

methylimidazolium 2-(2-methoxyethoxy)ethyl sulfate (Sigma-Aldrich, 95% purity) were analyzed on the LC/MS instrument to determine common product ions associated with sulfate esters. Additional samples were collected with the particle-into-liquid sampler (PILS) with subsequent offline analysis by ion chromatography (IC) (*31*). The PILS/IC technique allows for the quantitative measurement of water-soluble inorganic ions in aerosol; no IC peaks could be attributed to organosulfates, so for these experiments only inorganic ions are measured.

3.4 Results

3.4.1 Sulfate Ester Standards

(−)ESI-MS studies have shown that sulfate esters produce abundant $[M - H]^-$ ions, and upon collisional activation of these ions, yield *m/z* 97 (HSO_4^-) and 80 ($SO_3^{-\cdot}$) product ions (*21*, *24*, *25*). In conjunction with the known isotopic distribution of sulfur, which contains ^{34}S with a natural abundance of 4.2%, these product ions can be used to identify sulfate esters. As confirmation, authentic standards of sodium propyl sulfate (anionic mass = 139 Da), sodium lauryl sulfate (anionic mass = 265 Da), and 1-butyl-3-methylimidazolium 2-(2-methoxyethoxy)ethyl sulfate (anionic mass = 199 Da) were analyzed by the (−)LC/ESI-MS technique in the full scan mode of analysis followed by the upfront CID mode of analysis to generate MS and MS/MS data, respectively. As shown for the sodium propyl sulfate ester standard in Figure 3.1A, these authentic standards yielded *m/z* 97 and 80 product ions.

3.4.2 Sulfate Esters from Isoprene Oxidation

Previously characterized (*9*, *10*) isoprene SOA products were observed in these experiments and are shown in Table 3.3; however, the focus here will be on the identification of sulfate esters. Comparison of (−)ESI-MS data collected from experiments employing no sulfate aerosol to those with sulfate aerosol showed that numerous compounds were detected only when sulfate aerosol was present. To understand the nature of these compounds, tandem MS techniques were employed. Figure 3.1B-D shows the LC/ESI-MS upfront CID mass spectra collected for large chromatographic peaks common to many of the sulfate aerosol experiments listed in Table 3.1. The $[M - H]^-$ ions associated with these chromatographic peaks include *m/z* 215, 333, and 260, respectively. As was the case for the sulfate ester standards, the collisional activation of these $[M - H]^-$ ions yielded *m/z* 97 and 80 product ions. In addition, these ions also had an isotopic distribution common to sulfur, and as a result, these compounds were identified as sulfate esters. The other product ions, observed in the spectra shown in Figure 3.1, provided further information on the chemical structures of the identified sulfate esters. Proposed sulfate ester structures for these ions and all other ions listed in Table 3.1 are given in Table 3.3. Many of the sulfate esters shown in Table 3.3 were formed from previously identified isoprene SOA products, including aldehydes, dicarbonyls, hydroxycarbonyls, alcohols, and acids containing an alcohol moiety (*9*, *10*, *32*). Sulfate esters formed from small volatile oxidation products, such as glyoxal, hydroxyacetone, and glycolaldeyde, were only detected in experiments involving the highest aerosol acidity. All sulfate esters listed in Table 3.3 eluted from the reverse-phase LC column within 3 min, indicating their high water solubility. For example, the *m/z* 215 sulfate ester had a retention time of ~ 1.4 min, close to that of the inorganic sulfate (first peak to elute). On the other hand, the *m/z* 260 sulfate ester was found to be slightly less polar with isomers eluting at 2.4, 2.7, and 2.9 min. The presence of a nitrate group was confirmed by its even-mass $[M - H]^-$ ion and the observation of a 63 Da (HNO_3) neutral loss shown in Figure 1.1D. Sulfate ester products given in Table 3.3 containing nitrate groups were detected only in experiments containing NO_x.

In several previous studies, the presence of acidic sulfate aerosol was found to have a pronounced effect on the quantity of SOA formed by the photooxidation of isoprene (*9, 14, 15*). In the present study, it appears that sulfate ester formation may be similarly enhanced by the introduction of an acidic sulfate aerosol. In the absence of significant levels of inorganic sulfate, no sulfate esters were detected by LC/ESI-MS in any of the isoprene systems considered here. When experiments were carried out in the presence of AS aerosols, a few sulfate esters were detected, including $[M - H]^-$ ions at *m/z* 199, 215, 244, 260, or 333. Experiments carried out under acidic conditions with AAS aerosol produced a considerably wider array of detectable sulfate ester compounds. In addition, the peak areas of several ions observed in both the AS and AAS experiments were found to be larger in the AAS experiments. For example, in the low-NO_x experiments, the LC/MS peak area for the *m/z* 215 sulfate ester was found to double when AAS aerosol was used rather than non-acidic AS aerosol. Although quantitative data could not be obtained for either the sulfate ester concentrations or the effective acidity of the reaction system, these results suggest that sulfate ester formation is enhanced by the presence of an acidic sulfate aerosol, and that this enhanced sulfate ester formation may be contributing to the increased SOA mass detected previously under acidic conditions. Further work is needed in order to accurately quantify these sulfate esters. It was found that (−)LC/ESI-MS calibration curves generated by surrogate standards lacking sulfate groups (such as *meso*-erythritol) were not suitable for quantifying the identified sulfate esters, resulting from these standards having lower (−)ESI-MS sensitivities. The sulfate ester standards listed in the experimental section were also not suitable for quantification because these compounds had retention times much greater than +/- 1 min of the retention times for the isoprene sulfate esters. Also, these standards lack many structural features common to the identified sulfate esters; therefore, synthesis of more representative standards is needed in order to quantify sulfate esters by (−)LC/ESI-MS.

Sulfate ester aerosol was atomized from a standard solution of sodium propyl sulfate and analyzed directly by the PILS/IC technique; no significant levels of inorganic sulfate were detected, suggesting that organosulfates are thermally stable at the operating conditions of this instrument. In addition, no chromatographic peak in the IC data could be attributed to the sulfate ester standard. These results suggest that the PILS/IC technique will observe decreases in inorganic sulfate if sulfate ester formation occurs.

The time evolution of the SO_4^{2-} and NH_4^+ aerosol mass concentrations obtained using the PILS/IC technique for a Caltech low-NO_x isoprene AAS seed aerosol experiment is compared to that of a Caltech high-NO_x AS seed aerosol experiment in Figure 3.2. As shown in Figure 3.2A (although not evident from the time scale presented, SO_4^{2-} and NH_4^+ decay by ~ 20 and 14%, respectively, over 9 hours), a typical profile for most Caltech isoprene experiments in Table 3.1, ammonium and sulfate typically decreased slowly with time due to wall-loss processes. However, in the experiment shown in Figure 3.2B, in which sulfate ester concentrations were exceedingly high, the SO_4^{2-} aerosol mass concentration decreased much faster (i.e. SO_4^{2-} decayed by ~ 60% over 6 hours) than wall loss, suggesting an extra loss process, most likely due to chemical reaction. It should be noted that the initial NH_4:SO_4 molar ratio in Figure 3.2A was not exactly two due to a known source of ammonium volatilization previously characterized (*31*). The significant decrease in the SO_4^{2-} mass concentration observed for the Caltech low-NO_x AAS seed aerosol experiment is consistent with previously observed increases in SOA yields (*9*), strongly suggesting that particle-phase sulfate esterification is at least partly responsible for this "acid-effect." Filter sampling for most Caltech isoprene experiments began ~ 5-7 h after the experiment was initiated; sulfate esters are formed by this point in the experiments as shown in Figure 3.2.

3.4.3 Sulfate Esters from α-Pinene Oxidation

As in the isoprene experiments, α-pinene sulfate esters were found to produce abundant $[M - H]^-$ ions, corresponding ^{34}S isotopic ions, *m/z* 97 and 80 product ions, and were not observed in experiments without SO_2 (Table 3.2). Isoprene sulfate esters were formed also in experiments involving isoprene and SO_2 photooxidation; for simplicity, these esters are not listed in Table 3.2. Shown in Figure 3.3A-D are the (−)ESI-ITMS product ion spectra for representative α-pinene sulfate esters; these include esters containing a $[M - H]^-$ ion at *m/z* 294, 265, 310, and 326, respectively. Analogous to some of the isoprene sulfate esters, the *m/z* 294, 310, and 326 α-pinene sulfate esters also contain nitrate groups as suggested by their even-mass $[M - H]^-$ ions and observed neutral losses of 63 (HNO_3) and/or 47 Da (HONO). The MS/MS spectra of the $[M - H]^-$ ions for the four α-pinene sulfate esters yielded *m/z* 97 product ions. However, the *m/z* 80 product ion was observed only for the *m/z* 265 ion due to mass range limits on the mass spectrometer. It should be noted that the MS^3 spectra of high-mass product ions shown in Figure 3.3 (e.g. *m/z* 250 in Figure 3.1A) did yield the *m/z* 97 and *m/z* 80 product ions, thus supporting that the $[M - H]^-$ ions at *m/z* 294, 310, and 326 contain a sulfate group. These results were confirmed on the LC/MS instrument operated in the upfront CID mode of analysis.

Sulfate esters from α-pinene were found to elute from the reverse-phase LC column at much later RTs (~ 10 – 26 min) than those formed in isoprene oxidation, indicating differences in water solubility. Identified α-pinene sulfate esters listed in Table 3.4 were formed from the reactive uptake of previously identified gas-phase oxidation products (*33*, *34*), consistent with previous work (*17*, *18*). Except for pinonaldehyde, no sulfate esters have been identified to form from previously identified α-pinene SOA products; however, further investigation is warranted. For quality control purposes, solid phase extraction (SPE) was used on duplicate filters collected from selected experiments (EPA-211) to remove excess inorganic sulfate; it was found that the α-pinene sulfate esters were still detected, and in some cases at higher $[M - H]^-$ ion abundances, indicating that these sulfate esters are not a result of inorganic sulfate clusters in the mass spectrometer.

3.4.4 Sulfate Esters in Ambient Aerosol

Figures 3.4A-C compare the LC/MS extracted ion chromatograms (EICs) of *m/z* 215 obtained from a Caltech low-NO_x isoprene AAS experiment to that of two SEARCH field samples (JST and BHM, respectively). Both the RTs and mass spectra of the chromatographic peaks shown in the EICs of *m/z* 215 are the same in all samples, strongly suggesting that this isoprene sulfate ester is present in ambient aerosol. In addition, ambient aerosol recently collected at K-puszta, Hungary indicates that the *m/z* 199 and 260 isoprene sulfate esters are present (M. Claeys, unpublished results);

however, these compounds are only weakly detected on some days analyzed from the SEARCH network.

Figures 3.5A-C compare the LC/MS EICs of *m/z* 294 obtained from two α-pinene experiments (EPA-205 and EPA-326, respectively) and with a SEARCH field sample collected at the BHM field site in June 2004. This figure indicates that the α-pinene *m/z* 294 sulfate ester is a constituent of ambient aerosol, consistent with previous work (*22*). Other α-pinene sulfate esters identified in this study have been observed in ambient aerosol in the southeastern U.S (*22*). It is possible that the *m/z* 294 sulfate ester in the ambient aerosol could also result from the oxidation of other monoterpenes owing to the lack of detailed connectivity of specific functional groups (e.g. sulfate esters and hydroxyls) provided by ESI-MS/MS methods.

The results above suggest that the chemistry occurring in our laboratory experiments are relevant to the conditions in the southeastern U.S., even though the laboratory aerosol was generated from much higher VOC mixing ratios, lower RHs, and likely higher aerosol acidities observed in the southeastern U.S.

3.4.5 ESI-MS Quality Control Tests

To ensure that the sulfate esters elucidated in this study were formed only during SOA formation and not on the filter or during the ESI process, several quality control tests were conducted. First, a filter extract from a Caltech low-NO_x isoprene nucleation (i.e. no inorganic seed aerosol present) experiment was divided into two parts. One part was spiked with a high concentration of $(NH_4)_2SO_4$ and the other part was spiked with pure H_2SO_4. Both of these samples were analyzed by (−)LC/ESI-MS. The sulfate esters listed in Table 3.1 were not detected in these two test samples, demonstrating that the sulfate esters detected in this study are likely not artifacts formed in the ESI interface. The use of reverse phase chromatography allowed for inorganic sulfate not to be confused with organosulfates, where inorganic sulfate was the very first peak to elute from the column. In the two test samples discussed above, the inorganic sulfate peak was found to have some tailing, which was very similar to the seeded experiments listed in Table 3.1; however, this tailing seems to have no effect on the formation of sulfate esters.

As a second test, a *meso*-erythritol (a surrogate for the 2-methyltetrols produced from isoprene oxidation) standard was divided into two parts, where one was spiked with $(NH_4)_2SO_4$ and the other with pure H_2SO_4. As for the first quality control test above, these two samples produced no sulfate esters in (−)LC/ESI-MS.

Lastly, a filter extract from an EPA α-pinene experiment conducted without SO_2 (thus no sulfate aerosol present) was spiked with pure H_2SO_4. Again, no sulfate esters were detected. These results strongly suggest the organosulfates (sulfate esters) were formed in the aerosol phase and are not an artifact of sampling or measurement.

3.5 Discussion

3.5.1 Sulfate Esterification Reaction Mechanism

Reactive uptake of gas-phase alcohols (e.g. methanol and ethanol) and aldehydes (e.g. formaldehyde) in the upper troposphere and lower stratosphere have been suggested to occur in the presence of sulfate aerosols (*35−37*), where increased acidity was found to increase their uptake. Some of these studies proposed that the observed uptake of the alcohols and aldehydes likely occurred by sulfate ester formation, although no product studies were conducted. It has also been shown that reactive uptake of butanol and ethanol onto sulfate aerosols occurs at room temperature (*38*, *39*). Esterification was recently shown to occur from the photooxidation of isoprene in the presence of NO_x from condensation reactions of organic acids with alcohols (*9*, *10*). The large amounts of organic acids formed during the photooxidation were proposed to drive these reactions.

Figure 3.6 shows the general reactions proposed for the formation of sulfate esters from alcohols (2-methyltetrol used as model compound) and sulfate derivatives from carbonyl compounds (pinonaldehyde used as model compound). In the case of sulfate ester formation from alcohols, the proposed reactions likely involve nucleophilic substitution (SN_1), where the sulfuric acid protonates the alcoholic group, making water the leaving group. The resulting carbocation becomes a nucleophilic site for the unshared pair of electrons on one of the oxygen atoms of the sulfate (*40*). Due to the low relative humidities of these experiments, this likely shifts the equilibrium in favor of sulfate ester formation. In the case of sulfate ester formation from aldehydes, the proposed reaction likely involves the electron pair of the carbonyl oxygen accepting a proton from sulfuric acid, producing the oxonium ion, and making it more susceptible to nucleophilic attack from an unshared pair of electrons from one of the oxygen atoms on sulfate. It should be stressed that other reaction mechanisms are also possible, including: electrophilic addition of H_2SO_4 to an aliphatic double bond, addition of SO_3 through some radical process, or by some other unknown mechanism currently not understood. Sulfate diester ($ROSO_3R$) formation and sulfate ester oligomerization could also take place in the case of polyols; however, (−)ESI-MS is not sensitive to such neutral species, no such products have yet been identified. In prior work (*9*) we reported oligomeric signatures (14, 16, 18 Da differences) and compounds with masses up to ~ 620 Da in matrix-assisted laser desorption ionization (MALDI) – MS data collected for Caltech low-NO_x seeded experiments; AAS seed cases produced the most prominent signals, possibly providing evidence for the sulfate diester or sulfate ester oligomerization reactions.

3.5.2 Isoprene Sulfate Esters and the role of NO_x

Surratt et al. (*9*) observed a significant increase in the SOA yield in the low-NO_x AAS seed aerosol experiments, whereas very little (if any) increase in the SOA yield was observed in the high-NO_x AAS seed aerosol experiments. This difference likely occurs because of the large abundance of organic acids formed under high-NO_x conditions competing with sulfuric acid (or sulfate) for esterification with alcohols. The low-NO_x SOA was found to comprise largely of neutral polyols (e.g. 2-methyltetrols and hemiacetal dimers in Table 3.3) and hydroperoxides, which may react readily with sulfuric acid to produce sulfate esters. In previous work (*9*) we reported detecting no SOA components with (−)LC/ESI-MS for the low-NO_x seeded cases; reanalysis of that data indicates that sulfate esters (*m/z* 215, 333, and 415) were in fact detected, but because they eluted very closely to inorganic sulfate (within 1-1.5 minutes), they were believed to be an artifact.

3.5.3 Atmospheric Implications

Sulfate esters identified previously in ambient aerosol (*21*, *22*) appear to be secondary in nature, as demonstrated by the present study. Of particular significance is the detection of sulfate esters from isoprene and α-pinene in ambient aerosols, which could be indicators for the acid induced reaction pathway. There is also the possibility that oxidation of other hydrocarbons emitted into the atmosphere in high abundances, including monoterpenes other than α-pinene as well as sesquiterpenes, could lead to the formation of aerosol-bound sulfate esters. These esters could contribute significantly to the HULIS fraction of ambient aerosol due to their high water-solubility, acidity, thermally stability, and high molecular weights, all of which are common properties of HULIS (*41*). Strong chemical evidence is presented here for the substantial occurrence of sulfate esterification in both laboratory-generated and ambient aerosols. This evidence provides one concrete explanation for the observed increase in SOA yields in response to increasing aerosol acidity. Additional studies are needed to determine the mass fraction of sulfate esters in ambient aerosols and the factors that influence their formation, such as relative humidity, temperature, and initial sulfate aerosol mass concentrations, in order to better understand and model this chemistry.

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Table 3.1. Summary of experimental conditions and sulfate ester formation from isoprene photooxidation.

experiment	inorganic seed aerosol[a]	OH precursor	initial [isoprene] (ppb)	initial [NO_x] (ppb)	average T (°C)	$[M-H]^-$ detected sulfate ester ions (*m/z*)
Caltech Low-NO_x	none added	H_2O_2	500	none added	23.7	none detected
Caltech Low-NO_x	AS	H_2O_2	500	none added	23.9	215, 333
Caltech Low-NO_x	AAS	H_2O_2	500	none added	23.8	153, 155, 169, 215, 333, 451
Caltech High-NO_x	none added	H_2O_2 / NO	500	891	24.3	none detected
Caltech High-NO_x	AS	H_2O_2 / NO	500	963	24.9	199, 215, 244
Caltech High-NO_x	AAS	H_2O_2 / NO	500	904	24.6	139, 153, 155, 197, 199, 215, 244, 260, 301, 346
Caltech High-NO_x	none added	HONO	500	382	20.1	none detected
Caltech High-NO_x	AS	HONO	500	366	21.4	199, 215, 260, 333
EPA-299 Stage 1	AS[b]	[c]	2500	200	29.0	none detected
EPA-299 Stage 2	AAS	[c]	2500	200	29.0	153, 155, 167, 169, 181,197, 199, 215, 244, 260, 333
EPA-299 Stage 5	H_2SO_4 only	[c]	2500	200	29.0	153, 155, 157, 167, 169, 181, 197, 199, 215, 244, 260, 333
EPA-199 Stage 1	60 ppb SO_2	[c]	1598	475	24.6	197, 199, 215, 244, 260, 301, 317, 333
EPA-199 Stage 2	200 ppb SO_2	[c]	1598	475	24.6	155, 169, 197, 199, 215, 244, 260, 301, 317, 333, 346

[a] AS = 15 mM $(NH_4)_2SO_4$; AAS = 15 mM $(NH_4)_2SO_4$ + 15 mM H_2SO_4 for Caltech experiments and 0.31 mM $(NH_4)_2SO_4$ + 0.612 mM H_2SO_4 for EPA-299 experiments; H_2SO_4 only = 0.92 mM H_2SO_4 ; EPA-199 had no seed nebulized but instead used the photooxidation of SO_2 to generate sulfuric acid aerosol.

[b] Due to the low initial inorganic seed aerosol concentration, this condition is more conducive to nucleation.

[c] No OH precursor was used.

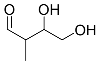
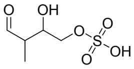
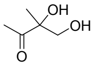
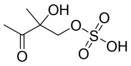
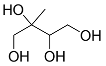
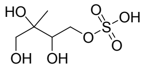
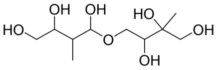
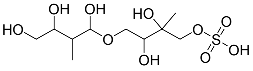
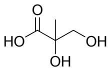
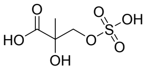
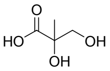
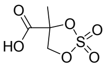
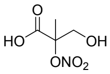
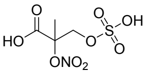
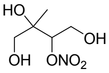
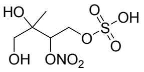
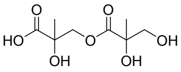
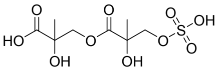
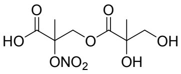
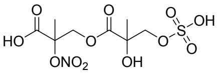
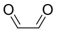
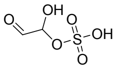
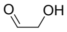
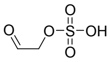
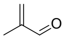
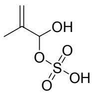
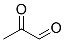
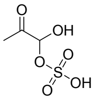
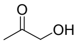
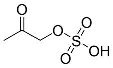
Table 3.2. Summary of experimental conditions and sulfate ester formation from α-pinene photooxidation.

experiment	initial [α-pinene] (ppb)	initial [isoprene] (ppb)	initial [toluene] (ppm)	initial [NO_x] (ppb)	SO_2 (ppb)	average T (°C)	$[M - H]^-$ detected sulfate ester ions (*m/z*)[a]
EPA-220	220	[b]	[b]	450	[b]	25.5	none detected
EPA-326	186	1108	[b]	248	287	20.5	249, 265, 294, 310, 412, 426
EPA-211 Stage 1	105	[b]	[b]	378	[b]	24.3	none detected
EPA-211 Stage 2	105	[b]	1.59	378	[b]	24.3	none detected
EPA-211 Stage 3	103	820	1.58	378	[b]	24.3	none detected
EPA-211 Stage 4	117	854	1.57	378	275	24.3	265, 279, 294, 310, 326, 412, 426
EPA-211 Stage 5	115	[b]	1.59	378	275	24.3	249, 265, 279, 294, 310, 326
EPA-211 Stage 6	[b]	794	1.56	378	[b]	24.3	none detected
EPA-205	106	592	1.45	599	278	24.0	265, 294, 310, 412, 426

[a] Isoprene sulfate ester products like those in Table 2 were also detected only when SO_2 and isoprene were copresent. No discernable toluene sulfate ester products were detected.

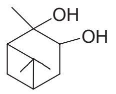
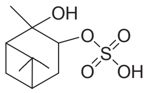
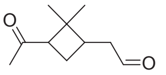
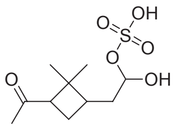
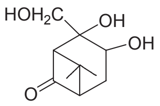
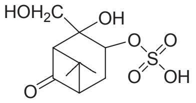
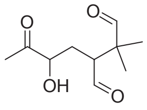
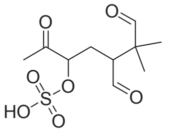
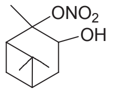
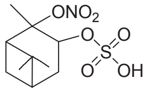
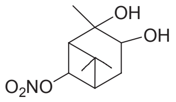
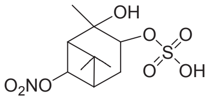
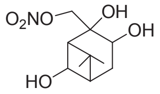
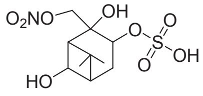
[b] This compound was not present during the experiment.

Table 3.3. Proposed isoprene sulfate ester SOA products.

	previously identified isoprene SOA product[a]	MW	proposed sulfate ester structure[a]	observed $[M-H]^-$ ion (m/z)	major $[M-H]^-$ product ions (m/z)
Low-NO_x	 C_5 alkene triol / ald form[b]	118		197	97 80
	 C_5 alkene triol / keto form[b]	118		197	97 80
	 2-methyltetrols[b]	136		215[c,d]	97 80
	 hemiacetal dimer[b]	254		333[d]	315 (- H_2O)[e] 215 (- C_5 alkene triol) 197 (- 2-methyltetrol) 97 80
High-NO_x	 2-methylglyceric acid (2-MG)[b]	120		199[c]	119 (- 2-MG) 97 80
	 2-methylglyceric acid (2-MG)[b]	120		181	97 80
	 2-MG acid nitrate[b]	165		244	226 (- H_2O) 197 (- HONO) 153 (- [CO_2 + HONO]) 97
	 2-MG dimer[b]	181		260[d]	197 (- HNO_3) 183 (- CH_3NO_3) 97 80
	 2-MG nitrate dimer[b]	222		301	257 (- CO_2) 119 97 80
	 C_5 trihydroxy nitrate[f]	267		346	[g]
Highest Acidity Conditions	 glyoxal	58		155	[g]
	 glycolaldehyde[h]	60		139	[g]
	 methacrolein	70		167	[g]
	 methylglyoxal[h]	72		169	[g]
	 hydroxyacetone[h]	74		153	[g]

[a] Positional isomers containing nitrate or sulfate groups at other hydroxylated positions are likely. [b] Isoprene SOA products previously identified in prior studies by Surratt et al. (*9*) and/or Szmigielski et al. (*10*) and/or Edney et al. (*15*). [c] Detected in ambient aerosol collected from SEARCH network (summer 2004) for first time. [d] Considered major product due to large MS abundance in chamber studies. [e] Compounds listed in parentheses are neutral losses observed upon (−) ESI-MS/MS. [f] Inferred precursor due to the MS/MS fragmentation of its respective organosulfate product; this parent isoprene product goes undetected by (−) ESI-MS and GC/MS methods. [g] Some evidence for its existence in first-order mass spectra. [h] Detected in ambient aerosol by Matsunaga et al. (32).

Table 3.4. Proposed α-pinene sulfate ester SOA products.

α-pinene oxidation product[a]	MW	proposed sulfate ester structure[a]	observed $[M - H]^-$ ion (*m/z*)	major $[M - H]^-$ product ions (*m/z*)
	170		249	231 (- H_2O)[b] 205 97 80
 pinonaldehyde	168[c]		265[d,e]	247 (- H_2O) 221 185 97 (- pinonaldehyde) 80
	200[c]		279[e,f]	261 (- H_2O) 235 199 181 97 80
	200[c]		279[e,f]	261 (- H_2O) 235 199 181 97 80
	215[c]		294[g]	247 (- HONO) 231 (- HNO_3) 220 96 80
	231[c]		310[g,h]	263 (- HONO) 236 247 (- HNO_3) 97
	247		326[e]	308 (- H_2O) 282 (- CO_2) 279 (- HONO) 252 97

[a] Positional isomers containing nitrate or sulfate groups at other hydroxylated positions are possible. [b] Compounds listed in parentheses are neutral losses observed upon ESI-MS/MS. [c] Previously detected α-pinene oxidation product by Aschmann et al. (*33*, *34*).
[d] Proposed by Liggio et al. (*17*) to form from pinonaldehyde reactive uptake onto acidic seed particles; however, structure was not confirmed. In the current study, we confirm its structure with (-)ESI-MS. [e] Detected in ambient aerosol collected from SEARCH network June 2004 for first time. [f] ESI-MS cannot differentiate between which product is being detected; for completeness both structures are shown here.
[g] Observed in an ambient study by Gao et al. (*22*). [h] No structural information was provided in the previous study by Gao et al. (*22*).

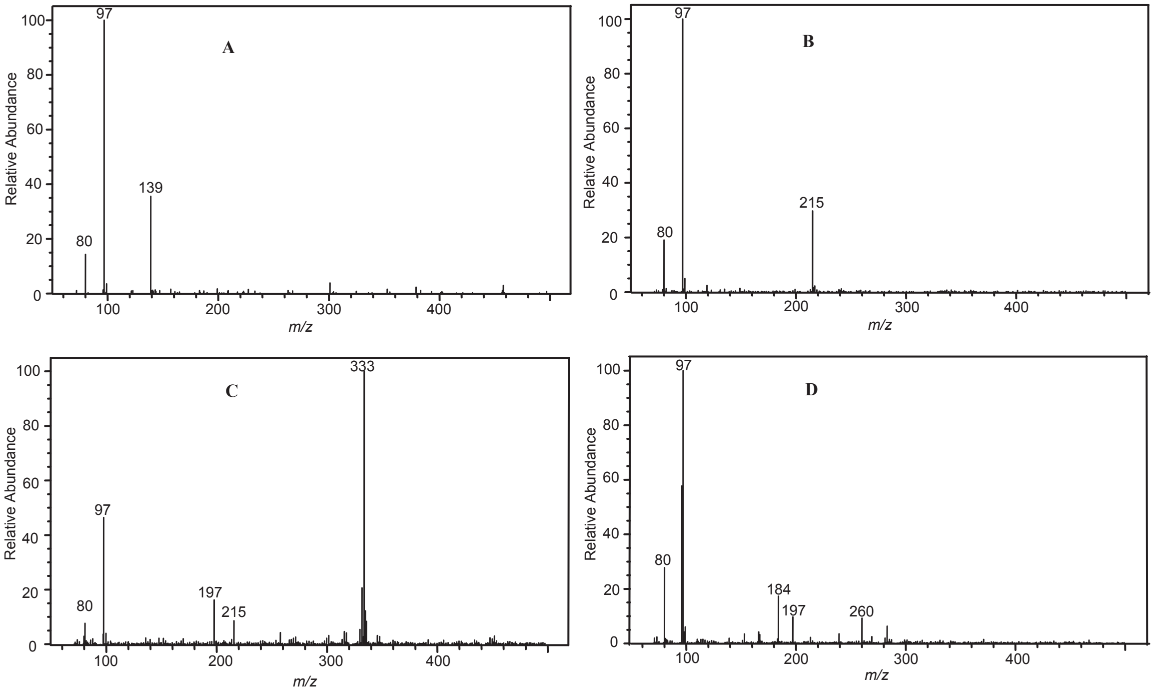


Figure 3.1. (–)LC/ESI-MS upfront CID mass spectra for selected isoprene sulfate ester SOA products shown in Table 3.2. (A) Product ion mass spectrum for sodium propyl sulfate standard (anionic mass of intact propyl sulfate ester = 139 Da). (B) Product ion mass spectrum for a 2-methyltetrol sulfate ester detected in a Caltech high-NO_x H_2O_2 AS seed photooxidation experiment. (C) Product ion mass spectrum for a hemiacetal dimer sulfate ester detected in a Caltech low-NO_x AAS seed photooxidation experiment. (D) Product ion mass spectrum for a C_5 trihydroxy nitrate sulfate ester detected in EPA-299 Stage 2.

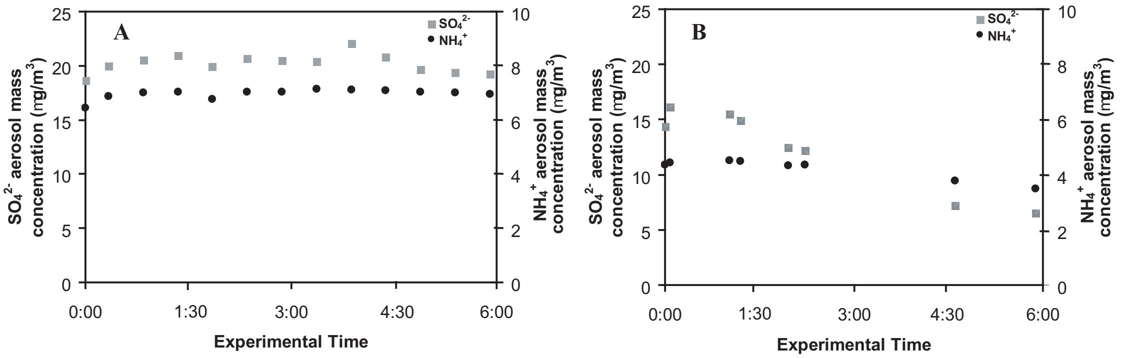


Figure 3.2. Time evolution of the SO_4^{2-} and NH_4^+ aerosol mass concentrations from the PILS/IC analysis. (A) Caltech high-NO_x H_2O_2 isoprene experiment with AS seed aerosol. (B) Caltech low-NO_x isoprene experiment with AAS seed aerosol. A control experiment was conducted in which seed aerosol is atomized from a solution of 0.015 M AS into the Caltech experimental chamber, and no other reactants such as VOCs or NO_x were present. This control experiment produced a similar result to that of Figure 3.2A, indicating that the only loss mechanism for sulfate in this case was wall loss. Of the Caltech isoprene experiments, only the low-NO_x AAS seed aerosol experiment showed a significant decrease in the SO_4^{2-} aerosol mass concentration, indicating that it was likely lost to reaction.

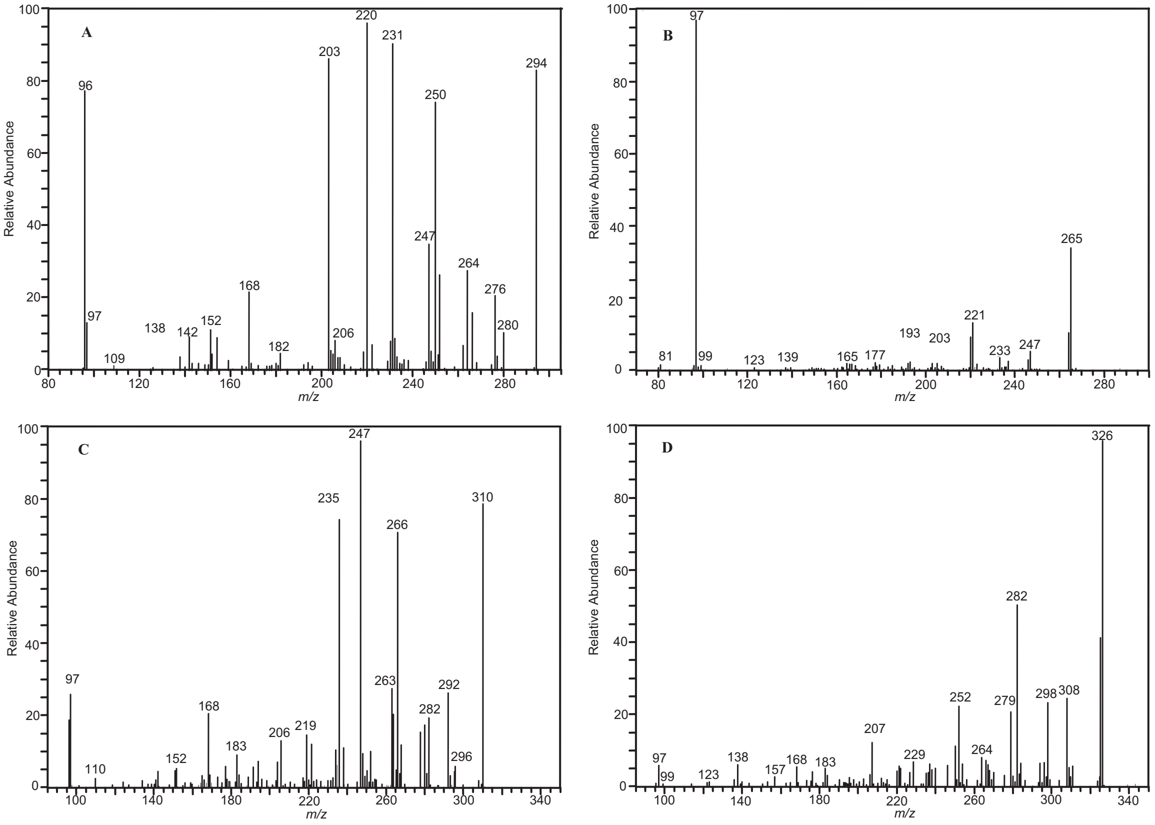


Figure 3.3. (–)ESI-ITMS product ion mass spectra for sulfate esters of α-pinene oxidation products. (A) Product ion mass spectrum for *m/z* 294 detected in EPA-211 Stage 5. (B) Product ion mass spectrum for *m/z* 265 detected in EPA-211 Stage 4. (C) Product ion mass spectrum for *m/z* 310 detected in EPA-211 Stage 5. (D) Product ion mass spectrum for *m/z* 326 detected in EPA-211 Stage 5. These sulfate esters were always present when α-pinene was photooxidized in the presence of SO_2.

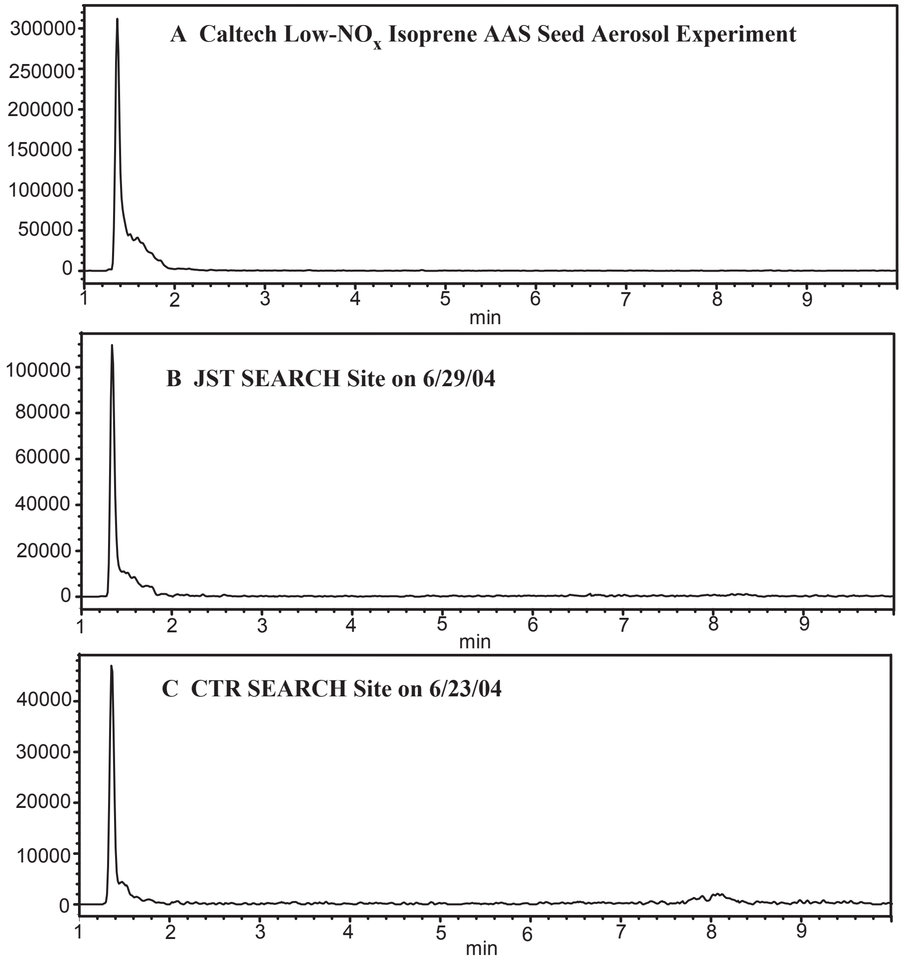


Figure 3.4. (–)LC/ESI-MS extracted ion chromatograms for *m/z* 215. The retention times of the *m/z* 215 EICs are the same as well as the mass spectra associated with each chromatographic peak; therefore, the comparison of these EICs suggests that the photooxidation of isoprene in the presence of acid seed produces these sulfate esters observed in the ambient aerosol. In all chamber experiments involving isoprene in the presence of AS seed aerosol, AAS seed aerosol, or SO_2, the *m/z* 215 ion was detected.

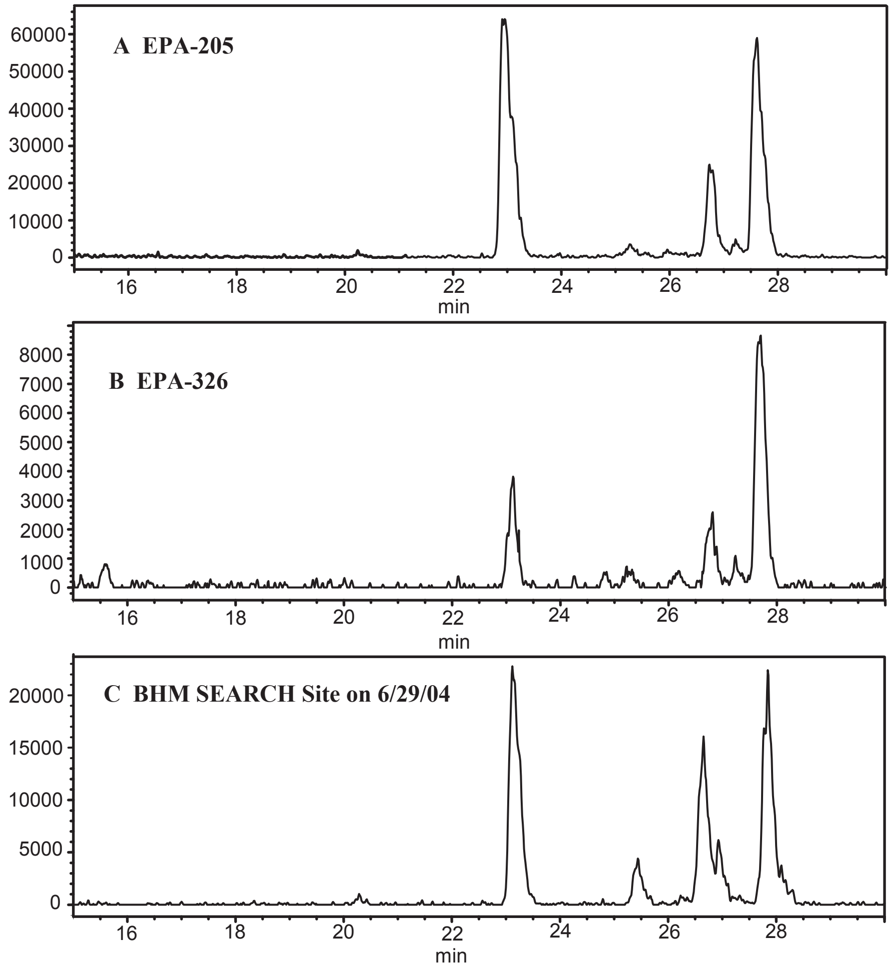


Figure 3.5. (–)LC/ESI-MS extracted ion chromatograms for *m/z* 294. The retention times of the *m/z* 294 compounds were the same as well as the mass spectra associated with each chromatographic peak; therefore, the comparison of these EICs suggests that the photooxidation of α-pinene in the presence of NO_x and acid seed produces these sulfate esters in ambient aerosol. No *m/z* 294 compounds were detected in experiments involving only isoprene and acid seed (or SO_2).

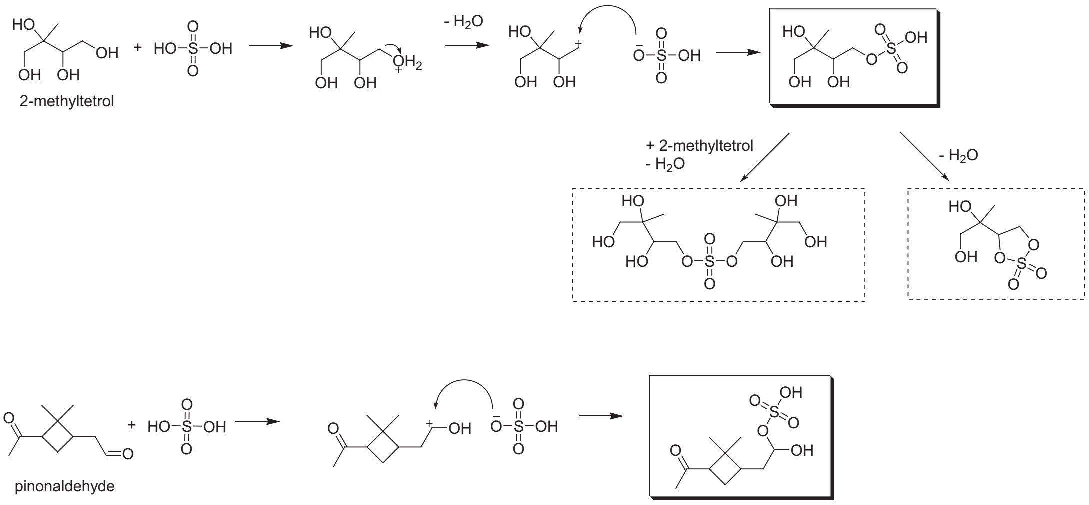


Figure 3.6. Proposed reactions for the formation of sulfate esters from 2-methyltetrol and pinonaldehyde, a representative alcohol and aldehyde generated by the photooxidation of isoprene and α-pinene, respectively. Solid boxes indicate (–)ESI-MS detected species. Dashed boxes indicate other proposed products possibly formed.