Chapter 5

Organosulfate Formation in Biogenic Secondary Organic Aerosol*

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5.1 Abstract

Organosulfates of isoprene, α -pinene, and β -pinene have recently been identified in both laboratory-generated and ambient secondary organic aerosol (SOA). In this study, the mechanism and ubiquity of organosulfate formation in biogenic SOA is investigated by a comprehensive series of laboratory photooxidation (i.e. OH-initiated oxidation) and nighttime-oxidation (i.e. NO₃-initiated oxidation under dark conditions) experiments using nine monoterpenes (α -pinene, β -pinene, d-limonene, l-limonene, α -terpinene, γ -terpinene, terpinolene, Δ^3 -carene, and β -phellandrene) and three monoterpenes (α -pinene, δ -limonene, and *l*-limonene), respectively. Organosulfates were characterized using liquid chromatographic techniques coupled to electrospray ionization combined with both linear ion trap and high-resolution time-of-flight mass spectrometry. Organosulfates are formed only when monoterpenes are oxidized in the presence of acidified sulfate seed aerosol, a result consistent with prior work. Archived laboratory-generated isoprene SOA and ambient filter samples collected from the southeastern U.S. were reexamined for organosulfates. By comparing the tandem mass measurements spectrometric collected for both and accurate mass the laboratory-generated and ambient aerosol, previously uncharacterized ambient organic aerosol components are found to be organosulfates of isoprene, α -pinene, β -pinene, and limonene-like monoterpenes (e.g. myrcene), demonstrating the ubiquity of organosulfate formation in ambient SOA. Several of the organosulfates of isoprene and of the monoterpenes characterized in this study are ambient tracer compounds for the occurrence of biogenic SOA formation under acidic conditions. Furthermore, the nighttime-oxidation experiments conducted under highly acidic conditions reveal a viable

mechanism for the formation of previously identified nitrooxy organosulfates found in ambient nighttime aerosol samples. We estimate that the organosulfate contribution to the total organic mass fraction of ambient aerosol collected from K-puszta, Hungary, a field site with a similar organosulfate composition as that found in the present study for the southeastern U.S., can be as high as 30%.

5.2 Introduction

The atmospheric oxidation of volatile organic compounds (VOCs) leads to secondary organic aerosol (SOA) formation through low-volatility products that partition into the aerosol phase. SOA can contribute a significant fraction to the organic mass found in tropospheric fine particulate matter (PM_{2.5}, with aerodynamic diameter < 2.5 mm);¹ high concentrations of PM_{2.5} are known to have adverse health effects² and play a role in global climate change.³ Of the known SOA-precursor classes of VOCs, biogenic volatile organic compounds (BVOCs), which include isoprene (2-methyl-1,3-butadiene, C₅H₈) and monoterpenes (C₁₀H₁₆), contribute significantly to the global SOA budget^{1,4,5} owing to their high reactivities with atmospheric oxidants, such as hydroxyl radicals (OH), ozone (O₃), and nitrate radicals (NO₃), and their large global emission rates.⁶

Laboratory work has shown that several factors need to be considered in order to understand and predict SOA formation mechanisms from BVOCs; these include the NO_x level,^{4,7–15} acidity of inorganic seed aerosol,^{16–26} relative humidity (RH),^{27–29} and temperature.^{30–32} Enhancements in laboratory-generated SOA from isoprene and a-pinene have recently been observed at increased acidity of preexisting sulfate seed aerosol.^{17–24, 33} Acid-catalyzed particle-phase reactions,^{16–20} some of which lead to the formation of high molecular weight (MW) species through oligomerization, have been

proposed to explain these observed enhancements. Detailed chemical analysis of laboratory-generated aerosol has revealed several types of particle-phase reactions formation,^{34,35} formation, including peroxyhemiacetal contributing SOA to formation,^{16,36} hydration followed by polymerization,¹⁶ aldol acetal/hemiacetal condensation,^{16,36} and organic esterification.^{33,37-40} Many of these reactions have been observed when particle-phase acidity is derived from sulfuric acid; however, recent work has shown that photochemically generated organic acids is a sufficient source of acidity, especially under dry conditions.^{28,33,37,41} The importance of particle-phase reactions to ambient SOA formation remains uncertain, as currently there is no chemical evidence for their respective products, and with the exception of organic esterification, many of these reactions are not thermodynamically favorable under ambient conditions.⁴²⁻⁴⁴ Additionally, some of these reactions may not be kinetically favorable in the atmosphere, as recently shown by Casale et al.⁴⁵ for aldol condensation reactions of aliphatic aldehydes.

Organosulfate formation (i.e. sulfate esters and/or sulfate derivatives) has recently been shown to occur in laboratory-generated SOA produced from the oxidation of several BVOCs, including isoprene,^{23,24,46} α -pinene,^{23,26,46,47} limonene,²⁵ and β -pinene,²⁶ and by the reactive uptake of known volatile aldehydes, such as glyoxal⁴⁸ and pinonaldeyde,^{49,50} in the presence of acidified sulfate seed aerosol. In addition, mass spectrometric evidence exists for organosulfates and nitrooxy organosulfates in ambient aerosol; however, direct evidence as to the sources and mechanism of formation for these compounds is lacking.^{47,51,52} Recent work from the Caltech laboratory, as well as the U.S. Environmental Protection Agency (EPA) and University of Antwerp laboratories,

has shown that organosulfate formation occurs from isoprene and α -pinene in both laboratory-generated SOA and ambient aerosol collected from the southeastern U.S.²³ and K-puszta, Hungary.⁴⁶ This work has identified ambient tracer compounds for the occurrence of biogenic SOA formation under acidic conditions as well as a relevant particle-phase reaction. Additionally, Iinuma et al.²⁶ have reported organosulfate formation from β -pinene in ambient aerosol, as well as have identified new organosulfates of monoterpenes likely containing two double bonds (e.g. limonene); however, laboratory experiments that confirm the initially proposed structures for the latter compounds were lacking. Interestingly, Iinuma et al.²⁶ showed that previously identified monoterpene nitrooxy organosulfates were detected only in nighttime samples, suggesting the importance of nighttime chemistry (i.e. NO₃ radical oxidation chemistry) to SOA formation. Despite these recent advances in identifying organosulfate formation in SOA, the ubiquity and abundance of organosulfates in ambient aerosol remain unclear. In addition, formation mechanisms and sources of several previously detected organosulfates in ambient aerosol are unknown.

In the present work, we investigate in detail the mechanism of organosulfate formation in biogenic SOA on the basis of a series of laboratory oxidation experiments under varying particle-phase acidities and oxidative conditions. Laboratory photooxidation (i.e. OH-initiated oxidation) experiments were conducted using nine monoterpenes: α -pinene, β -pinene, *d*-limonene, *l*-limonene, α -terpinene, γ -terpinene, β -phellandrene, Δ^3 -carene and terpinolene. In addition, laboratory nighttime-oxidation (i.e. NO₃-initiated oxidation) experiments were conducted using three monoterpenes (α -pinene, *d*-limonene, and *l*-limonene). Filters were collected from all the laboratory

experiments for offline chemical composition analysis. Furthermore, archived isoprene SOA and ambient filter samples collected from prior studies^{33,47} were reexamined for organosulfates using highly sensitive and advanced mass spectrometric techniques. Both high-performance liquid chromatography (HPLC) combined with electrospray ionization (ESI)-linear ion trap mass spectrometry (LITMS) and ultra-performance liquid chromatography (UPLC) combined with ESI-high-resolution time-of-flight mass spectrometry (TOFMS), which provide tandem MS (i.e. structural elucidation) and accurate mass measurements (i.e. elemental composition/molecular formulae), respectively, were employed to characterize the detailed chemical structures of the organosulfates; particular attention is focused on those compounds detected in both laboratory-generated SOA and in ambient aerosol collected from the Southeastern Aerosol Research and Characterization (SEARCH) network in the southeastern U.S. during the June 2004 campaign. In a previous study from our laboratories, many of the chemical structures of the compounds detected during the June 2004 campaign remained uncharacterized because of the use of less advanced mass spectrometric techniques as compared to the current study; it was found that many of these compounds were likely secondary in nature and resulted from terpene oxidation.⁴⁷ As will be presented, many of these previously uncharacterized products, as well as newly identified compounds, are found to be organosulfates of isoprene and of prevalent monoterpenes, including α -pinene, β -pinene, and limonene-like monoterpenes (i.e. monoterpenes, such as myrcene and ocimene, containing at least two or more double bonds, with the requirement of one of these double bonds being in a terminal position).

5.3 Experimental Section

5.3.1 Chamber Experiments

Organosulfate formation was studied in SOA generated from the following nine monoterpenes: α -pinene (98+%, Sigma-Aldrich), β -pinene (98%, Lancaster), *d*-limonene (puriss. p.a. terpene standard for GC, \geq 99%, Fluka), *l*-limonene (puriss. p.a. terpene standard for GC, \geq 99%, Fluka), α -terpinene (purum \geq 95%, Fluka), γ -terpinene (puriss. p.a. terpene standard for GC, \geq 98.5%, Fluka), terpinolene (purum \geq 97%, Fluka), Δ^3 -carene (puriss. p.a. terpene standard for GC, \geq 98.5%, Fluka), and β -phellandrene/d-limonene standard mixture (40:60 v/v, generously provided by Professor Roger Atkinson of the University of California, Riverside).⁵³ To establish better understanding of organosulfate formation in limonene SOA, the further oxidation of limonaketone (4-acetyl-1-methylcyclohexene, C₉H₁₄O, Sigma-Aldrich, library of rare chemicals), which is a known first-generation gas-phase product from limonene,⁵⁴ was conducted in a single photooxidation experiment. In addition to these monoterpenes, organosulfate formation was reexamined in isoprene SOA; archived isoprene SOA samples were available from both the Caltech and EPA chamber experiments, and were used for the high-resolution MS analysis to confirm previous identifications. Details of the experimental conditions employed for the generation of isoprene SOA can be found elsewhere;^{4,13,23,33} it should be noted that the EPA isoprene SOA came from the EPA-199 stage 2 photooxidation experiment, in which experimental conditions (i.e. 1598 ppb initial isoprene, 475 ppb initial NO_x, and 200 ppb SO₂) were previously outlined in Surratt et al.²³ and were used solely for the tandem MS analysis of organosulfates of isoprene. Table 5.1 lists the chemical structures of isoprene and of the monoterpenes

studied, as well as the rate constants of these VOCs for reaction with OH, O_3 , and NO_3 .⁵⁵ Table 5.2 summarizes the experimental conditions and results for the suite of monoterpene oxidation experiments conducted.

All monoterpene experiments were performed in the Caltech dual 28 m³ Teflon environmental chambers. Details of the facilities have been described elsewhere.^{56,57} Before each experiment, the chambers were flushed continuously for at least 24 h. The aerosol number concentration, size distribution, and volume concentration were measured by a Differential Mobility Analyzer (DMA, TSI model 3081) coupled with a condensation nucleus counter (TSI model 3760). All aerosol growth data were corrected for wall loss, in which size dependent particle loss coefficients were determined from inert particle loss experiments.⁵⁷ Temperature, relative humidity, and concentrations of O₃, NO and NO_x were continuously monitored.

Seed particles were generated by atomizing an aqueous solution with a constant-rate atomizer. The neutral seed consisted of 15 mM (NH₄)₂SO₄, while the acidic seed contained a mixture of 15 mM (NH₄)₂SO₄ and 15 mM H₂SO₄, and the highly acidic seed contained a mixture of 30 mM MgSO₄ and 50 mM H₂SO₄. The initial particle number concentration was about 20,000 particles cm⁻³, with a geometric mean diameter of ~55 nm (for the neutral and acid seed) or ~70 nm (for the highly acidic seed). The initial seed volume was ~15 μ m³ cm⁻³. After introduction of the seed aerosol, a known volume of the parent hydrocarbon was injected into a glass bulb and introduced into the chambers by an air stream. The mixing ratio of the hydrocarbon was monitored with a gas chromatograph (Agilent model 6890N) coupled with a flame ionization detector (GC-FID).

In the monoterpene photooxidation experiments, aerosol was generated under either high-, intermediate-, or low-NO_x conditions. Of the monoterpenes investigated, α -pinene was the only compound studied over all NO_x conditions, thus providing a model system for organosulfate formation from monoterpenes. The experimental protocols are similar to those in previous NO_x-dependence studies.^{14,15} In the high-NO_x experiments, nitrous acid (HONO) was used as the source of oxidant (OH). HONO was prepared by dropwise addition of 15 mL of 1 wt% NaNO₂ into 30 mL of 10 wt% H₂SO₄ in a glass bulb, and introduced into the chambers with an air stream. Additional NO from a 500 ppm gas cylinder (Scott Marrin, Inc.) was added until the total concentration of NO_x was ~1 ppm (upper limit of NO_x monitor). This relatively high concentration was used in the high-NO_x experiments to prevent a switch in NO_x regimes (i.e. high- to low- NO_x conditions) during the course of oxidation. In the low- NO_x experiments, hydrogen peroxide (H₂O₂) served as the OH precursor. Prior to introduction of seed particles and parent hydrocarbon, about 3–5 ppm H₂O₂ was introduced into the chambers by bubbling a 50% aqueous H_2O_2 solution for 2.5 h at 5 L min⁻¹. In most experiments, 300–500 ppb of NO was introduced into the chamber after addition of H₂O₂. In these experiments, the concentration of NO drops to zero rapidly during the experiment, resulting in a switch from high- to low-NO_x conditions. These latter experiments are designated as intermediate-NO_x experiments (denoted as H_2O_2/NO in the text). In all the photooxidation experiments, the reaction was initiated by irradiating the chamber with blacklights, after the concentrations of seed, parent hydrocarbon and NO_x stabilized.

To study the nighttime chemistry of selected monoterpenes (i.e. α -pinene, *d*-limonene, and *l*-limonene), oxidation by nitrate radicals (NO₃) was performed in the

dark. O_3 at a level of 200 ppb, generated with a UV lamp ozone generator (EnMet Corporation, MI), was injected into the chambers at 5 L min⁻¹ after introduction of the seed particles. Approximately 600 ppb of NO₂ was then added. When the O₃ concentration drops to ~45 ppb, the parent hydrocarbon was introduced into the chambers, marking the beginning of the experiment. Based on the concentrations of NO₂ and O₃ employed, it is estimated that about 500 ppt of NO₃ radical was initially present; based on the applicable rate constants, NO₃ initially dominates the oxidation of the monoterpenes rather than O₃. The initial concentration of the hydrocarbon was estimated from the volume of hydrocarbon injected.

5.3.2 Chamber Filter Sample Collection and Extraction Protocols

Duplicate Teflon filters (PALL Life Sciences, 47-mm diameter, 1.0- μ m pore size, teflo membrane) were collected from each of the monoterpene chamber experiments for offline chemical analysis. The flow rate for filter collection was ~ 17 and 23 L min⁻¹ for the first and second filter sampler, respectively. The difference between flow rates for the two filter samplers was found not to affect the chemical characterization results, as the total mass sampled on the duplicate filters was approximately the same for each experiment. Filter sampling was initiated when the aerosol volume reached its maximum (constant) value, as determined by the DMA. Depending on the total volume concentration of aerosol in the chamber, the duration of filter sampling was 2 – 3.5 h, which resulted in ~ 1.6 – 4.6 m³ of total chamber air sampled.

Teflon filters used for the high-resolution mass spectrometry (MS) analysis were extracted in 5 mL of high-purity methanol (LC-MS CHROMASOLV-Grade, Sigma-Aldrich) by 45 min of sonication. Methanol extracts were blown dry under a gentle N₂ stream at ambient temperature. Dried residues were then reconstituted with 500 mL of a 1:1 (v/v) solvent mixture of 0.1% acetic acid in water (LC-MS CHROMASOLV-Grade, Sigma-Aldrich) and 0.1% acetic acid in methanol (LC-MS CHROMASOLV-Grade, Sigma Aldrich). Blank Teflon filters were extracted and treated in the same manner as the samples; none of the organosulfates detected in the filter samples collected from the chamber experiments was observed in these blanks, indicating that organosulfates were not introduced during sample storage and/or preparation. Furthermore, to ensure that organosulfate formation was not an artifact simply formed from the collection of seed aerosol onto filter media, blank filters were collected under dark conditions from the Caltech chamber containing typical experimental well-mixed concentrations of the VOC (i.e. individual runs of isoprene and α -pinene), seed aerosol, and the OH precursor (i.e. H_2O_2 or HONO), and were extracted and analyzed by our high-resolution MS technique. The chamber air mixture was sampled on these blanks for the same duration as a sample filter. Besides the observation of inorganic sulfate, no organosulfates characterized in the present study or significant contaminants were observed by the high-resolution MS technique from these blank filters, consistent with the lack of observed aerosol growth under dark conditions. Additionally, it is worth mentioning that our initial study on organosulfate formation also included several quality control tests to ensure that organosulfate formation occurred only during SOA formation.²³ All Teflon filters used for high-resolution MS analysis were examined within 1-2 days of the filter extraction/sample preparation. Following their initial analysis, sample extract solutions were stored at -20 °C. Several samples were reanalyzed a month after their initial extraction and showed no signs of degradation due to hydrolysis, a result consistent with previous work.²⁶ Additionally, it should be noted that a prior systematic study has shown that extractions of aliphatic sulfate esters and sulfonic acids in deionized water do not release any detectable inorganic sulfate by ion chromatography.⁵⁸

Teflon filters used for linear ion trap mass spectrometry analysis were extracted two times for 30 min in an ultrasonic bath with 20 mL of methanol. The extracts were combined and concentrated in a rotary evaporator at 35 °C to approximately 1 mL and filtered through a Teflon filter (0.45 μ m), then evaporated to dryness under a N₂ stream at ambient temperature and reconstituted in 300 μ L of a solvent mixture of methanol:water (2:1; v/v). Quality control tests were made to ensure that the filtration step did not introduce artifacts or interferences.

5.3.3 Ambient Aerosol Sample Collection and Extraction Protocols

Details of the SEARCH network, which includes descriptions of each site, sample collection protocols, and gas- and particle-phase measurements conducted, can be found elsewhere.^{59,60} In the present study, archived quartz fiber filters collected from the June 2004 campaign⁴⁷ were analyzed, and were collected from the following three sites: Birmingham, Alabama (BHM – urban site), Centerville, Alabama (CTR – rural site), and Atlanta, Georgia (JST – Jefferson Street – downtown urban site). Quartz fiber filter extraction and sample preparation procedures have been described elsewhere;⁴⁷ however, it should be noted that solid-phase extraction (SPE) was not employed in the current study to desalt the ambient filter samples before MS analysis. This was not done owing to the risk of removing early-eluting organosulfates of isoprene in C₁₈ reversed phase LC; therefore, preventing their detection by MS.

5.3.4 Ultra-Performance Liquid Chromatography/Electrospray Ionization – Timeof-Flight High-Resolution Mass Spectrometry (UPLC/ESI-TOFMS)

Both chamber and field sample extracts were analyzed by a Waters ACQUITY ultra-performance liquid chromatography (UPLC) system, coupled to a Waters LCT Premier XT time-of-flight mass spectrometer (TOFMS) equipped with an electrospray ionization (ESI) source. The ESI source on this instrument contains two individual orthogonal sprays; one spray is for the column eluent and the other is for lock-mass correction. Optimum ESI conditions were found using a 2.5 kV capillary voltage, 40 V sample cone voltage, 350 °C desolvation temperature, 130 °C source temperature, 20 L hr⁻¹ cone gas flow rate, and a 650 L hr⁻¹ desolvation gas flow rate. Data were collected from m/z 50 – 1000 in the negative (-) ionization mode with the TOFMS instrument operated in the W geometry reflectron mode. The W reflectron mode offers the highest mass resolution, which is approximately 12,000, and allows for accurate mass measurements to be conducted on detected organosulfates, resulting in the determination of elemental compositions for these compounds. All organosulfates were detected as their deprotonated molecules $([M - H]^{-})$. The chromatographic separations were carried out using a Waters ACQUITY UPLC HSS (high strength Silica) column (2.1 x 100 mm, 1.8 mm particle size) at 45 °C. The mobile phases consisted of (A) 0.1% acetic acid in water (LC-MS CHROMASOLV-Grade, Sigma-Aldrich) and (B) 0.1% acetic acid in methanol (LC-MS CHROMASOLV-Grade, Sigma-Aldrich). The applied 12-min gradient elution program was as follows: the concentration of eluent B is 0% for the first 2 min, increased to 90% from 2 to 10 min, held at 90% from 10 to 10.2 min, and then

decreased back to 0% from 10.2 to 12 min. The flow rate and sample injection volume were 0.3 mL min⁻¹ and 2 mL, respectively.

The Waters ACQUITY UPLC HSS column was selected to separate organosulfates in this study because of its increased retention of water-soluble polar organosulfates as compared to the Waters ACQUITY BEH C₁₈ column. The latter column is essentially analogous to that of the C₁₈ HPLC column previously employed by Surratt et al.^{23,24} Both C₁₈ columns failed to separate inorganic sulfate from many of the organosulfates of isoprene previously identified in these studies. On the Waters ACQUITY UPLC HSS column, a separation was achieved between inorganic sulfate (detected as m/z 97 and its adduct m/z 195), which elutes first from the column (Figure 5.1, RT 0.79 min), and the organosulfates of the 2-methyltetrols previously identified by Surratt et al.^{23,24} (Figure 5.1, RT 0.91 min). Separation was achieved as a result of trifunctionally-bonded (T3) C_{18} alkyl residues on this column, which prevent stationary phase collapse when a 100% aqueous mobile phase is used, thus, resulting in better retention of water-soluble polar organic compounds. The newly acquired separation between inorganic sulfate and organosulfates of isoprene further confirms that these latter compounds are not artifacts formed in the electrospray ionization source during MS analysis due to co-elution.

At the beginning of each analysis period, the TOFMS instrument was calibrated using a 1:1 (v/v) solvent mixture of acetonitrile and 0.1% phosphoric acid aqueous solution. During each chromatographic run, 2 ng mL⁻¹ of leucine enkephalin (MW = 555) was used for the lock-mass spray for lock-mass correction to obtain accurate masses for each SOA component eluting from the column. The lock-mass syringe pump was operated at 20 μ L min⁻¹. In addition to using the lock-mass spray, the dynamic range enhancement feature of this mass spectrometer was applied to prevent dead time, which decreases mass accuracy, from occurring. Data were acquired and processed using the MassLynx version 4.1 software. As a confirmation that the accurate mass measurement was reliable from the UPLC/(-)ESI-TOFMS technique, a standard sample containing known isoprene and a-pinene organosulfates previously characterized by Surratt et al.²³ was analyzed. The known elemental compositions (i.e. molecular formulae) of the previously characterized organosulfates²³ were in excellent agreement with their measured exact masses (i.e. within ± 2 mDa or ± 2 ppm, which is excellent for small In addition to accurate mass measurements, further insights into the molecules). structures of the organosulfates were obtained by generating tandem MS data, which was done by increasing the first aperature voltage on the TOFMS instrument from 10 V to 25 V; however, it should be noted that the tandem MS data generated from the linear ion trap instrument, as will be described in the next section, was the preferred method for this type of analysis. The tandem MS analysis conducted on the UPLC/ESI-TOFMS instrument served only as a further confirmation of the presence of a sulfate or nitrooxy group.

5.3.5 High-Performance Liquid Chromatography/Electrospray Ionization – Linear Ion Trap Mass Spectrometry (HPLC/ESI-LITMS)

Selected chamber and field sample extracts were also analyzed by a Thermo Fisher Surveyor plus HPLC system (pump and autosampler) coupled to a Thermo Fisher LXQ linear ion trap analyzer equipped with an electrospray ionization source. Data were acquired and processed using Xcalibur version 2.0 software. A Waters Atlantis dC18 column (3 μ m; 2.1 x 150 mm; 3 μ m particle size) was employed, which is similar to the Waters ACQUITY UPLC HSS column used for UPLC/ESI-TOFMS analysis, except that the stationary phase contained difunctionally- instead of trifunctionally-bonded C₁₈ alkyl chains. The mobile phases consisted of acetic acid 0.1 % (v/v) (A) and methanol (B). The applied 45-min gradient elution program was as follows: the concentration of eluent B was kept at 3% for 2 min, then increased to 90% in 18 min, kept at 90% for 10 min, then decreased to 3% in 5 min, and kept at 3% for 10 min. The injection volume and flow rate were 5 μ L and 0.2 mL min⁻¹, respectively.

The linear ion trap was operated under the following conditions: sheath gas flow (nitrogen), 50 arbitrary units; auxiliary gas flow (nitrogen), 5 arbitrary units; source voltage, -4.5 kV; capillary temperature, 350 °C; and maximum ion injection time, 200 ms. For MS² and MS³ experiments, an isolation width of 2 m/z units and a normalized collision energy level of 35% were applied. The [M – H]⁻ signal optimization was done by introducing a 50 µg mL⁻¹ malic acid standard solution.

5.4 Atmospheric Significance of Organosulfates

In the subsequent sections, the detailed chemical characterization of several high-mass organosulfates detected in ambient fine aerosol collected from the southeastern U.S. will be presented; however, before presenting our detailed chemical characterization results, we estimate the total contribution of organosulfates to aerosol collected during summertime conditions from an independent European field site to demonstrate the potential significance of these compounds to ambient organic aerosol formation. Although authentic and/or suitable surrogate standards are not currently available to quantify the characterized organosulfates by the UPLC/(–)ESI-TOFMS and

HPLC/(–)ESI-LITMS techniques employed in the present study, an upper limit estimate of the contribution from organosulfates to the particulate organic matter (OM) can be derived from the analysis of aerosol samples for total sulfur and water-soluble sulfate. Water-soluble sulfate is commonly measured by ion chromatography (IC), and organosulfates do not appear in this type of measurement, consistent with previous work.²³ Total sulfur can be measured by X-ray emission techniques, such as X-ray fluorescence (XRF) or particle-induced X-ray emission spectrometry (PIXE), and this measurement will include the sulfur from water-soluble sulfate and other inorganic sulfur species (e.g., sulfite), the insoluble sulfur which may be associated with primary biogenic particles.⁶¹ and also the sulfur of the organosulfates. Subtracting the IC sulfate-sulfur from the XRF or PIXE sulfur can thus provide an upper limit for the sulfur that is associated with organosulfates. XRF, PIXE, and IC analyses have an associated uncertainty of the order of 5% or more, so the uncertainty that is associated with the difference can be substantial. Even though such data sets were not available for the SEARCH samples analyzed in the present study, one can estimate the maximum amount of sulfur associated with organosulfates for PM₁₀ samples that were collected during a 2003 summer field campaign at the forested site of K-puszta in Hungary,^{62,63} where organosulfates found in the K-puszta aerosol are generally the same as those characterized in the present study, and are likely present in substantial concentrations.⁴⁶ The difference between the PIXE sulfur data and the IC sulfate-sulfur data for the 63 PM_{10} samples ranged from 32 to 850 ng m⁻³, and was, on average, 330 ng m⁻³, which represents 20% of the average PIXE total PM₁₀ sulfur concentration (Maenhaut, unpublished results). The average concentration of particulate organic carbon (OC) in

the PM_{10} samples of the campaign was 5.8 µg m⁻³, which, using an OC-to-OM conversion factor of 1.8 that was adopted for the site,⁶³ corresponds to 10.4 μ g m⁻³ of OM. The mass percentages of sulfur in some common BSOA organosulfates, i.e. those of the characterized 2-methyltetrols and the nitrooxy organosulfates from α -pinene SOA with a MW of 295, are 14.8% and 10.8%, respectively. Using the latter percentage, the 330 ng m⁻³ of non-sulfate-sulfur mentioned above would correspond to 3.1 µg m⁻³ of OM for the 2003 summer campaign at K-puszta and thus represent about 30% of the total PM_{10} OM. Despite the uncertainties associated with this estimate, it is clear that organosulfates may be responsible for a sizeable fraction of ambient OM. In addition to our estimates, Lukács et al.⁶⁴ recently showed that organosulfates in water-soluble fine aerosol, also collected from the K-puszta field site during the 2006 summer campaign, contribute 6-12% to the total sulfur concentration. Due to the likely importance of these estimates, it is essential that the detailed chemical characterization of organosulfates be conducted, as this will lead to improved understanding of their formation pathways in ambient organic aerosol. In the following sections, we first present the results of our laboratory chamber experiments in order to reveal conditions under which organosulfate formation is favorable. Even though our chamber experiments employ higher VOC mixing ratios, higher levels of seed aerosol acidity, and drier conditions than typically observed in the atmosphere, it will be shown that many of the laboratory-generated organosulfates are also detected in the ambient aerosol collected from the southeastern U.S. Those organosulfates detected in both laboratory-generated and ambient organic aerosol will then be the focus of our detailed chemical characterization efforts. Since

most of these compounds are characterized for the first time, a substantial amount of analytical detail is provided.

5.5 Laboratory-Generated Organosulfates

5.5.1 Monoterpene Oxidation Experiments

Experimental conditions and results of the monoterpene oxidation experiments are summarized in Table 5.2. As in recent work,^{23,46} only two types of organosulfates are considered in the present study: (i) sulfate esters formed from the particle-phase esterification of a semivolatile product containing one or more hydroxyl groups by sulfuric acid; and (ii) sulfate derivatives formed from a semivolatile product containing an aldehyde or a keto group and sulfuric acid. The latter organosulfates require gem-diol formation followed by esterification with sulfuric acid.

As stated previously, organosulfates were identified by using both UPLC/(–)ESI-TOFMS and HPLC/(–)ESI-LITMS techniques. Accurate mass measurements for all the organosulfate ions listed in Table 5.2 are provided in Tables 5.3–5.8; however, as noted in Table 5.2, no separate table for accurate mass measurements is provided for the Δ^3 -carene experiment owing to the fact that only one organosulfate isomer was identified at *m/z* 342 using the UPLC/(–)ESI-TOFMS technique. The differences between the theoretical masses of the TOFMS suggested molecular formulae and the measured masses found in Tables 5.3–5.8 are minimal, and are generally well within acceptable errors (i.e., approximately ±1–2 mDa and/or ±5 ppm error). The accurate mass data shown in these tables indicate that these ions have molecular formulae containing at least one sulfur atom, and based on the degree of oxidation indicated by their respective molecular formulae, suggest the presence of a sulfate group. Additionally, some of these ions were also found to contain at least one nitrogen atom, thus being identified as nitrooxy organosulfates. In addition to the accurate mass data, MS^2 spectra for all the organosulfate ions listed in Table 5.2 showed prominent m/z 97 (HSO_4^-) product ions, as well as m/z 80 (SO_3^-) product ions in some cases, both of which have been previously shown to serve as indicator ions for the presence of a sulfate group.^{23–26,51,65,66} MS² product ion spectra for all nitrooxy organosulfates yield a neutral loss of 63 u (HNO_3 ; nitric acid), further confirming the presence of a nitrooxy group. Based on these accurate mass and tandem MS results, all the [M - H]⁻ ions listed in Table 5.2 were classified only as organosulfates and/or nitrooxy organosulfates.

Detailed study of organosulfate formation in laboratory-generated SOA produced from the photooxidation (i.e., OH-initiated oxidation) and/or nighttime-oxidation (i.e., NO₃-initiated oxidation) of monoterpenes has been limited. Previous work, in collaboration with the EPA laboratory, observed organosulfates, as well as nitrooxy organosulfates, from the photooxidation of α -pinene in the presence of NO_x and SO₂.²³ Limited experiments were conducted in this prior study; specifically, a series of experiments in which mixtures of hydrocarbons (toluene, isoprene) containing α -pinene were irradiated in the presence of NO_x, and for selected experiments, in the presence of SO₂. Organosulfates of α -pinene were observed in this prior study only when both a-pinene and SO₂ were present; particle-phase acidity was generated from the photochemical conversion of SO₂ to condensable H₂SO₄. Owing to the complexity of this previous study (i.e., the use of hydrocarbon mixtures to investigate organosulfate formation from α -pinene), organosulfate formation in α -pinene SOA was investigated in much greater detail in the present work.

A number of α -pinene experiments were conducted, in which both the acidity of the sulfate seed aerosol and the oxidation conditions employed were varied (Table 5.2). Organosulfates were formed only when α -pinene was oxidized (under light or dark conditions) in the presence of acidic and/or highly acidic sulfate seed aerosol; higher acidity led to a wider array of organosulfate products detected, consistent with prior work.^{23–26} In the photooxidation experiments, organosulfate formation occurred at all NO_x levels examined, a result previously observed in isoprene SOA.²³ Additionally, nitrooxy organosulfates were observed only under either intermediate- or high-NO_x conditions (denoted as H₂O₂/NO and HONO, respectively). This thorough investigation of organosulfate formation from α -pinene served as a model system for the experimental design of other monoterpenes examined in this study. In particular, since no organosulfate formation from α -pinene was observed under neutral sulfate seed aerosol conditions, which is consistent with previous work,^{25,26} all other monoterpene experiments were conducted only under acidic and/or highly acidic conditions. For the remaining monoterpene experiments, intermediate-NO_x conditions were employed (in most cases) to favor the formation of both organosulfates and nitrooxy organosulfates, as previously observed in isoprene SOA.²³ As shown in Tables 5.3–5.8, organosulfates and nitrooxy organosulfates of all monoterpenes studied under these conditions were detected. Tentative structures and likely precursor oxidation products for many of these organosulfates are given in these tables; however, in subsequent sections, detailed chemical characterization will focus only on those ions detected in both laboratorygenerated and ambient aerosol.

5.5.2 Isoprene Oxidation Experiments

Recent work from our laboratories has examined the detailed chemical composition of isoprene SOA formed under differing combinations of NO_x levels and sulfate seed aerosol acidities.^{23,24,33,37} In these previous studies, organosulfates of isoprene were observed at all NO_x levels and in the presence of sulfate seed aerosol. Interestingly, organosulfates of isoprene were observed in the presence of neutral sulfate seed aerosol,²³ differing from the behavior of the monoterpenes examined in the present study; however, isoprene produced a wider array of organosulfates with enhanced acidity of the sulfate seed aerosol. Chemical characterization of these products was conducted using less advanced mass spectrometric approaches as compared to the present study. No high-resolution (-)ESI-MS data were obtained in the initial study by Surratt et al.²³ As a further confirmation of the initial identifications made in the latter study, Table 5.9 shows the accurate mass measurements obtained in the present study for previously observed organosulfates of isoprene formed in the Caltech isoprene chamber experiments. With the exception of the nitrooxy organosulfates of isoprene detected at m/z 244, in conjunction with recent detailed tandem MS analysis, 23,46 the $[M - H]^{-}$ ion formulae, as determined from the accurate mass data, correspond exactly to the deprotonated forms of the previously proposed isoprene organosulfate structures, hence now providing a more complete characterization of these chamber-generated SOA products. As for the monoterpene organosulfates, only those organosulfates of isoprene detected in both laboratory-generated and ambient aerosol will be further discussed and thoroughly characterized in subsequent sections; particular attention is focused on those ions detected for the first time in ambient aerosol.

5.6 Organosulfates in Ambient Aerosol

Figure 5.1 shows the UPLC/(–)ESI-TOFMS base peak ion chromatograms (BPCs) for 24-h integrated ambient aerosol samples collected from three different sites, and on three different days, across the southeastern U.S. during the summer of 2004. Several of the chromatographic peaks in these BPCs are labeled with their respective [M – H][–] ion. Comparison of these BPCs demonstrates that the chemical composition of PM_{2.5} in this region is rather constant during summertime polluted conditions, consistent with our initial investigation of this region.⁴⁷ It should be noted that not all organosulfates detected are labeled in this figure; Table 5.10 shows the accurate mass data for all organosulfates detected in each analyzed field sample.

In our previous study, the chemical composition of aerosol collected from this region was investigated; however, very few organic components identified in Figure 5.1 (and Table 5.10) were fully characterized, and in some cases not even detected, owing to the use of less-sensitive mass spectrometric approaches.⁴⁷ Besides the identification of known terpenoic acids (denoted with an asterisk in Figure 5.1), such as norpinic (MW 172), pinic (MW 186), and pinonic (MW 184) acids, as well the commonly observed MW 204 compound found in ambient aerosol,^{47,67–70} which was recently characterized as 3-methyl-1,2,3-butanetricarboxylic acid,⁷¹ only one organosulfate (i.e., *m/z* 294) was identified in this previous study.⁴⁷ In addition to characterizing *m/z* 294 as a nitrooxy organosulfate of α -pinene,²³ recent work has reported that ions at *m/z* 215 and 260 shown in Figure 5.1 (as well as *m/z* 199 not shown) are organosulfates of isoprene;^{23,46} specifically, it was found that *m/z* 215, 260, and 199 corresponded to organosulfates of the 2-methyltetrols, nitrooxy organosulfates of the 2-methyltetrol mononitrates, and

organosulfates of 2-methylglyceric acid, respectively. It should be noted that both the 2-methyletrols and 2-methylglyceric acid have been previously identified as tracer compounds for the occurrence of SOA formation in ambient aerosol from isoprene phootooxidation.^{21,72} In the following sections, detailed mass spectrometric evidence is presented, characterizing most of the previously uncharacterized and partially characterized organic components observed in the field samples (Figure 5.1) as organosulfates of monoterpenes and isoprene. Except for the organosulfates of glyoxal (i.e. m/z 155) and methylglyoxal (i.e. m/z 169), which could form from the oxidation of both anthropogenic and biogenic VOCs in the presence of acidified sulfate seed aerosol, all other organosulfates characterized in this study appear to be unique tracer compounds for the occurrence of biogenic SOA formation under acidic conditions.

5.6.1 Organosulfates of Monoterpenes in Ambient Aerosol

5.6.1.1. m/z 294

 $[M - H]^-$ ions at *m/z* 294 have been observed using (–)ESI-MS techniques in ambient PM_{2.5} collected from several regions of the U.S.^{23,47} as well as Europe,^{26,46,51,73} and have been only partially characterized as nitrooxy organosulfates using high-resolution and tandem MS. It should be noted that it is critical that the latter MS techniques be used in combination when establishing the chemical identity of an unknown compound measured by (–)ESI-MS, as many isobaric compounds (i.e., compounds of the same molecular mass but of different elemental composition) exist in ambient organic aerosol, and as a result, low-resolution MS instruments (e.g., quadrupole and ion trap mass analyzers) will not allow the determination of the mass difference between isobaric compounds. By using a surrogate standard, the total m/z 294 nitrooxy organosulfate aerosol mass concentration (i.e. sum of three major isomers observed) was previously estimated to range from 27 – 140 ng m⁻³ for all days and field sites analyzed from the southeastern U.S.,⁴⁷ resulting in this ion being the most abundant organic species detected by (–)ESI-MS for this region. However, it is noted that the latter is only true when the filters are extracted in methanol. There may be other more abundant organic components in ambient aerosol collected from this region not extractable by methanol, as well as not observed in the (–)ESI-MS analysis due to not being eluted from the chromatographic column previously employed or not being detected in the negative ion mode.

(-)ESI-TOFMS accurate mass data for the m/z 294 ions indicated that the [M – H]⁻ ion formula is C₁₀H₁₆NO₇S^{-,26,47} consistent with the accurate mass data shown in Table 5.10. Based on these ion formulae, it was suggested that monoterpenes (C₁₀H₁₆) serve as a likely source for these ambient nitrooxy organosulfates.^{26,47} Surratt et al.²³ recently reported that the m/z 294 nitrooxy organosulfates detected in southeastern U.S. aerosol could arise from the photooxidation of α -pinene in the presence of NO_x and SO₂ (i.e., acidified sulfate seed aerosol); however, it was noted in this prior study, as well as in Iinuma et al.,²⁶ that other monoterpenes might also contribute to the formation of these compounds. Interestingly, previous studies have found that these compounds were more abundant in nighttime samples collected from Europe, indicating an additional formation mechanism is possible (i.e., NO₃-initiated oxidation).^{26,46} No such distinction between daytime and nighttime chemistry could be made in previous studies from the SEARCH campaign,^{23,47} as well as in the present study, owing to the fact that the samples were collected over a 24-h integrated period.

Figure 5.2 compares the UPLC/(-)ESI-TOFMS extracted ion chromatograms (EICs) of m/z 294 obtained from one representative SEARCH field sample (CTR experiments. 6/11/04) and four selected monoterpene oxidation including α -pinene/H₂O₂/NO/neutral seed, α -pinene/H₂O₂/NO/highly acidic seed, α -pinene/NO₃/highly acidic seed, and β -pinene/H₂O₂/NO/highly acidic seed experiments, respectively. It is noted that the m/z 294 compounds were detected for all days in which samples were collected from each SEARCH field site (Table 5.10), consistent with our previous field study.⁴⁷ Although isomeric m/z 294 nitrooxy organosulfates were also formed in the α -terpinene and terpinolene photooxidation experiments conducted under highly acidic conditions (Tables 5.5 and 5.7), these two monoterpenes are not considered as possible sources for these nitrooxy organosulfates found in the SEARCH samples since the retention times (RTs) of their single isomers do not correspond to those of the ambient samples. The photooxidation and nighttime-oxidation of α -pinene in the presence of highly acidic seed aerosol is shown in Figure 5.2 to produce three m/z 294 nitrooxy organosulfates with the same RTs and accurate masses as those observed in the SEARCH samples (RTs 8.19, 8.80, and 8.99 min; Figure 5.2a). As shown in Figure 5.2b, the photooxidation of α -pinene in the presence of neutral sulfate seed aerosol does not produce m/z 294 compounds, which was also the result for the α -pinene/NO₃/neutral seed the experiment (Table 5.2). Additionally, Figure 5.2e shows that β -pinene/H₂O₂/NO/highly acidic seed experiment produced one *m/z* 294 nitrooxy organosulfate isomer with the same RT and accurate mass found in the field samples; however, tandem MS data will be discussed subsequently in order to confirm whether α -pinene, as well as β -pinene, are in fact the monoterpene precursors required for the formation of these compounds in ambient aerosol.

Figures 5.3 and 5.4 show MS²/MS³ data obtained with the HPLC/(–)ESI-LITMS technique for the three m/z 294 compounds formed in the α -pinene/NO₃/highly acidic seed experiment, and MS²/MS³ data for the three m/z 294 compounds present from a selected SEARCH sample (CTR 6/11/04), respectively. MS² data similar to those for the α -pinene/NO₃/highly acidic seed experiment were also obtained in the case of the α -pinene/H₂O₂/NO/highly acidic seed experiment (see Figure 5.35); in addition, similar MS² data were also recorded for two other field samples (JST 6/26/04 and BHM 6/20/04; data not shown). Comparison of these data establishes that the NO₃ and H₂O₂/NO highly acidic sulfate seed experiments yield the same m/z 294 nitrooxy organosulfates as those present in the field samples and originate from either the nighttime-oxidation or photooxidation of α -pinene, with the latter in the presence of NO_x.

Isomeric structural assignments, taking into account that these compounds originate from the oxidation of α -pinene, and explanations for the formation of product ions produced in the tandem MS data supporting these structural assignments are outlined in Scheme 5.1 [where numerals 1–3(295) indicate the protonated compounds proposed]; however, in the absence of reference compounds, these attributions should be regarded as tentative. The *m/z* 294 MS² product spectra of compounds **2** and **3**(295) are very similar, suggesting positional isomers with sulfate and nitrate groups at different positions. The *m/z* 294 MS² spectra for compounds **2** and **3**(295) contain an abundant *m/z* 231 ion due to the loss of 63 u (HNO₃), which shows a different fragmentation behavior for the two compounds; in the case of compound **2**(295) multiple product ions are formed upon MS³

of the m/z 231 ion, while in the case of compound 3(295) m/z 151 is the only product ion. The abundant m/z 203 ion in the m/z 294 $\rightarrow m/z$ 231 MS³ spectrum of compound **2**(295) corresponds to the loss of 28 u (CH₂=CH₂). This can be explained by a retro-Diels Alder (RDA) fragmentation and points to a nitrooxy group at the secondary carbon position of the 2,2-dimethylcyclobutane ring. On the other hand, the m/z 142 ion in the m/z 294 MS² spectrum of compound 3(295) points to neighboring OSO₃⁻ and ONO₂ groups and thus supports the proposed structure shown in Scheme 5.1. In regards to compound 1(295), it is noted that the m/z 294 MS² spectrum is remarkably similar to those shown in Figure 5.36 for β -pinene SOA; however, the product ions at m/z 247, 220 and 96 exhibit different relative abundances, consistent with isomeric differences, and indicate that β -pinene is not responsible for the formation of these nitrooxy organosulfates in ambient aerosol. This conclusion is further supported by the MS³ data, which reveal more distinct differences between compound 1(295) and the two m/z 294 compounds present in β -pinene SOA. The *m/z* 247 ion (loss of HNO₂) in the *m/z* 294 MS² spectrum of compound 1(295) is consistent with a primary nitrooxy group, while the base peak at m/z96 (SO₄^{-•}) points to a sulfate group at a tertiary position. The absence of a m/z 151 ion suggests that a hydrogen required for loss of HNO₃ is not available at a neighboring position within compound 1(295). The abundant m/z 220 ion can be explained by the combined loss of CO and a NO₂ radical (74 u); however, a simple mechanism for this fragmentation could not be formulated.

Based upon the interpretation of both the accurate mass and tandem MS data, Figure 5.5 shows the proposed formation mechanism for the three major isomers of the m/z 294 nitrooxy organosulfates observed in ambient aerosol. As previously shown for pinonaldehyde, 49,50 a known first-generation gas-phase product from α -pinene oxidation, it is proposed that isomeric hydroxynitrate gas-phase products of MW 215 from α -pinene reactively uptake onto acidified sulfate seed aerosol through esterification of the hydroxyl group with sulfuric acid, yielding the characterized nitrooxy organosulfates shown in Scheme 5.1. Prior work done by Aschmann et al.^{74,75} has detected a hydroxynitrate species of MW 215 in the gas phase produced from an α -pinene photooxidation experiment conducted in the presence of NO when using an atmospheric pressure ionization tandem mass spectrometer, and as a result, supporting the feasibility of our proposed reaction mechanism; in addition, Jay and Stieglitz⁷⁶ also observed hydroxynitrates from the NO₃-initiated oxidation of α -pinene using gas chromatography(GC)/mass spectrometry(MS) and FTIR analysis. Despite the structure for the hydroxynitrate gas-phase precursor of compound 3(295) being the only isomer conforming to known RO₂ chemistry, other structural isomers of the hydroxynitrate likely correspond to the detailed chemical structures shown in Scheme 5.1. In order to form compounds 1 and 2(295) from the photooxidation of α -pinene in the presence of NO_x, we propose that the β-hydroxyalkyl radical that forms after the initial OH radical addition to the double bond isomerizes the radical by H-abstraction to another carbon within the α -pinene skeleton (or undergoes a hydrogen rearrangement), followed by the immediate reaction with O_2 to form the respective hydroxyperoxy radicals shown in Figure 5.5. Similar isomerization behavior has been proposed by Jay and Stieglitz⁷⁶ for β nitrooxyalkyl radicals formed from the NO₃-initiated oxidation of α -pinene; however, it remains unclear at this time how such an isomerization would yield the hydroxynitrates needed to produce compounds 1 and 2(295) under nighttime oxidation conditions, even

though the MS data clearly show that both nighttime and daytime chemistry of α -pinene produce the same three isomers of the m/z 294 nitrooxy organosulfates. Conversely, we only discuss and propose the formation of compounds 1 and 2(295) from the photooxidation pathway in Figure 5.5. Upon the formation of the hydroxyperoxy radicals from the isomerization of the initial β -hydroxyalkyl radical and subsequent addition of O₂, under intermediate- and/or high-NO_x conditions, the former radicals react with NO to yield the hydroxynitrate precursors shown for compounds 1 and 2(295). Alternatively, previous work has shown that large hydroxyalkoxy (RO) radicals, produced from the reaction of the RO₂ radical with NO, readily isomerize rather than fragment,^{12,74,75} especially if the RO radical has at least 4 or more carbons and can form a 6-membered transition state.^{77,78} The isomerization of the RO radical was not considered in the present study owing to the fact that if the initial RO radical of α -pinene isomerizes, as previously observed by Aschmann et al.,^{74,75} this results in the formation of a dihvdroxvalkyl radical. The latter radical immediately reacts with O2 to form a dihydroxyperoxy radical, and in the presence of NO, forms a dihydroxynitrate gas-phase product of MW 231, thus failing to explain the formation of compounds 1 and 2(295)from the photooxidation of α -pinene.

Recent emission data show that α -pinene is the most abundant monoterpene emitted from loblolly pine (*Pinus taeda* L.), which is one of the most predominant timber species found in southeastern U.S. forests, followed by β -pinene, myrcene, *d*-limonene, and β -phellandrene.^{79,80} Considering our chemical characterization results and the known emission rates from loblolly pine, it appears that the *m/z* 294 nitrooxy organosulfates we observe in the SEARCH field samples arise solely from either the photooxidation of

 α -pinene in the presence of NO_x or the nighttime oxidation of α -pinene, both of which require the presence of acidified sulfate seed aerosol. It should be noted that future laboratory chamber experiments of myrcene and ocimene are needed in order to determine their potential contribution to the *m/z* 294 nitrooxy organosulfates found in ambient aerosol, especially considering that new emission data for the U.S. indicate that these two monoterpenes are emitted abundantly from deciduous (broadleaf) and coniferous (needle) trees.⁸¹ Additionally, it would be worthwhile to analyze nighttimesegregated filter samples collected from the SEARCH network to evaluate the importance of nighttime chemistry to the formation of the *m/z* 294 nitrooxy organosulfates.

5.6.1.2 *m/z* 296

Previous field studies have reported $[M - H]^-$ ions at m/z 296 when using (-)ESI-MS techniques to characterize organic aerosol collected from both the southeastern and southwestern U.S.^{47,52} Despite the recent identification of a m/z 296 compound as a nitrooxy organosulfate in southwestern U.S. aerosol,⁵² the source and formation mechanism of this compound remained unclear in both regions previously studied. Figure 5.37 compares the UPLC/(–)ESI-TOFMS EICs of m/z 296 obtained from three selected monoterpene oxidation experiments, which includes the β-phellandrene *d*-limonene/H₂O₂/NO/highly acidic seed, +*d*-limonene mixture/H2O2/NO/highly acidic seed, and limonaketone/H2O2/NO/highly acidic seed experiments, to that of one representative SEARCH field sample (JST 6/26/04), respectively. Although not shown, it should be noted that the *l*-limonene/H₂O₂/NO/highly acidic seed experiment also produced three m/z 296

compounds with the same RTs and accurate masses as those highlighted in Figure 5.37 for the *d*-limonene experiments. From all the monoterpene oxidation experiments conducted, d-/l-limonene and β -phellandrene, as well as limonaketone (C₉H₁₄O), which is a known first-generation oxidation product of limonene,^{54,82} were the only precursors in this study to produce m/z 296 compounds; specifically, the photooxidation of these BVOC precursors in the presence of NOx and highly acidified sulfate seed aerosol produced these compounds. Interestingly, no m/z 296 compounds formed in the NO₃/highly acidic seed experiments of *d*- and *l*-limonene, which is likely attributable to the large nucleation events observed at the start of these experiments; specifically, the NO₃-initiated oxidation of these monoterpenes led to a large number of particles being formed by nucleation, and as a result, likely prevented the formation of the m/z 296 compounds by not allowing for the reactive uptake of the gas-phase semivolatile products onto the acidified sulfate seed aerosol. Accurate mass data for all chromatographic peaks highlighted in Figure 5.37 indicate that the $[M - H]^{-}$ ion formulae for both the laboratorygenerated (Figure 5.37a-c) and ambient m/z 296 compounds (Figure 5.37d) are $C_9H_{14}NO_8S^{-}$.

Figure 5.6 shows the m/z 296 MS² TICs obtained using the HPLC/(–)ESI-LITMS technique for the *d*-limonene/H₂O₂/NO/highly acidic seed experiment and a SEARCH sample (BHM 6/20/04), respectively. As observed in the UPLC/(–)ESI-TOFMS EICs of m/z 296 (Figure 5.37), the RTs for the three m/z 296 compounds in *d*-limonene SOA were slightly shifted to longer times when compared to the ambient m/z 296 compounds. It is noted that the signals observed between 36 and 48 min in Figure 5.6b are due to 34 S/ 18 O isotopic contributions of m/z 294 α -pinene SOA nitrooxy organosulfates that are very

abundant in the ambient sample. The MS^2/MS^3 data for the three m/z 296 compounds from d-limonene SOA (Figure 5.6a) eluting at 24.1, 25.4 and 28.3 min, are given in Figure 5.7a-c, respectively. It can be seen that the m/z 296 MS² and m/z 296 $\rightarrow m/z$ 233 MS^3 spectra are remarkably similar for the three compounds in *d*-limonene SOA. Tentative structures based on the interpretation of both the MS^2/MS^3 (Figure 5.7) and accurate mass data for the three m/z 296 compounds observed in *d*-limonene SOA, and explanations for the observed product ions supporting these structural assignments, are given in Scheme 5.2 [where numerals 1-3(297) indicate the protonated compounds proposed]. The m/z 233 ion is explained by the loss of HNO₃ (63 u), indicating that a hydrogen is available for HNO₃ loss in the three compounds. The two first-eluting compounds [1 and 2(297)] also reveal a weak m/z 142 ion, indicating that the sulfate and nitrooxy groups are spatially close. Furthermore, in addition to m/z 97 [HSO₄⁻], it can be seen that the $m/z 296 \rightarrow m/z 233 \text{ MS}^3$ spectra show a m/z 81 ion corresponding to HSO₃⁻. It is worth noting that this ion is not formed from the corresponding m/z 294 α -pinene derivatives, where instead m/z 80 [SO₃^{-•}] is generated upon fragmentation of m/z 231.

In order to further support the proposed structures shown in Scheme 5.2 and gain insight into the formation mechanism of these compounds in *d*-limonene SOA, a limonaketone/H₂O₂/NO/highly acidic seed experiment was conducted. As shown in Figure 5.37, this experiment (Figure 5.37c) produced three m/z 296 compounds with the same RTs and accurate masses as those observed in the *d*-limonene and β -phellandrene + *d*-limonene experiments (Figures 5.37a and 5.37b, respectively). Additionally, comparison of the MS²/MS³ data collected for the three m/z 296 compounds observed in both the *d*-limonene (Figure 5.7) and limonaketone (Figure 5.38) H₂O₂/NO/highly acidic seed experiments show comparable mass spectral properties, and as a result, conclusively indicate that the further oxidation of limonaketone in the presence of NO_x and highly acidified sulfate seed aerosol produces these m/z 296 nitrooxy organosulfates in *d*-limonene SOA. Based upon the interpretation of both the accurate mass and tandem MS data, Figure 5.8 shows the proposed formation mechanism for the three major m/z296 nitrooxy organosulfates observed in the laboratory-generated d-limonene SOA. As proposed for the m/z 294 α -pinene derivatives, the m/z 296 compounds are formed from the reactive uptake of isomeric hydroxynitrate gas-phase products by esterification of the hydroxyl groups with sulfuric acid. Notably, previous gas-phase measurements using proton transfer reaction (PTR)-MS for *d*-limonene/NO_x photooxidation experiments observed an organic nitrate species of MW 217 in the gas phase,⁸² thus further supporting the proposed reaction mechanism. Compounds 1 and 2(297) are likely stereoisomers (i.e. enantiomers) formed directly from the reactive uptake of the hydroxynitrate that results from the reaction of the RO₂ radical of limonaketone with NO; however, analogous to the proposed formation mechanism of compounds 1 and 2(295) in a-pinene SOA, compound 3(297) likely forms from the hydroxynitrate that results from isomerization (i.e. hydrogen rearrangement) of the β -hydroxyalkyl radical of limonaketone.

The three m/z 296 compounds observed in the ambient sample (Figure 5.37d and Figure 5.6b) were initially considered as *d*-limonene SOA products since their elemental compositions (i.e. C₉H₁₄NO₈S⁻) were exactly the same as those observed in the limonene SOA experiments (Figure 5.37a-c). Despite some differences in the RTs, careful inspection of the MS²/MS³ data shown in Figure 5.39 revealed notable differences in the mass spectral properties of the ambient m/z 296 compounds as compared to those in the

d-limonene SOA experiments (Figure 5.7). The trace m/z 296 compound eluting at 24.0 min in Figure 5.6b corresponds with the second-eluting m/z 296 compound from *d*-limonene SOA [2(297)]. Comparison of their respective MS²/MS³ spectra (Figure 5.7b) and Figure 5.39b) supports this conclusion; the MS² spectrum obtained for the trace m/z296 compound in the ambient sample reveals some additional interfering ions (i.e. at m/z237, 179 and 137) compared to that of *d*-limonene SOA but the $m/z 296 \rightarrow m/z 233 \text{ MS}^3$ spectra compare reasonably well, suggesting that the precursor of this compound is likely *d*-limonene. However, the two other major m/2 296 compounds from the ambient sample have RTs at 22.4 and 27.5 min that are different from those of the d-limonene SOA compounds. The third-eluting compounds from both samples have slightly different RTs (difference of only 0.8 min), but their MS^2/MS^3 data are virtually similar, suggesting a very close structural relationship. These results allowed us to conclude that the m/z 296 compounds observed in the ambient samples could originate from limonene-like monoterpene precursors; specifically, these precursors require the presence of two or more double bonds, with at least one of these double bonds located at a terminal position, whereupon oxidation of this bond-type under intermediate/high-NO_x conditions, allows for the formation of a C_9 ketone/aldehyde precursor. Importantly, it should be noted that the other monoterpenes with two double bonds (i.e. α -/ γ -terpinene and terpinolene), neither of which are at a terminal position, which were examined in the present study (Table 5.2) did not produce m/z 296 compounds.

As previously noted, emissions of myrcene have been measured to be substantial during summertime conditions from loblolly pine (*Pinus taeda* L.).^{79,80} Even though α -/ β -pinene are the most abundant monoterpenes emitted from this prevalent timber

species found in the southeastern U.S., prior studies have shown that myrcene is emitted more abundantly than limonene,^{79,80} making myrcene a likely candidate for the source of the major m/z 296 compounds found in ambient aerosol collected from this region. It would be worthwhile to evaluate whether myrcene, as well as ocimene (a known isomer of myrcene that is abundantly emitted from broad leaf trees),⁸¹ serves as the precursor for the m/z 296 compounds observed in ambient aerosol by conducting further laboratory investigations. In addition, it should be kept in mind that there are still unknown terpene-like compounds in the atmosphere that show substantial OH reactivity and remain to be identified.⁸³

5.6.1.3 *m/z* 249

Figure 5.9 compares the UPLC/(–)ESI-TOFMS EICs of *m/z* 249 obtained from three selected monoterpene oxidation experiments, which include α-pinene/NO₃/highly acidic seed, α-pinene/H₂O₂/NO/highly acidic seed, and β-pinene/H₂O₂/NO/highly acidic seed experiments, to that of one representative SEARCH field sample (CTR 6/11/04), respectively. Accurate mass data for all chromatographic peaks highlighted in this figure indicate that the $[M - H]^-$ ion formulae for both the laboratory-generated (Figure 5.9a-c) and ambient *m/z* 249 compounds (Figure 5.9d) are C₁₀H₁₇O₅S⁻. Even though other monoterpenes shown in Tables 5.3–5.8 also produced *m/z* 249 compounds (i.e., *d-/l*-limonene and terpinolene), α- and β-pinene were the only monoterpenes in this study to produce these compounds with the same RTs as those detected in filter samples collected from the SEARCH network (Table 5.10), and as a result, detailed tandem MS experiments were conducted in order to confirm that α-pinene and/or β-pinene were the source of these compounds in ambient aerosol collected from the southeastern U.S.
Figure 5.10 shows the MS² spectra for the two m/z 249 compounds from the β-pinene/H₂O₂/NO/highly acidic seed experiment and a SEARCH sample (BHM 6/20/04), which have exactly the same RTs (i.e., 24.4 and 29.3 min using the HPLC/ESI-LITMS technique). In addition, Figure 5.11 shows the MS² spectra for the two m/z 249 compounds from the α -pinene/H₂O₂/NO/highly acidic seed experiment and a SEARCH sample (CTR 6/11/04), which also have exactly the same RTs (i.e., 31.2 and 32.2 min using the HPLC/ESI-LITMS technique). It should be noted that the two ambient m/z 249 compounds with the same RTs as those found in the α -pinene SOA were not detected in every field sample using the UPLC/(–)ESI-TOFMS technique (Table 5.10); in fact, only trace amounts were observed for those samples containing these compounds, differing from the relatively large signals observed for the β -pinene m/z 249 organosulfates in ambient aerosol. It can be seen that the m/z 249 MS² spectra of the compounds from both the β -pinene and ambient samples with the same RTs perfectly agree. Plausible isomeric structures are given in Figure 5.12 and Scheme 5.3 [where numerals 1-4(250) indicate the protonated compounds proposed]; the second-eluting β -pinene compound 2(250) is assigned to the isomer with a terminal hydroxyl group based on the loss of a hydrogen molecule giving rise to m/z 247 and subsequent loss of SO₃ (80 u) yielding m/z 167 in its m/z 249 MS² spectrum. The fragmentation behavior of both β -pinene isomers [i.e., compounds 1 and 2(250)] is distinctly different with regard to the formation of m/z 97 [HSO₄]; while m/z 97 is virtually absent from the m/z 249 MS² spectrum of the secondeluting isomer 2(250), the formation of m/z 97 is favored in the first-eluting isomer 1(250) resulting in the base peak. The α -pinene isomers [i.e., compounds 3 and 4(250)] also reveal a quite different fragmentation behavior. The m/z 249 MS² spectrum of the first-eluting α -pinene isomer shows m/z 249 as base peak and product ions at m/z 231 and 151, due to the loss of water and the combined loss of water and SO₃, respectively. As in the case of the β -pinene isomers, notable abundance differences are observed for m/z 97 [HSO₄⁻]; while m/z 97 is virtually absent from the m/z 249 MS² spectrum of the first-eluting isomer **3**(250), the formation of m/z 97 is favored in the second-eluting isomer **4**(250).

In addition to the tentatively proposed structures, Figure 5.12 shows the proposed reaction scheme for the formation of the m/z 249 organosulfates observed in ambient aerosol collected from the southeastern U.S. The oxidation of α - and β -pinene is expected to occur primarily through reaction with OH radicals, owing to the fact that H₂O₂ was employed as the OH radical source in both photooxidation experiments; however, as shown in Figure 5.9a, α -pinene + NO₃ cannot be ruled as a source for compounds 3 and 4(250) until nighttime-segregated samples from the southeastern U.S. are analyzed. Based on the latter result, β -pinene + NO₃ may also contribute to the formation of compounds 1 and 2(250), thus this route cannot be excluded a possible source at this time. Even though negligible amounts of O₃ were initially present at the start of each experiment, O₃ formation occurs during the course of the experiments resulting from the photochemical conversion of NO to NO_2 . In the case of β -pinene, even at ~500 ppb O_3 , which is the maximum mixing ratio of O_3 when β -pinene was still present, the reaction rate of β -pinene + OH is still 9 times that of β -pinene + O₃. As previously observed in isoprene photooxidation experiments,^{4,13,33} the NO mixing ratio needs to approach zero before significant levels of O_3 form; however, by this time, most of the hydrocarbon is typically reacted away by OH radicals.

Although we propose that the OH radical oxidation is primarily responsible for the formation of the m/z 249 organosulfates in southeastern U.S. aerosol, Iinuma et al.²⁶ have shown that β -pinene ozonolysis in the presence of acidified sulfate seed aerosol can also produce compound 1(250) in PM_{2.5} aerosol from a German Norway sprucedominated forest; specifically, similar tandem MS and accurate mass data were obtained for compound 1(250) of this study, suggesting that O_3 may play a role in forming these compounds under polluted conditions. Instead of forming the m/z 249 organosulfates by reactive uptake of pinanediol gas-phase intermediates, as shown in Figure 5.12, Iinuma et al.²⁶ have proposed that these compounds also form by the reactive uptake of β -pinene oxide when the oxidation of β -pinene is initiated by O₃. Interestingly, this prior study found that α -pinene ozonolysis in the presence of acidic seed particles exhibited a distinctly different behavior; specifically, this experiment did not produce a corresponding organosulfate at m/z 249, which was attributed to α -pinene + O₃ likely following a ring-opening primary ozonide pathway rather than a ring-retaining oxirane pathway (like that for β -pinene) owing to the fact that the α -pinene primary ozonide structure is relatively strained.

Similar to previous work done with glyoxal and pinonaldehyde,^{48–50} it would be worthwhile to perform reactive uptake experiments using the pinanediol and epoxide intermediates only in the presence of acidified sulfate seed aerosol, as this could help establish the reaction mechanism responsible for the formation of these organosulfates in ambient aerosol. Considering that the α -pinene/NO₃/highly acidic seed experiment (Figure 5.9a) also produced the *m/z* 249 α -pinene organosulfates detected in ambient aerosol (Figure 5.9d), as well as α -pinene oxide being detected in the gas-phase at measurable yields under nighttime-oxidation conditions,^{84–86} it will be crucial to analyze nighttime-segregated filter samples collected from the SEARCH network in order to evaluate the importance of this reaction pathway to the formation of these compounds in ambient aerosol. Additionally, β -pinene/NO₃/highly acidic seed experiments should be conducted in the future owing to the fact that measurable quantities of β -pinene oxide have also been observed in the gas phase from β -pinene + NO₃ reactions.⁸⁷ Further work should also investigate the source for the differences in the relative abundances of the *m/z* 249 α - and β -pinene organosulfates.

5.6.1.4 *m/z* 227

show m/z227 MS^2 TICs obtained Figures 5.13-5.14 from the α-pinene/H₂O₂/NO/highly acidic seed experiment and a SEARCH sample (BHM 6/20/04), and MS²/MS³ data for the *m/z* 227 compounds from the α -pinene SOA sample and m/z 227 compounds eluting at the same RT from the ambient sample, respectively. In a prior study by Gómez-González et al.⁴⁶, polar early-eluting m/z 227 compounds from K-puszta aerosol with comparable RTs as those found in the present study were identified as sulfate esters of 2- and 3-hydroxyglutaric acid, as shown in Scheme 5.4 [where numerals 1-2(228) indicate the protonated forms of 3- and 2-hydroxyglutaric acids, respectively], of which 3-hydroxyglutaric acid was attributed to an α -pinene SOA product⁸⁸ and 2-hydroxyglutaric acid was proposed to be an oxidation product of unsaturated fatty acids. It can be seen in the $m/z 227 \rightarrow m/z 147 \text{ MS}^3$ spectrum of the a-pinene SOA product (Figure 5.14a) that both m/z 129 and m/z 85 are produced, which are characteristic product ions of deprotonated 2- and 3-hydroxyglutaric acid,⁴⁶ respectively; these data indicate that the m/z 227 α -pinene SOA product is a mixture of sulfated 2- and 3-hydroxyglutaric acids. Furthermore, the UPLC/(–)ESI-TOFMS accurate mass data indicated that the elemental compositions of both the laboratory-generated and ambient m/z 227 compounds are C₅H₇O₈S⁻, confirming that these compounds are likely formed from either 2- or 3-hydroxyglutaric acids in ambient aerosol.

The m/z 227 MS²/MS³ data obtained from the SEARCH sample (BHM 6/20/04) are comparable with those reported from K-puszta aerosol.⁴⁶ It is noted that m/z 129 dominates the m/z 227 $\rightarrow m/z$ 147 MS³ spectrum (Figure 5.14b), indicating that sulfated 2-hydroxyglutaric acid is the prevalent isomer in the SEARCH sample. This suggests that 2-hydroxyglutaric acid has precursors other than α -pinene, possibly unsaturated fatty acids as proposed in our prior study.⁴⁶ Besides the α -pinene/H₂O₂/NO/highly acidic seed experiment, none of the other monoterpenes studied in the present work produced laboratory-generated m/z 227 organosulfates (see Tables 5.2 and Tables 5.3–5.8); however, owing to substantial emission rates of myrcene and ocimene in the southeastern U.S. during summertime conditions,^{79–81} future laboratory experiments are needed to determine their potential for the formation of m/z 227 organosulfates found in ambient aerosol. Additionally, from our experimental work, it appears that the formation of the m/z 227 α -pinene organosulfates in ambient aerosol requires the presence of NO_x, consistent with recent work showing that the 3-hydroxyglutaric acid precursors, and likely 2-hydroxyglutaric acid, form from the further oxidation of *cis*-pinonic acid by OH radicals in the presence of NO.^{88,89}

Even though recent work identified an m/z 279 compound as an organosulfate in southwestern U.S. aerosol,⁵² the source and formation mechanism of this compound remained unclear. Our initial characterization of organic aerosol collected from the SEARCH network did not observe an ion at m/z 279, likely owing to the lower sensitivity of the (-)ESI-MS techniques employed.⁴⁷ Figure 5.15 compares the UPLC/(-)ESI-TOFMS EICs of m/z 279 obtained from three selected monoterpene oxidation experiments, which include α -pinene/H₂O₂/NO/highly acidic seed, α -pinene/NO₃/highly acidic seed and β -pinene/H₂O₂/NO/highly acidic seed experiments, to that of one representative SEARCH field sample (CTR 6/11/04), respectively. Accurate mass data for all chromatographic peaks highlighted in this figure indicate the $[M - H]^{-}$ ion formulae for both the laboratory-generated (Figure 5.15a-c) and ambient m/z 279 compounds (Figure 5.15d) are $C_{10}H_{15}O_7S^-$. Although other monoterpene oxidation experiments (i.e. *d*-/*l*-limonene and α -/ γ -terpinene) produced *m*/*z* 279 SOA compounds with the same elemental compositions as those observed in ambient aerosol, α - and β -pinene were the only monoterpenes in this study to produce these compounds with the same RTs as those detected in all SEARCH filter samples (Table 5.10), and as a result, detailed tandem MS experiments were conducted in order to confirm that α - and β -pinene were the source of these compounds.

Figures 5.16–5.19 show m/z 279 MS² TICs from an α -pinene/H₂O₂/NO/highly acidic seed experiment, a β -pinene/H₂O₂/NO/highly acidic seed experiment and a SEARCH sample (CTR 6/11/04), and MS²/MS³ data for the two first-eluting m/z 279 compounds from the α -pinene and β -pinene SOA samples and the two m/z 279

compounds eluting at the same RTs in the ambient sample, respectively. It can be seen that the m/z 279 MS² spectra are distinctly different for the two first-eluting α -pinene SOA products (Figure 5.17): m/z 97 [HSO₄⁻] is the base peak in the case of the firsteluting compound 1(280), while m/z 199 due to loss of SO₃ dominates the m/z 279 MS² spectrum of the second-eluting isomer 2(280). Different possible isomeric structures corresponding to sulfated hydroxypinonic acids can be suggested for the m/z 279 compounds. In this respect, it is worth mentioning that 10-hydroxypinonic acid (MW 200) has been reported by Larsen et al.⁹⁰ as a photooxidation product formed through reaction of the OH radical of both α - and β -pinene, but that multiple isomers of MW 200 were observed in each case. In addition, three isomeric hydroxypinonic acids with hydroxyl groups at the 1-, 4- and 10-positions have been considered as α -pinene SOA products formed under photooxidation and ozonolysis conditions by Winterhalter et al.⁹¹ It can be seen that the MS^2/MS^3 data of the α -pinene SOA compounds (Figure 5.17) and those eluting at the same RTs of the ambient sample (Figure 5.19) are fairly similar. However, comparison of the MS^2/MS^3 data of the α -pinene SOA compounds (Figure 5.17) with those of the β -pinene SOA compounds with exactly the same RTs reveals some differences which are at present not understood; more specifically, the m/z 279 \rightarrow m/z 199 MS³ spectra are similar in the case of the β -pinene compounds in contrast to those obtained for the α -pinene compounds. Based on the interpretation of the MS²/MS³ data and the known elemental composition of the m/z 279 ions determined from the accurate mass measurements, tentative structures and explanations for the observed product ions are proposed in Scheme 5.5 [where numerals 1-2(280) indicate the protonated compounds proposed] for the two m/z 279 organosulfates found in southeastern U.S. organic aerosol. Additional research is required to confirm the chemical structures of the m/z 279 compounds and understand the MS behaviors of these compounds.

5.6.1.6 *m/z* 310

Figures 5.20–5.21 show m/z 310 MS² TICs obtained from the α - and β-pinene/H₂O₂/NO/highly acidic seed experiments and a representative SEARCH sample (BHM 6/20/04), and MS²/MS³ data for the two major m/z 310 compounds from the ambient sample, respectively. MS^2/MS^3 data for the m/z 310 compounds eluting at similar RTs from the α - and β -pinene SOA samples are given in Figure 5.40. Interestingly, in addition to α - and β -pinene, the α - and γ -terpinene/H₂O₂/NO/highly acidic seed experiments also produced m/z 310 compounds (Tables 5.5 and 5.6); however, their RTs did not correspond to any of the ambient m/z 310 compounds, and as a result, were not considered as possible sources for these compounds. It is worth noting that the MS²/MS³ data for the selected compounds from the α - and β -pinene SOA, as well as from the ambient sample, are strikingly different. On the basis of these data, it may be concluded that the m/z 310 compounds from the ambient sample originate from BVOC precursors other than α - and β -pinene, even though both the laboratory and ambient m/z 310 compounds share a common elemental composition of C₁₀H₁₆NO₈S⁻ (Tables 5.3, 5.8, and 5.10). In the following discussion, we will consider only the two m/z 310 compounds from the ambient sample. The m/z 310 MS² spectrum of the firsteluting compound 1(311) contains m/z 247 due to loss of HNO₃, consistent with the presence of a nitrooxy group, while the $m/z 310 \rightarrow m/z 247 \text{ MS}^3$ spectrum reveals m/z 97[HSO₄] and $m/z \approx [SO_3^{-1}]$, characteristic features of a sulfate group. Another

characteristic fragmentation is the loss of 76 u (m/z 234), corresponding to a CH₂-ONO₂ radical and pointing to a terminal CH_2 -ONO₂ group. The m/z 310 MS² spectrum of the second-eluting major compound 2(311) shows m/z 142, indicating that the sulfate and nitrooxy groups in the molecule are proximate. Other diagnostic ions include m/z 263 due the combined loss of H and NO₂ radicals, and m/z 245, 219 and 193 due to a subsequent loss of H_2O , C_3H_8 and C_5H_{10} , respectively. Taking into account the fragmentation behaviors and the elemental compositions, tentative structures are proposed for the m/z 310 compounds from the ambient sample in Scheme 5.6 [where numerals 1-2(311) indicate the protonated compounds proposed]. The major nitrooxyorganosulfate compound 2(311) can be related to *p*-menth-6-en-2-one, a known constituent of the essential oil of many plants, e.g., *Eucalyptus* species.⁹² Additionally, as suggested for the m/z 294, 296, and 279 organosulfates, photooxidation experiments of myrcene and ocimene in the presence of NO_x and acidified sulfate seed aerosol may provide additional insights into the sources of the m/z 310 compounds, especially owing to their high emission strengths from coniferous and deciduous trees during summertime conditions in the U.S. $^{79-81}$

5.6.1.7 *m/z* 373

Iinuma et al.²⁶ previously determined that the elemental compositions of $[M - H]^$ ions at *m/z* 373 detected in ambient aerosol collected from a forested site in Europe by (–)ESI-MS techniques are C₁₀H₁₇N₂O₁₁S⁻. This prior study observed these compounds only in nighttime samples. Based on the mass spectral behaviors of these previously detected compounds, tentative structures were proposed containing two nitrooxy groups, and monoterpenes containing two double bonds (e.g., limonene) were suggested as the BVOC precursors; however, no laboratory experiments were conducted to confirm these structures.

Figure 5.41 compares the UPLC/(–)ESI-TOFMS EICs of m/z 373 obtained from two monoterpene experiments conducted in the present study, which include the *d*-limonene/H₂O₂/NO/highly acidic seed and β -phellandrene + *d*-limonene/H₂O₂/highly acidic seed experiments, to that of one representative SEARCH field sample (BHM $\frac{6}{20}$, respectively. Accurate mass data for all chromatographic peaks highlighted in this figure indicates that the $[M - H]^-$ ion formulae for both the laboratory-generated (Figure 5.41a–c) and ambient m/z 373 compounds (Figure 5.41d) are C₁₀H₁₇N₂O₁₁S⁻. In addition to d-limonene and β -phellandrene, the photooxidation of all other monoterpenes containing two double bonds, which included α -terpinene, γ -terpinene, and terpinolene (Tables 5.5–5.7, respectively), also produced m/z 373 compounds with the same elemental compositions as those observed in the ambient samples (Table 5.10); however, none of these compounds have the same RTs as those found in the ambient samples, indicating that some other monoterpene not examined in the present study is likely the Unlike the photooxidation experiments, it is worth noting that the source. d-limonene/NO₃/highly acidic experiment did not produce m/z 373 compounds, likely resulting from the large nucleation event observed at the start of the experiment, and as a result, preventing the reactive uptake of gas-phase precursors. From our set of laboratory data (Tables 5.2 and Tables 5.3–5.8), it now appears that monoterpenes with one double bond do not contribute to the formation of these compounds in ambient aerosol.

To gain insight into the source of the compounds, Figures 5.22–5.23 show m/z 373 MS² TICs obtained from a representative SEARCH sample (BHM 6/20/04) and the

 MS^2/MS^3 data for the two major compounds 1–2(373) found in the ambient aerosol. respectively; it should be noted that both the HPLC/(-)ESI-LITMS and UPLC/(-)ESI-TOFMS techniques observed these two major late-eluting m/z 373 compounds (Figures Figure 5.22 and Figure 5.41c). In agreement with the findings of Iinuma et al.²⁶, the m/z373 MS^2 spectra are very similar for the two compounds, revealing m/z 310 (loss of HNO₃) as the base peak. Subsequent fragmentation of m/z 310 proceeds through a second loss of HNO₃, affording m/z 247. In the case of compound 2(373), the m/z 373 \rightarrow m/z 310 MS³ spectrum also shows an ion at m/z 234 due to the loss of a CH₂-ONO₂ radical (76 u) and m/z 233 due to subsequent loss of a hydrogen radical. Furthermore, the weak m/z 142 ion suggests that the sulfate and nitrooxy groups in the m/z 310 precursor ion are spatially close. Taking into account this fragmentation behavior and the elemental compositions determined from the accurate mass measurements (Table 5.10), a tentative structure with a myrcene skeleton is proposed in Scheme 5.7 [where numerals 1–2(374) indicate the protonated compounds proposed] for the m/z 373 compounds from the ambient sample. Since myrcene is one of the five major monoterpenes that are emitted from the loblolly pine (*Pinus taeda* L.),^{79,80} a species native to the southeastern U.S., it would be worthwhile to evaluate whether myrcene serves as a precursor for the m/z 373 compounds. Additionally, other monoterpenes with multiple double bonds, such as ocimene, should also be evaluated in future laboratory experiments.

5.6.1.8 Uncharacterized organosulfates detected at *m/z* 239, 281, 283, 324, 326, 342,

and 387 in SEARCH samples likely attributable to monoterpenes

In addition to the ions already characterized in this study, close examination of Table 5.10 reveals that many other $[M - H]^-$ ions detected in the field samples by the

UPLC/(–)ESI-TOFMS technique have elemental compositions containing 9 or 10 carbon atoms, which indicate monoterpenes as a potential source. The $[M - H]^{-}$ ion formulae determined from the UPLC/(–)ESI-TOFMS accurate mass data were $C_{10}H_{17}O_7S^-$, $C_9H_{15}O_8S^-$, $C_{10}H_{14}NO_9S^-$, $C_{10}H_{16}NO_9S^-$, $C_{10}H_{16}NO_{10}S^-$, and $C_{10}H_{15}N_2O_{12}S^-$, for m/z 281, 283, 324, 326, 342, and 387, respectively. Although both m/z 239 isomers observed in the SEARCH samples have an elemental composition of $C_7H_{11}O_7S^-$, which does not clearly support a monoterpene source, the early-eluting isomer has the same RT and elemental composition as that of the *d*-limonene SOA m/z 239 compound; however, additional research and characterization is needed in order to confirm d-limonene as the source of this early-eluting compound. Notably, Lee et al.⁸² observed a gas-phase product of MW 142 from the photooxidation of d-limonene in the presence of NO_x, and suggested that this product corresponds to a C_7 -diketone aldehyde. As indicated in Table Table 5.4, the laboratory-generated limonene m/z 239 organosulfate is proposed to form as the sulfate derivative of this MW 142 product; specifically, the aldehyde function forms a gem-diol followed by esterification with sulfuric acid.

The m/z 281 compounds observed in the SEARCH samples have the same elemental composition of the single isomer previously observed in SOA produced from the ozonolysis of *d*-limonene in the presence of acidic seed aerosol;²⁵ however, it was found in the present study that the m/z 281 compounds produced in the *d*-limonene SOA (Table 5.4) do not have the same RTs as those in the ambient samples (Table 5.10). Further work is needed to confirm whether limonene or a limonene-like precursor is the source of these compounds. Although other monoterpenes, including α -pinene (i.e., only the H₂O₂/highly acidic seed experiment), *l*-limonene, α -terpinene, terpinolene, and

 β -pinene, examined in this study produced *m/z* 281 compounds with the same elemental compositions as those observed in the ambient aerosol, these monoterpenes are not considered as the source of these compounds owing to the differences in the RTs.

The *m/z* 283 organosulfate was detected only on one day (6/17/04) from the BHM SEARCH site (Table 5.10). Although the α -terpinene/H₂O₂/NO/highly acidic seed experiment produced one *m/z* 283 compound with the same elemental composition (i.e., C₉H₁₅O₈S⁻) as the compound observed in the ambient sample, this monoterpene was not considered as a source for this compound owing to the differences in the RTs. Additionally, the β -pinene and terpinolene experiments produced *m/z* 283 compounds; however, these monoterpenes were also ruled out as potential sources for this compound in the ambient aerosol due to the differences in the elemental compositions. Based on the current laboratory findings (Tables 5.3–5.8), monoterpenes with more than one double bond, such as myrcene and ocimene, are candidate precursors of this compound.

Despite the absence of m/z 324 nitrooxy organosulfates in the current set of monoterpene experiments (Table 5.2), several of the monoterpenes, including *d*-limonene, *l*-limonene, terpinolene, and β -pinene, were found to produce m/z 326 nitrooxy organosulfates. The accurate mass data for all these laboratory-generated m/z 326 compounds indicate that these ions have an elemental composition of C₁₀H₁₆NO₉S⁻, consistent with the ambient compounds (Table 5.10); however, the oxidation of these monoterpenes did not produce these compounds with the same RTs and corresponding tandem MS data. As for the m/z 283 compound, our laboratory data suggest that an unidentified monoterpene is the likely source for the m/z 326 nitrooxy organosulfates.

Inuma et al.²⁶ previously detected m/z 342 compounds in aerosol collected from a forested site in Germany with the same elemental compositions (i.e., C₁₀H₁₆NO₁₀S⁻) as those observed in the SEARCH field samples. Interestingly, this prior study observed the m/z 342 nitrooxy organosulfates only in nighttime samples. None of the monoterpene (i.e., α -pinene, *d*-limonene, and *l*-limonene) nighttime oxidation experiments in the present study produced m/z 342 compounds; however, the photooxidation of α -pinene, β -pinene, and α -terpinene in the presence of NO_x and highly acidic seed aerosol did produce m/z 342 compounds with the same elemental compositions as those observed in the ambient samples. Although the latter experiments produced m/z 342 compounds, the monoterpenes examined in the present study are not considered as sources for these compounds in ambient aerosol owing to the differences in the RTs and in the tandem MS data. Further experimental work is needed in order to confirm and identify the source of the m/z 342 nitrooxy organosulfates, especially since these compounds have relatively large signals and many isomeric forms in the ambient aerosol.

Similar to the m/z 342 compounds, the m/z 387 compound was previously observed using (–)ESI-MS techniques in our initial characterization of ambient PM_{2.5} collected from the southeastern U.S.; however, the formation mechanism and structure of this compound was also not determined. As shown in Figure 5.1, the m/z 387 compound was abundantly detected on some days in the ambient aerosol. Although none of the monoterpene oxidation experiments formed a m/z 387 nitrooxy organosulfate, it is likely that this compound is formed from a monoterpene (e.g., myrcene) not examined in the current study since its elemental composition (i.e., C₁₀H₁₅N₂O₁₂S⁻) determined from the accurate mass measurements (Table 5.10) suggests a monoterpene part.

5.6.2 Organosulfates of Isoprene in Ambient Aerosol

5.6.2.1 *m/z* 244

Figures 5.24 and 5.25 show m/z 244 MS² TICs obtained from an isoprene/NO_x/SO₂ EPA photooxidation experiment and a SEARCH sample (CTR 6/11/04), and MS²/MS³ data for the m/z 244 compounds from both samples, respectively. As shown in Tables 5.9 and 5.10, both the Caltech isoprene/H₂O₂/NO/acidic seed and isoprene/HONO/neutral seed experiments also produced m/z 244 compounds with the same RTs and elemental compositions (i.e., C₅H₁₀NO₈S⁻) as those observed in the SEARCH samples. Even though not previously detected in ambient aerosol, Surratt et al.²³ previously proposed that these laboratory-generated compounds formed from the esterification of a hydroxyl group contained within a 2-methylglyceric acid nitrate with sulfuric acid. This previous proposal now appears incorrect owing to the elemental compositions determined from the accurate mass data collected in the present study (Tables 5.9 and 5.10), as well as the MS²/MS³ data not supporting such a structure.

It can be seen that the m/z 244 MS² spectra shown in Figure 5.25 reveal some differences; the spectrum obtained for the ambient sample is more complex, however. In both cases m/z 226 and 197, due to the loss of water and the combined loss of hydrogen and NO₂ radicals, respectively, are the most abundant product ions. Furthermore, it can be noted that the m/z 244 $\rightarrow m/z$ 197 MS³ spectra are similar, and moreover, show the same product ions as the m/z 260 $\rightarrow m/z$ 197 MS³ spectra obtained for nitrooxy organosulfates of 2-methyltetrols in the prior study by Gómez-González et al.⁴⁶ This leads us to propose nitrooxy organosulfate structures of C₅-alkane triols for the m/z 244 compounds. Based on the interpretation of the MS²/MS³ data and the known elemental composition of the m/z 244 ions determined from the accurate mass measurements, tentative structures and explanations for the observed product ions are proposed in Scheme 5.8 [where numerals 1–2(245) indicate the protonated compounds proposed]. In the case of the isoprene SOA sample, the mass spectral behavior of the m/z 244 compound can be addressed with a structure of a nitrooxy organosulfate of 2-methyl-1,2,3-butanetriol 1 (245). In regards to the m/z 244 MS² spectrum of the ambient sample, it can be noted that an ion at m/z 211 is present, corresponding to the combined loss of water and a methyl radical. This suggests that the ambient sample contains one or more additional m/z 244 isomeric compounds; the structure of a nitrooxy organosulfate of 3-methyl-1,2,4-butanetriol 2 (245) allows us to explain quite readily m/z 211 in the m/z 244 MS² spectrum, as well as the abundant m/z 149 ion in the m/z 244 $\rightarrow m/z$ 226 MS³ spectrum. The formation of C₅-alkane triols through photooxidation of isoprene has to our knowledge not yet been documented in the literature.

5.6.2.2 *m/z* 305

Figures 5.26–5.28 show m/z 305 MS² TICs obtained from an isoprene/NO_x/SO₂ EPA photooxidation experiment and a SEARCH sample (CTR 6/11/04), and MS²/MS³ data for the m/z 305 compounds from both samples, respectively. The m/z 305 compounds correspond to 2-methyltetrols containing one sulfate and two nitrooxy groups; hence, many stereo- and positional isomers are possible, as shown by the number of chromatographic peaks in Figure 5.26. Recent work of the Caltech laboratory has shown that the NO₃-initiated oxidation of isoprene under dark conditions, in the presence of either non-acidified or highly acidified sulfate seed aerosol, also produces m/z 305 compounds.⁹³ The further oxidation of a C₅-hydroxynitrate, a known first-generation gas-

phase product, by NO₃ was shown to yield a dihydroxydinitrate that subsequently reacts in the particle-phase by esterification with sulfuric acid. Interestingly, UPLC/(–)ESI-TOFMS accurate mass measurements made in this prior study indicated that the elemental composition of these ions is $C_5H_9N_2O_{11}S^{-,93}$ consistent with the accurate mass measurements made for the *m/z* 305 compounds found in both the SEARCH (Table 5.10) and Caltech isoprene SOA samples (Table 5.9), and as a result, shows that either the photooxidation (in the presence of NO_x) or nighttime oxidation of isoprene in the presence of sulfate seed aerosol leads to the formation of these compounds.

While eight isomeric m/z 305 compounds are detected in the laboratory SOA sample (Figure 5.26a), only the five first-eluting isomers are seen in the ambient samples. In the following discussion, we will address only the structures of two of the four major m/z 305 isomers from the ambient sample, namely, those with RTs 15.7 min [2(306)] and 19.0 min [4(306)]. Possible structures for these compounds are proposed and supported in Scheme 5.9 [where numerals 2 and 4(306) indicate the protonated compounds proposed]; insufficient MS structural information was available in the case of the three The four major m/z 305 compounds have as base peak m/z 242, other isomers. corresponding to the loss of HNO₃ (63 u). In regards to compound 2(306), the ion at m/z165 due to the combined loss of CH₃ and ONO₂ radicals (77 u) in the m/z 305 $\rightarrow m/z$ 242 MS³ spectrum is consistent with a nitrooxy group and a methyl substituent at neighboring positions. The ion at m/z 139 in the m/z 305 MS² spectrum of compound 4(306) points to a sulfated nitrooxy diol part and a terminal sulfate group. Furthermore, the m/z 305 \rightarrow m/z 242 MS³ spectrum reveals ions at m/z 142, indicating that the sulfate and nitrooxy group in the m/z 242 precursor ion are proximate, at m/z 195, due to the combined loss of a hydrogen and a NO₂ radical (47 u), and, at m/z 179 and 165, which can be attributed to further loss of CH₄ and CH₂O, respectively, from m/z 195.

Based upon the interpretation of both the accurate mass and tandem MS data, Figure 5.29 shows the proposed formation mechanism for the two characterized m/z 305 nitrooxy organosulfates [i.e., compounds **2** and **4**(306)] observed in the ambient aerosol. In conjunction with our previous analysis of SOA produced from the NO₃-initiated oxidation of isoprene under dark conditions in the presence of sulfate seed aerosol,⁹³ it now appears that both the photooxidation (in the presence of NO_x) and the nighttime oxidation of isoprene could yield these products in ambient aerosol; however, nighttimesegregated samples need to be analyzed from the SEARCH network in order to determine which pathway is more important for ambient aerosol. As for many of the ions already discussed, these nitrooxy organosulfates should form from the particle-phase esterification of one of the hydroxyl groups contained within a dihydroxy dinitrate with sulfuric acid.

5.6.2.3 *m/z* 333 and 331

Figures 5.30–5.34 show m/z 333 and 331 MS² TICs obtained from an isoprene/NO_x/SO₂ EPA photooxidation experiment and a SEARCH sample (CTR 6/11/04), and MS²/MS³ data for m/z 333 and 331 compounds from both samples. Surratt et al.²³ tentatively identified the m/z 333 compounds as the sulfated form of hemiacetals formed between 2-methyltetrols and a C₅-dihydroxycarbonyl, i.e., 1,2-dihydroxy-3-methylbutane-4-one. It can be seen that the m/z 333 compounds elute as broad peaks in both samples, which is as expected since many stereo- and positional isomers are possible. In this respect it is worth mentioning that six partly resolved

hemiacetal dimers could be observed by GC/MS with prior trimethylsilylation for SOA from an isoprene photooxidation experiment at low-NO_x.³³ Again, as in the case of the m/z 244 and 305 compounds discussed above, isomeric differences can be noted between the m/z 333 compounds from isoprene SOA and the ambient sample. The m/z 333 MS² spectra for the middle sections of the peaks with RTs 3.8 and 4.9 min from isoprene SOA reveal clear differences for the relative abundances of the product ions at m/z 215 and 197, indicating that the sulfate group is primarily located in the 2-methyltetrol and C₅-dihydroxycarbonyl part for the isomeric mixtures with RTs 3.8 and 4.9 min, respectively. Possible structures for m/z 333 compounds are given and supported in Scheme 5.10 [where numerals 1-2(334) indicate the protonated compounds proposed]; accurate mass measurements of both the Caltech laboratory-generated and SEARCH m/z333 compounds indicates that these ions share the same elemental composition of $C_{10}H_{21}O_{10}S^{-}$, and as a result, further confirm the proposed structures. The m/z 333 $\rightarrow m/z$ 215 MS³ spectrum obtained for the m/z 333 isomeric mixture eluting at 3.8 min is exactly the same as the m/z 215 MS² spectrum reported in the prior study by Gómez-González et al.⁴⁶ for sulfated 2-methyltetrol isomers, demonstrating that the sulfate group in the m/z333 compounds is located in the 2-methyltetrol part. It is noted that the m/z 333 $\rightarrow m/z$ 197 MS^3 spectrum of the m/z 333 compounds eluting at 4.9 min is strikingly similar to the $m/z 244 \rightarrow m/z 197 \text{ MS}^3$ spectrum of the m/z 244 compounds. This led us to revise the structure of the C_5 -dihydroxycarbonyl part as 2,3-dihydroxy-2-methylbutane-1-one. It is worth mentioning that the C5-dihydroxycarbonyl part, tentatively attributed to 1,2-dihydroxy-3-methylbutane-4-one in the prior study by Surratt et al.,³³ was based on MS data of trimethylsilyl derivatives obtained in a preceding study for the corresponding

non-sulfated products with MW 254. It was verified here that the latter MS data are also consistent with the new revised C₅-dihydroxycarbonyl structure. The m/z 333 $\rightarrow m/z$ 197 MS³ spectrum reveals m/z 97 [HSO₄⁻] as base peak and product ions at m/z 179, 167, 153 and 139, which are all readily explained with the revised sulfated C₅-dihydroxycarbonyl structure.

In regards to the m/z 331 compounds, it can be seen that the m/z 331 MS² spectra (Figures 5.33 and 5.34) show features that are similar to those of the m/z 333 compounds, i.e. the presence of m/z 215 and 197, of which the latter ion shows exactly the same fragmentation behavior as for the m/z 333 compounds. In addition, a product ion at m/z195 can be observed in the m/z 331 MS² spectra; however, the fate of this ion is not the same for isoprene SOA and the ambient sample. While m/z 331 fragments to m/z 123 in isoprene SOA (Figure 5.33), fragmentation to m/z 137 occurs for the ambient sample (Figure 5.34b). Possible structures for the m/z 331 compounds from isoprene SOA (RT 5 min) [1(332)] and the ambient sample (RT 5.1 min) [2(332)] taking into account their fragmentation behaviors are given in Scheme 5.11 [where numerals 1-3(332) indicate the protonated compounds proposed]. The proposed C₅-hydroxydicarbonyl part in the m/z331 compound from the ambient sample has likely a precursor that is different from isoprene. The m/z 331 compound with RT 4.1 min [3(332)] from the ambient sample shows m/z 133 as a base peak in its MS² spectrum, an ion that was elucidated in the prior study by Gómez-González et al.⁴⁶ and attributed to a sulfate derivative of 4,5-dihydroxypentanoic acid, which is believed to originate from the photooxidation of 4-pentenal, which in turn may result from the oxidative decay of unsaturated fatty acids. The m/z 331 $\rightarrow m/z$ 133 MS³ spectrum perfectly agrees with the m/z 133 MS² spectrum

reported for sulfated 4,5-dihydroxypentanoic acid in the cited study. A possible structure for the first-eluting m/z 331 compound [3(332)] in the ambient sample is presented in Scheme 5.11.

5.6.2.4 Other Organosulfates of Isoprene detected at m/z 155, 169, 211, 213 and 260

Similar to previously characterized organic aerosol collected from K-puszta, Hungary and an isoprene/NO_x/SO₂ EPA photooxidation experiment,⁴⁶ the $[M - H]^-$ ions at m/z 155 and 169 detected in the SEARCH (5.10) and the Caltech laboratory-generated isoprene SOA samples (Table 5.9) are attributed to organosulfates (i.e., sulfate derivatives) of glyoxal and methylglyoxal, respectively. The accurate mass measurements obtained for the m/z 155 and 169 compounds in the latter two samples indicate that the elemental compositions of these ions are $C_2H_3O_6S^-$ and $C_3H_5O_6S^-$, respectively. MS² product-ion spectra (not shown) for both of these organosulfates show a major product ion at m/z 97 [HSO₄⁻], consistent with prior work⁴⁶ and the neutral nature of the non-sulfated part of these compounds, as well as further confirming our characterization. It is worth mentioning that Gómez-González et al.⁴⁶ observed two chromatographic peaks for m/z 155 glyoxal organosulfates; the first-eluting compound co-eluted with inorganic sulfate and was explained by reaction of glyoxal and inorganic sulfate in the electrospray ionization source, while the second-eluting compound was attributed to the α -hydroxysulfate ester of glyoxal present in the sample. In addition, this prior study also considered the non-covalent adduct formed between glyoxal and sulfuric acid; theoretical calculations indicate that the organosulfate of glyoxal exists in the a-hydroxysulfate ester (i.e., sulfate derivative) form rather than the non-covalent adduct form. As shown in Figure 5.1, chromatographic separation was achieved between

inorganic sulfate and the organosulfate of glyoxal in the present study, providing further confirmation that the organosulfate of glyoxal is not an artifact or non-covalent adduct formed in the electrospray ionization source. Our previous characterization of organic aerosol collected from the June 2004 SEARCH campaign failed to detect the organosulfates of glyoxal and methylglyoxal owing to the solid-phase extraction (SPE) technique employed to desalt the filter samples before MS analysis.⁴⁷ Interestingly, from our detailed investigation of organosulfate formation in both isoprene and monoterpene SOA (Tables 5.2 and Tables 5.3-5.9), it appears that isoprene is the only BVOC in this study to yield organosulfates of glyoxal and methylglyoxal; this is an important finding owing to the fact that recent global estimates indicate that isoprene oxidation is the most important precursor for both dicarbonyls (i.e., contributing 47% of glyoxal and 79% of methylglyoxal globally).⁹⁴ As shown in Table 5.9, only the photooxidation of isoprene under intermediate (H₂O₂/NO)- and/or high (HONO)-NO_x conditions in the presence of sulfate seed aerosol produces the organosulfates of glyoxal and methylglyoxal, suggesting that this pathway is responsible for a large fraction of these compounds found in ambient aerosol. Oxidation of anthropogenic VOCs, such as aromatic compounds and acetylene, are also known to be a significant source of glyoxal and methylglyoxal,⁹⁴ and as a result, may potentially contribute to the organosulfate formation of both these compounds. Laboratory chamber experiments are needed in order to establish whether organosulfates of glyoxal and methylglyoxal form from the oxidation of aromatics in the presence of acidified sulfate seed aerosol.

Organosulfates at m/z 211 and 213 have previously been observed in ambient aerosol collected from K-puszta, Hungary; however, chemical structures were elucidated

only for the m/z 213 organosulfates, resulting in the source of the m/z 211 remaining unknown.⁴⁶ In this prior study the m/z 213 compounds were attributed to isomeric organosulfates of 4,5-dihydroxypentanoic and 2,3-dihydroxypentanoic acids, and it was suggested that 4-pentenal, a likely gas-phase product from the oxidative decay of unsaturated fatty acids, and 2-pentenal, a photolysis product of the plant-leaf volatile Z-3-hexenal, were the VOC precursors for these organosulfates. Notably, we find that both the Caltech isoprene/H₂O₂/acidic seed photooxidation experiment and the SEARCH samples contain m/z 213 organosulfates (Tables 5.9 and 5.10, respectively) with the same elemental composition (i.e., C₅H₉O₇S⁻) as those previously observed by Gómez-González et al.⁴⁶ for K-puszta aerosol. In addition to sharing the same elemental composition, the m/z 213 organosulfates detected in both the Caltech isoprene/H₂O₂/acidic seed experiment and the SEARCH samples were found to have the same RTs, suggesting that isoprene is a likely source for these compounds. It should be noted that the m/z 213 compounds were not detected by Gómez-González et al.⁴⁶ in the aerosol collected from an isoprene/ NO_x/SO_2 EPA photooxidation experiment. It appears that the photooxidation of isoprene under low-NO_x (or NO_x-free) conditions in the presence of acidified sulfate seed aerosol produces m/z 213 organosulfates in ambient aerosol; however, work is needed in order to further characterize these products as well as identify their detailed formation mechanism. Although the source for the m/z 211 compounds remained unknown in K-puszta aerosol analyzed by Gómez-González et al.,⁴⁶ the Caltech isoprene/H₂O₂/acidic seed experiment (Table 5.9) produced an m/z 211 organosulfate with the same elemental composition (i.e., $C_5H_7O_7S^-$) and RT as that of one of the isomeric m/z 211 compounds detected in the SEARCH samples (Table 5.10).

Interestingly, the three remaining, later-eluting isomeric m/z 211 organosulfates observed in the SEARCH samples were not detected in the Caltech isoprene photooxidation experiments, suggesting that some other VOC precursor, such as unsaturated fatty acids, are responsible for the formation of these compounds. It is noted that isoprene was the only BVOC in this study to produce the m/z 211 and 213 organosulfates in the laboratory-generated BSOA.

Although m/z 260 compounds have been previously detected and thoroughly characterized as isomeric organosulfates of the 2-methyltetrol mononitrates in K-puszta aerosol⁴⁶ and in isoprene SOA,^{23,46} these compounds were not previously detected in the initial analysis of aerosol collected from the SEARCH network,⁴⁷ owing to the use of less advanced mass spectrometric techniques. As shown in Tables 5.9 and 5.10, the accurate mass measurements indicate that these compounds have an elemental composition of C₅H₁₀NO₉S⁻, confirming the initial characterization of these compounds in SOA as well as identifying isoprene as the VOC precursor.

5.7 Conclusions

The presence of organosulfates and nitrooxy organosulfates of both monoterpenes and isoprene in ambient samples is confirmed. With the exception of the organosulfates of glyoxal and methylglyoxal, our results indicate that all of the organosulfates characterized in this study should be considered as unique tracers for the occurrence of biogenic SOA formation under acidic conditions. Owing to the fact that glyoxal and methylglyoxal are also oxidation products from anthropogenic VOCs (such as aromatics – e.g. toluene), oxidation experiments of these VOCs under acidic conditions are needed in order to confirm whether they serve as additional sources of organosulfates of glyoxal and methylglyoxal in ambient fine aerosol.

Laboratory studies of isoprene and monoterpene oxidation have tended to employ levels of seed aerosol acidity that exceed those expected in ambient aerosol. These studies have established seed aerosol acidity either by adding sulfuric acid to ammonium sulfate solutions or by oxidizing gas-phase SO₂, resulting in sulfate aerosol mass. These approaches leave it unclear as to whether organosulfate formation is dependent upon either the sulfate aerosol mass concentration or acidity. In this regard, Surratt et al.²³ found that organosulfates and nitrooxy organosulfates of isoprene form in the presence of non-acidified sulfate seed aerosol; however, it was found that as the sulfuric acid concentration increased in the atomization solution, so did the number of organosulfate and nitrooxy organosulfate products. Further work is required to elucidate the extent to which sulfate aerosol mass concentration, level of acidity, and ionic strength affect the organosulfate formation potential from isoprene and monoterpenes in ambient aerosol. Furthermore, it has been suggested that organosulfate formation occurs on the acidic surface (and not in the bulk) of a fine ambient aerosol particle, as a result of condensation of semi-volatile organic vapors and subsequent reaction with sulfuric acid, and gives rise to a refractory organic film.^{64,95} It would be worthwhile to confirm in further studies with suitable analytical techniques (e.g., transmission electron microscopy) the occurrence of organosulfates on the surface of ambient fine aerosols.

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compound	structure	formula (MW)	k _{он} ,ª cm³ molec ⁻¹ s ⁻¹	k ₀₃ , ^{<i>a,b,c</i>} cm ³ molec ⁻¹ s ⁻¹	k _{NO3} , ^{a,d} cm ³ molec ⁻¹ s ⁻¹
isoprene		C₅H ₈ (68)	9.9 x 10 ⁻¹¹	1.3 x 10 ⁻¹⁷	7.0 x 10 ⁻¹³
α-pinene	\bigwedge	C ₁₀ H ₁₆ (136)	5.3 x 10 ⁻¹¹	8.4 x 10 ⁻¹⁷	6.2 x 10 ⁻¹²
β-pinene		C ₁₀ H ₁₆ (136)	7.4 x 10 ⁻¹¹	1.5 x 10 ⁻¹⁷	2.5 x 10 ⁻¹²
limonene	$\sum_{i=1}^{i}$	C ₁₀ H ₁₆ (136)	1.7 x 10 ⁻¹⁰	2.1 x 10 ⁻¹⁶	1.2 x 10 ⁻¹⁰
a-terpinene		C ₁₀ H ₁₆ (136)	3.6 x 10 ⁻¹⁰	2.1 x 10 ⁻¹⁴	1.4 x 10 ⁻¹⁰
γ-terpinene	¢ ¢	C ₁₀ H ₁₆ (136)	1.8 x 10 ⁻¹⁰	1.4 x 10 ⁻¹⁶	2.9 x 10 ⁻¹¹
terpinolene	$\left \right\rangle$	C ₁₀ H ₁₆ (136)	2.3 x 10 ⁻¹⁰	1.9 x 10 ⁻¹⁵	9.7 x 10 ⁻¹¹
Δ^3 -carene	Þ	C ₁₀ H ₁₆ (136)	8.8 x 10 ⁻¹¹	3.7 x 10 ⁻¹⁷	9.1 x 10 ⁻¹²
β -phellandrene		C ₁₀ H ₁₆ (136)	1.7 x 10 ⁻¹⁰	4.7 x 10 ⁻¹⁷	8.0 x 10 ⁻¹²
limonaketone	\diamond	C₃H₁₄O (138)	-	2.7 x 10 ⁻¹⁶	-

 Table 5.1. Biogenic volatile organic compounds studied.

^aRate constants were obtained from Atkinson and Arey⁵⁵ [and references therein].

^bNo ozonolysis experiments were conducted; however, rates are reported here to show that

under the conditions of the chamber experiments, OH and NO3 radicals dominate the initial oxidation

of the BVOCs during photooxidation and nighttime-oxidation experiments, respectively.

 $^{\circ}\text{Rate}$ constant for limonaketone was measured by Donahue et al. 54

 ${}^{d}\alpha$ -Pinene and d-//-limonene were the only three BVOCs for which reactions with NO₃ radicals was studied.

bydrocarbon	initial [HC]	oxidant	sood typob	initial [NO]	initial [NO₂] (nnh)	initial [O₃]	T° (°C)	RH°	total SOA volume ^c (um ³ cm ⁻³)	$[M - H]^{-}$ detected organosulfate ions $(m/2)$
α-pinene	41	H ₂ O ₂	neutral	<u>(ppb)</u> < 2	<u>(ppb)</u> < 2	2	31.2	3.8	(µm cm) 82	none detected
α-pinene	46	H ₂ O ₂	highly acidic	< 2	< 2	2	26.4	5.5	145	237, 279 ^d , 281, 297
α-pinene	47	H ₂ O ₂ /NO	neutral	303	4	3	25.6	7.2	104	none detected
α-pinene	61	H ₂ O ₂ /NO	acidic	488	12	2	27.1	4.3	151	279 ^{<i>d</i>} , 342
α-pinene	53	H ₂ O ₂ /NO	highly acidic	507	5	3	25.7	5.7	189	223, 227 ^d , 237, 249 ^d , 265, 279 ^d , 294 ^d , 310 ^d , 342
α -pinene	81	HONO	neutral	463	447	2	23.8	< 4.5	78	none detected
α-pinene	78	HONO	acidic	509	468	2	29.1	3.4	62	265, 279 ^d , 310 ^d , 342
α-pinene	104	HONO	highly acidic	522	429	< 2	25.2	4.5	96	247, 249 ^d , 265, 279 ^d , 294 ^d , 310 ^d , 342
α-pinene	~100	$NO_2 + O_3 / dark$	netural	< 2	170	45	20.3	6.3	52	none detected
α -pinene	~100	$NO_2 + O_3 / dark$	highly acidic	< 2	212	47	21.0	5.8	107	247, 249 ^d , 279 ^d , 294 ^d , 310 ^d , 339, 355
d-limonene	93	HONO	acidic	499	479	3	27.1	4.0	92	251, 281, 312, 330, 389
d-limonene	91	H ₂ O ₂ /NO	highly acidic	504	< 2	2	27.2	5.0	340	239 ^d , 249, 251, 267, 279, 296 ^d , 312, 326, 328, 373 ^d
d-limonene	~100	$NO_2 + O_3 / dark$	highly acidic	< 2	140	54	19.0	5.8	525	312, 328
I-limonene	86	H ₂ O ₂ /NO	highly acidic	508	12	2	27.8	4.4	186	239 ^d , 249, 251, 267, 279, 281, 296 ^d , 312, 326, 330, 373
I-limonene	~50	$NO_2 + O_3 / dark$	highly acidic	< 2	186	38	21.4	5.4	373	239 ^{<i>d</i>} , 279, 312, 328, 389
phellandrene /d-limonene	~100 (total)	H ₂ O ₂ /NO	highly acidic	428	< 2	< 2	26.9	3.7	169	239ª, 251, 267, 296ª, 326, 238, 373
limonaketone	~150	H ₂ O ₂ /NO	highly acidic	< 2	494	< 2	26.8	5.9	384	249, 251, 267, 296 ^d , 312
α -terpinene	141	HONO	acidic	489	479	4	26.6	3.8	57	265, 281, 283, 297, 373
α -terpinene	123	H ₂ O ₂ /NO	highly acidic	505	10	< 2	26.5	4.9	153	253, 265, 279, 281, 283, 294, 297, 310, 342, 373
γ-terpinene	85	H ₂ O ₂ /NO	highly acidic	497	8	3	26.4	8.3	142	279, 310, 373
terpinolene	34	H ₂ O ₂ /NO	highly acidic	483	17	< 2	25.5	8.6	101	249, 265, 281, 283, 294, 297, 326, 373
β -pinene	62	H ₂ O ₂ /NO	highly acidic	469	< 2	3	26.2	5.9	232	249 ^d , 263, 279 ^d , 281, 283, 294 ^d , 310 ^d , 326, 342
Δ^3 -carene	~100	H ₂ O ₂ /NO	highly acidic	496	< 2	< 2	26.6	3.7	123	342 ^e

Table 5.2. Summary of experimental conditions and organosulfate formation from monoterpene oxidation chamber experiments.

^a H₂O₂ and HONO serve as OH radical sources in photooxidation experiments. NO₂ + O₃ reaction serves as NO₃ radical source in dark experiments.

^bAtomizing solution compositions: neutral = 15 mM (NH₄)₂SO₄; acidic = 15 mM (NH₄)₂SO₄ + 15 mM H₂SO₄;

highly acidic = 30 mM MgSO₄ + 50 mM H₂SO₄.

^cAveraged over the course of filter sampling.

^d At least one of the isomers has the same RT and exact mass as compared to the corresponding ion detected in the field samples collected from the southeastern U.S. (see Table 8S, Supporting Information).

* Unlike Tables 1S-6S (Supporting Information), no separate table for this monoterpene is provided owing to the fact that there was only one organosulfate isomer observed. The RT = 6.59 min; measured mass = 342.0529; mDa error = 3.3 mDa; ppm error = 9.6 ppm; elemental composition = C₁₀H₁₆NO₁₀S⁻.

[M − H] ⁻ ion (<i>m/z</i>)	α-pinene experiment	retention time (min)	measured mass	TOFMS suggested formula	error (mDa)	error (ppm)	proposed precursor α-pinene oxidation product	proposed organosulfate structure ^{a,b}
223	$H_2O_2/NO/highly$ acidic seed	4.07	223.0248	C7H11O6S⁻	-1.7	-7.6	not identified	not identified
227°	$H_2O_2/NO/highly$ acidic seed	0.92	226.9875	C₅H7O8S⁻	1.3	5.7	see section 5.1.4.	see section 5.1.4.
237 —	H_2O_2 /highly acidic seed	4.88	237.0432	$C_8H_{13}O_6S^{-}$	-0.1	-0.4	not identified	not identified
	H ₂ O ₂ /NO/highly acidic seed	4.87	237.0428	C ₈ H ₁₃ O ₆ S⁻	-0.5	-2.1	notidentilled	
247 —	HONO/highly acidic seed	6.62	247.0684	$C_{10}H_{15}O_5S^-$	2.4	9.7		not identified
	NO ₃ /highly acidic seed	6.62	247.0649	$C_{10}H_{15}O_5S^-$	0.9	3.6	not identified	
249°	H ₂ O ₂ /NO/highly acidic seed	6.48	249.0819	C ₁₀ H ₁₇ O ₅ S ⁻	2.2	8.8		see section 5.1.3.
		6.50	249.0809	$C_{10}H_{17}O_5S^-$	1.2	4.8	see section 5.1.3.	
	HONO/nignly acidic seed	7.32	249.0793	$C_{10}H_{17}O_5S^-$	-0.4	-1.6		
	NO ₂ /highly acidic seed	6.47	249.0803	$C_{10}H_{17}O_5S^-$	0.6	2.4		
	NO3/Highly actuic seed	7.30	249.0805	$C_{10}H_{17}O_5S^-$	0.8	3.2		
	$H_2O_2/NO/highly$ acidic seed	5.87	265.0763	$C_{10}H_{17}O_6S^-$	1.7	6.4	• • · ·	A HO AND
265	HONO/acidic seed	5.91	265.0757	C ₁₀ H ₁₇ O ₆ S⁻	1.1	4.1		
	HONO/highly acidic seed	5.92	265.0738	$C_{10}H_{17}O_6S^-$	-0.8	-3.0	MW 168 ^{d,e}	
	H.O./bighly acidic seed	5.22	279.0545	$C_{10}H_{15}O_7S^-$	0.7	2.5		see section 5.1.5.
_		5.41	279.0543	$C_{10}H_{15}O_7S^-$	0.5	1.8		
	$H_2O_2/NO/acidic seed$	5.40	279.0542	$C_{10}H_{15}O_7S^-$	0.4	1.4	see section 5.1.5.	
		5.28	279.0539	$C_{10}H_{15}O_7S^-$	0.1	0.4		
279° 	H ₂ O ₂ /NO/highly acidic seed	5.38	279.0538	$C_{10}H_{15}O_7S^-$	0.0	0.0		
		5.89	279.0542	$C_{10}H_{15}O_7S^-$	0.4	1.4		
	HONO/acidic seed	5.40	279.0524	$C_{10}H_{15}O_7S^-$	-1.4	-5.0		
	HONO/highly acidic seed	5.41	279.0540	$C_{10}H_{15}O_7S^-$	0.2	0.7	-	
	NO. /highly poidio cood	5.30	279.0550	$C_{10}H_{15}O_7S^-$	1.2	4.3		
	NO 3/Highly acture seed	5.42	279.0546	$C_{10}H_{15}O_7S^-$	0.8	2.9		
281	H_2O_2 /highly acidic seed	5.86	281.0692	C ₁₀ H ₁₇ O ₇ S ⁻	-0.3	-1.1	not identified	not identified

Table 5.3. Organosulfates of α -pinene.
		8.19	294.0670	$C_{10}H_{16}NO_7S^-$	2.3	7.8		
	H ₂ O ₂ /NO/highly acidic seed	8.80	294.0666	$C_{10}H_{16}NO_7S^-$	1.9	6.5		
		8.96	294.0656	$C_{10}H_{16}NO_7S^-$	0.9	3.1		
		8.24	294.068	$C_{10}H_{16}NO_7S^{-}$	3.3	11.2		
294°	HONO/highly acidic seed'	9.04	294.0685	$C_{10}H_{16}NO_7S^{-}$	3.8	12.9	see section 5.1.1.	see section 5.1.1.
		8.21	294.0663	C ₁₀ H ₁₆ NO ₇ S ⁻	1.6	5.4		
	NO ₃ /highly acidic seed	8.81	294.0657	$C_{10}H_{16}NO_7S^-$	1.0	3.4		
		9.00	294.0649	$C_{10}H_{16}NO_7S^-$	0.2	0.7		
297	H_2O_2 /highly acidic seed	6.27	297.0644	C ₁₀ H ₁₇ O ₈ S⁻	0.0	0.0		OH OSO3
		6.74	310.0608	C ₁₀ H ₁₆ NO ₈ S ⁻	1.1	3.5	10100 200	
		7 00	310 0599		02	0.6		
	H ₂ O ₂ /NO/highly acidic seed	7.47	310.0607	C10H16NO8S	1.0	3.2		
		7.79	310.0588	C ₁₀ H ₁₆ NO ₈ S ⁻	-0.9	-2.9		
		8.08	310.0589	C ₁₀ H ₁₆ NO ₈ S ⁻	-0.8	-2.6) OH	
	HONO/acidic seed	7.20	310.0605	C ₁₀ H ₁₆ NO ₈ S	0.8	2.6	С С ОН	oso3-
310		6.77	310.0591	C ₁₀ H ₁₆ NO ₈ S	-0.6	-1.9	O2NO	O2NO
	HONO/highly acidic seed	7.51	310.0602	C ₁₀ H ₁₆ NO ₈ S	0.5	1.6	 MW 231 ^e	-
		7.02	310.0600	$C_{10}H_{16}NO_8S^-$	0.3	1.0		
	NO /highly poidio apod	7.50	310.0595	$C_{10}H_{16}NO_8S^-$	-0.2	-0.6		
	NO ₃ /highly actuic seed	7.80	310.0603	$C_{10}H_{16}NO_8S^-$	0.6	1.9		
		8.09	310.0618	$C_{10}H_{16}NO_8S^-$	2.1	6.8		
339	NO_3 /highly acidic seed	8.65	339.0498	$C_{10}H_{15}N_2O_9S^-$	0.0	0.0	not identified	not identified
	H ₂ O ₂ /NO/acidic seed	6.76	342.0544	$C_{10}H_{16}NO_{10}S^{-}$	4.9	14.3		
2426	H ₂ O ₂ /NO/highly acidic seed	6.74	342.0529	C ₁₀ H ₁₆ NO ₁₀ S ⁻	3.4	9.9		
342	HONO/acidic seed	6.74	342.0515	C ₁₀ H ₁₆ NO ₁₀ S ⁻	0.8	2.3	notidentilled	noridentined
	HONO/highly acidic seed	6.77	342.0505	C ₁₀ H ₁₆ NO ₁₀ S ⁻	1.0	2.9		
355	NO₃/highly acidic seed	9.16	355.0429	C ₁₀ H ₁₅ N ₂ O ₁₀ S [.]	-1.8	-5.1	0N02 02N0 MW 276	0N02 02N0

^aPositional isomers containing nitrate or sulfate groups at other hydroxylated positions are likely.

^bTwo types of organosulfates are considered: (i) sulfate esters formed from the particle-phase esterification of a semivolatile product containing one or more hydroxyl groups by sulfuric acid; and (ii) sulfate derivatives formed from a semivolatile product containing an aldehyde or a keto group and sulfuric acid. The latter organosulfates require gem-diol formation followed by esterification with sulfuric acid. *At least one of the isomers has the same RT and exact mass as compared to the corresponding ion detected in the field samples collected from

the southeastern US (see Table 8S, Supporting Information).

^dA corresponding [M + H]⁺ ion was detected in the gas-phase by PTR-MS analysis done by Lee et al.⁸²

ePreviously detected and proposed α -pinene gas-phase oxidation products by Aschmann et al.^{74,75}

'Weak signals observed for these ions from this experiment.

[M − H] ⁻ ion (<i>m/z</i>)	limonene experiment	retention time (min)	measured mass	TOFMS suggested formula	error (mDa)	error (ppm)	proposed precursor limonene oxidation product	proposed organosulfate structure ^{a,b}
	<i>d</i> -limonene/H ₂ O ₂ /NO/highly acidic seed	0.95	239.0225	C7H11O7S ⁻	0.0	0.0		
230 <i>c.d</i>	/-limonene/H2O2/NO/highly acidic seed	0.94	239.023	C7H11O7S ⁻	0.5	2.1		О НО ОСО3-
200	I-limonene/NO ₃ /highly acidic seed	0.94	239.0233	C ₇ H ₁₁ O ₇ S ⁻	0.8	3.3	MW 142°	
	β-phellandrene + <i>d</i> - limonene/H ₂ O ₂ /NO/highly acidic seed	0.94	239.0219	C ₇ H ₁₁ O ₇ S ⁻	-0.6	-2.5	-	
	d-limonene/H ₂ O ₂ /NO/highly acidic seed	4.67	249.0446	C ₉ H ₁₃ O ₆ S⁻	1.3	5.2	X ^{OH}	Voso3.
249	/-limonene/H2O2/NO/highly acidic seed	4.73	249.0451	C ₉ H ₁₃ O ₆ S⁻	1.8	7.2	Q [*]	$\nabla^{\mathbf{u}}$
	limonaketone/H ₂ O ₂ /NO/highly acidic seed	4.69	249.0435	$C_9H_{13}O_6S^-$	0.2	0.8	->>> MW 170°	∕∽₀
	d-limonene/HONO/acidic seed	4.53	251.0597	$C_9H_{15}O_6S^-$	0.8	3.2		
	d-limonene/H ₂ O ₂ /NO/highly acidic seed	4.54	251.0600	C ₉ H ₁₅ O ₆ S⁻	1.1	4.4	Сонон	OH OSO3"
251	/-limonene/H2O2/NO/highly acidic seed	4.59	251.0583	C ₉ H ₁₅ O ₆ S ⁻	-0.6	-2.4	X	Y
	β-phellandrene + d- limonene/H ₂ O ₂ /NO/highly acidic seed	4.54	251.0603	$C_9H_{15}O_6S^-$	1.9	5.6	0 MW 172	~~0
	limonaketone/H ₂ O ₂ /NO/highly acidic seed	4.54	251.0576	C ₉ H ₁₅ O ₆ S⁻	-1.3	-5.2	-	
	d-limonene/H2O2/NO/highly acidic seed	4.97	267.0546	C ₉ H ₁₅ O ₇ S⁻	0.8	3.0	_	
267	/-limonene/H2O2/NO/highly acidic seed	5.02	267.0549	C ₉ H ₁₅ O ₇ S⁻	1.1	4.1		<u> </u>
207	β -phellandrene + d- limonene/H ₂ O ₂ /NO/highly acidic seed	4.99	267.0550	$C_9H_{15}O_7S^-$	1.2	4.5	\mathbf{x}_{0}	С он
	limonaketone/H ₂ O ₂ /NO/highly acidic seed	4.97	267.0543	C ₉ H ₁₅ O ₇ S⁻	0.5	1.9	MW 170 ^e	
	d limenana (H. O. (NO/highly agidis agod	4.15	279.0529	C ₁₀ H ₁₅ O ₇ S ⁻	-0.9	-3.2		
	a-informerie/r1202/NO/highly actuic seed	4.30	279.0529	C ₁₀ H ₁₅ O ₇ S⁻	-0.9	-3.2		
279	/-limonene/H2O2/NO/highly acidic seed	4.82	279.0547	$C_{10}H_{15}O_7S^-$	0.9	3.2	- OH	- oso3.
		4.85	279.0546	C ₁₀ H ₁₅ O ₇ S ⁻	0.8	2.9	MW 200	5
	I-IIMONENE/NO₃/Nighly acidic seed	5.06	279.0542	C ₁₀ H ₁₅ O ₇ S⁻	0.4	1.4		

Table 5.4. Organosulfates of limonene.

		4.84	281.0664	C ₁₀ H ₁₇ O ₇ S ⁻	-3.1	-11.0		
	d-limonene/HONO/acidic seed	5.12	281.0667	C ₁₀ H ₁₇ O ₇ S [−]	-2.8	-10.0	, k	4
281		5.37	281.0695	C ₁₀ H ₁₇ O ₇ S ⁻	0.0	0.0		
		4.92	281.0698	C ₁₀ H ₁₇ O ₇ S ⁻	0.3	1.1	OH MW 202	oso3.
	I-limonene/H2O2/NO/highly acidic seed	5.43	281.0676	C ₁₀ H ₁₇ O ₇ S⁻	-1.9	-6.8	10100 202	
	d-limonene/H ₂ O ₂ /NO/highly acidic seed	7.05	296.0431	C ₉ H ₁₄ NO ₈ S⁻	-0.9	-3.0		
		6.63	296.0443	C ₉ H ₁₄ NO ₈ S⁻	0.3	1.0		
	/-limonene/H ₂ O ₂ /NO/highly acidic seed	7.10	296.0427	C ₉ H ₁₄ NO ₈ S⁻	-1.3	-4.4		
296°		6.59	296.0457	C ₉ H ₁₄ NO ₈ S⁻	1.7	5.7	see section 5.1.2.	see section 5.1.2.
	β -preliandrene + a - limonene/H ₂ O ₂ /NO/highly acidic seed	7.06	296.0436	C ₉ H ₁₄ NO ₈ S⁻	-0.4	-1.4		
	limonaketone/H ₂ O ₂ /NO/highly acidic seed	7.06	296.0444	C ₉ H ₁₄ NO ₈ S⁻	0.4	1.4		
		4.94	312.0389	C ₉ H ₁₄ NO ₉ S⁻	0.0	0.0		
	d-limonene/HONO/acidic seed	5.36	312.0403	C ₉ H ₁₄ NO ₉ S⁻	1.4	4.5		
		5.22	312.0377	C ₉ H ₁₄ NO ₉ S [−]	-1.2	-3.8		
	d-limonene/H ₂ O ₂ /NO/highly acidic seed	6.30	312.0396	C ₉ H ₁₄ NO ₉ S⁻	0.7	2.2		
		6.61	312.0420	C ₉ H ₁₄ NO ₉ S⁻	3.1	9.9		
	d-limonene/NO ₃ /highly acidic seed	5.23	312.0402	C ₉ H ₁₄ NO ₉ S⁻	1.3	4.2		
312		5.29	312.0384	C ₉ H ₁₄ NO ₉ S ⁻	-0.5	-1.6	not identified	not identiifed
	I-limonene/H2O2/NO/highly acidic seed	5.41	312.0382	C ₉ H ₁₄ NO ₉ S⁻	-0.7	-2.2		
		6.35	312.0397	C ₉ H ₁₄ NO ₉ S⁻	0.8	2.6		
	/-limonene/NO₃/highly acidic seed	5.22	312.0389	$C_9H_{14}NO_9S^-$	0.0	0.0		
	limonaketone/H ₂ O ₂ /NO/highly acidic	4.94	312.0396	C ₉ H ₁₄ NO ₉ S⁻	0.7	2.2		
	seed	5.23	312.0368	C ₉ H ₁₄ NO ₉ S⁻	-2.1	-6.7		
	d-limonene/H ₂ O ₂ /NO/highly acidic seed	8.24	326.0529	$C_{10}H_{16}NO_9S^-$	-1.7	-5.2	4	, Lo
326	/-limonene/H2O2/NO/highly acidic seed	8.32	326.0530	$C_{10}H_{16}NO_9S^-$	-1.6	-4.9		
	β -phellandrene + d- limonene/H ₂ O ₂ /NO/highly acidic seed	8.29	326.0542	$C_{10}H_{16}NO_9S^-$	-0.4	-1.2	∽он MW 247	└─OSO3 ⁻
	d-limonene/H2O2/NO/highly acidic seed	5.75	328.0719	C 10H 18NO 9S ⁻	1.7	5.7		
		5.23	328.0703	C ₁₀ H ₁₈ NO ₉ S ⁻	0.1	0.3		
	d-limonene/NO ₃ /highly acidic seed	5.54	328.0710	C ₁₀ H ₁₈ NO ₉ S⁻	0.8	2.4		
328		5.76	328.0706	C ₁₀ H ₁₈ NO ₉ S⁻	-2.3	-7.0		
		5.31	328.0693	C ₁₀ H ₁₈ NO ₉ S ⁻	-0.9	-2.7	Кон	Coso3-
	/-limonene/NO ₃ /highly acidic seed	5.84	328.0688	C ₁₀ H ₁₈ NO ₉ S ⁻	-1.4	-4.3	WW 249	
	β-phellandrene + <i>d</i> - limonene/H ₂ O ₂ /NO/highly acidic seed	6.77	328.0688	C ₁₀ H ₁₈ NO ₉ S ⁻	-1.4	-4.3		

330	d-limonene/HONO/acidic seed	5.02	330.0491	C ₉ H ₁₆ NO ₁₀ S ⁻	-0.4	-1.2	not identified	not identiifed
	d-limonene/H2O2/NO/highly acidic seed	7.87	373.0577	$C_{10}H_{17}N_2O_{11}$ S ⁻	2.4	6.4		
		7.94	373.0558	$\begin{array}{c} C_{10}H_{17}N_2O_{11}\\S^-\end{array}$	0.5	1.3		
	/-limonene/H2O2/NO/highly acidic seed	8.27	373.0569	C ₁₀ H ₁₇ N ₂ O ₁₁ S ⁻	1.6	4.3		
		8.73	373.0569	C ₁₀ H ₁₇ N ₂ O ₁₁ S ⁻	1.6	4.3		
		8.20	373.0556	$\begin{array}{c} C_{10}H_{17}N_2O_{11}\\ S^{-} \end{array}$	0.3	0.8	see section 5.1.7.	see section 5.1.7.
	β -phellandrene + d- limonene/H $_2O_2/NO/highly acidic seed$	8.82	373.0543	C ₁₀ H ₁₇ N ₂ O ₁₁ S ⁻	-1.0	-2.7		
		8.97	373.0547	$C_{10}H_{17}N_2O_{11}$ S ⁻	-0.6	-1.6		
		9.28	373.0552	$C_{10}H_{17}N_2O_{11}$ S ⁻	-0.1	-0.3		
		9.43	373.0541	$C_{10}H_{17}N_2O_{11}$ S ⁻	-1.2	-3.2		
	d limenana/LIONO/asidia asad	6.04	389.0510	C ₁₀ H ₁₇ N ₂ O ₁₂ S ⁻	0.8	2.1		
	a-imonene/HONO/actuic seed	6.23	389.0507	$C_{10}H_{17}N_2O_{12}$ S ⁻	0.5	1.3		
		6.61	389.0502	$C_{10}H_{17}N_2O_{12}$ S ⁻	-1.0	-2.6		
389		6.82	389.0519	$\begin{array}{c} C_{10}H_{17}N_{2}O_{12}\\ S^{-}\end{array}$	1.7	4.4	not identified	not identiifed
	I-limonene/NO ₃ /highly acidic seed	7.11	389.0516	$C_{10}H_{17}N_2O_{12}$ S ⁻	0.6	1.5		
		7.26	389.0505	C ₁₀ H ₁₇ N ₂ O ₁₂ S⁻	0.3	0.8		

^aPositional isomers containing nitrate or sulfate groups at other hydroxylated positions are likely.
^bTwo types of organosulfates are considered: (i) sulfate esters formed from the particle-phase esterification of a semivolatile product containing one or more hydroxyl groups by sulfuric acid; and (ii) sulfate derivatives formed from a semivolatile product containing an aldehyde or a keto group and sulfuric acid. The latter organosulfates require gem-diol formation followed by esterification with sulfuric acid.

°At least one of the isomers has the same RT and exact mass as compared to the corresponding ion detected in the field samples collected

from the southeastern US (see Table 8S, Supporting Information).

^dObserved for the first time by Gomez-Gonzalez et al.⁴⁶ in ambient aerosol collected from K-puszta, Hungary.

A corresponding [M + H] ion was detected in the gas-phase by PTR-MS analysis done by Lee et al.;82 this prior study examined gas-phase products produced from the photooxidation of limonene in the presence of NO_x.

[M − H] ⁻ ion (<i>m/z</i>)	α-terpinene experiment	retention time (min)	measured mass	TOFMS Suggested Formula	error (mDa)	error (ppm)	precursor α-terpinene oxidation product	proposed organosulfate structure ^{a,b}
253	$H_2O_2/NO/highly$ acidic seed	5.96	253.0392	C ₈ H ₁₃ O ₇ S⁻	1.0	4.0	not identified	not identified
		6.60	265.0736	C ₁₀ H ₁₇ O ₆ S [−]	-1.0	-3.8		
		0.71	200.0742		-0.4	-1.5		
	HONO/acidic seed	7.01	265.0751	C ₁₀ H ₁₇ O ₆ S [−]	0.5	1.9		
		7.10	265.0751	C ₁₀ H ₁₇ O ₆ S ⁻	0.5	1.9		
		7.44	265.0761	C ₁₀ H ₁₇ O ₆ S⁻	1.5	5.7	, ko	o
265		6.43	265.0753	$C_{10}H_{17}O_6S^-$	0.7	2.6	~~°	Voso3-
		6.53	265.0718	$C_{10}H_{17}O_6S^-$	-2.8	-10.6	\downarrow	🔨 о́н
		6.57	265.0755	$C_{10}H_{17}O_6S^-$	0.9	3.4	MW 168°	
	H ₂ O ₂ /NO/highly acidic seed	6.77	265.0742	C ₁₀ H ₁₇ O ₆ S ⁻	-0.4	-1.5		
		6.96	265.0748	$C_{10}H_{17}O_6S^-$	0.2	0.8		
		7.01	265.0753	$C_{10}H_{17}O_6S^-$	0.7	2.6		
		7.16	265.0755	$C_{10}H_{17}O_6S^-$	0.9	3.4		
279	$H_2O_2/NO/highly$ acidic seed	5.47	279.0548	C 10H15O7S⁻	1.0	3.6	not identified	not identified
		5.21	281.0696	$C_{10}H_{17}O_7S^-$	0.1	0.4		
	HONO/acidic seed	5.31	281.0693	C ₁₀ H ₁₇ O ₇ S ⁻	-0.2	-0.7		
		5.96	281.0704	$C_{10}H_{17}O_7S^-$	0.9	3.2	,OH	OH LOH
		5.04	281.0704	$C_{10}H_{17}O_7S^-$	0.9	3.2	0	-03SO
		5.41	281.0697	$C_{10}H_{17}O_7S^-$	0.2	0.7	° T	°
	H ₂ O ₂ /NO/highly acidic seed	5.52	281.0698	C ₁₀ H ₁₇ O ₇ S ⁻	0.3	1.1	\sim	\sim
		7.58	281.0702	C ₁₀ H ₁₇ O ₇ S ⁻	0.7	2.5		
283 isobar 1	H ₂ O ₂ /NO/highly acidic seed	4.80	283.0489	C ₉ H ₁₅ O ₈ S⁻	0.1	0.4	not identified	not identified

Table 5.5. Organosulfates of α -terpinene.

		5.46	283.0839	$C_{10}H_{19}O_7S^-$	-1.3	-4.6	. ОН	, OH
202	HONO/acidic seed	5.67	283.0848	$C_{10}H_{19}O_7S^-$	-0.4	-1.4	— Спон	ССОН
isobar 2		5.90	283.0838	$C_{10}H_{19}O_7S^-$	-1.4	-4.9	ОН	oso3-
_	$H_2O_2/NO/highly$ acidic seed	5.69	283.0838	$C_{10}H_{19}O_7S^-$	-1.4	-4.9	√ он	\ OH
294	H ₂ O ₂ /NO/highly acidic seed	6.58	294.0654	C10H16NO7S ⁻	0.7	2.4	ONO ₂ OH	ONO2 OSO3
		4.63	297.0651	C ₁₀ H ₁₇ O ₈ S ⁻	0.7	2.4		
	HONO/acidic seed	5.42	297.0650	$C_{10}H_{17}O_8S^-$	0.6	2.0		
-		4.60	297.0640	C ₁₀ H ₁₇ O ₈ S [−]	-0.4	-1.3		
297	H ₂ O ₂ /NO/highly acidic seed	5.21	297.0631	$C_{10}H_{17}O_8S^-$	-1.3	-4.4	not identified	not identified
		7.00	297.0648	$C_{10}H_{17}O_8S^-$	0.4	1.3		
		7.64	297.0677	$C_{10}H_{17}O_8S^-$	3.3	11.1		
310	$H_2O_2/NO/highly$ acidic seed	8.47	310.0625	C₁₀H₁₅NO₅S⁻	2.8	9.0	not identified	not identified
		7.12	342.0524	C ₁₀ H ₁₆ NO ₁₀ S ⁻	2.9	8.5		
342	$H_2O_2/NO/highly$ acidic seed	7.15	342.0525	C ₁₀ H ₁₆ NO ₁₀ S ⁻	3.0	8.8	not identified	not identified
		7.17	373.0559	$C_{10}H_{17}N_2O_{11}S^-$	0.6	1.6		
	HONO/acidic seed	7.54	373.0567	$C_{10}H_{17}N_2O_{11}S^-$	1.4	3.8		
272		8.71	373.0565	$C_{10}H_{17}N_2O_{11}S^-$	1.2	3.2		
373		9.06	373.0558	$C_{10}H_{17}N_2O_{11}S^-$	0.5	1.3		
	H-O-/NO/highly acidic seed	8.24	373.0587	$C_{10}H_{17}N_2O_{11}S^-$	3.2	8.6		
	H202/NO/Highly acidic Seeu	9.15	373.0592	C ₁₀ H ₁₇ N ₂ O ₁₁ S⁻	3.9	10.5		

^aPositional isomers containing nitrate or sulfate groups at other hydroxylated positions are likely.

^bTwo types of organosulfates are considered: (i) sulfate esters formed from the particle-phase esterification of a semivolatile product containing one or more hydroxyl groups by sulfuric acid; and (ii) sulfate derivatives formed from a semivolatile product containing an aldehyde or a keto group

and sulfuric acid. The latter organosulfates require gem-diol formation followed by esterification with sulfuric acid.

^cA corresponding [M + H]⁺ ion was detected in the gas-phase by PTR-MS analysis done by Lee et al.,^{s2} this prior study examined

gas-phase products produced from the photooxidation of α -terpinene in the presence of NO_x.

[M − H] ⁻ ion (<i>m/</i> z)	retention time (min)	measured mass	TOFMS suggested formula	error (mDa)	error (ppm)	γ-terpinene precursor oxidation product	proposed sulfate ester structure ^{b.c}
279	5.80	279.0549	$C_{10}H_{15}O_7S^-$	1.1	3.9	not identified	not identified
	5.90	279.0548	$C_{10}H_{15}O_7S^-$	1.0	3.6		
310	7.53	310.0609	C ₁₀ H ₁₆ NO ₈ S⁻	1.2	3.9	not identified	not identified
	7.78	373.0566	$C_{10}H_{17}N_2O_{11}S^-$	1.3	3.5		
070	8.21	373.0565	$C_{10}H_{17}N_2O_{11}S^-$	1.2	3.2		0503
373	9.01	373.0563	$C_{10}H_{17}N_2O_{11}S^-$	1.0	2.7	HO O ₂ NO	HO O2NO
	9.32	373.0571	$C_{10}H_{17}N_2O_{11}S^-$	1.8	4.8	MW 294	/

Table 5.6. Organosulfates of γ -terpinene^{*a*}

^aOnly one experiment was conducted; specifically, H₂O₂/NO/highly acidic seed photooxidation experiment.

^bPositional isomers containing nitrate or sulfate groups at other hydroxylated positions are likely.

^cTwo types of organosulfates are considered: (i) sulfate esters formed from the particle-phase esterification of a semivolatile product containing one or more hydroxyl groups by sulfuric acid; and (ii) sulfate derivatives formed from a semivolatile product containing an aldehyde or a keto group and sulfuric acid. The latter organosulfates require gem-diol formation followed by esterification with sulfuric acid.

[M – H]⁻	retention		TOFMS	-			
ion	time (min)	measured	suggested	error	error	terpinolene precursor	proposed sulfate actor structure ^{b.c}
(11/2)	(1111)	IIId55	Torniula	(IIIDa)	(ppiii)		proposed sunate ester structure
249 isobar 1	4.65	249.0442	C₀H₁₃O ₆ S⁻	0.9	3.6	not identified	not identified
249 isobar 2	7.89	249.0800	$C_{10}H_{17}O_5S^-$	0.3	1.2	ОНОН	OH OSO3
265	5.08	265.0750	$C_{10}H_{17}O_6S^-$	0.4	1.5		
	5.71	265.0735	$C_{10}H_{17}O_6S^-$	-1.1	-4.1	MW 168 ^d	Д ОН
	4.70	281.0706	C ₁₀ H ₁₇ O ₇ S ⁻	1.1	3.9		
	4.87	281.0698	C ₁₀ H ₁₇ O ₇ S ⁻	0.3	1.1		
	5.01	281.0695	C10H17O7S ⁻	0.0	0.0		
	5.14	281.0704	C ₁₀ H ₁₇ O ₇ S ⁻	0.9	3.2	1	1
	5 18	281 0707	C10H17O7S	12	43	<u>∕</u> ~o	<i>∼</i> ₀
	5.23	281.0685	CHO-S-	-1.0	-3.6	S~_⁰	o
201	5.52	281.0000	C40H47O7S	-0.5	-1.8	HOTOH	OH OH
201	5.75	281 0718		2.0	8.2		
	5.75	201.0710		2.5	0.2		
	6.14	281.0703	C ₁₀ H ₁₇ O ₇ S ⁻	0.8	2.8		
	7.10	281.0695	C ₁₀ H ₁₇ O ₇ S [−]	0.0	0.0		
	7.20	281.0685	C ₁₀ H ₁₇ O ₇ S [−]	-1.0	-3.6		
	7.40	281.0709	$C_{10}H_{17}O_7S^-$	1.4	5		
	7.56	281.0694	C ₁₀ H ₁₇ O ₇ S ⁻	-0.1	-0.4		
283	6.72	283.0867	C 10H 19O7S [−]	1.5	5.3	он но он	HO OH
294	6.53	294.0640	C10H16NO7S⁻	-0.7	-2.4	0 ₂ NO OH	O2NO Oso3.
297	4.75	297.0661	$C_{10}H_{17}O_8S^-$	1.7	5.7	not identified	not identified
326	6.19	326.0535	C ₁₀ H ₁₆ NO ₉ S ⁻	-1.1	-3.4	02N0 НО ОН	HO OH
373	8.04	373.0563	$C_{10}H_{17}N_2O_{11}S^-$	1.0	2.7	O2NO O2NO OH	O2NO O2NO OH

Table 5.7. Organosulfates of terpinolene.

^aOnly one experiment was conducted; specifically, H₂O₂/NO/highly acidic seed photooxidation experiment.

^bPositional isomers containing nitrate or sulfate groups at other hydroxylated positions are likely.

^cTwo types of organosulfates are considered: (i) sulfate esters formed from the particle-phase esterification of a semivolatile product containing one or more hydroxyl groups by sulfuric acid; and (ii) sulfate derivatives formed from a semivolatile product containing an aldehyde or a keto group and sulfuric acid. The latter organosulfates require gem-diol formation followed by esterification with sulfuric acid.

^dA corresponding [M + H]⁺ ion was detected in the gas-phase by PTR-MS analysis done by Lee et al.;⁸² this prior study examined

gas-phase products produced from the photooxidation of terpinolene in the presence of NO_{x} .

[M – H] ⁻	retention		TOFMS				
ion	time (min)	measured	suggested	error	error	terpinolene precursor	proposed sulfate actor structure
(11/2)	(min)	mass	Tormula	(mDa)	(ppm)	oxidation product	proposed sunate ester structure.
249 isobar 1	4.65	249.0442	C ₉ H ₁₃ O ₆ S⁻	0.9	3.6	not identified	not identified
249 isobar 2	7.89	249.0800	C ₁₀ H ₁₇ O ₅ S ⁻	0.3	1.2	ОНОН	OH OSO3
265	5.08	3 265.0750 C ₁₀ H ₁₇ O ₆ S ⁻ 0.4 1.5		1.5			
203	5.71	265.0735	C ₁₀ H ₁₇ O ₆ S ⁻	-1.1	-4.1	MW 168 ^d	ОН
	4.70	281.0706	C ₁₀ H ₁₇ O ₇ S [−]	1.1	3.9		
	4 87	281 0698	C40H47O7S ⁻	0.3	11		
	5.01	281 0605		0.0	0.0		
	5.01	201.0095		0.0	0.0	1	
	5.14	201.0704		0.9	3.2	~	
	5.18	281.0707	C ₁₀ H ₁₇ O ₇ S	1.2	4.3		
	5.23	281.0685	C ₁₀ H ₁₇ O ₇ S ⁻	-1.0	-3.6	но јон	O3SO OH
281	5.52	281.0690	C ₁₀ H ₁₇ O ₇ S ⁻	-0.5	-1.8		\sim
	5.75	281.0718	$C_{10}H_{17}O_7S^-$	2.3	8.2		
	6.14	281.0703	$C_{10}H_{17}O_7S^-$	0.8	2.8		
	7.10	281.0695	C ₁₀ H ₁₇ O ₇ S [−]	0.0	0.0		
	7.20	281.0685	C ₁₀ H ₁₇ O ₇ S ⁻	-1.0	-3.6		
	7.40	281.0709	C ₁₀ H ₁₇ O ₇ S⁻	1.4	5		
	7.56	281.0694	C10H17O7S ⁻	-0.1	-0.4		
283	6.72	283.0867	C 10H 19O7S⁻	1.5	5.3	он но он	HO OH OSO3.
294	6.53	294.0640	C ₁₀ H ₁₆ NO7S ⁻	-0.7	-2.4	0 ₂ NO OH	O ₂ NO OSO3 ⁻
297	4.75	297.0661	C ₁₀ H ₁₇ O ₈ S⁻	1.7	5.7	not identified	not identified
326	6.19	326.0535	C 10H 16NO9S⁻	-1.1	-3.4	02NO HO OH	HO OH
373	8.04	373.0563	$C_{10}H_{17}N_2O_{11}S^{-}$	1.0	2.7	O ₂ NO OH O ₂ NO OH	O2NO OSO3

Table 5.8. Organosulfates of β -pinene.

^aOnly one experiment was conducted; specifically, H₂O₂/NO/highly acidic seed photooxidation experiment.

^bPositional isomers containing nitrate or sulfate groups at other hydroxylated positions are likely.

^cTwo types of organosulfates are considered: (i) sulfate esters formed from the particle-phase esterification of a semivolatile product containing one or more hydroxyl groups by sulfuric acid; and (ii) sulfate derivatives formed from a semivolatile product containing an aldehyde or a keto group and sulfuric acid. The latter organosulfates require gem-diol formation followed by esterification with sulfuric acid.

 d A corresponding [M + H]⁺ ion was detected in the gas-phase by PTR-MS analysis done by Lee et al.,⁸² this prior study examined gas-phase products produced from the photooxidation of terpinolene in the presence of NO_x.

[M − H] ⁻ ion (<i>m/z</i>) ^a	isoprene experiment ^b	retention time (min)	measured mass	TOFMS suggested formula	error (mDa)	error (ppm)	previoulsy proposed organosulfate structure ^{c.d}
139	$H_2O_2/NO/acidic seed$	0.92	138.9716	$C_2H_3O_5S^-$	1.5	10.8	00= 0= 0- 0= 0-
	H ₂ O ₂ /NO/acidic seed	0.92	152.9861	$C_3H_5O_5S^-$	0.3	2.0	9 Q
153° -	HONO/neutral seed	0.94	152.9869	$C_3H_5O_5S^-$	1.1	7.2	0, s, o,
	H ₂ O ₂ /NO/acidic seed	0.84	154.9663	$C_2H_3O_6S^-$	1.3	8.4	o, OH o
155%' -	HONO/neutral seed	0.85	154.9651	$C_2H_3O_6S^-$	-0.8	5.3	0-\$-0 0
169 ^{e,f}	HONO/neutral seed	0.95	168.9816	C₃H₅O ₆ S⁻	0.9	5.3	OH O O O O O O O O O O O O O O O O O O
100%[H ₂ O ₂ /NO/acidic seed	0.92	198.9907	C ₄ H ₇ O ₇ S ⁻	-0.5	-2.5	
199 -	HONO/neutral seed	0.92	198.9906	C₄H ₇ O ₇ S⁻	-0.6	-3.0	HO Y O'NO
211°	$H_2O_2/acidic seed$	0.94	210.9910	C₅H ₇ O ₇ S⁻	-0.2	-0.9	not previously observed
213 ^e	$H_2O_2/acidic seed$	0.94	213.0060	C₅H₀O7S⁻	-0.9	-4.2	not previously observed
	H ₂ O ₂ /NO/acidic seed	0.92	215.0215	$C_5H_{11}O_7S^-$	-1.0	-4.7	HO
- 215¢.f	HONO/neutral seed	0.95	215.0219	$C_5H_{11}O_7S^-$	-0.6	-2.8	
215 -	H ₂ O ₂ /neutral seed	0.91	215.0218	$C_5H_{11}O_7S^-$	-0.7	-3.3	он он
-	H ₂ O ₂ /acidic seed	0.95	215.0222	$C_5H_{11}O_7S^-$	-0.3	-1.4	
		0.97	244.0136	$C_5H_{10}NO_8S^-$	0.9	3.7	
	H ₂ O ₂ /NO/acidic seed	1.55	244.0127	C₅H ₁₀ NO ₈ S⁻	0.0	0.0	
244 ^{e,g}		1.63	244.0135	C₅H ₁₀ NO ₈ S⁻	0.8	3.3	see section 5.2.1.
-		0.96	244.0140	C₅H ₁₀ NO ₈ S ⁻	1.3	5.3	
	HONO/neutral seed	1.60	244.0134	C₅H ₁₀ NO ₈ S⁻	0.7	2.9	

 Table 5.9.
 Organosulfates of isoprene.

$ \begin{array}{ c c c c } & \begin{array}{c c c c } & 1, & 200, & 00, & 0, & 0, & 0, & 0, & 0, $			1.02	260.0076	C₅H ₁₀ NO ₉ S⁻	0.0	0.0	
$ \begin{array}{ c c c c c } & 1 \\ & 1 \\ & 1 \\ & 1 \\ & 1 \\ & 1 \\ & 260^{1/1} O() \mbox{ locidit c seed} & 1 \\ & 260 0073 & C_1 h_1 NO, S & 0.5 & 1.9 \\ & 1 $			1.47	260.0076	C₅H ₁₀ NO ₉ S⁻	0.0	0.0	
$ \begin{array}{ c c c c } & 1 \\ \hline 1 \\ 1 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\$			1.68	260.0063	C₅H ₁₀ NO ₉ S⁻	-1.3	-5.0	
$ \begin{array}{ c c c c c c } & 260 & 260 0073 & C_{H^{1} \otimes NO_{1}S} & 0.3 & -12 \\ 2.61 & 260 0081 & C_{H^{1} \otimes NO_{2}S} & 0.3 & 1.9 \\ 1.67 & 260 0081 & C_{H^{1} \otimes NO_{2}S} & 0.3 & 1.2 \\ 2.72 & 260 0074 & C_{H^{1} \otimes NO_{2}S} & 0.3 & 1.2 \\ 2.27 & 260 0074 & C_{H^{1} \otimes NO_{2}S} & 0.3 & 1.2 \\ 2.45 & 260 0080 & C_{H^{1} \otimes NO_{2}S} & 0.5 & 1.7 \\ 2.45 & 260 0080 & C_{H^{1} \otimes NO_{2}S} & 0.5 & 1.7 \\ 2.78 & 301 0.24 & C_{4} H_{0} O_{0}S & 0.5 & 1.7 \\ 2.78 & 301 0.24 & C_{4} H_{0} O_{0}S & 0.5 & 1.7 \\ 1.83 & 301 0.24 & C_{4} H_{0} O_{0}S & 0.5 & 1.7 \\ 1.83 & 301 0.24 & C_{4} H_{0} O_{0}S & 0.5 & 1.7 \\ 1.83 & 301 0.24 & C_{4} H_{0} O_{0}S & 0.6 & 11.8 \\ 5.46 & 304 993 & C_{3} H_{N} O_{1}S & 2.1 & 6.9 \\ 5.52 & 304 993 & C_{3} H_{N} O_{1}S & 1.6 & 5.2 \\ 5.64 & 304 993 & C_{3} H_{N} O_{1}S & 1.6 & 5.2 \\ 5.68 & 304 993 & C_{3} H_{N} O_{1}S & 1.6 & 5.2 \\ 5.68 & 304 993 & C_{3} H_{N} O_{1}S & 1.6 & 5.2 \\ 6.68 & 304 993 & C_{3} H_{N} O_{1}S & 0.8 & 2.6 \\ 6.01 & 304 995 & C_{3} H_{N} O_{1}S & 0.8 & 2.6 \\ 6.08 & 304 992 & C_{3} H_{N} O_{1}S & 0.7 & 2.3 \\ 6.01 & 304 995 & C_{3} H_{N} O_{1}S & 0.7 & 2.3 \\ 6.64 & 304 993 & C_{3} H_{N} O_{1}S & 0.7 & 2.3 \\ 6.64 & 304 993 & C_{3} H_{N} O_{1}S & 0.7 & 2.3 \\ 6.64 & 304 993 & C_{3} H_{N} O_{1}S & 0.9 & 5. \\ 6.08 & 304 992 & C_{3} H_{N} O_{1}S & 0.9 & 5. \\ 6.08 & 304 992 & C_{3} H_{N} O_{1}S & 0.9 & 2.7 \\ \hline HONOlneutral seed & 0.95 & 331.071 & C_{10} H_{10} O_{1}S & 0.9 & 2.7 \\ 1.83 & 331.067 & C_{10} H_{10} O_{1}S & 0.1 & 0.3 \\ \hline H_{1} O_{1}/actidic seed & 0.94 & 33.087 & C_{1} H_{1} O_{2}S & 0.6 \\ 1.83 & 330.087 & C_{1} H_{1} O_{2}S & 0.6 & 1.8 \\ 1.63 & 330.087 & C_{1} H_{1} O_{2}S & 0.6 & 1.8 \\ 1.64 & 330.087 & C_{1} H_{1} O_{2}S & 0.6 & 1.8 \\ 1.60 & 330.087 & C_{1} H_{1} O_{2}S & 0.6 & 1.8 \\ 1.60 & 330.087 & C_{1} H_{1} O_{2}S & 0.6 & 1.8 \\ 1.60 & 330.087 & C_{1} H_{1} O_{2}S & 0.6 & 1.8 \\ 1.60 & 330.087 & C_{1} H_{1} O_{2}S & 0.6 & 1.8 \\ 1.60 & 330.087 & C_{1} H_{1} O_{2}S & 0.6 & 1.8 \\ 1.60 & 330.087 & C_{1} H_{1} O_{2}S & 0.6 & 0.0 \\ \end{array} \right)$		H ₂ U ₂ /NU/acidic seed	2.06	260.0088	C₅H₁₀NO₀S⁻	1.2	4.6	
$\begin{array}{ c c c c } \hline & 2.51 & 26.0081 & C_{4}H_{3}N_{0}S & 0.5 & 1.9 \\ \hline & 100O/neutral seed \\ \hline & 2.13 & 260.0081 & C_{4}H_{3}N_{0}S & 0.2 & 0.8 \\ \hline & 2.13 & 260.007 & C_{4}H_{3}N_{0}S & 0.2 & 0.8 \\ \hline & 2.27 & 260.007 & C_{4}H_{3}N_{0}S & 0.2 & 0.8 \\ \hline & 2.45 & 260.008 & C_{4}H_{3}N_{0}S & 1.3 & 5.0 \\ \hline & 1.33 & 301.0248 & C_{4}H_{3}O_{3}S & 1.2 & 5.0 \\ \hline & 1.33 & 301.0248 & C_{4}H_{3}O_{3}S & 0.2 & 0.6 & 5 \\ \hline & 1.33 & 301.0248 & C_{4}H_{3}O_{3}S & 1.3 & 5.0 \\ \hline & 1.33 & 301.0248 & C_{4}H_{3}O_{3}S & 1.3 & 5.0 \\ \hline & 1.33 & 301.0248 & C_{4}H_{3}O_{3}S & 1.6 & 5.1 \\ \hline & 1.33 & 301.0248 & C_{4}H_{3}O_{3}S & 1.6 & 5.1 \\ \hline & 1.33 & 301.0248 & C_{4}H_{3}O_{3}S & 1.6 & 5.1 \\ \hline & 1.33 & 301.0248 & C_{4}H_{3}O_{3}S & 1.6 & 5.2 \\ \hline & 1.35 & 301.0248 & C_{4}H_{3}O_{3}S & 1.6 & 5.2 \\ \hline & 5.46 & 304.993 & C_{4}H_{3}O_{3}S & 1.6 & 5.2 \\ \hline & 5.64 & 304.993 & C_{4}H_{3}O_{3}S & 1.6 & 5.2 \\ \hline & 5.68 & 304.993 & C_{4}H_{3}O_{3}S & 1.0 & 3.3 \\ \hline & 6.01 & 304.995 & C_{4}H_{3}O_{3}S & 1.0 & 3.3 \\ \hline & 6.01 & 304.995 & C_{4}H_{3}O_{3}S & 0.9 & 5. \\ \hline & 6.08 & 304.993 & C_{4}H_{3}O_{3}S & 0.9 & 5. \\ \hline & HONO/neutral seed & 5.47 & 304.995 & C_{4}H_{3}O_{3}S & 0.9 & 2.7 \\ \hline & HONO/neutral seed & 0.95 & 331.0713 & C_{9}H_{9}O_{9}S & 0.1 & 0.3 \\ \hline & H_{2}O_{4}/acidic seed & 1.63 & 331.0698 & C_{9}H_{3}O_{3}S & 0.7 & 2.1 \\ \hline & H_{2}O_{4}/acidic seed & 1.63 & 331.0698 & C_{9}H_{9}O_{9}S & 0.7 & 2.1 \\ \hline & H_{2}O_{4}/acidic seed & 1.63 & 331.0698 & C_{9}H_{9}O_{9}S & 0.7 & 2.1 \\ \hline & H_{2}O_{4}/acidic seed & 0.95 & 331.0713 & C_{9}H_{9}O_{9}S & 0.7 & 2.1 \\ \hline & H_{2}O_{4}/acidic seed & 0.95 & 331.0877 & C_{4}H_{9}O_{8}S & 0.7 & 2.1 \\ \hline & H_{2}O_{4}/acidic seed & 0.95 & 333.0871 & C_{9}H_{9}O_{9}S & 0.7 & 2.1 \\ \hline & H_{2}O_{4}/acidic seed & 0.95 & 333.0871 & C_{9}H_{9}O_{9}S & 0.7 & 2.1 \\ \hline & H_{2}O_{4}/acidic seed & 0.95 & 333.0871 & C_{9}H_{9}O_{8}S & 0.1 & 0.3 \\ \hline & H_{1}O_{2}/acidic seed & 0.95 & 333.0871 & C_{9}H_{9}O_{8}S & 0.1 & 0.3 \\ \hline & H_{1}O_{2}/acidic seed & 0.95 & 333.0872 & C_{9}H_{9}O_{9}S & 0.1 & 0.3 \\ \hline & H_{1}O_{2}/acidic seed & 0$	00004		2.40	260.0073	$C_5H_{10}NO_9S^-$	-0.3	-1.2	HO Q O
$\frac{1}{1000/\text{neutral seed}} = \frac{1.67}{2.23} = \frac{260.0081}{2.20070} C_{\text{cH} \text{s}} NO_{15}^{\text{c}} 0.5 = 1.9}{0.3 1.2}$ $\frac{1}{2.27} = \frac{260.0074}{2.64} C_{\text{cH} \text{s}} NO_{5}^{\text{c}} 0.2 = 0.8}{0.3 1.2} = 0.8$ $\frac{1}{2.45} = \frac{260.0089}{260.0074} C_{\text{cH} \text{s}} NO_{5}^{\text{c}} 1.9 = 6.3}{0.5 1.3} = 5.0$ $\frac{1}{2.78} = \frac{301.024}{2.78} C_{\text{cH} \text{s}} NO_{15}^{\text{c}} 1.9 = 6.3}{0.5 1.3} = 5.0$ $\frac{1}{2.78} = \frac{301.024}{2.78} C_{\text{cH} \text{s}} NO_{15}^{\text{c}} 2.2 = 0.8}{0.5} = 1.7$ $\frac{1}{2.78} = \frac{301.024}{2.78} C_{\text{cH} \text{s}} NO_{15}^{\text{c}} 2.0 = 6.6$ $\frac{1}{2.78} = \frac{301.0249}{2.78} C_{\text{cH} \text{s}} NO_{15}^{\text{c}} 3.6 = 11.8}{0.4994} C_{\text{cH} \text{s}} O_{15}^{\text{c}} 3.6 = 11.8$ $\frac{1}{1.67} = \frac{1}{304.9963} C_{\text{cH} \text{s}} NO_{15}^{\text{c}} 3.6 = 11.8$ $\frac{1}{1.67} = \frac{1}{304.9963} C_{\text{cH} \text{s}} NO_{15}^{\text{c}} 3.6 = 11.8$ $\frac{1}{1.60}/\text{acidic seed} = \frac{5.77}{304.9953} C_{\text{cH} \text{s}} NO_{15}^{\text{c}} 3.6 = 1.6 = 5.2$ $\frac{1}{1.60} NO_{16} = \frac{1}{1.63} = \frac{1}{304.9953} C_{\text{cH} \text{s}} NO_{15}^{\text{c}} 3.0 = 9.5$ $\frac{1}{1.60} NO_{16} = \frac{1}{1.63} = \frac{1}{1.64} = \frac{1}{1.64} = \frac{1}{1.63} = \frac{1}{1.64} = \frac{1}$	260 ^{e,r}		2.51	260.0081	C₅H ₁₀ NO ₉ S⁻	0.5	1.9	~~~o~ ^{\$}
$\begin{array}{ c c c c c } \\ HONO/neutral seed & 2.13 & 260.007 & C_1H_{10}NO_5N & 0.3 & 1.2 \\ 2.27 & 200.007 & C_1H_{10}NO_5N & 3.5 & 0.2 & 0.6 \\ 2.45 & 200.008 & C_1H_{10}O_5N & 1.9 & 6.3 \\ \\ \hline \\ 1.0 & 301.024 & C_8H_{10}O_8N & 1.9 & 6.3 \\ \hline \\ 1.0 & 301.024 & C_8H_{10}O_8N & 2.0 & 6.6 \\ \hline \\ 1.0 & 301.024 & C_8H_{10}O_8N & 2.0 & 6.6 \\ \hline \\ 1.0 & 301.024 & C_8H_{10}O_8N & 3.6 & 11.8 \\ \hline \\ 1.0 & 301.024 & C_8H_{10}O_8N & 3.6 & 11.8 \\ \hline \\ 1.0 & 304.995 & C_8H_{1N}O_1N & 3.6 & 11.8 \\ \hline \\ 1.0 & 304.995 & C_8H_{1N}O_1N & 1.6 & 5.2 \\ \hline \\ 1.0 & 304.995 & C_8H_{1N}O_1N & 2.6 & 8.5 \\ \hline \\ 1.0 & 304.995 & C_8H_{1N}O_1N & 2.6 & 8.5 \\ \hline \\ 1.0 & 304.995 & C_8H_{1N}O_1N & 2.6 & 8.5 \\ \hline \\ 1.0 & 304.995 & C_8H_{1N}O_1N & 0.8 & 2.6 \\ \hline \\ 1.0 & 304.995 & C_8H_{1N}O_1N & 0.7 & 2.3 \\ \hline \\ 1.0 & 304.995 & C_8H_{1N}O_1N & 0.7 & 2.3 \\ \hline \\ 1.0 & 304.995 & C_8H_{1N}O_1N & 0.9 & 2.7 \\ \hline \\ 1.0 & 304.995 & C_8H_{1N}O_1N & 0.9 & 2.7 \\ \hline \\ 1.0 & 331.0670 & C_{9H_{10}O_8N & 0.1 & 0.3 \\ \hline \\ 1.0 & 333.0670 & C_{9H_{10}O_8N & 0$	-		1.67	260.0081	C₅H ₁₀ NO ₉ S⁻	0.5	1.9	ÓH ÓNO2
$\begin{array}{ c c c c c c } \hline HONOlneutral seed $$ 227 & 260.0074 & C_{3}H_{10}NO_{3}S & -0.2 & -0.8 \\ 2.44 & 260.0089 & C_{3}H_{10}NO_{3}S & -0.2 & -0.8 \\ 1.3 & 5.0 \\ \hline 1.3 & 301.024 & C_{4}H_{10}O_{1}S & 1.9 & 6.3 \\ \hline 1.3 & 301.024 & C_{4}H_{10}O_{1}S & 0.5 & 1.7 \\ \hline 1.6 & 301.024 & C_{4}H_{10}O_{1}S & 0.5 & 1.7 \\ \hline 1.6 & 301.024 & C_{4}H_{10}O_{1}S & 0.5 & 1.7 \\ \hline 1.6 & 301.024 & C_{4}H_{10}O_{1}S & 0.6 & 11.8 \\ \hline 1.6 & 301.024 & C_{4}H_{10}O_{1}S & 0.6 & 11.8 \\ \hline 1.6 & 301.024 & C_{4}H_{10}O_{1}S & 0.6 & 11.8 \\ \hline 1.6 & 301.9993 & C_{4}H_{1N}O_{1}S & 0.6 & 11.8 \\ \hline 1.6 & 304.9993 & C_{4}H_{N}O_{1}S & 0.8 & 2.6 \\ \hline 1.6 & 304.9993 & C_{4}H_{N}O_{1}S & 0.8 & 2.6 \\ \hline 1.6 & 304.9993 & C_{4}H_{N}O_{1}S & 0.8 & 2.6 \\ \hline 1.6 & 304.9995 & C_{4}H_{N}O_{1}S & 0.8 & 2.6 \\ \hline 1.6 & 304.9995 & C_{4}H_{N}O_{1}S & 0.8 & 2.6 \\ \hline 1.6 & 304.9995 & C_{4}H_{N}O_{1}S & 0.2 & -0.7 \\ \hline 1.6 & 304.9995 & C_{4}H_{N}O_{1}S & 0.7 & 2.3 \\ \hline 1.6 & 304.9995 & C_{4}H_{N}O_{1}S & 0.7 & 2.3 \\ \hline 1.6 & 304.9995 & C_{4}H_{N}O_{1}S & 0.9 & 2.7 \\ \hline 1.6 & 304.9995 & C_{2}H_{1}O_{1}S & 0.9 & 2.7 \\ \hline 1.6 & 301.0699 & C_{2}H_{10}O_{1}S & 0.1 & 0.3 \\ \hline 1.6 & 301.0699 & C_{2}H_{10}O_{1}S & 0.1 & 0.3 \\ \hline 1.6 & 303.0662 & C_{2}H_{10}O_{1}S & 0.1 & 0.3 \\ \hline 1.6 & 303.0662 & C_{2}H_{10}O_{1}S & 0.1 & 0.3 \\ \hline 1.6 & 303.0662 & C_{2}H_{10}O_{1}S & 0.1 & 0.3 \\ \hline 1.6 & 303.0662 & C_{2}H_{10}O_{1}S & 0.1 & 0.3 \\ \hline 1.6 & 303.0662 & C_{2}H_{10}O_{1}S & 0.1 & 0.3 \\ \hline 1.6 & 303.0662 & C_{2}H_{10}O_{1}S & 0.1 & 0.3 \\ \hline 1.6 & 333.0671 & C_{2}H_{10}O_{1}S & 0.1 & 0.3 \\ \hline 1.6 & 333.0671 & C_{2}H_{10}O_{1}S & 0.2 & 0.6 \\ \hline 1.6 & 333.0672 & C_{2}H_{10}O_{1}S & 0.1 & 0.3 \\ \hline 1.6 & 333.0672 & C_{2}H_{10}O_{1}S & 0.2 & 0.6 \\ \hline 1.6 & 333.0672 & C_{2}H_{10}O_{1}S & 0.1 & 0.3 \\ \hline 1.6 & 333.0672 & C_{2}H_{10}O_{1}S & 0.1 & 0.3 \\ \hline 1.6 & 333.0672 & C_{2}H_{10}O_{1}S & 0.1 & 0.3 \\ \hline 1.6 & 333.0672 & C_{2}H_{10}O_{1}S & 0.1 & 0.3 \\ \hline 1.6 & 333.0672 & C_{2}H_{10}O_{1}S & 0.1 & 0.3 \\ \hline 1.6 & 333.0672 & C_{2}H_{10}O_{1}S & 0.1 & 0.3 \\ \hline 1.6 & 333.0672 & C_{2}H_{10}O_{1}S & 0.1 & 0.3 \\ \hline 1.6 & 333.$			2.13	260.0079	C₅H₁₀NO₀S⁻	0.3	1.2	
$\begin{array}{ c c c c c } \hline 1.245 & 260.0089 & C_{1}H_{10}NO_{15} & 1.3 & 5.0 \\ \hline 1.33 & 301.0248 & C_{4}H_{10}O_{15} & 1.9 & 6.3 \\ \hline 1.33 & 301.0248 & C_{4}H_{10}O_{15} & 1.5 & 1.7 \\ \hline 1.73 & 301.0249 & C_{4}H_{10}O_{15} & 2.0 & 6.6 \\ \hline 1.74 & 301.0249 & C_{4}H_{10}O_{15} & 2.0 & 6.6 \\ \hline 1.75 & 301.0249 & C_{4}H_{10}O_{15} & 3.6 & 11.8 \\ \hline 1.75 & 301.0249 & C_{4}H_{10}O_{15} & 1.6 & 5.2 \\ \hline 1.75 & 304.9963 & C_{4}H_{10}O_{15} & 1.6 & 5.2 \\ \hline 1.75 & 304.9953 & C_{4}H_{10}O_{15} & 1.6 & 5.2 \\ \hline 1.75 & 304.9953 & C_{4}H_{10}O_{15} & 1.6 & 5.2 \\ \hline 1.75 & 304.9953 & C_{4}H_{10}O_{15} & 1.6 & 5.2 \\ \hline 1.75 & 304.9953 & C_{4}H_{10}O_{15} & 1.0 & 3.3 \\ \hline 1.75 & 304.9957 & C_{4}H_{10}O_{15} & 1.0 & 3.3 \\ \hline 1.75 & 304.9957 & C_{4}H_{10}O_{15} & 1.0 & 3.3 \\ \hline 1.75 & 304.9957 & C_{4}H_{10}O_{15} & 1.0 & 3.3 \\ \hline 1.75 & 304.9957 & C_{4}H_{10}O_{15} & 1.0 & 3.3 \\ \hline 1.75 & 304.9957 & C_{4}H_{10}O_{15} & 1.0 & 3.3 \\ \hline 1.75 & 304.9957 & C_{4}H_{10}O_{15} & 1.0 & 3.3 \\ \hline 1.75 & 304.9957 & C_{4}H_{10}O_{15} & 1.0 & 3.3 \\ \hline 1.75 & 304.9957 & C_{4}H_{10}O_{15} & 1.0 & 3.3 \\ \hline 1.75 & 304.9957 & C_{4}H_{10}O_{15} & 1.0 & 3.3 \\ \hline 1.75 & 304.9957 & C_{4}H_{10}O_{15} & 0.7 & 2.3 \\ \hline 1.75 & 304.9957 & C_{4}H_{10}O_{15} & 0.7 & 2.3 \\ \hline 1.75 & 311.013 & C_{10}H_{10}O_{15} & 1.4 & 4.2 \\ \hline 1.75 & 311.019 & C_{10}H_{10}O_{15} & 0.7 & 2.1 \\ \hline 1.75 & 311.019 & C_{10}H_{10}O_{15} & 0.7 & 2.1 \\ \hline 1.75 & 311.019 & C_{10}H_{10}O_{15} & 0.7 & 2.1 \\ \hline 1.75 & 311.019 & C_{10}H_{10}O_{15} & 0.7 & 2.1 \\ \hline 1.75 & 311.019 & C_{10}H_{10}O_{15} & 0.7 & 2.1 \\ \hline 1.75 & 311.019 & C_{10}H_{10}O_{15} & 0.7 & 2.1 \\ \hline 1.75 & 311.019 & C_{10}H_{10}O_{15} & 0.7 & 2.1 \\ \hline 1.75 & 311.019 & C_{10}H_{10}O_{15} & 0.7 & 2.1 \\ \hline 1.75 & 311.019 & C_{10}H_{10}O_{15} & 0.7 & 2.1 \\ \hline 1.75 & 311.019 & C_{10}H_{10}O_{15} & 0.7 & 2.1 \\ \hline 1.75 & 311.019 & C_{10}H_{10}O_{15} & 0.7 & 0.1 \\ \hline 1.75 & 311.019 & C_{10}H_{10}O_{15} & 0.7 & 0.1 \\ \hline 1.75 & 311.019 & C_{10}H_{10}O_{15} & 0.7 & 0.1 \\ \hline 1.75 & 311.019 & C_{10}H_{10}O_{15} & 0.7 & 0.1 \\ \hline 1.75 & 311.019 & C_{10}H_{10}O_{15} & 0.7 & 0.1 $		HONO/neutral seed	2.27	260.0074	C₅H ₁₀ NO ₉ S⁻	-0.2	-0.8	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			2.45	260.0089	C₅H₁₀NO₀S⁻	1.3	5.0	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			1.33	301.0248	$C_8H_{13}O_{10}S^-$	1.9	6.3	
$ \begin{array}{ c c c c c c } \hline 1.78 & 301.024 & C_{8}H_{10}O_{18}S & 2.0 & 6.6 \\ \hline OH & OH \\ \hline $	301	$H_2O_2/NO/acidic seed$	1.83	301.0234	$C_8H_{13}O_{10}S^-$	0.5	1.7	но цело в с
9085.13304.9635.4h,9k,2k,3c3.61.185.44304.90435.4h,9k,2k,3c5.16.95.52304.90435.4h,9k,2k,3c5.65.25.64304.90355.4h,9k,2k,3c5.65.65.77304.90375.4h,9k,2k,3c5.65.65.78304.90375.4h,9k,2k,3c5.65.75.86304.99375.4h,9k,2k,3c5.05.65.86304.99375.4h,9k,2k,3c5.05.66.01304.99575.4h,9k,2k,3c5.05.66.02304.99575.4h,9k,2k,3c5.25.76.03304.99575.4h,9k,2k,3c5.25.76.04304.99585.4h,9k,2k,3c5.25.76.0531.07135.4h,9k,2k,3c5.25.37411.6231.07135.4h,9k,2k,3c5.95.77421.6331.07135.4h,9k,2k,3c5.95.77431**1.4231.07135.4h,9k,2k,3c5.95.77431**1.4231.07135.4h,9k,2k,3c5.95.77431**1.4231.07135.4h,9k,2k,3c5.15.3744131.07135.4h,9k,2k,3c5.15.37451**1.4333.06975.4h,9k,2k,3c5.15.37451**1.4333.06975.4h,9k,2k,3c5.15.27451**1.4333.06975.4h,9k,2k,3c5.15.17451**1.4333.0697			2.78	301.0249	$C_8H_{13}O_{10}S^-$	2.0	6.6	он он
4.2 4.2			5.13	304.9963	$C_5H_9N_2O_{11}S^-$	3.6	11.8	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			5.46	304.9948	$C_5H_9N_2O_{11}S^-$	2.1	6.9	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			5.52	304.9943	$C_5H_9N_2O_{11}S^-$	1.6	5.2	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		$H_2O_2/NO/acidic seed$	5.64	304.9935	$C_5H_9N_2O_{11}S^-$	0.8	2.6	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	305°		5.77	304.9953	$C_5H_9N_2O_{11}S^-$	2.6	8.5	see section 5.2.2
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	303		5.86	304.9937	$C_5H_9N_2O_{11}S^-$	1.0	3.3	300 30000 J.Z.Z.
$ \begin{array}{c c c c c c c c } \hline & 6.08 & 304.9925 & C_5H_9N_2O_{11}S^- & -0.2 & -0.7 \\ \hline & & & & & & & & & & & & & & & & & &$			6.01	304.9957	$C_5H_9N_2O_{11}S^-$	3.0	9.5	
$ \frac{1}{10000/neutral seed} \begin{cases} 5.47 & 304.9934 & C_5H_9N_2O_{11}S^{-} & 0.7 & 2.3 \\ 5.64 & 304.9956 & C_6H_9N_2O_{11}S^{-} & 2.9 & 9.5 \end{cases} \\ \frac{1}{10000000000000000000000000000000000$			6.08	304.9925	$C_5H_9N_2O_{11}S^-$	-0.2	-0.7	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	-		5.47	304.9934	$C_5H_9N_2O_{11}S^-$	0.7	2.3	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		HONO/neutral seed	5.64	304.9956	$C_5H_9N_2O_{11}S^-$	2.9	9.5	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		H ₂ O ₂ /neutral seed	0.95	331.0713	$C_{10}H_{19}O_{10}S^{-}$	0.9	2.7	
$\frac{11202}{331000} = \frac{11202}{31000000000000000000000000000000000000$	331°	H. O. /asidia sood	0.99	331.0713	$C_{10}H_{19}O_{10}S^{-}$	1.4	4.2	see section 5.2.3.
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			1.63	331.0699	$C_{10}H_{19}O_{10}S^{-}$	0.1	0.3	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			0.94	333.0862	$C_{10}H_{21}O_{10}S^{-}$	0.7	2.1	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			1.96	333.0871	$C_{10}H_{21}O_{10}S^{-}$	1.6	4.8	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	-		0.95	333.0857	C ₁₀ H ₂₁ O ₁₀ S ⁻	0.2	0.6	
$\frac{2.22}{HONO/neutral seed} \frac{2.22}{2.26} \frac{333.0854}{333.0872} \frac{C_{10}H_{21}O_{10}S^{-}}{C_{10}H_{21}O_{10}S^{-}} \frac{-0.1}{1.7} \frac{-0.3}{5.1}$	333°	H ₂ O ₂ /acidic seed	2.00	333.0849	$C_{10}H_{21}O_{10}S^{-}$	-0.6	-1.8	see section 5.2.3.
HONO/neutral seed $\begin{array}{cccccccccccccccccccccccccccccccccccc$			2.22	333.0854	$C_{10}H_{21}O_{10}S^{-}$	-0.1	-0.3	
HONO/neutral seed 2.26 333.0855 C ₁₀ H ₂₁ O ₁₀ S ⁻ 0.0 0.0			0.96	333.0872	C ₁₀ H ₂₁ O ₁₀ S ⁻	1.7	5.1	
		HONO/neutral seed	2.26	333.0855	C ₁₀ H ₂₁ O ₁₀ S ⁻	0.0	0.0	



^aAll ions listed were observed previously by Surratt et al.;²³ however, these were only partially characterized, as accurate mass

measurements were not presented in this prior study and detailed tandem MS analysis was not provided.

^bDetails of the experimental conditions used to generate SOA from isoprene can be found in Surratt et al.³³ and Kroll et al.⁴

^ePositional isomers containing nitrate or sulfate groups at other hydroxylated positions are likely. ^dTwo types of organosulfates are considered: (i) sulfate esters formed from the particle-phase esterification of a semivolatile product containing one or more hydroxyl groups by sulfuric acid; and (ii) sulfate derivatives formed from a semivolatile product containing an aldehyde or a keto group and sulfuric acid. The latter organosulfates require gem-diol formation followed by esterification with sulfuric acid.

eAt least one of the isomers has the same RT and exact mass as compared to the corresponding ion detected in the field samples collected from the southeastern US (see Table 8S, Supporting Information).

Proposed structure is consistent with recent detailed interpretations of MS² and MS³ behaviors of these ions by Gomez-Gonzalez et al.,⁴⁶only one of the possible structural isomers is shown.

^gThe previously proposed structure for this ion was found to be incorrect in the current study.

observed			retention	measured	TOFMS			
[M – H]⁻	SEARCH		time	[M – H]⁻	suggested	error	error	
ion (m/z)	site	date	(min)	ion (Da)	formula	(mDa)	(nnm)	proposed VOC precursor
	JST	20 June 2004	0.94	152 9855	CaHEOEST	-0.3	-2.0	propossa i sis prosares
	JST	23 June 2004	0.04	152 9861	C.H.O.S ⁻	0.0	2.0	
	101	26 June 2004	0.02	152.0001	C.H.O.S ⁻	0.0	0.7	
	331	20 June 2004	0.92	152.9659	C3H5O5S	0.1	0.7	
150	СТР	11 June 2004	0.04	152 0957		0.1	07	
100		11 June 2004	0.94	152.9057		-0.1	-0.7	hydroxyacetone
Isomer 1	CIR	23 June 2004	0.95	152.9850		-0.2	-1.3	5 5
	CIR	29 June 2004	0.94	152.9855	$C_3H_5O_5S$	-0.3	-2.0	
					<u> </u>		- -	
	BHM	17 June 2004	0.92	152.9857	C ₃ H₅O ₅ S [−]	-0.1	-0.7	
	BHM	20 June 2004	0.92	152.9860	C₃H₅O₅S⁻	0.2	1.3	
	JST	20 June 2004	-	-	-	-	-	
	JST	23 June 2004	-	-	-	-	-	
	JST	26 June 2004	1.18	152.9860	C₃H₅O₅S⁻	0.2	1.3	
153	CTR	11 June 2004	1.18	152.9867	C₃H₅O₅S⁻	0.9	5.9	bydroxyacetone
isomer 2	CTR	23 June 2004	-	-	-	-	-	nydroxyacetorie
	CTR	29 June 2004	1.20	152.9852	C₃H₅O₅S⁻	-0.6	-3.9	
	BHM	17 June 2004	-	-	-	-	-	
	BHM	20 June 2004	1.18	152.9856	C ₃ H ₅ O ₅ S [−]	-0.2	-1.3	
	JST	20 June 2004	0.85	154.9637	C ₂ H ₃ O ₆ S ⁻	-1.3	-8.4	
	JST	23 June 2004	0.84	154,9655	C ₂ H ₃ O ₆ S ⁻	0.5	3.2	
	JST	26 June 2004	0.84	154 9650	C2H2O25	0.0	0.0	
	001	20 00110 200 1	0.01	101.0000	02113060	0.0	0.0	
	CTR	11 June 2004	0.85	154 9642	C.H.O.S ⁻	-0.8	-52	
155	CTR	23 June 2004	0.84	154.9655	C_H_O_S^	-0.0	3.2	glyoxal
	CTP	20 June 2004	0.04	154.0652		0.0	1.0	
	UIK	29 June 2004	0.04	154.9055	C2H3O63	0.5	1.9	
		17 June 2004	0.04	454 0050		0.0	10	
	BHIM	17 June 2004	0.84	154.9653		0.3	1.9	
	BHM	20 June 2004	0.82	154.9650	C ₂ H ₃ O ₆ S	0.0	0.0	
	JST	20 June 2004	0.94	168.9812	$C_3H_5O_6S$	0.5	3.0	
	JST	23 June 2004	-	-		-	-	
	JST	26 June 2004	0.94	168.9810	C₃H₅O ₆ S⁻	0.3	1.8	
169	CTR	11 June 2004	0.94	168.9818	C₃H₅O ₆ S⁻	1.1	6.5	methylalvoxal
	CTR	23 June 2004	-	-	-	-	-	ine ing ig i y estai
	CTR	29 June 2004	0.94	168.9835	C₃H₅O ₆ S⁻	2.8	16.6	
	BHM	17 June 2004	0.94	168.9817	C₃H₅O ₆ S⁻	1.0	5.9	
	BHM	20 June 2004	0.94	168.9806	C₃H₅O ₆ S⁻	-0.1	-0.6	
-	JST	20 June 2004	0.92	198.9905	C₄H ₇ O ₇ S⁻	-0.7	-3.5	
	JST	23 June 2004	0.92	198.9910	C₄H ₇ O ₇ S [−]	-0.2	-1.0	
	JST	26 June 2004	0.92	198.9916	C₄H ₇ O ₇ S ⁻	0.4	2.0	
	CTR	11 June 2004	0.94	198.9914	C₄H ₇ O ₇ S⁻	0.2	1.0	
199	CTR	23 June 2004	0.94	198 9915	C4H2O2S	0.3	15	isoprene
	CTR	29 June 2004	0.92	198 9911	C ₄ H ₇ O ₇ S ⁻	-0.1	-0.5	
	0.11	20 00.10 200 1	0.01		04.17070	••••	0.0	
	BHM	17 June 2004	0 94	198 9915	$C_4H_7O_7S^-$	0.3	15	
	BHM	20 June 2004	0.04	198 9912	C.H-0-S-	0.0	0.0	
	191	20 June 2004	0.04	210 0012	C_H_O_S^	0.0	0.0	
	IST	23 June 2004	0.02	210.0014	C-H-O-S ⁻	0.2	0.5	
	IST	26 June 2004	0.92	210.9914	C-H-O-S-	0.2	10	
	301	20 June 2004	0.92	210.3310	05117070	0.4	1.9	
211	CTD	11 June 2004	0.04	210 0010	C-H-O 8-	0.2	0.0	
211		11 June 2004	0.94	210.9910		-0.2	-0.9	isoprene
Isomer 1		23 June 2004	0.97	210.9934		2.2	10.4	-
	CIR	29 June 2004	0.92	210.9903	C5H7O7S	-0.9	-4.3	
	DI	47 1 000		040.0040		~ ·	o -	
	BHM	17 June 2004	0.94	210.9913	C₅H ₇ O ₇ S [−]	0.1	0.5	
	BHM	20 June 2004	0.92	210.9917	C₅H ₇ O ₇ S⁻	0.5	2.4	
	JST	20 June 2004	-	-	-	-	-	
	JST	23 June 2004	-	-	-	-	-	
	JST	26 June 2004	1.25	210.9916	C₅H ₇ O ₇ S [−]	0.4	1.9	
211	CTR	11 June 2004	1.25	210.9922	C₅H ₇ O ₇ S ⁻	1.0	4.7	unknown
isomer 2	CTR	23 June 2004	-	-	-	-	-	UTIKHOWN
	CTR	29 June 2004	-	-	-	-	-	
	BHM	17 June 2004	1.23	210.9912	C₅H ₇ O ₇ S [−]	0.0	0.0	
	BHM	20 June 2004	1.21	210.9909	C₅H ₇ O ₇ S [−]	-0.3	-1.4	

 Table 5.10.
 Organosulfates observed in southeastern U.S. aerosol.

	JST	20 June 2004	-	-	-	-	-	
	JST	23 June 2004	-	-	-	-	-	
	JST	26 June 2004	1 54	210 9909	CrH-0-S	-0.3	-14	
	001	20 June 2004	1.54	210.0000	0517070	-0.5	-1.4	
014		44 1	4 57	040 0004		0.0	4.0	
211	CIR	11 June 2004	1.57	210.9921	C5H7O7S	0.9	4.3	unknown
isomer 3	CIR	23 June 2004	-	-	-	-	-	
	CTR	29 June 2004	1.54	210.9919	C₅H ₇ O ₇ S⁻	0.7	3.3	
	BHM	17 June 2004	1.59	210.9916	C₅H ₇ O ₇ S [−]	0.4	1.9	
	BHM	20 June 2004	1 58	210 9902	C-H-0-S	-10	-47	
		20 June 2004	1.00	210.0002	0511/0/0	1.0	4.1	
	J31	20 June 2004	-	-	-	-	-	
	121	23 June 2004	-	-	-	-	-	
	JST	26 June 2004	1.65	210.9913	C₅H ₇ O ₇ S [−]	0.1	0.5	
211	CTR	11 June 2004	1.62	210.9913	C ₅ H ₇ O ₇ S [−]	0.1	0.5	
somer 4	CTR	23 June 2004	-	-	-	-	-	UNKNOWN
	CTR	20 June 2004	_	_	_	_	_	
	OIK	20 00110 2004	-	-	_	_	_	
					<u> </u>		~ ~	
	BHM	17 June 2004	1.64	210.9906	C ₅ H ₇ O ₇ S ⁻	-0.6	-2.8	
	BHM	20 June 2004	1.63	210.9913	C₅HァOァS⁻	0.1	0.5	
	JST	20 June 2004	0.91	213.0064	C₅H₀O7S⁻	-0.5	-2.3	
	JST	23 June 2004	0.92	213.0065	C₅H₀O ₇ S [−]	-0.4	-1.9	
	IST	26 June 2004	0.02	213 0072	C-H-O-S-	03	1 /	
	501	20 June 2004	0.52	210.0072	05119070	0.5	1.4	
	070	44 1	0.00	040 0005	0 11 0 0-	<u> </u>	4.0	
213	CIR	11 June 2004	0.92	213.0065	C₅H ₉ O ₇ S [−]	-0.4	-1.9	isoprene
	CTR	23 June 2004	0.95	213.0079	C₅H₀O7S⁻	1.0	4.7	
	CTR	29 June 2004	0.91	213.0059	C₅H₀O7S⁻	-1.0	-4.7	
	BHM	17 June 2004	0.01	213 0066	C-H-O-S-	-03	-14	
		20 June 2004	0.01	213.0000		-0.5	-1.4	
		20 June 2004	0.91	213.0074		0.5	2.3	
	JST	20 June 2004	0.90	215.0232	$C_5H_{11}O_7S$	0.7	3.3	
	JST	23 June 2004	0.91	215.0226	C₅H₁₁O₂S⁻	0.1	0.5	
	JST	26 June 2004	0.90	215.0223	C₅H ₁₁ O ₇ S⁻	-0.2	-0.9	
	CTR	11 June 2004	0 90	215 0224	CrH40-S	-0 1	-0.5	
215	CTR	22 June 2004	0.00	215.0224		-0.1	-0.5	isoprene
		23 June 2004	0.92	215.0220	C5H11O7S	0.1	0.5	
	CIR	29 June 2004	0.92	215.0222	C ₅ H ₁₁ O ₇ S	-0.3	-1.4	
	BHM	17 June 2004	0.90	215.0223	C₅H₁1O7S⁻	-0.2	-0.9	
	BHM	20 June 2004	0.90	215.0194	C₅H₁1O7S [−]	-3.1	-14.4	
	JST	20 June 2004	0.92	226 9866	C _E H ₇ O ₈ S ⁻	0.4	18	
	IST	23 Juno 2004	0.04	226.0000	C L O S-	2.6	11 5	
	101	20 June 2004	0.34	220.9000	05117080	2.0	40.0	
	121	26 June 2004	0.94	226.9892	C5H7O8S	3.0	13.2	
227	CTR	11 June 2004	0.94	226.9892	C₅H7O8S⁻	3.0	13.2	a pipopo
221	CTR	23 June 2004	0.96	226.9861	C ₅ H ₇ O ₈ S [−]	-0.1	-0.4	a-pillelle
	CTR	29 June 2004	-	-	-	-	-	
	••••	20 00.10 200 .						
	рым	17 June 2004	0.04	226 0002		2.0	12.0	
			0.94	220.9092		3.0	13.2	
	BHM	20 June 2004	0.92	226.9872	C5H7O8S	1.0	4.4	
	JST	20 June 2004	0.86	229.0015	C₅H₀O₀S⁻	-0.3	-1.3	
	JST	23 June 2004	0.87	229.0025	C₅H₀O₀S⁻	0.7	3.1	
	JST	26 June 2004	0.87	229,0023	C₅H₀O₀S⁻	0.5	2.2	
	СТР	11 Juno 2004	0 97	220 0040	0-10 0-	0.1	04	
229			0.07	229.0019		0.1	0.4	unknown
	CIR	23 June 2004	0.86	229.0017	C₅H ₉ O ₈ S [−]	-0.1	-0.4	
	CTR	29 June 2004	0.86	229.0017	C₅H₀O₀S⁻	-0.1	-0.4	
	BHM	17 June 2004	0.85	229.0017	C₅H₀O₀S⁻	-0.1	-0.4	
	BHM	20 June 2004				••••		
		20 June 2004	4 60	235 0295	C.HO. 8-	0.0	2.0	
	101		4.09	200.0200	08111063	0.9	5.0	
	121	23 June 2004	-	-	-	-	-	
	JST	26 June 2004	-	-	-	-	-	
235	CTR	11 June 2004	-	-	-	-	-	
isobar 1	CTR	23 June 2004	-	-	-	-	-	unknown
	СТР	20 June 2004	_	_	_	_	_	
	UIK	29 JUNE 2004	-	-	-	-	-	
	B 1 ··· ·	(- ·	
	BHM	17 June 2004	4.72	235.0288	C ₈ H ₁₁ O ₆ S⁻	1.2	5.1	
	BHM	20 June 2004	4.69	235.0274	C ₈ H ₁₁ O ₆ S⁻	-1.1	-4.7	

	JST	20 June 2004	5.80	235.0649	C ₉ H ₁₅ O ₅ S [−]	0.9	3.8	
	JST	23 June 2004	5.82	235.0646	C ₉ H ₁₅ O ₅ S [−]	0.6	2.6	
	JST	26 June 2004	5.80	235.0640	C ₉ H ₁₅ O ₅ S [−]	0.0	0.0	
235	CTR	11 June 2004	5 79	235 0641	C₀H₁₅O₅S⁻	01	04	
isobar 2	CTR	23 June 2004	5 79	235 0645	CoH40cS	0.5	21	unknown
1300001 2	CTD	20 June 2004	5.00	235 0637		0.0	12	
	UIK	29 June 2004	0.02	235.0037	09115055	-0.5	-1.5	
		17 June 0004	F 00	005 0004		0.4	• •	
	BHIM	17 June 2004	5.82	235.0661		2.1	8.9	
	BHW	20 June 2004	5.79	235.0641	$C_9H_{15}O_5S$	0.1	0.4	
	JST	20 June 2004	0.96	239.0231	$C_7H_{11}O_7S^{-1}$	0.6	2.5	
	JST	23 June 2004	0.96	239.0228	C7H11O7S⁻	0.3	1.3	
	JST	26 June 2004	-	-	-	-	-	
239	CTR	11 June 2004	0.96	239.0233	C7H11O2S ⁻	0.8	3.3	limonono
isomer 1	CTR	23 June 2004	-	-	-	-	-	limonene
	CTR	29 June 2004	0.96	239.0238	C ₇ H ₁₁ O ₇ S [−]	1.3	5.4	
	BHM	17 June 2004	0.96	239.0225	C7H11O7S [−]	0.0	0.0	
	BHM	20 June 2004	-		-	-	-	
	JST	20 June 2004	4 20	239 0230	C-H40-S	0.5	21	
	IST	23 June 2004		200.0200	0/1110/0	-	-	
	ICT	26 June 2004						
	331	20 June 2004	-	-	-	-	-	
000	отр	11	2 22	000 0000		~ ~	2.2	
239		11 June 2004	3.20	239.0233	C7H11O7S	0.8	3.3	unknown
isomer 2	CIR	23 June 2004	-	-	-	-	-	
	CTR	29 June 2004	-	-	-	-	-	
	BHM	17 June 2004	3.32	239.0221	C7H11O2S⁻	-0.4	-1.7	
	BHM	20 June 2004	4.20	239.0223	C ₇ H ₁₁ O ₇ S [−]	-0.2	-0.8	
	JST	20 June 2004	1.57	244.0134	C₅H ₁₀ NO ₈ S⁻	0.7	2.9	
	JST	23 June 2004	-	-	-	-	-	
	JST	26 June 2004	1.58	244.0127	C₅H ₁₀ NO ₈ S⁻	0.0	0.0	
	CTR	11 June 2004	1 55	244 0138	C₅H₁₀NO₀S⁻	11	45	
244	CTR	23 June 2004	-	-	-	-	-	isoprene
	CTR	20 June 2004	_	_	_	_	_	
	OIK	29 June 2004	-	-	-	-	-	
	рцм	17 June 2004	1 57	244 0120		0.2	0 0	
		17 June 2004	1.57	244.0129		0.2	0.0	
		20 June 2004	1.57	244.0125	C5H10NO8S	-0.2	-0.8	
	JST	20 June 2004	6.47	249.0807	$C_{10}H_{17}O_5S$	1.0	4.0	
	JST	23 June 2004	-	-		-	-	
	JST	26 June 2004	6.47	249.0826	$C_{10}H_{17}O_5S^{-1}$	2.9	11.6	
249	CTR	11 June 2004	6.47	249.0820	C ₁₀ H ₁₇ O₅S ⁻	2.3	9.2	<i>a</i> -ninene
isomer 1	CTR	23 June 2004	-	-	-	-	-	a-pinene
	CTR	29 June 2004	6.52	249.0807	C ₁₀ H ₁₇ O ₅ S [−]	1.0	4.0	
	BHM	17 June 2004	6.49	249.0817	C ₁₀ H ₁₇ O ₅ S ⁻	2.0	8.0	
	BHM	20 June 2004	-	-	-	-	-	
	JST	20 June 2004	7.30	249.0810	C ₁₀ H ₁₇ O ₅ S [−]	1.3	5.2	
	JST	23 June 2004	7.31	249.0813	C ₁₀ H ₁₇ O ₅ S [−]	1.6	6.4	
	JST	26 June 2004	7.30	249.0813	C10H17O5S ⁻	1.6	6.4	
		20 00.10 200 .			010.17030		••••	
249	CTP	11 June 2004	7 20	249 0808	C.,,H.,-O-S-	11	44	
isomer 2	CTP	23 June 2004	7 20	240.0812	CHO.S ⁻	1.1	6.0	α-pinene
ISOINEI Z	CTD	20 June 2004	7.20	249.0012		1.0	4.0	
		23 JUNE 2004	1.52	273.0001	0101117050	1.0	4.0	
	DLIM	17 June 2004	7 2 2	240.0024		24	0.6	
		17 June 2004	1.32	249.0021		2.4	9.0 0 0	
		20 June 2004	7.40	249.0017		2.0	0.0	
	121	20 June 2004	7.49	249.0801		0.4	1.6	
	JST	23 June 2004	7.51	249.0810	C ₁₀ H ₁₇ O ₅ S [−]	1.3	5.2	
	JST	26 June 2004	7.49	249.0813	C ₁₀ H ₁₇ O ₅ S⁻	1.6	6.4	
249	CTR	11 June 2004	7.47	249.0799	C ₁₀ H ₁₇ O ₅ S [−]	0.2	0.8	ß-ninene
isomer 3	CTR	23 June 2004	7.49	249.0811	C ₁₀ H ₁₇ O ₅ S [−]	1.4	5.6	P-buoue
	CTR	29 June 2004	-	-	-	-	-	
	BHM	17 June 2004	7.51	249.0808	C ₁₀ H ₁₇ O ₅ S [−]	1.1	4.4	
	BHM	20 June 2004	7 4 9	249 0799	CueHurOrS ⁻	02	0.8	

	JST	20 June 2004	7.57	249.0812	$C_{10}H_{17}O_5S^{-}$	1.5	6.0	
	JST	23 June 2004	7 59	249 0811	C10H17O5S ⁻	14	56	
	JST	26 June 2004	7 59	249 0814	C40H47O2S	17	6.8	
	001	20 00110 2001	1.00	210.0011	010117050		0.0	
249	CTR	11 June 2004	7 50	240 0708	CHO-S-	0.1	04	
inomor 4	СТР	22 June 2004	7.55	240.0900		1.2	10.4	β-pinene
Isomer 4		23 June 2004	7.50	249.0009		1.2	4.0	
	CIR	29 June 2004	7.54	249.0790	$C_{10}\Pi_{17}O_5S$	-0.1	-0.4	
		17 1	7.04	040.0705	0 11 0 0-	10	4.0	
	BHM	17 June 2004	7.61	249.0785	$C_{10}H_{17}O_5S$	-1.2	-4.8	
	BHM	20 June 2004	7.59	249.0811	$C_{10}H_{17}O_5S^-$	1.4	5.6	
	JST	20 June 2004	1.79	260.0059	C₅H₁₀NO₀S⁻	-1.7	-6.5	
	JST	23 June 2004	1.91	260.0092	C₅H₁₀NO₀S⁻	1.6	6.2	
	JST	26 June 2004	1.84	260.0053	C₅H₁₀NO₀S⁻	-2.3	-8.8	
260	CTR	11 June 2004	1.81	260.0082	C₅H₁₀NO₀S⁻	0.6	2.3	icontono
isomer 1	CTR	23 June 2004	-	-	-	-	-	isoprene
	CTR	29 June 2004	1.86	260.0085	C₅H₁₀NO₀S⁻	0.9	3.5	
	BHM	17 June 2004	1 86	260 0071	C. H. NO S	-0.5	-19	
	BHM	20 June 2004	1.00	260.0071		0.0	1.0	
		20 June 2004	2.16	200.0075		1 2	5.0	
	101	20 June 2004	2.10	200.0069		1.5	5.0	
	121	23 June 2004	2.25	200.0001		-1.5	-5.0	
	JST	26 June 2004	2.21	260.0076	$C_5H_{10}NO_9S$	0.0	0.0	
260	CTR	11 June 2004	2.12	260.0082	C₅H₁₀NO₀S⁻	0.6	2.3	isoprene
isomer 2	CTR	23 June 2004	-	-	-	-	-	leoprono
	CTR	29 June 2004	2.15	260.0074	C₅H₁₀NO₀S⁻	-0.2	-0.8	
	BHM	17 June 2004	2.16	260.0076	C₅H₁₀NO₀S⁻	0.0	0.0	
	BHM	20 June 2004	2.15	260.0076	C₅H₁₀NO₀S⁻	0.0	0.0	
	JST	20 June 2004	2.41	260.0074	C₅H ₁₀ NO ₉ S [−]	-0.2	-0.8	
	JST	23 June 2004	2.46	260.0084	C₅H10NO9S ⁻	0.9	3.5	
	JST	26 June 2004	2 4 9	260 0067	C ₅ H ₁₀ NO ₀ S ⁻	-0.9	-35	
	001	20 00110 2001	2.10	200.0001	0311010090	0.0	0.0	
260	CTR	11 June 2004	2 16	260 0078	C. H. NO S	02	0.8	
isomer 3	CTP	23 June 2004	2.10	200.0070	051101090	0.2	0.0	isoprene
isonici o	СТР	20 June 2004	2 40	260 0060		1.6	6.2	
	UIK	29 June 2004	2.40	200.0000	C5111010095	-1.0	-0.2	
		17 1	0.45	000 0077		0.4	0.4	
	BHIM	17 June 2004	2.45	260.0077		0.1	0.4	
	BHM	20 June 2004	2.41	260.0077	C ₅ H ₁₀ NO ₉ S	0.1	0.4	
	JST	20 June 2004	3.01	260.007	C₅H₁₀NO₀S⁻	-0.6	-2.3	
	JST	23 June 2004	-	-	-	-	-	
	JST	26 June 2004	2.66	260.0067	C₅H₁₀NO₀S⁻	-0.9	-3.5	
260	CTR	11 June 2004	2.42	260.0080	C₅H₁₀NO₀S⁻	0.4	1.5	isoprene
isomer 4	CTR	23 June 2004	-	-	-	-	-	looprene
	CTR	29 June 2004	-	-	-	-	-	
	BHM	17 June 2004	3.18	260.0076	C₅H₁₀NO₀S⁻	-0.1	-0.4	
	BHM	20 June 2004	2.64	260.0079	C₅H ₁₀ NO ₉ S [−]	0.3	1.2	
	JST	20 June 2004	4 56	279 0531	$C_{10}H_{15}O_7S^-$	-0.7	-25	
	JST	23 June 2004	4 59	279 0536	C10H15O7S	-0.2	-0.7	
	IST	26 June 2004	4 59	279 0529	CHO-S ⁻	_0 Q	-3.2	
	001	20 00110 2004	4.00	210.0020	010115070	-0.5	-0.2	
270	СТР	11 Juno 2004	1 55	270 0529	CH. 0.9-	_1 0	-3 6	
LIS icomor 1		23 June 2004	4.00	213.0020		-1.0	-3.0	unknown monoterpene
ISUTIEL L		20 June 2004	4.00	219.0000		2.2	1.9	
	CIR	29 June 2004	4.59	219.0535	U ₁₀ H ₁₅ U ₇ S	-0.3	-1.1	
		17 has 000 f	4 = 0	070 0505	0 11 0 0-	C 1	~ ·	
	BHM	17 June 2004	4.58	2/9.0537	C ₁₀ H ₁₅ O ₇ S ⁻	-0.1	-0.4	
	BHM	20 June 2004	4.56	279.0536	C ₁₀ H ₁₅ O ₇ S⁻	-0.2	-0.7	

	JST	20 June 2004	5.27	279.0548	C ₁₀ H ₁₅ O ₇ S ⁻	1.0	3.6	
	JST	23 June 2004	5 31	279 0554	C10H15O7S ⁻	16	57	
	JST	26 June 2004	5.31	279 0542	C40H45O7S	17	6.1	
	001	20 00110 2001	0.01	210.0012	010115070		0.1	
279	CTR	11 June 2004	5 27	279 0534	C.H.O.S-	-0.4	-14	
inomor 2	СТР	22 June 2004	5.27	270.0525		0.7	-1.4	α -/ β -pinene
Isomer 2		23 June 2004	5.27	279.0555	U10H15U73	-0.5	-1.1	
	CIR	29 June 2004	-	-	-	-	-	
		17	F 00	070 0540	0 11 0 0-			
	BHM	17 June 2004	5.28	279.0549	C ₁₀ H ₁₅ O ₇ S	1.1	3.9	
	BHM	20 June 2004	5.28	279.0539	$C_{10}H_{15}O_7S^{-1}$	0.1	0.4	
	JST	20 June 2004	5.41	279.0542	C ₁₀ H ₁₅ O ₇ S⁻	0.4	1.4	
	JST	23 June 2004	5.42	279.0536	C ₁₀ H ₁₅ O ₇ S⁻	-0.2	-0.7	
	JST	26 June 2004	5.41	279.0541	C ₁₀ H ₁₅ O ₇ S [−]	0.3	1.1	
279	CTR	11 June 2004	5.40	279.0544	C ₁₀ H ₁₅ O ₇ S [−]	0.6	2.2	- 10 pipepe
isomer 3	CTR	23 June 2004	5.40	279.0529	C ₁₀ H ₁₅ O ₇ S [−]	-0.9	-3.2	α-/p-pinene
	CTR	29 June 2004	5.45	279.0554	C10H15O7S [−]	1.6	5.7	
					- 10: 110 - 7 -			
	BHM	17 June 2004	5 4 3	279 0551	CueHarO-S	13	47	
	BHM	20 June 2004	5.40	279.0541	CHO-S-	03	1 1	
		20 June 2004	5.50	270.0528		1.0	3.6	
	101	20 June 2004	5.50	279.0520		-1.0	-3.0	
	121	23 June 2004	5.01	279.0547		0.9	3.Z	
	121	26 June 2004	5.66	279.0545	$C_{10}H_{15}O_7S$	0.7	2.5	
070	OTD	44.4 0004		070 0554	<u> </u>	4.0		
279	CIR	11 June 2004	5.64	279.0554	$C_{10}H_{15}O_7S$	1.6	5.7	unknown monoterpene
isomer 4	CTR	23 June 2004	-	-	-	-	-	
	CTR	29 June 2004	-	-	-	-	-	
	BHM	17 June 2004	5.53	279.0546	C ₁₀ H ₁₅ O ₇ S [−]	0.8	2.9	
	BHM	20 June 2004	5.57	279.0541	C ₁₀ H ₁₅ O ₇ S [−]	0.3	1.1	
	JST	20 June 2004	-	-	-	-	-	
	JST	23 June 2004	-	-	-	-	-	
	JST	26 June 2004	-	-	-	-	-	
281	CTR	11 June 2004	4.75	281.0695	C10H17O7S ⁻	0.0	0.0	
	-		-		- 10 11 - 1 -			Unknown monotornono
Isomer 1	CTR	23 June 2004	-	-	-	-	-	unknown monoterpene
Isomer 1	CTR CTR	23 June 2004 29 June 2004	-	-	-	-	-	unknown monoterpene
Isomer 1	CTR CTR	23 June 2004 29 June 2004	-	-	-	-	-	unknown monoterpene
Isomer 1	CTR CTR BHM	23 June 2004 29 June 2004	-	-	-	-	-	unknown monoterpene
Isomer 1	CTR CTR BHM BHM	23 June 2004 29 June 2004 17 June 2004	-	-	-	-	-	
	CTR CTR BHM BHM	23 June 2004 29 June 2004 17 June 2004 20 June 2004 20 June 2004	- - -	- - -	- - -	- - -	- - -	
Isomer 1	CTR CTR BHM BHM JST	23 June 2004 29 June 2004 20 June 2004 20 June 2004 20 June 2004 20 June 2004	- - - -	- - - - - -	-		- - - - - 2 1	
Isomer 1	CTR CTR BHM BHM JST JST	11 June 2004 23 June 2004 29 June 2004 17 June 2004 20 June 2004 20 June 2004 20 June 2004 23 June 2004 20 June 2004 20 June 2004 20 June 2004	- - - 6.00	- - - 281.0701	- - - C ₁₀ H ₁₇ O ₇ S ⁻	- - - 0.6	- - - 2.1	
Isomer 1	CTR CTR BHM BHM JST JST JST	11 June 2004 23 June 2004 29 June 2004 17 June 2004 20 June 2004 20 June 2004 23 June 2004 26 June 2004	- - - 6.00 5.98	- - - 281.0701 281.0704	- - - - C ₁₀ H ₁₇ O ₇ S ⁻ C ₁₀ H ₁₇ O ₇ S ⁻	- - - 0.6 0.9	- - - 2.1 3.2	
	CTR CTR BHM BHM JST JST JST	11 June 2004 23 June 2004 29 June 2004 17 June 2004 20 June 2004 21 June 2004 22 June 2004 23 June 2004 26 June 2004	- - - 6.00 5.98		- - - - C ₁₀ H ₁₇ O ₇ S ⁻ C ₁₀ H ₁₇ O ₇ S ⁻	- - - 0.6 0.9	- - 2.1 3.2	
281	CTR CTR BHM BHM JST JST JST CTR	11 June 2004 23 June 2004 29 June 2004 20 June 2004 20 June 2004 23 June 2004 26 June 2004 11 June 2004	- - - 6.00 5.98 5.99	- - 281.0701 281.0704 281.0704	- - - C ₁₀ H ₁₇ O ₇ S ⁻ C ₁₀ H ₁₇ O ₇ S ⁻ C ₁₀ H ₁₇ O ₇ S ⁻	- - - 0.6 0.9 0.9	- - 2.1 3.2 3.2	unknown monoterpene
281 isomer 2	CTR CTR BHM JST JST JST CTR CTR CTR	11 June 2004 23 June 2004 29 June 2004 20 June 2004 20 June 2004 20 June 2004 23 June 2004 26 June 2004 11 June 2004 23 June 2004	- - - 6.00 5.98 5.99 5.99	- - 281.0701 281.0704 281.0704 281.0706	- - - C ₁₀ H ₁₇ O ₇ S ⁻ C ₁₀ H ₁₇ O ₇ S ⁻ C ₁₀ H ₁₇ O ₇ S ⁻ C ₁₀ H ₁₇ O ₇ S ⁻	- - - 0.6 0.9 0.9 1.1	- - 2.1 3.2 3.2 3.9	unknown monoterpene
281 isomer 2	CTR CTR BHM JST JST JST CTR CTR CTR CTR	11 June 2004 23 June 2004 29 June 2004 20 June 2004 20 June 2004 20 June 2004 23 June 2004 26 June 2004 11 June 2004 23 June 2004 29 June 2004	- - - 6.00 5.98 5.99 5.98 6.01	- - 281.0701 281.0704 281.0704 281.0706 281.0697	- - - C ₁₀ H ₁₇ O ₇ S ⁻ C ₁₀ H ₁₇ O ₇ S ⁻	- - - 0.6 0.9 0.9 1.1 0.2	- - 2.1 3.2 3.2 3.9 0.7	unknown monoterpene
281 isomer 2	CTR CTR BHM JST JST JST CTR CTR CTR	11 June 2004 23 June 2004 29 June 2004 20 June 2004 20 June 2004 20 June 2004 23 June 2004 26 June 2004 11 June 2004 23 June 2004 29 June 2004	- - 6.00 5.98 5.99 5.98 6.01	- - 281.0701 281.0704 281.0704 281.0706 281.0697	- - - C ₁₀ H ₁₇ O ₇ S ⁻ C ₁₀ H ₁₇ O ₇ S ⁻	- - 0.6 0.9 0.9 1.1 0.2	- 2.1 3.2 3.2 3.9 0.7	unknown monoterpene
281 isomer 2	CTR CTR BHM JST JST JST CTR CTR CTR CTR BHM	11 June 2004 23 June 2004 29 June 2004 20 June 2004 20 June 2004 20 June 2004 23 June 2004 26 June 2004 11 June 2004 23 June 2004 29 June 2004 17 June 2004	- - 6.00 5.98 5.99 5.98 6.01	- 281.0701 281.0704 281.0704 281.0706 281.0697 -	- - C ₁₀ H ₁₇ O ₇ S ⁻ C ₁₀ H ₁₇ O ₇ S ⁻	- - - 0.6 0.9 0.9 1.1 0.2	- 2.1 3.2 3.2 3.9 0.7	unknown monoterpene
281 isomer 2	CTR CTR BHM JST JST JST CTR CTR CTR CTR BHM BHM	11 June 2004 23 June 2004 29 June 2004 17 June 2004 20 June 2004 20 June 2004 20 June 2004 23 June 2004 26 June 2004 11 June 2004 23 June 2004 11 June 2004 29 June 2004 11 June 2004 29 June 2004 20 June 2004 20 June 2004 20 June 2004 17 June 2004 20 June 2004	- - 6.00 5.98 5.99 5.98 6.01 - 5.84	- - 281.0701 281.0704 281.0704 281.0706 281.0697 - 281.0696	- - - C ₁₀ H ₁₇ O ₇ S ⁻ C ₁₀ H ₁₇ O ₇ S ⁻	- - 0.6 0.9 0.9 1.1 0.2 - 0.1	- 2.1 3.2 3.2 3.9 0.7	unknown monoterpene
281 isomer 2	CTR CTR BHM JST JST JST CTR CTR CTR CTR BHM BHM JST	13 June 2004 23 June 2004 29 June 2004 17 June 2004 20 June 2004 20 June 2004 20 June 2004 23 June 2004 26 June 2004 21 June 2004 23 June 2004 24 June 2004 25 June 2004 29 June 2004 17 June 2004 20 June 2004	- - 6.00 5.98 5.99 5.98 6.01 - 5.84 6.45	- - 281.0701 281.0704 281.0704 281.0706 281.0697 - 281.0696 281.0702	- - - C ₁₀ H ₁₇ O ₇ S ⁻ C ₁₀ H ₁₇ O ₇ S ⁻	- - 0.6 0.9 0.9 1.1 0.2 - 0.1 0.7	- - 2.1 3.2 3.9 0.7 - 0.4 2.5	unknown monoterpene
281 isomer 2	CTR CTR BHM JST JST JST CTR CTR CTR BHM BHM JST JST	13 June 2004 23 June 2004 29 June 2004 17 June 2004 20 June 2004 20 June 2004 20 June 2004 23 June 2004 26 June 2004 23 June 2004 29 June 2004 11 June 2004 29 June 2004 29 June 2004 20 June 2004	- - 6.00 5.98 5.99 5.98 6.01 - 5.84 6.45 6.50	- - 281.0701 281.0704 281.0704 281.0706 281.0697 - 281.0696 281.0702 281.0700	- - - C ₁₀ H ₁₇ O ₇ S ⁻ C ₁₀ H ₁₇ O ₇ S ⁻	- - 0.6 0.9 0.9 1.1 0.2 - 0.1 0.7 0.5	- 2.1 3.2 3.9 0.7 - 0.4 2.5 1.8	unknown monoterpene
281 isomer 2	CTR CTR BHM JST JST JST CTR CTR CTR BHM BHM JST JST JST	13 June 2004 23 June 2004 29 June 2004 17 June 2004 20 June 2004 20 June 2004 20 June 2004 23 June 2004 26 June 2004 23 June 2004 29 June 2004 11 June 2004 29 June 2004 17 June 2004 20 June 2004 17 June 2004 20 June 2004	- - - 6.00 5.98 5.99 5.98 6.01 - 5.84 6.45 6.50 6.48	- - 281.0701 281.0704 281.0704 281.0706 281.0697 - 281.0696 281.0702 281.0700 281.0702	- - - C ₁₀ H ₁₇ O ₇ S ⁻ C ₁₀ H ₁₇ O ₇ S ⁻	- - 0.6 0.9 0.9 1.1 0.2 - 0.1 0.7 0.5 0.7	- 2.1 3.2 3.9 0.7 - 0.4 2.5 1.8 2.5	unknown monoterpene
281 isomer 2	CTR CTR JST JST JST CTR CTR CTR CTR BHM BHM JST JST JST	11 June 2004 23 June 2004 29 June 2004 17 June 2004 20 June 2004 20 June 2004 20 June 2004 23 June 2004 26 June 2004 23 June 2004 29 June 2004 11 June 2004 29 June 2004 17 June 2004 20 June 2004	- - 6.00 5.98 5.99 5.98 6.01 - 5.84 6.45 6.50 6.48	- 281.0701 281.0704 281.0704 281.0706 281.0697 - 281.0696 281.0702 281.0700 281.0702	$\begin{array}{c} - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ - $	- - 0.6 0.9 0.9 1.1 0.2 - 0.1 0.7 0.5 0.7	- 2.1 3.2 3.9 0.7 - 0.4 2.5 1.8 2.5	unknown monoterpene
281 isomer 2	CTR CTR BHM JST JST JST CTR CTR CTR CTR BHM BHM JST JST JST CTR	11 June 2004 23 June 2004 29 June 2004 17 June 2004 20 June 2004 20 June 2004 20 June 2004 23 June 2004 26 June 2004 23 June 2004 29 June 2004 20 June 2004 23 June 2004 26 June 2004 26 June 2004 11 June 2004 11 June 2004	- - - - - - - - - - - - - - - - - - -	- - 281.0701 281.0704 281.0704 281.0706 281.0697 - 281.0696 281.0702 281.0702 281.0702 281.0702	- - - - - - - - - - - - - - - - - - -	- - 0.6 0.9 0.9 1.1 0.2 - 0.1 0.7 0.5 0.7 -0.1	- 2.1 3.2 3.9 0.7 - - 0.4 2.5 1.8 2.5 -0.4	unknown monoterpene
281 isomer 2 281 isomer 3	CTR CTR BHM JST JST JST CTR CTR CTR BHM BHM JST JST JST CTR CTR	11 June 2004 23 June 2004 29 June 2004 17 June 2004 20 June 2004 20 June 2004 20 June 2004 20 June 2004 23 June 2004 24 June 2004 25 June 2004 26 June 2004 20 June 2004 21 June 2004 23 June 2004 24 June 2004 25 June 2004 26 June 2004 21 June 2004 22 June 2004 23 June 2004	- - 6.00 5.98 5.99 5.98 6.01 - 5.84 6.45 6.50 6.48 6.45 6.45 6.47	- 281.0701 281.0704 281.0704 281.0704 281.0706 281.0697 - 281.0696 281.0702 281.0702 281.0702 281.0694 281.0694 281.0688	- - - C ₁₀ H ₁₇ O ₇ S ⁻ C ₁₀ H ₁₇ O ₇ S ⁻	- - - 0.6 0.9 1.1 0.2 - 0.1 0.7 0.5 0.7 -0.1 -0.7	- 2.1 3.2 3.2 3.9 0.7 - - 0.4 2.5 1.8 2.5 -0.4 -2 5	unknown monoterpene unknown monoterpene
281 isomer 2 281 isomer 3	CTR CTR BHM JST JST JST CTR CTR CTR BHM BHM JST JST JST CTR CTR CTR CTR	11 June 2004 23 June 2004 29 June 2004 17 June 2004 20 June 2004 20 June 2004 20 June 2004 20 June 2004 23 June 2004 24 June 2004 25 June 2004 26 June 2004 29 June 2004 20 June 2004 21 June 2004 23 June 2004 21 June 2004 23 June 2004 24 June 2004 25 June 2004 26 June 2004 27 June 2004 28 June 2004	- - 6.00 5.98 5.99 5.98 6.01 - 5.84 6.45 6.50 6.48 6.45 6.47 6.52	- 281.0701 281.0704 281.0704 281.0704 281.0706 281.0697 - 281.0696 281.0700 281.0700 281.0702 281.0694 281.0688 281.0697	- - - C ₁₀ H ₁₇ O ₇ S ⁻ C ₁₀ H ₁₇ O ₇ S ⁻	- - 0.6 0.9 0.9 1.1 0.2 - 0.1 0.7 0.5 0.7 -0.1 -0.7 0.2	- 2.1 3.2 3.9 0.7 - 0.4 2.5 1.8 2.5 -0.4 -2.5 0.7	unknown monoterpene unknown monoterpene
281 isomer 2 281 isomer 3	CTR CTR JST JST JST CTR CTR CTR BHM BHM JST JST JST JST CTR CTR CTR CTR	11 June 2004 23 June 2004 29 June 2004 17 June 2004 20 June 2004 20 June 2004 20 June 2004 20 June 2004 23 June 2004 24 June 2004 25 June 2004 26 June 2004 29 June 2004 20 June 2004 23 June 2004 24 June 2004 25 June 2004 26 June 2004 27 June 2004 28 June 2004 29 June 2004	- - 6.00 5.98 5.99 5.98 6.01 - 5.84 6.45 6.45 6.45 6.45 6.47 6.52	- 281.0701 281.0704 281.0704 281.0704 281.0697 - 281.0696 281.0702 281.0702 281.0702 281.0694 281.0694 281.0697	$\begin{array}{c} - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ - \\ - $	- - - 0.6 0.9 0.9 1.1 0.2 - 0.1 0.7 0.5 0.7 -0.1 -0.7 0.2	- 2.1 3.2 3.9 0.7 - 0.4 2.5 1.8 2.5 -0.4 -2.5 0.7	unknown monoterpene unknown monoterpene
281 isomer 2 281 isomer 3	CTR CTR JST JST JST CTR CTR CTR BHM BHM JST JST JST CTR CTR CTR CTR CTR	13 June 2004 23 June 2004 29 June 2004 17 June 2004 20 June 2004 20 June 2004 20 June 2004 20 June 2004 23 June 2004 26 June 2004 21 June 2004 23 June 2004 29 June 2004 20 June 2004 21 June 2004 23 June 2004 21 June 2004 23 June 2004 21 June 2004 21 June 2004	- - 6.00 5.98 5.99 5.98 6.01 - 5.84 6.45 6.45 6.45 6.45 6.47 6.52	- 281.0701 281.0704 281.0704 281.0706 281.0697 - 281.0696 281.0702 281.0702 281.0702 281.0694 281.0694 281.0697	- - - - - - - - - - - - - - - - - - -	- - 0.6 0.9 0.9 1.1 0.2 - 0.1 0.7 0.5 0.7 -0.1 -0.7 0.2	- 2.1 3.2 3.9 0.7 - 0.4 2.5 1.8 2.5 -0.4 -2.5 0.7	unknown monoterpene unknown monoterpene
281 isomer 2 281 isomer 3	CTR CTR JST JST JST CTR CTR CTR CTR BHM BHM ST JST JST CTR CTR CTR CTR CTR BHM BHM	13 June 2004 23 June 2004 29 June 2004 17 June 2004 20 June 2004 20 June 2004 20 June 2004 20 June 2004 23 June 2004 26 June 2004 29 June 2004 21 June 2004 29 June 2004 20 June 2004 21 June 2004 23 June 2004 21 June 2004 23 June 2004 11 June 2004 23 June 2004 11 June 2004 29 June 2004 11 June 2004 20 June 2004 20 June 2004	- - - - - - - - - - - - - - - - - - -	- 281.0701 281.0704 281.0704 281.0704 281.0706 281.0697 - 281.0696 281.0702 281.0702 281.0694 281.0694 281.0697	- - C ₁₀ H ₁₇ O ₇ S ⁻ C ₁₀ H ₁₀ O ₇ S ⁻	- - - - 0.6 0.9 0.9 1.1 0.2 - 0.1 - 0.7 0.5 0.7 -0.1 -0.7 0.2 - 0.8	- 2.1 3.2 3.9 0.7 - 0.4 2.5 1.8 2.5 -0.4 -2.5 0.7	unknown monoterpene unknown monoterpene

	JST	20 June 2004	-	-	-	-	-	
	JST	23 June 2004	-	-	-	-	-	
	JST	26 June 2004	-	-	-	-	-	
	CTR	11 June 2004	-	-	-	-	-	
283	CTR	23 June 2004	_	-	-	-	_	unknown monoterpene
	CTR	29 June 2004	_	_	_	-	_	
	OII	20 00110 2004						
	вни	17 June 2004	1 60	283 0504	C.HO.S-	16	57	
		20 June 2004	4.00	200.0004	09115080	1.0	5.7	
		20 June 2004	7 60	204 0654	- CHNO-S ⁻	- 0.7	2.5	
	101	20 June 2004	7.09	294.0034		0.7	2.0	
	101	25 June 2004	7.73	294.0074		2.7	9.Z	
	101	20 June 2004	1.12	294.0002	C 101 1161 1073	1.5	5.1	
204	отр	11 June 2004	7 74	204.0000		2.2	7 5	
294		11 June 2004	7.71	294.0009	$C_{10}\Pi_{16}NO_7S$	2.2	7.5	unknown monoterpene
Isomer 1		23 June 2004	7.71	294.0071	$C_{10}\Pi_{16}NO_7S$	2.4	0.2	
	CIR	29 June 2004	1.16	294.0667	$C_{10}H_{16}NO_7S$	2.0	6.8	
		47 1 0004						
	BHM	17 June 2004		-	-	-		
	BHW	20 June 2004	1./1	294.0643	C ₁₀ H ₁₆ NO ₇ S	-0.4	-1.4	
	JST	20 June 2004	8.20	294.0637	C ₁₀ H ₁₆ NO ₇ S	-1.0	-3.4	
	JST	23 June 2004	8.19	294.0646	C ₁₀ H ₁₆ NO ₇ S [−]	-0.1	-0.3	
	JST	26 June 2004	8.18	294.0661	C ₁₀ H ₁₆ NO ₇ S⁻	1.4	4.8	
_			_		. .			
294	CTR	11 June 2004	8.19	294.0654	C ₁₀ H ₁₆ NO ₇ S⁻	0.7	2.4	a-ninene
isomer 2	CTR	23 June 2004	8.18	294.0647	C ₁₀ H ₁₆ NO ₇ S⁻	0.0	0.0	a-pinene
	CTR	29 June 2004	8.24	294.0642	C ₁₀ H ₁₆ NO ₇ S⁻	-0.5	-1.7	
	BHM	17 June 2004	8.24	294.0647	C ₁₀ H ₁₆ NO ₇ S⁻	0.0	0.0	
	BHM	20 June 2004	8.17	294.0606	C ₁₀ H ₁₆ NO ₇ S [−]	-4.1	-13.9	
	JST	20 June 2004	8.75	294.0619	C ₁₀ H ₁₆ NO ₇ S ⁻	-2.8	-9.5	
	JST	23 June 2004	8.62	294.0658	C10H16NO7S [−]	1.1	3.7	
	JST	26 June 2004	8.60	294.0679	C10H16NO7S [−]	3.2	10.9	
294	CTR	11 June 2004	8 78	294 0644		-0.3	-10	
isomer 3	CTR	23 June 2004	8 77	294 0645		-0.2	-0.7	α -pinene
	CTR	29 June 2004	8 66	294 0663	C10H10NO7S	16	54	
	0111	20 00110 200 1	0.00	201.0000		1.0	0.1	
	BHM	17 June 2004	_	_	_	-	_	
	BHM	20 June 2004	8 77	204 0622	CHNO-S-	-25	-85	
		20 June 2004	8.77	204.0626	C H NO-S	-2.5	-0.5	
	IST	23 June 2004	8.80	204.0630	C H NO-S ⁻	-2.1	-2.7	
	101	26 June 2004	9 70	204.0655		-0.0	2.7	
	101	20 June 2004	0.79	294.0000	C 101 1161 1073	0.0	2.1	
204	СТР	11 June 2004						
294	CTD	22 June 2004	-	-	-	-	-	α -pinene
ISOITIEI 4		23 June 2004	-	-		-	-	
	UR	29 June 2004	0.02	294.0048	C ₁₀ Π ₁₆ NO ₇ S	0.1	0.3	
		17 June 0004	0.00	004 0054		0.4		
	BHIM	17 June 2004	8.83	294.0651	$C_{10}H_{16}NO_7S$	0.4	1.4	
	BHIM	20 June 2004	-	-	-	-	-	
	JST	20 June 2004	8.95	294.0647	C ₁₀ H ₁₆ NO ₇ S	-2.9	-9.9	
	JST	23 June 2004	8.99	294.0645	C ₁₀ H ₁₆ NO ₇ S	-0.2	-0.7	
	JST	26 June 2004	8.99	294.0648	C ₁₀ H ₁₆ NO ₇ S⁻	0.1	0.3	
294	CTR	11 June 2004	8.99	294.0645	C ₁₀ H ₁₆ NO ₇ S⁻	-0.2	-0.7	a-ninene
isomer 5	CTR	23 June 2004	8.97	294.0643	C ₁₀ H ₁₆ NO ₇ S⁻	-0.4	-1.4	a-pinene
	CTR	29 June 2004	-	-	-	-	-	
	BHM	17 June 2004	-	-	-	-	-	
	BHM	20 June 2004	8.97	294.0626	C ₁₀ H ₁₆ NO ₇ S [−]	-2.1	-7.1	
	JST	20 June 2004	9.02	294.0649	C ₁₀ H ₁₆ NO ₇ S ⁻	0.2	0.7	
	JST	23 June 2004	9.06	294.0643	C ₁₀ H ₁₆ NO ₇ S⁻	-0.4	-1.4	
	JST	26 June 2004	9.05	294.0663	C ₁₀ H ₁₆ NO ₇ S [−]	1.6	5.4	
294	CTR	11 June 2004	9.05	294.0648	C ₁₀ H ₁₆ NO ₇ S [−]	0.1	0.3	
isomer 6	CTR	23 June 2004	9.04	294.0665	C ₁₀ H ₁₆ NO ₇ S [−]	1.8	6.1	α-pinene
	CTR	29 June 2004	9.04	294.0644	C ₁₀ H ₁₆ NO ₇ S [−]	-0.3	-1.0	
					- 10 - 10 - 070			
	BHM	17 June 2004	9.04	294,0671	C₁₀H₁₅NO₂S⁻	24	82	
	BHM	20 June 2004	9.05	294.0640	C ₁₀ H ₁₆ NO ₇ S [−]	-0.7	-2.4	
					- 10. 10. 0 / 0	÷.,		

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isomer 1 CTR 23 June 2004 5.86 296.0444 $C_9H_{14}NO_9S^{-}$ 0.4 1.4 Infinite Heritik CTR 29 June 2004 5.91 296.0444 $C_9H_{14}NO_9S^{-}$ 0.4 1.4 Infinite Heritik 20 June 2004 5.86 296.0444 $C_9H_{14}NO_9S^{-}$ 0.4 1.4 JST 20 June 2004 6.08 296.0447 $C_9H_{14}NO_9S^{-}$ 0.3 -1.0 JST 23 June 2004 6.11 296.0437 $C_9H_{14}NO_9S^{-}$ -0.3 -1.0 JST 26 June 2004 6.10 296.0456 $C_9H_{14}NO_9S^{-}$ 1.6 5.4 If NO_9S^{-} 1.6 5.4 CTR 23 June 2004 6.13 296.0436 $C_9H_{14}NO_9S^{-}$ 1.0 3.4 If monene-lik CTR 29 June 2004 6.13 296.0436 $C_9H_{14}NO_9S^{-}$ -0.4 -1.4 If NO_9S^{-} 2.7 CTR 23 June 2004 6.13 296.0436 $C_9H_{14}NO_9S^{-}$ -0.4 -1.4 If NO_9S^{-} 2.7 CTR 29 June 2004 6.98 296.0438 $C_9H_{14}NO_9S^{-}$ -0.4 -1.4 If NO_9S^{-} 2.2 CTR 23 June 2004 6.98 296.0438 $C_9H_{14}NO_9S^{-}$ -0.2 -0.7 JST 26 June 2004 7.02 296.0435 $C_9H_{14}NO_9S^{-}$ -0.3 -1.0 JST 20 June 2004 7.01 296.0433 $C_9H_{14}NO_9S^{-}$ -0.3 -1.0 JST 26 June 2004 7.01 296.0433 $C_9H_{14}NO_9S^{-}$ -0.3 -1.0 JST 20 June 2004 7.01 296.0433 $C_9H_{14}NO_9S^{-}$ -0.3 -1.0 JST 20 June 2004 7.01 296.0433 $C_9H_{14}NO_9S^{-}$ -0.3 -1.0 JST 20 June 2004 7.06 296.0436 $C_9H_{14}NO_9S^{-}$ -0.3 -1.0 JST 20 June 2004 7.01 296.0443 $C_9H_{14}NO_9S^{-}$ -0.3 -1.0 JST 20 June 2004 7.06 296.0436 $C_9H_{14}NO_9S^{-}$ -0.3 -1.0 JST 20 June 2004 7.06 296.0436 $C_9H_{14}NO_9S^{-}$ -0.3 -1.0 JST 20 June 2004 7.06 296.0433 $C_9H_{14}NO_9S^{-}$ -0.4 -1.4 If monene-lik BHM 17 June 2004 7.06 296.0443 $C_9H_{14}NO_9S^{-}$ -0.3 -1.0 JST 20 June 2004 7.06 296.0443 $C_9H_{14}NO_9S^{-}$ -0.3 -1.0 JST 20 June 2004 7.06 296.0443 $C_9H_{14}NO_9S^{-}$ -1.1 -3.6 JST 20 June 2004 4 4.67 304.9916 $C_9H_{9}N_2O_{11}S^{-}$ -1.1 -3.6 JST 20 June 2004 4 4.67 304.9916 $C_9H_9N_2O_{11}S^{-}$ -1.1 -3.6 JST 26 June 2004 4 4.67 304.9939 $C_9H_9N_2O_{11}S^{-}$ -1.1 -3.6 JST 20 June 2004 4 4.67 304.9939 $C_9H_9N_2O_{11}S^{-}$ -1.1 -3.6 JST 20 June 2004 4 4.67 304.9939 $C_9H_9N_2O_{11}S^{-}$ -1.1 -3.6 JST 20 June 2004 4 4.67 304.9939 $C_9H_9N_2O_{11}S^{-}$ -1.1 -3.6 JSO SO SO SO SO SO SO S	
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isomer 1 CTR 23 June 2004	
CTR 29 June 2004	
BHM 17 June 2004 4.68 304.9945 C₅H₀N₂O₁1S⁻ 1.8 5.9	
BHM 20 June 2004 4 65 304 9932 C Ho 2015 0 5 1 6	
JST 20 June 2004 4.80 304.9915 CsHaN2O11S -1.2 -3.9	
JST 23 June 2004	
JST 26 June 2004 4 80 304 9922 Cr HoN2Q11ST -0.5 -1.6	
305 CTR 11. June 2004 4.80 304.9948 C₅H₀N₂O₁₁S ⁻ 2.1 6.9	
isomer 2 CTR 23 June 2004	
CTR 29 June 2004	
BHM 17 June 2004 4.82 304.9925 C₅H₀N₂O₁₁S⁻ -0.2 -0.7	
BHM 20 June 2004 4.82 304.9937 C5H3N2O11S ⁻ 1.0 3.3	
JST 20 June 2004 5.13 304.9943 CsHaN2O11S 1.6 5.2	
JST 23 June 2004	
JST 26 June 2004 5.13 304.9911 CsHut N2OuS ⁻ -1.6 -5.2	
305 CTR 11 June 2004	
isomer 3 CTR 23 June 2004 isoprene	
CTR 29 June 2004	
BHM 17 June 2004 5.16 304.9944 C₅H₀N₂O₁₁S⁻ 1.7 5.6	
BHM 20 June 2004 5.13 304.9952 C H N 2018 2.5 8.2	
JST 20 June 2004 5.40 304.9923 CsHaN2O11S -0.4 -1.3	
JST 23 June 2004 5 45 304 9951 C H N 2015 2 4 7 9	
JST 26 June 2004 5.37 304 9905 CaHoN204822 - 72	
305 CTR 11 June 2004 5.41 304.9942 C₅H₅N₂O↔S⁻ 1.5 4.9	
isomer 4 CTR 23 June 2004 isoprene	
CTR 29 June 2004	
BHM 17 June 2004 5.42 304.9943 C₅H₅N₂O↔S⁻ 1.6 5.2	
BHM 20 June 2004 5.42 304.9919 C ₅ H ₉ N ₂ O ₁₁ S ⁻ -0.8 -2.6	

	JST	20 June 2004	-	-	-	-	-	
	IST	23 June 2004	_	_	_	_	_	
	100	26 Juno 2004	6 05	304 0016		07	23	
	101	20 June 2004	0.05	304.9910	$C_5 \Pi_9 \Pi_2 O_{11} O_$	-0.7	-2.5	
005	OTD	44 1						
305	CIR	11 June 2004	-	-	-	-	-	isoprene
isomer 5	CTR	23 June 2004	-	-	-	-	-	
	CTR	29 June 2004	-	-	-	-	-	
	BHM	17 June 2004	6.10	304.9933	C₅H ₉ N ₂ O ₁₁ S ⁻	0.6	2.0	
	BHM	20 June 2004	6.06	304,9959	C5H0N2O11S	3.2	10.5	
	JST	20 June 2004	7 20	310 0590	CasHasNOsS ⁻	-0.7	-2.3	
	IST	23 June 2004	1.20	010.0000	010111611080	0.7	2.0	
	101	20 June 2004	-	-		~ ~	1.0	
	121	26 June 2004	1.21	310.0002	C10H16NO85	0.5	1.0	
240								
310	CIR	11 June 2004	7.21	310.0608	$C_{10}H_{16}NO_8S$	1.1	3.5	unknown monoterpene
isomer 1	CTR	23 June 2004	-	-	-	-	-	
	CTR	29 June 2004	-	-	-	-	-	
	BHM	17 June 2004	-	-	-	-	-	
	BHM	20 June 2004	-	-	-	-	-	
	JST	20 June 2004	7 93	310 0603	C40H40NO0ST	0.6	19	
	IST	23 June 2004	7.05	310.0602	C.H.NO.S	0.5	1.6	
	101	25 June 2004	7.95	210.0002		1.5	1.0	
	121	26 June 2004	7.92	310.0612	$C_{10}H_{16}NO_8S$	1.5	4.8	
310	CTR	11 June 2004	7.93	310.0594	C ₁₀ H ₁₆ NO ₈ S⁻	-0.3	-1.0	unknown monoternene
isomer 2	CTR	23 June 2004	7.92	310.0586	C ₁₀ H ₁₆ NO ₈ S⁻	-1.1	-3.5	unition in monoterpene
	CTR	29 June 2004	7.99	310.0598	C ₁₀ H ₁₆ NO ₈ S⁻	0.1	0.3	
	BHM	17 June 2004	7.97	310.0603	C₁₀H₁₀NO₀S⁻	0.6	1.9	
	BHM	20 June 2004	7 93	310 0602	C40H40NO ₀ S ⁻	0.5	1.6	
		20 June 2004	6.78	324 0387		_0.2	-0.6	
	101	20 June 2004	6.02	324.0307	$C_{10} \Pi_{14} \Pi O_9 S$	-0.2	-0.0	
	121	23 June 2004	0.03	324.0309		0.0	0.0	
	JST	26 June 2004	6.80	324.0392	$C_{10}H_{14}NO_9S$	0.3	0.9	
324	CTR	11 June 2004	6.78	324.0412	C₁₀H₁₄NO₀S⁻	2.3	7.1	unknown monotornono
524	CTR	23 June 2004	6.79	324.0380	C ₁₀ H ₁₄ NO ₉ S⁻	-0.9	-2.8	unknown monoterpene
	CTR	29 June 2004	6.84	324.0388	C ₁₀ H ₁₄ NO ₉ S [−]	-0.1	-0.3	
	BHM	17 June 2004	6.83	324 0381	C ₄₀ H ₄₄ NO ₀ S [−]	-0.8	-25	
	BHM	20 June 2004	6 79	324 0302		0.0	<u> </u>	
		20 June 2004	5.50	226.0550		0.0	1.2	
	101	20 June 2004	5.56	320.0550	$C_{10}\Pi_{16}NO_{9}S$	0.4	1.2	
	121	23 June 2004	5.60	326.0556	C ₁₀ H ₁₆ NO ₉ S	1.0	3.1	
	JST	26 June 2004	5.59	326.0557	$C_{10}H_{16}NO_9S$	1.1	3.4	
326	CTR	11 June 2004	5.57	326.0574	C₁₀H₁₀NO₀S⁻	2.8	8.6	unknown monoternene
isomer 1	CTR	23 June 2004	5.57	326.0536	C ₁₀ H ₁₆ NO ₉ S⁻	-1.0	-3.1	unknown monoterpene
	CTR	29 June 2004	-	-	-	-	-	
	BHM	17 June 2004	-	-	_	-	-	
	BHM	20 June 2004	5 57	326 0554	Cultur NO ST	0.8	25	
		20 June 2004	6.25	226.0544		0.0	2.5	
	101	20 JUINE 2004	6.00	320.0344		-0.2	-0.0	
	101	23 June 2004	0.20	320.0343		-0.1	-0.5	
	121	26 June 2004	6.27	326.0544	$C_{10}H_{16}NO_9S^-$	-0.2	-0.6	
326	CTR	11 June 2004	6.25	326.0564	C ₁₀ H ₁₆ NO ₉ S⁻	1.8	5.5	unknown monoterneno
isomer 2	CTR	23 June 2004	6.25	326.0546	C ₁₀ H ₁₆ NO ₉ S⁻	0.0	0.0	and own monoterpelle
	CTR	29 June 2004	6.30	326.0546	C ₁₀ H ₁₆ NO ₉ S⁻	1.3	4	
	BHM	17 June 2004	6 29	326 0535	C₁₀H₁₀NO₀S⁻	-1 1	-34	
	BHM	20 June 2004	6 25	326 0538		-0 8	-25	
	D 1100		0.20	0-0.0000		0.0		

	JST	20 June 2004	-	-	-	-	-	
	JST	23 June 2004	7.41	326.0552	C ₁₀ H ₁₆ NO ₉ S⁻	0.6	1.8	
	JST	26 June 2004	7.40	326.0562	C ₁₀ H ₁₆ NO ₉ S⁻	1.6	4.9	
326	CTR	11 June 2004	7.39	326.0576	$C_{10}H_{16}NO_9S^-$	3.0	9.2	unknown monoterpene
isomer 3	CTR	23 June 2004	7.40	326.0556	C ₁₀ H ₁₆ NO ₉ S⁻	1.0	3.1	
	CIR	29 June 2004	-	-	-	-	-	
	DUM	17 June 0004	7 40	200 0500		~ ~	0.7	
	BHIM	17 June 2004	7.42	326.0568	$C_{10}H_{16}NO_{9}S$	2.2	6.7	
		20 June 2004	- 7.09	-		-	-	
	JST IST	20 June 2004	7.90	326.0543	C	-0.3	-0.9	
	JST	26 June 2004	7.98	326 0555	C10H16NO9S	1.7	0.2	
	001	20 00110 2004	1.00	020.0000	0 101 1161 00 90			
326	CTR	11 June 2004	7 97	326 0569	C₁₀H₁₀NO₀S⁻	23	71	
isomer 4	CTR	23 June 2004	7.97	326.0535	C10H16NO9S [−]	-1.1	-3.4	unknown monoterpene
	CTR	29 June 2004	_	-	-	-	-	
	BHM	17 June 2004	-	-	-	-	-	
	BHM	20 June 2004	7.97	326.0556	C ₁₀ H ₁₆ NO ₉ S⁻	1.0	3.1	
	JST	20 June 2004	8.05	326.0571	C ₁₀ H ₁₆ NO ₉ S⁻	2.5	7.7	
	JST	23 June 2004	-	-	-	-	-	
	JST	26 June 2004	-	-	-	-	-	
326	CTR	11 June 2004	8.03	326.0570	C ₁₀ H ₁₆ NO ₉ S⁻	2.4	7.4	unknown monoterpene
isomer 5	CTR	23 June 2004	-	-	-	-	-	
	CIR	29 June 2004	-	-	-	-	-	
		47 1 0004						
	BHM	17 June 2004	-	-	-	-	-	
		20 June 2004	- 0 40	-		-	-	
	JOI	20 June 2004	0.49	320.0559	C ₁₀ П ₁₆ NO ₉ S	-0.7	-2.1	
	JOT IST	25 June 2004	- 8/8	326 0577	- CHNO.S ⁻	- 31	0.5	
	001	20 June 2004	0.40	520.0577	C10111610095	5.1	9.5	
326	CTR	11 June 2004	-	-	_	-	-	
isomer 6	CTR	23 June 2004	-	-	-	-	-	unknown monoterpene
	CTR	29 June 2004	-	-	-	-	-	
	BHM	17 June 2004	-	-	-	-	-	
	BHM	20 June 2004	8.48	326.0542	C ₁₀ H ₁₆ NO ₉ S⁻	-0.4	-1.2	
	JST	20 June 2004	-	-	-	-	-	
	JST	23 June 2004	-	-	-	-	-	
	JST	26 June 2004	-	-	-	-	-	
331	CTR	11 June 2004	0.92	331.0688	C ₁₀ H ₁₉ O ₁₀ S⁻	-1.1	-3.3	isoprene
	CTR	23 June 2004	-	-	-	-	-	
	CIR	29 June 2004	-	-	-	-	-	
	DUM	17 June 2004						
		17 June 2004	-	-	-	-	-	
		20 June 2004	- 0.02	- 333 0866	- 	- 1 1	33	
	JST	20 June 2004	0.52	-	-	-	-	
	JST	26 June 2004	-	-	_	-	-	
		20 00.10 200 1						
333	CTR	11 June 2004	0.94	333.0860	C10H21O10S ⁻	0.5	1.5	
isomer 1	CTR	23 June 2004	_	-	-	-	-	isoprene
	CTR	29 June 2004	0.95	333.0875	C ₁₀ H ₂₁ O ₁₀ S [−]	2.0	6.0	
					-			
	BHM	17 June 2004	0.95	333.0847	C ₁₀ H ₂₁ O ₁₀ S [−]	-0.8	-2.4	
	BHM	20 June 2004	-	-		-	-	
	JST	20 June 2004	-	-	-	-	-	
	JST	23 June 2004	-	-	-	-	-	
	JST	26 June 2004	-	-	-	-	-	
0.00	<u></u>	44.1 666.						
333	CTR	11 June 2004	-	-	-	-	-	isoprene
isomer 2		23 June 2004	-	-	-	-	-	
	UR	29 June 2004	-	-	-	-	-	
	впи	17 June 2004	1 02	333 0073	CHO S-	1.0	51	
	BHM	20 June 2004	-	-	-	-	-	

	JST	20 June 2004	-	-	-	-	-	
	JST	23 June 2004	-	-	-	-	-	
	JST	26 June 2004	-	-	-	-	-	
	001	20 00110 2001						
333	CTP	11 June 2004	2 16	333 0857		0.2	0.6	
inomor 2	CTD	22 June 2004	2.10	333.0037	01011210100	0.2	0.0	isoprene
isomer 3		23 June 2004	-	-	-	-	-	
	UIR	29 June 2004	-	-	-	-	-	
	D 1114	47 1 0004	0.44	000 00 17	0 11 0 0-		~ (
	BHM	17 June 2004	2.11	333.0847	$C_{10}H_{21}O_{10}S$	-0.8	-2.4	
	BHM	20 June 2004	-	-	-	-	-	
	JST	20 June 2004	5.55	342.0489	C ₁₀ H ₁₆ NO ₁₀ S⁻	-0.6	-1.8	
	JST	23 June 2004	-	-	-	-	-	
	JST	26 June 2004	5.56	342.0502	C ₁₀ H ₁₆ NO ₁₀ S ⁻	0.7	2.0	
342	CTR	11 June 2004	-	-	-	-	-	unknown monotornono
isomer 1	CTR	23 June 2004	5.56	342.0470	C ₁₀ H ₁₆ NO ₁₀ S ⁻	-2.5	-7.3	unknown monoterpene
	CTR	29 June 2004	-	-	-	-	-	
	••••	20 00.10 200 1						
	BHM	17 June 2004	_	_	_	_	_	
	BHM	20 June 2004		_		_		
		20 June 2004	5 70	242 0400			1 2	
	101	20 June 2004	5.70	342.0499	$C_{10}\Pi_{16}NO_{10}S$	0.4	1.2	
	121	23 June 2004	5.74	342.0499	C ₁₀ H ₁₆ NO ₁₀ S	0.4	1.2	
	JST	26 June 2004	5.74	342.0503	$C_{10}H_{16}NO_{10}S$	0.8	2.3	
342	CTR	11 June 2004	5.72	342.0491	C ₁₀ H ₁₆ NO ₁₀ S ⁻	-0.4	-1.2	unknown monoternene
isomer 2	CTR	23 June 2004	5.72	342.0486	C ₁₀ H ₁₆ NO ₁₀ S⁻	-0.8	-2.6	unknown monoterpene
	CTR	29 June 2004	5.76	342.0483	C ₁₀ H ₁₆ NO ₁₀ S ⁻	-1.2	-3.5	
	BHM	17 June 2004	-	-	-	-	-	
	BHM	20 June 2004	5.72	342.0515	C ₁₀ H ₁₆ NO ₁₀ S ⁻	2.0	5.8	
	JST	20 June 2004	5.91	342.0486	C10H16NO10S ⁻	-0.9	-2.6	
	JST	23 June 2004	5 94	342 0501	C10H16NO10S ⁻	0.6	1.8	
	JST	26 June 2004	5 99	342 0505		1.0	29	
	001		0.00	042.0000	010110100100	1.0	2.0	
342	CTP	11 June 2004	5 90	342 0500	C.H.NO.S	05	15	
inomor 2	CTD	22 June 2004	5.00	242.0300		10	5.2	unknown monoterpene
Isomer 3		23 June 2004	5.90	342.0477	C10H16NO103	-1.0	-5.5	
	CIR	29 June 2004	-	-	-	-	-	
	D 1114	47 1 0004						
	BHM	17 June 2004		-	-	-	-	
	BHM	20 June 2004	5.91	342.0497	C ₁₀ H ₁₆ NO ₁₀ S [−]	0.2	0.6	
	JST	20 June 2004	6.16	342.0501	C ₁₀ H ₁₆ NO ₁₀ S⁻	0.6	1.8	
	JST	23 June 2004	6.10	342.0500	C ₁₀ H ₁₆ NO ₁₀ S⁻	0.5	1.5	
	JST	26 June 2004	6.18	342.0506	C ₁₀ H ₁₆ NO ₁₀ S ⁻	1.1	3.2	
342	CTR	11 June 2004	6.16	342.0511	C ₁₀ H ₁₆ NO ₁₀ S ⁻	1.6	4.7	unknown monotornono
isomer 4	CTR	23 June 2004	6.19	342.0499	C ₁₀ H ₁₆ NO ₁₀ S ⁻	0.4	1.2	unknown monoterpene
	CTR	29 June 2004	-	-	-	-	-	
	BHM	17 June 2004	-	-	-	-	-	
	BHM	20 June 2004	6 18	342 0504	CasHasNOas ⁻	09	26	
		20 June 2004	0.10		010116100100	0.0	2.0	
	ICT	20 June 2004	6 5 3	342 0403		0.2	0.6	
	101	20 June 2004	0.00	342.0493 242.0493		-0.2	-0.0	
	121	20 June 2004	0.52	342.0495	U10H16NU10S	0.0	0.0	
240	070	11 lun - 000 f	0.50	040.0540		0.0	o 7	
342	OTR	11 June 2004	0.58	342.0518	$C_{10}H_{16}NO_{10}S$	2.3	b./	unknown monoterpene
isomer 5	CIR	23 June 2004	6.58	342.0484	C ₁₀ H ₁₆ NO ₁₀ S ⁻	-1.1	-3.2	
	CTR	29 June 2004	6.54	342.0508	C ₁₀ H ₁₆ NO ₁₀ S [−]	1.3	3.8	
	BHM	17 June 2004	6.39	342.0494	C ₁₀ H ₁₆ NO ₁₀ S ⁻	-0.1	-0.3	
	BHM	20 June 2004	6.37	342.0526	C ₁₀ H ₁₆ NO ₁₀ S ⁻	3.1	9.1	

	JST	20 June 2004	-	-	-	-	-	
	JST	23 June 2004	6 74	342 0490	C10H16NO10S [−]	-0.5	-15	
	JST	26 June 2004	6 74	342 0512		17	5.0	
	001		0.74	042.0012	010116100100	1.7	0.0	
342	CTP	11 June 2004	_	_	_	_	_	
inomor 6	CTD	22 June 2004	-	-	-	-	-	unknown monoterpene
Isomer 6		23 June 2004	-	-	-	-	-	
	CIR	29 June 2004	-	-	-	-	-	
	D 1114	47 1 0004						
	BHM	17 June 2004	-	-	-	-	-	
	BHM	20 June 2004	-	-	-	-	-	
	JST	20 June 2004	7.20	342.0482	C ₁₀ H ₁₆ NO ₁₀ S⁻	-1.3	-3.8	
	JST	23 June 2004	7.22	342.0517	C ₁₀ H ₁₆ NO ₁₀ S⁻	2.2	6.4	
	JST	26 June 2004	7.21	342.0520	C ₁₀ H ₁₆ NO ₁₀ S ⁻	2.5	7.3	
342	CTR	11 June 2004	7.21	342.0496	C ₁₀ H ₁₆ NO ₁₀ S ⁻	0.1	0.3	unknown manatarnana
isomer 7	CTR	23 June 2004	7.20	342.0512	C ₁₀ H ₁₆ NO ₁₀ S [−]	1.7	5.0	unknown monoterpene
	CTR	29 June 2004	-	-	-	-	-	
	••••	20 00.10 200 1						
	BHM	17 June 2004	-	_	_	_	-	
	BHM	20 June 2004	7 21	342 0408	C.H.NO.S-	03	0 0	
		20 June 2004	7.26	242.0400		0.0	2.5	
	101	20 June 2004	7.30	342.0303	$C_{10}\Pi_{16}NO_{10}S$	0.0	2.3	
	121	23 June 2004	7.37	342.0514	C ₁₀ H ₁₆ NO ₁₀ S	1.9	5.0	
	JST	26 June 2004	7.36	342.0500	$C_{10}H_{16}NO_{10}S$	0.5	1.5	
342	CTR	11 June 2004	7.34	342.0489	C ₁₀ H ₁₆ NO ₁₀ S [−]	-0.6	-1.8	unknown monoterpene
isomer 8	CTR	23 June 2004	7.34	342.0485	C ₁₀ H ₁₆ NO ₁₀ S⁻	-1.0	-2.9	
	CTR	29 June 2004	-	-	-	-	-	
	BHM	17 June 2004	-	-	-	-	-	
	BHM	20 June 2004	7.34	342.0494	C ₁₀ H ₁₆ NO ₁₀ S ⁻	-0.1	-0.3	
	JST	20 June 2004	7.69	342.0490	C ₁₀ H ₁₆ NO ₁₀ S [−]	-0.5	-1.5	
	JST	23 June 2004	7.71	342.0496	C10H16NO10S ⁻	0.1	0.3	
	JST	26 June 2004	7 69	342 0498		03	0.9	
		20 00.10 200 1		0.210.000	0 10. 110. 00 100	0.0	0.0	
342	CTR	11 June 2004	7 69	342 0501	Cultur NOus ⁻	0.6	18	
isomer 9	CTR	23 June 2004	7.68	342.0001		-1.6	_4.7	unknown monoterpene
isomer 5	CTD	20 June 2004	7.00	342.0473	C101116100105	-1.0	-4.7	
	UIK	29 June 2004	-	-	-	-	-	
		47	7 70	0.40.0500		0.4	0.0	
	BHM	17 June 2004	7.73	342.0529	$C_{10}H_{16}NO_{10}S$	3.4	9.9	
	BHM	20 June 2004	7.70	342.0500	C ₁₀ H ₁₆ NO ₁₀ S	0.5	1.5	
	JST	20 June 2004	7.73	342.0494	C ₁₀ H ₁₆ NO ₁₀ S [−]	-0.1	-0.3	
	JST	23 June 2004	7.76	342.0498	C ₁₀ H ₁₆ NO ₁₀ S⁻	-1.0	-2.9	
	JST	26 June 2004	7.75	342.0507	C ₁₀ H ₁₆ NO ₁₀ S ⁻	1.2	3.5	
342	CTR	11 June 2004	7.74	342.0494	C ₁₀ H ₁₆ NO ₁₀ S ⁻	-0.1	-0.3	unknown monotornono
isomer 10	CTR	23 June 2004	7.73	342.0478	C ₁₀ H ₁₆ NO ₁₀ S ⁻	-1.7	-5.0	unknown monoterpene
	CTR	29 June 2004	7.80	342.0515	C ₁₀ H ₁₆ NO ₁₀ S ⁻	2.0	5.8	
	BHM	17 June 2004	7.79	342.0509	C10H16NO10S ⁻	1.4	4.1	
	BHM	20 June 2004	7.74	342,0488	C10H16NO10S ⁻	-0.7	-2.0	
	JST	20 June 2004	6.69	373 0569	$C_{10}H_{17}N_2O_{11}S^-$	1.6	4.3	
	JST	23 June 2004	6.73	373 0562	C40H47N2O44S	0.9	24	
	IST	26 June 2004	0.70	010.0002		0.0	2.7	
	001	20 June 2004	-	-	-	-	-	
372	СТР	11 June 2004						
3/3		11 June 2004	-	-	-	-	-	limonene-like
isomer 1		23 June 2004	-	-	-	-	-	
	CIR	29 June 2004	-	-	-	-	-	
	B							
	BHM	17 June 2004	6.74	373.0569	$C_{10}H_{17}N_2O_{11}S^-$	1.6	4.3	
	BHM	20 June 2004	6.72	373.0568	$C_{10}H_{17}N_2O_{11}S^-$	1.5	4.0	

	JST	20 June 2004	6.94	373.0568	$C_{10}H_{17}N_2O_{11}S^-$	1.5	4.0	
	JST	23 June 2004	6.96	373.0569	C ₁₀ H ₁₇ N ₂ O ₁₁ S [−]	1.6	4.3	
	JST	26 June 2004	6.95	373.0552	C ₁₀ H ₁₇ N ₂ O ₁₁ S ⁻	-0.1	-0.3	
373	CTR	11 June 2004	-	-	-	-	-	P
isomer 2	CTR	23 June 2004	-	-	-	-	-	limonene-like
	CTR	29 June 2004	-	-	-	-	-	
	BHM	17 June 2004	6.97	373.0567	C10H17N2O11S ⁻	1.4	3.8	
	BHM	20 June 2004	6.93	373.0563	$C_{10}H_{17}N_2O_{11}S^{-1}$	1.0	2.7	
	JST	20 June 2004	7.20	373.0569	C ₁₀ H ₁₇ N ₂ O ₁₁ S ⁻	1.6	4.3	
	JST	23 June 2004	7.22	373.0563	$C_{10}H_{17}N_2O_{11}S^{-1}$	1.0	2.7	
	JST	26 June 2004	-	-	-	-	-	
373	CTR	11 June 2004	-	-	-	-	_	
isomer 3	CTR	23 June 2004	-	-	-	-	-	limonene-like
	CTR	29 June 2004	-	-	-	-	_	
	•	20 00.10 200 1						
	BHM	17 June 2004	7 23	373 0576	$C_{10}H_{17}N_2O_{11}S^{-}$	23	62	
	BHM	20 June 2004	-	-	-		-	
	JST	20 June 2004	7 35	373 0573	$C_{40}H_{47}N_{2}O_{44}S^{-}$	2.0	54	
	JST	23 June 2004	7.36	373 0571	C10H17N2O11S	1.8	4.8	
	JST	26 June 2004	7.35	373 0569	C 10H 17N2O 11S ⁻	1.6	4.3	
	001	20 00110 2004	1.00	070.0000	010111/1020110	1.0	4.0	
373	CTR	11 June 2004	-	_	_	_	-	
isomer 4	CTP	23 June 2004						limonene-like
13011161 4	CTP	20 June 2004	-	_	_	-	-	
	UIK	29 June 2004	-	-	-	-	-	
	рци	17 Juno 2004	7 27	373 0527		26	70	
		20 June 2004	7.37	373.0527	$C_{10} \Pi_{17} \Pi_2 O_{11} S$	-2.0	-1.0	
		20 June 2004	7.50	373.0505	$C_{10} H_{17} N_2 O_{11} S$	2.4	<u> </u>	
	101	20 June 2004	7.52	272 0561	$C_{10} \Pi_{17} \Pi_2 O_{11} S$	2.4	0.4	
	101	25 June 2004	7.52	373.0501	$C_{10}\Pi_{17}N_2O_{11}S$	0.0	2.1	
	191	20 June 2004	7.51	373.0559	$C_{10}\Pi_{17}\Pi_2 O_{11}S$	0.0	1.0	
272	отр	11 June 2004						
373 jacmar E		11 June 2004	-	-		-	-	limonene-like
Isomer 5		23 June 2004	7.50	373.0571	$C_{10}\Pi_{17}N_2O_{11}S$	1.0	4.0	
	CIR	29 June 2004	-	-	-	-	-	
		17 June 0004	7 66	070 0544		4.0	~ ~	
	BHM	17 June 2004	7.55	373.0541	$C_{10}H_{17}N_2O_{11}S$	-1.2	-3.2	
	BHW	20 June 2004	7.51	373.0562	$C_{10}H_{17}N_2O_{11}S$	0.9	2.4	
	JST	20 June 2004	7.84	373.0524	$C_{10}H_{17}N_2O_{11}S^-$	-1.1	-2.9	
	JST	23 June 2004	7.88	373.0560	$C_{10}H_{17}N_2O_{11}S^-$	0.7	1.9	
	JST	26 June 2004	7.85	373.0560	$C_{10}H_{17}N_2O_{11}S$	0.7	1.9	
	~							
373	CIR	11 June 2004	7.85	373.0581	$C_{10}H_{17}N_2O_{11}S^{-1}$	2.8	7.5	limonene-like
isomer 6	CTR	23 June 2004	7.84	373.0531	$C_{10}H_{17}N_2O_{11}S^{-1}$	-2.2	-5.9	
	CIR	29 June 2004	7.90	373.057	$C_{10}H_{17}N_2O_{11}S^{-1}$	1.7	4.6	
	BHM	17 June 2004	7.88	373.0553	C ₁₀ H ₁₇ N ₂ O ₁₁ S ⁻	0.0	0.0	
	BHM	20 June 2004	7.84	373.0543	C ₁₀ H ₁₇ N ₂ O ₁₁ S ⁻	-1.0	-2.7	
	JST	20 June 2004	7.93	373.0560	$C_{10}H_{17}N_2O_{11}S^{-1}$	0.7	1.9	
	JST	23 June 2004	7.95	373.0554	$C_{10}H_{17}N_2O_{11}S^{-1}$	-3.3	-8.8	
	JST	26 June 2004	7.94	373.0570	C ₁₀ H ₁₇ N ₂ O ₁₁ S⁻	1.7	4.6	
			_					
373	CTR	11 June 2004	7.93	373.0594	$C_{10}H_{17}N_2O_{11}S^-$	4.1	11.0	limonene-like
isomer 7	CTR	23 June 2004	7.93	373.0531	C ₁₀ H ₁₇ N ₂ O ₁₁ S⁻	-2.2	-5.9	
	CTR	29 June 2004	7.95	373.0576	C ₁₀ H ₁₇ N ₂ O ₁₁ S [−]	2.3	6.2	
	_		_		_			
	BHM	17 June 2004	7.97	373.0556	$C_{10}H_{17}N_2O_{11}S^-$	0.3	0.8	
	BHM	20 June 2004	7.94	373.0544	$C_{10}H_{17}N_2O_{11}S^-$	-0.9	-2.4	
	JST	20 June 2004	8.46	387.0337	$C_{10}H_{15}N_2O_{12}S^-$	-0.9	-2.3	
	JST	23 June 2004	8.48	387.0323	$C_{10}H_{15}N_2O_{12}S^-$	-2.3	-5.9	
	JST	26 June 2004	8.45	387.0338	$C_{10}H_{15}N_2O_{12}S^-$	-0.8	-2.1	
387	CTR	11 June 2004	8.48	387.0342	$C_{10}H_{15}N_2O_{12}S^-$	-0.4	-1.0	limonene-like
507	CTR	23 June 2004	8.46	387.0343	$C_{10}H_{15}N_2O_{12}S^-$	-0.3	-0.8	
	CTR	29 June 2004	8.52	387.0317	$C_{10}H_{15}N_2O_{12}S^-$	-2.9	-7.5	
	BHM	17 June 2004	8.51	387.0328	$C_{10}H_{15}N_2O_{12}S^-$	-1.8	-4.7	
	BHM	20 June 2004	8.47	387.0320	$C_{10}H_{15}N_2O_{12}S^-$	-2.6	-6.7	



Figure 5.1. UPLC/(–)ESI-TOFMS base peak chromatograms (BPCs) for filter extracts of PM_{2.5} aerosol collected from the SEARCH network during the June 2004 campaign. Chromatographic peaks are marked with corresponding $[M - H]^-$ ion. Besides the *m/z* 97 (i.e. inorganic sulfate) peak and peaks marked with an asterisk, which correspond to known SOA acidic products (i.e. *m/z* 187, azelaic acid; m/z 203, 3-methyl-1,2,3-butanetricarboxylic acid; *m/z* 171, norpinic acid; *m/z* 185, pinic acid), all other peaks correspond to organosulfates or nitrooxy organosulfates formed from the oxidation of isoprene and/or monoterpenes. The source of the *m/z* 239 organosulfates remains unknown. Although most of the chromatographic peaks correspond to organosulfates, this does not mean that all of the organic mass on the filters is from these compounds. Due to the use of methanol as the extraction solvent, the type of chromatographic column and the mobile phase system employed, some of the organic mass on the filter will not be extracted and/or observed by the UPLC/(–)ESI-TOFMS technique due to some of the organic mass not being eluted from the column or not being detected in the negative ion mode.



Figure 5.2. UPLC/(–)ESI-TOFMS extracted ion chromatograms (EICs) of m/z 294. The RTs, accurate masses, and mDa errors between the theoretical masses of the TOFMS suggested molecular formulae and the accurate masses of the detected m/z 294 ions are listed above each chromatographic peak. All the chromatographic peaks highlighted in the figure share the same elemental composition of $C_{10}H_{16}NO_7S^-$. In order to form the m/z 294 nitrooxy organosulfates in the monoterpene photooxidation experiments, the presence of both NO_x (i.e., intermediate-NO_x or high-NO_x levels) and highly acidified sulfate seed aerosol is required (Table 5.2). Additionally, the m/z 294 nitrooxy organosulfates can form from the nighttime (NO₃-initiated) oxidation of α -pinene; however, the presence of highly acidified sulfate seed aerosol is also required (Table 5.2). Although the β -pinene experiment produced one of the m/z 294 isomers observed in the ambient aerosol, in subsequent figures the tandem MS data reveal that α -pinene is the only monoterpene examined in this study that appears to be the sole source of these compounds in ambient aerosol collected from the southeastern U.S. Besides the suite of monoterpenes examined in this study, other known highly emitted monoterpenes (e.g., myrcene and ocimene) 79,80 in the southeastern U.S. should be examined in future experiments to determine their potential for forming the m/z 294 nitrooxy organosulfates in organic aerosol.



Figure 5.3. MS^2/MS^3 data obtained for *m/z* 294 compounds from an α -pinene/NO₃/highly acidic seed experiment with RTs (a) 37.6, (b) 43.6 and (c) 45.3 min. These compounds are denoted in the text and Scheme 5.1 by **1**(295), **2**(295) and **3**(295), respectively.



Figure 5.4. MS^2/MS^3 data obtained for m/z 294 compounds from a SEARCH sample (BHM 6/20/04) with RTs (a) 37.4, (b) 43.4 and (c) 45.1 min. These compounds are denoted in the text and Scheme 5.1 by 1(295), 2(295) and 3(295), respectively.



Figure 5.5. Proposed formation mechanism for the three major isomers of the m/z 294 nitrooxy organosulfates observed in ambient aerosol from the oxidation of α -pinene. Numerals **1–3**(295) correspond to the isomeric structural assignments based upon the explanations shown in Scheme 5.1 for the observed product ions formed in the tandem MS experiments. For isomers **1** and **2**(295), it remains unclear how the NO₃-initiated oxidation produces these compounds in the presence of highly acidified sulfate seed aerosol. ^{*a*} Aschmann et al.^{74,75} observed a hydroxynitrate of this MW in the gas-phase from the OH-initiated oxidation of α -pinene in the presence of NO.



Figure 5.6. MS^2 (*m/z* 296) TICs obtained from (a) a *d*-limonene/H₂O₂/NO/highly acidic seed experiment and (b) a SEARCH sample (Birmingham, Alabama 6/20/04).



Figure 5.7. MS^2/MS^3 data obtained for the three m/z 296 compounds from a *d*-limonene/ $H_2O_2/NO/highly$ acidic seed experiment with RTs 24.1, 25.4 and 28.3 min. The compounds are denoted by 1–3(297) in the text and Scheme 5.2.



Figure 5.8. Proposed formation mechanism for the three major m/z 296 nitrooxyorganosulfate isomers observed from the photooxidation of limonene/limonaketone in the presence of NO_x and highly acidified sulfate seed aerosol. Numerals 1–3(297) correspond to the isomeric structural assignments based upon the explanations shown in Scheme 5.2 for the observed product ions formed in the tandem MS experiments. ^{*a*} Lee et al.⁸² observed an organic nitrate species of this MW in the gas-phase from the photooxidation of limonene in the presence of NO_x as the $[M + H]^+$ ion using PTR-MS.



Figure 5.9. UPLC/(–)ESI-TOFMS extracted ion chromatograms (EICs) of *m/z* 249 for the following: (a) α -pinene/NO₃/highly acidic seed experiment; (b) α -pinene/H₂O₂/NO/highly acidic seed experiment; (c) β -pinene/H₂O₂/NO/highly acidic seed experiment; (d) SEARCH sample collected from the CTR field site on 6/11/2004. The RTs, accurate masses, and mDa errors between the theoretical masses of the TOFMS suggested molecular formulas and the accurate masses of the detected *m/z* 249 ions are listed above each chromatographic peak. All the chromatographic peaks highlighted in the figure share the same elemental composition of C₁₀H₁₇O₅S-. α -/ β -Pinene were the only monoterpenes found in this study to produce the *m/z* 249 organosulfates with the same RTs, accurate masses, and elemental compositions as those observed in the SEARCH field samples.



Figure 5.10. MS^2 spectra obtained for the two *m/z* 249 compounds with RTs 31.2 and 32.2 min from (a, b) a β -pinene/H₂O₂/NO/highly acidic seed experiment and (c, d) a SEARCH field sample (BHM 6/20/04). The compounds are denoted by 1(250) and 2(250) in the text, Figure 5.12 and Scheme 5.3.



Figure 5.11. MS^2 spectra obtained for the two m/z 249 compounds with RTs 24.4 and 29.3 min from (a, b) an α -pinene/H₂O₂/NO/highly acidic seed experiment and (c, d) a SEARCH field sample (CTR 6/11/24). The compounds are denoted by **3**(250) and **4**(250) in the text, Figure 5.12 and Scheme 5.3. The ion at m/z 205 is due to an interference.


Figure 5.12. Proposed formation mechanism for the four m/z 249 organosulfates observed in ambient aerosol from the OH-initiated oxidation of β -pinene and α -pinene. Numerals 1–2(250) correspond to the isomeric structural assignments for the m/z 249 β pinene organosulfates, which are based upon the explanations for the observed product ions formed in the tandem MS experiments (Figure 5.10). Iinuma et al.²⁶ also observed the formation of isomer 1(250) from a β -pinene ozonolysis acid seed experiment, and detected this same isomer in a Norway spruce-dominated forest in Bavaria, Germany. Numerals 3–4(250) correspond to the isomeric structural assignments for the m/z 249 α pinene organosulfates, which are based upon the explanations for the observed product ions formed in the tandem MS experiments (Figure 5.11).



Figure 5.13. MS² (*m/z* 227) TICs obtained from (a) an α -pinene/H₂O₂/NO/highly acidic seed experiment and (b) a SEARCH sample (BHM 6/20/04).



Figure 5.14. MS^2/MS^3 data for the *m/z* 227 compounds from (a) an α -pinene/H₂O₂/NO/highly acidic seed experiment with RT 4.3 min and (b) a SEARCH sample (BHM 6/20/04) with RT 4.1 min.



Figure 5.15. UPLC/(–)ESI-TOFMS extracted ion chromatograms (EICs) of *m/z* 279 for the following: (a) α -pinene/H₂O₂/NO/highly acidic seed experiment; (b) α -pinene/NO₃/highly acidic seed experiment; (c) β -pinene/H₂O₂/NO/highly acidic seed experiment; (d) SEARCH sample collected from the CTR field site on 6/11/2004. The RTs, accurate masses, and mDa errors between the theoretical masses of the TOFMS suggested molecular formulae and the accurate masses of the detected *m/z* 279 ions are listed above each chromatographic peak. All the chromatographic peaks highlighted in the figure share the same elemental composition of C₁₀H₁₅O₇S⁻.



Figure 5.16. MS^2 (*m/z* 279) TICs obtained from (a) an α -pinene/H₂O₂/NO/highly acidic seed experiment and (b) a SEARCH sample (CTR 6/11/24). The compounds with RTs 19.1 (or 18.9) and 19.9 min are denoted by **1**(280) and **2**(280) in the text and in Scheme 5.5.



Figure 5.17. MS^2/MS^3 data for (a) the first- (19.1 min) and (b) second-eluting (19.9 min) m/z 279 compounds from the α -pinene/H₂O₂/NO/highly acidic seed experiment.



Figure 5.18. MS^2/MS^3 data for (a) the first- (19.1 min) and (b) second-eluting (19.9 min) m/z 279 compounds from the β -pinene/H₂O₂/NO/highly acidic seed experiment.



Figure 5.19. MS^2/MS^3 data for the first- (18.9 min) and second-eluting (19.7 min) m/z 279 compounds from the SEARCH sample (CTR 6/11/04).



Figure 5.20. MS^2 (*m/z* 310) TICs obtained from (a) an α -pinene/H₂O₂/NO/highly acidic seed experiment, (b) a β -pinene/H₂O₂/NO/highly acidic seed experiment and (c) a SEARCH sample (BHM 6/20/04). The compounds with RTs 27.0 and 34.5 min from the ambient sample are denoted by **1–2**(311) in the text and Scheme 5.6.



Figure 5.21. MS^2/MS^3 data for the *m/z* 310 compounds with RTs (a) 27.0 and (b) 34.5 min from the SEARCH sample (BHM 6/20/04).



Figure 5.22. MS^2 (*m/z* 373) TIC obtained from a SEARCH sample (BHM 6/20/04). The compounds with RTs 31.9 and 32.6 min are denoted by **1**(374) and **2**(374) in the text and Scheme 5.7.



Figure 5.23. MS^2/MS^3 data for the *m/z* 373 compounds with RTs (a) 31.9 and (b) 32.6 min) from a SEARCH sample (BHM 6/20/04).



Figure 5.24. MS^2 (*m/z* 244) TICs obtained from (a) an isoprene/NO_x/SO₂ EPA photooxidation experiment and (b) a SEARCH sample (CTR 6/11/04).



Figure 5.25. MS^2/MS^3 data for the *m/z* 244 compounds from (a) an isoprene/NO_x/SO₂ EPA photooxidation experiment and (b) a SEARCH sample (CTR 6/11/04).



Figure 5.26. MS^2 (*m/z* 305) TICs obtained from (a) an isoprene/NO_x/SO₂ EPA photooxidation experiment and (b) a SEARCH sample (CTR 6/11/04). The compounds with RTs 15.7 and 19.0 min in the ambient sample are denoted by **2**(306) and **4**(306) in the text and Scheme 5.9.



Figure 5.27. MS^2/MS^3 data obtained for the five first-eluting m/z 305 compounds from an isoprene/NO_x/SO₂ EPA photooxidation experiment. It is noted that MS^2/MS^3 data obtained for the three last-eluting m/z 305 compounds from the same isoprene experiment (Figure 5.26a) are shown in Figure 5.42.



Figure 5.28. MS^2/MS^3 data obtained for the five *m/z* 305 compounds from a SEARCH sample (CTR 6/11/04).



Figure 5.29. Proposed formation mechanism for the two major m/z 305 nitrooxyorganosulfate isomers observed in ambient aerosol (Figure 5.26b) from either the photooxidation of isoprene in the presence of NO_x or NO₃-initiated oxidation of isoprene under dark conditions, with both in the presence of acidified sulfate seed aerosol. Numerals **2** and **4**(306) correspond to the isomeric structural assignments based upon the explanations shown in Scheme 5.9 for the observed product ions formed in the tandem MS experiments. ^{*a*} Ng et al.⁹³ observed a hydroxynitrate species of this MW in the gasphase from the NO₃-initiated oxidation of isoprene under dark conditions as the [M + CF3O⁻] ion using chemical ionization MS.



Figure 5.30. MS^2 (*m/z* 334 and 332) TICs obtained from (a, c) an isoprene/NO_x/SO₂ EPA photooxidation experiment and (b, d) a SEARCH sample (CTR 6/11/04), respectively.



Figure 5.31. MS^2/MS^3 data obtained for the *m/z* 333 compounds from an isoprene/NO_x/SO₂ EPA photooxidation experiment eluting at (a) 3.8 and (b) 4.2 min.



Figure 5.32. MS^2/MS^3 data obtained for *m/z* 333 compounds from a SEARCH sample (CTR 6/11/04) eluting at 4.8 min.



Figure 5.33. MS^2/MS^3 data obtained for *m/z* 331 compounds from an isoprene/NO_x/SO₂ EPA photooxidation experiment eluting at 5.0 min.



Figure 5.34. MS^2/MS^3 data obtained for *m/z* 331 compounds from a SEARCH sample (CTR 6/11/04) eluting at (a) 4.1 and (b) 5.1 min.



Figure 5.35. MS² spectra obtained for m/z 294 compounds from an α -pinene/H₂O₂/NO/highly acidic seed experiment with RTs (a) 37.6, (b) 43.6 and (c) 45.3 min.



Figure 5.36. MS^2/MS^3 data obtained for *m/z* 294 compounds from a β -pinene/ $H_2O_2/NO/highly$ acidic seed experiment with RTs (a) 43.7 and (b) 46.4 min.



Figure 5.37. UPLC/(–)ESI-TOFMS extracted ion chromatograms (EICs) of *m/z* 296 for the following: (a) d-limonene/H₂O₂/NO/highly acidic seed experiment; (b) β -phellandrene + d-limonene/H₂O₂/NO/highly acidic seed experiment; (c) limonaketone/H₂O₂/NO/highly acidic seed experiment; (d) SEARCH sample collected from the JST field site (i.e., Downtown Atlanta, Georgia) on 6/26/2004. The RTs, accurate masses, and mDa errors between the theoretical masses of the TOFMS suggested molecular formulas and the accurate masses of the detected *m/z* 296 ions are listed above each chromatographic peak. All the chromatographic peaks highlighted in the figure share the same elemental composition of C₉H₁₄NO₈S⁻.



Figure 5.38. MS^2/MS^3 data obtained for the three *m/z* 296 compounds 1–3(297) from a limonaketone/H₂O₂/NO/highly acidic seed experiment. The compounds are denoted by 1–3(297) in the text and Scheme 5.2.



Figure 5.39. MS^2/MS^3 data obtained for the three *m/z* 296 compounds from a SEARCH sample (BHM 6/20/04) with RTs 22.4, 24.0 and 27.5 min.



Figure 5.40. MS^2/MS^3 data for the *m/z* 310 compounds with RTs (a) 27.2 min from an α -pinene/H₂O₂/NO/highly acidic seed experiment and (b) 34.0 min from a β -pinene/H₂O₂/NO/highly acidic seed experiment.



Figure 5.41. UPLC/(–)ESI-TOFMS extracted ion chromatograms (EICs) of *m/z* 373 for the following: (a) d-limonene/H₂O₂/NO/highly acidic seed experiment; (b) β -phellandrene + d-limonene/H₂O₂/NO/highly acidic seed experiment; (c) SEARCH sample collected from the BHM field site on 6/20/2004. The RTs, accurate masses, and mDa errors between the theoretical masses of the TOFMS suggested molecular formulas and the accurate masses of the detected *m/z* 373 ions are listed above each chromatographic peak. All the chromatographic peaks highlighted in the figure share the same elemental composition of C₁₀H₁₇N₂O₁₁S⁻.



Figure 5.42. MS^2/MS^3 data obtained for the three last-eluting *m/z* 305 compounds from an isoprene/NO_x/SO₂ EPA photooxidation experiment (Figure 5.26a).









SCHEME 5.2



SCHEME 5.3



303

SCHEME 5.4




m/z 247







307









