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Organosulfate Formation in Biogenic Secondary Organic Aerosol

Jason D. Surratt,[†] Yadian Gómez-González,[‡] Arthur W. H. Chan,[§] Reinhilde Vermeylen,[‡] Mona Shahgholi,[†] Tadeusz E. Kleindienst,[⊥] Edward O. Edney,[⊥] John H. Offenberg,[⊥] Michael Lewandowski,[⊥] Mohammed Jaoui,[#] Willy Maenhaut,[¶] Magda Claeys,[‡] Richard C. Flagan,[§,+] and John H. Seinfeld*[,§,+]

Department of Chemistry, California Institute of Technology, Pasadena, California 91125, Department of Pharmaceutical Sciences, University of Antwerp (Campus Drie Eiken), Universiteitsplein 1, BE-2610 Antwerp, Belgium, Department of Chemical Engineering, California Institute of Technology, Pasadena, California 91125, National Exposure Laboratory, Office of Research and Development, Environmental Protection Agency, Research Triangle Park, North Carolina 27711, Alion Science and Technology, P.O. Box 1231, Research Triangle Park, North Carolina 27709, Department of Analytical Chemistry, Institute for Nuclear Sciences, Ghent University, Proeftuinstraat 86, BE-9000 Gent, Belgium, and Department of Environmental Science and Engineering, California Institute of Technology, Pasadena, California 91125

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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., NO_3-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, *d*-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 spectrometric and accurate mass measurements collected for both 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%.

1. 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 μm);[1] high concentrations of $PM_{2.5}$ are known to have adverse health effects[2] 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, C_5H_8) and monoterpenes ($C_{10}H_{16}$), contribute significantly to the global SOA budget[1,4,5] owing to their high reactivities with atmospheric oxidants, such as hydroxyl radicals (OH), ozone (O_3), and nitrate radicals (NO_3), 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 α-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 contributing to SOA formation, including peroxyhemiacetal formation,[34,35] acetal/hemiacetal formation,[16,36] hy-

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* To whom correspondence should be addressed. Phone: (626) 395-4635. Fax: (626) 796-2591. E-mail: seinfeld@caltech.edu.

[†] Department of Chemistry, California Institute of Technology, Pasadena.

[‡] University of Antwerp.

[§] Department of Chemical Engineering, California Institute of Technology.

[⊥] Environmental Protection Agency.

[#] Alion Science and Technology.

[¶] Ghent University.

[+] Department of Environmental Science and Engineering, California Institute of Technology.

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dration followed by polymerization,[16] aldol 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 are 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 glyoxal[48] 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 and 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., NO_3 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.

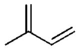
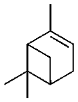
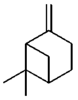
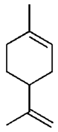
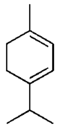
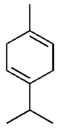
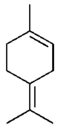
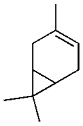
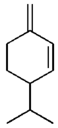
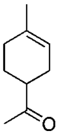
In the present work, we investigate in detail the mechanism of organosulfate formation in biogenic SOA on the basis of a series of laboratory oxidation experiments under varying particle-phase acidities and oxidative conditions. Laboratory photooxidation (i.e., OH-initiated oxidation) experiments were 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., NO_3-initiated oxidation) experiments were conducted using three monoterpenes (α-pinene, *d*-limonene, and *l*-limonene). Filters were collected from all of the laboratory experiments for off-line 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 formulas), respectively, were employed to characterize the detailed chemical structures of the organosulfates; particular attention was focused on those compounds detected in both laboratory-generated SOA and 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 those in 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).

2. Experimental Section

2.1. 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, ≥99%, Fluka), *l*-limonene (puriss. p.a. terpene standard for GC, ≥99%, Fluka), α-terpinene (purum ≥95%, Fluka), γ-terpinene (puriss. p.a. terpene standard for GC, ≥98.5%, Fluka), terpinolene (purum ≥97%, Fluka), Δ^3-carene (puriss. p.a. terpene standard for GC, ≥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, $C_9H_{14}O$, 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 of initial isoprene, 475 ppb of initial NO_x, and 200 ppb of SO_2) were previously outlined in Surratt et al.[23] and were used solely for the tandem MS analysis of organosulfates of isoprene. Table 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 2summarizes the experimental conditions and results for the suite of monoterpene oxidation experiments conducted.

All monoterpene experiments were performed in the Caltech dual 28 m^3 Teflon environmental chambers. Details of the facilities have been described elsewhere.[56,57] Before each

TABLE 1: Biogenic Volatile Organic Compounds Studied

compound	structure	formula (MW)	k_{OH},[a] cm^3 $molec^{-1}$ s^{-1}	k_{O3},[a,b,c] cm^3 $molec^{-1}$ s^{-1}	k_{NO3},[a,d] cm^3 $molec^{-1}$ s^{-1}
isoprene		C_5H_8 (68)	9.9×10^{-11}	1.3×10^{-17}	7.0×10^{-13}
α-pinene		$C_{10}H_{16}$ (136)	5.3×10^{-11}	8.4×10^{-17}	6.2×10^{-12}
β-pinene		$C_{10}H_{16}$ (136)	7.4×10^{-11}	1.5×10^{-17}	2.5×10^{-12}
limonene		$C_{10}H_{16}$ (136)	1.7×10^{-10}	2.1×10^{-16}	1.2×10^{-11}
α-terpinene		$C_{10}H_{16}$ (136)	3.6×10^{-10}	2.1×10^{-14}	1.4×10^{-10}
γ-terpinene		$C_{10}H_{16}$ (136)	1.8×10^{-10}	1.4×10^{-16}	2.9×10^{-11}
terpinolene		$C_{10}H_{16}$ (136)	2.3×10^{-10}	1.9×10^{-15}	9.7×10^{-11}
Δ^3-carene		$C_{10}H_{16}$ (136)	8.8×10^{-11}	3.7×10^{-17}	9.1×10^{-12}
β-phellandrene		$C_{10}H_{16}$ (136)	1.7×10^{-10}	4.7×10^{-17}	8.0×10^{-12}
limonaketone		$C_9H_{14}O$ (138)	-	2.7×10^{-16}	-

[a] Rate constants were obtained from Atkinson and Arey[55] (and references therein). [b] No ozonolysis experiments were conducted; however, rates are reported here to show that under the conditions of the chamber experiments, OH and NO_3 radicals dominate the initial oxidation of the BVOCs during photooxidation and nighttime oxidation experiments, respectively. [c] The rate constant for limonaketone was measured by Donahue et al.[54] [d] α-Pinene and *d-/l*-limonene were the only three BVOCs for which reactions with NO_3 radicals were studied.

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] The temperature, relative humidity, and concentrations of O_3, 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 $(NH_4)_2SO_4$, while the acidic seed contained a mixture of 15 mM $(NH_4)_2SO_4$ and 15 mM H_2SO_4, and the highly acidic seed contained a mixture of 30 mM $MgSO_4$ and 50 mM H_2SO_4. The initial particle number concentration was about 20 000 particles cm^{-3}, with a geometric mean diameter of ~55 (for the neutral and acid seed) or ~70 nm (for the highly acidic seed). The initial seed volume was ~15 μm^3 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).

TABLE 2: Summary of Experimental Conditions and Organosulfate Formation from Monoterpene Oxidation Chamber Experiments

hydrocarbon	initial [HC] (ppb)	oxidant precursor[a]	seed type[b]	initial [NO] (ppb)	initial $[NO_2]$ (ppb)	initial $[O_3]$ (ppb)	T^c (°C)	RH^c (%)	total SOA volume[c] ($\mu m^3 cm^{-3}$)	$[M - H]^-$ detected organosulfate ions (*m/z*)
α-pinene	41	H_2O_2	neutral	<2	<2	2	31.2	3.8	82	none detected
α-pinene	46	H_2O_2	highly acidic	<2	<2	2	26.4	5.5	145	237, 279^d, 281, 297
α-pinene	47	H_2O_2/NO	neutral	303	4	3	25.6	7.2	104	none detected
α-pinene	61	H_2O_2/NO	acidic	488	12	2	27.1	4.3	151	279^d, 342
α-pinene	53	H_2O_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_2O_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
l-limonene	86	H_2O_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
l-limonene	~50	$NO_2 + O_3$/dark	highly acidic	<2	186	38	21.4	5.4	373	239^d, 279, 312, 328, 389
β-phellandrene *ld*-limonene mixture	~100 (total)	H_2O_2/NO	highly acidic	428	<2	<2	26.9	3.7	169	239^d, 251, 267, 296^d, 326, 238, 373
limonaketone	~150	H_2O_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_2O_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_2O_2/NO	highly acidic	497	8	3	26.4	8.3	142	279, 310, 373
terpinolene	34	H_2O_2/NO	highly acidic	483	17	<2	25.5	8.6	101	249, 265, 281, 283, 294, 297, 326, 373
β-pinene	62	H_2O_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_2O_2/NO	highly acidic	496	<2	<2	26.6	3.7	123	342^e

[a] H_2O_2 and HONO serve as OH radical sources in photooxidation experiments. The $NO_2 + O_3$ reaction serves as the NO_3 radical source in dark experiments. [b] Atomizing solution compositions: neutral = 15 mM $(NH_4)_2SO_4$; acidic = 15 mM $(NH_4)_2SO_4$ + 15 mM H_2SO_4; highly acidic = 30 mM $MgSO_4$ + 50 mM H_2SO_4. [c] Averaged over the course of filter sampling. [d] At least one of the isomers has the same RT and exact mass as compared to those of the corresponding ion detected in the field samples collected from the southeastern U.S. (see Table 8S, Supporting Information). [e] 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. RT = 6.59 min; measured mass = 342.0529; mDa error = 3.3 mDa; ppm error = 9.6 ppm; elemental composition = $C_{10}H_{16}NO_{10}S^-$.

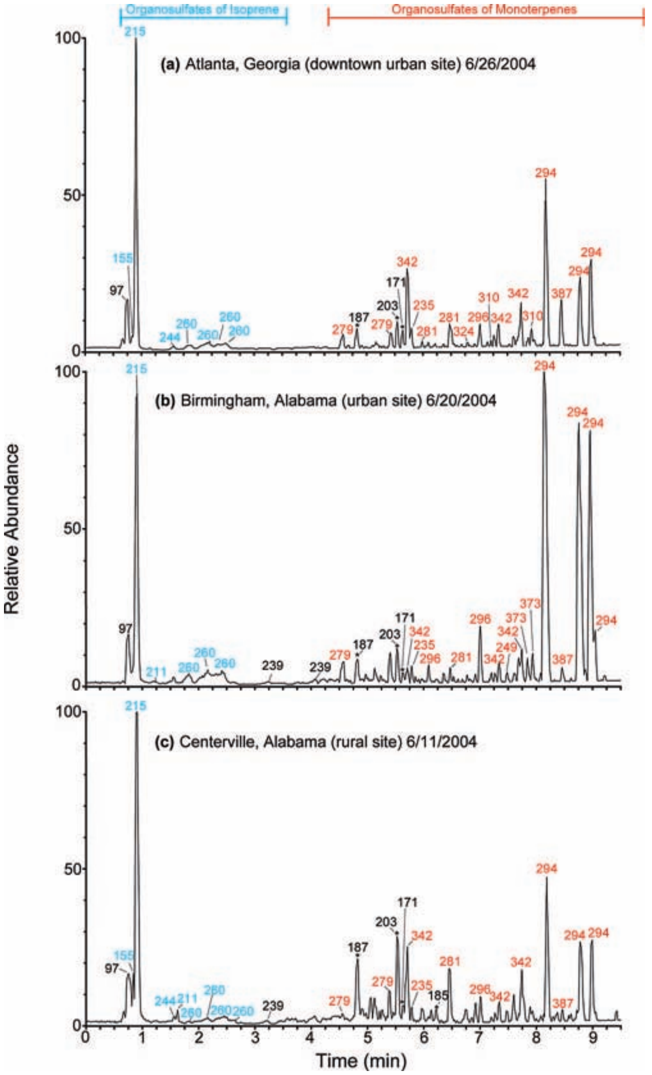


Figure 1. UPLC/(−)ESI-TOFMS base peak chromatograms (BPCs) for filter extracts of $PM_{2.5}$ aerosol collected from the SEARCH network during the June 2004 campaign. Chromatographic peaks are marked with corresponding $[M - H]^-$ ion. Besides the *m/z* 97 (i.e., inorganic sulfate) peak and peaks marked 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.

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% $NaNO_2$ into 30 mL of 10 wt% H_2SO_4 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 (H_2O_2) served as the OH precursor. Prior to the introduction of seed particles and the parent hydrocarbon, about 3−5 ppm of H_2O_2 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 H_2O_2. 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 of the photooxidation experiments, the reaction was initiated by irradiating the chamber with blacklights, after the concentrations of the 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 (NO_3) 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 NO_2 was then added. When the O_3 concentration dropped to ~45 ppb, the parent hydrocarbon was introduced into the chambers, marking the beginning of the experiment. On the basis of the concentrations of NO_2 and O_3 employed, it is estimated that about 500 ppt of NO_3 radical was initially present; on the basis of the applicable rate constants, NO_3 initially dominates the oxidation of the monoterpenes rather than O_3. The initial concentration of the hydrocarbon was estimated from the volume of hydrocarbon injected.

2.2. Chamber Filter Sample Collection and Extraction Protocols. Duplicate Teflon filters (PALL Life Sciences, 47 mm diameter, 1.0 μm pore size, teflo membrane) were collected from each of the monoterpene chamber experiments for off-line chemical analysis. The flow rate for filter collection was ~17 and 23 L min^{-1} for the first and second filter samplers, 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 m^3 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 N_2 stream at ambient temperature. Dried residues were then reconstituted with 500 μL 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 were 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

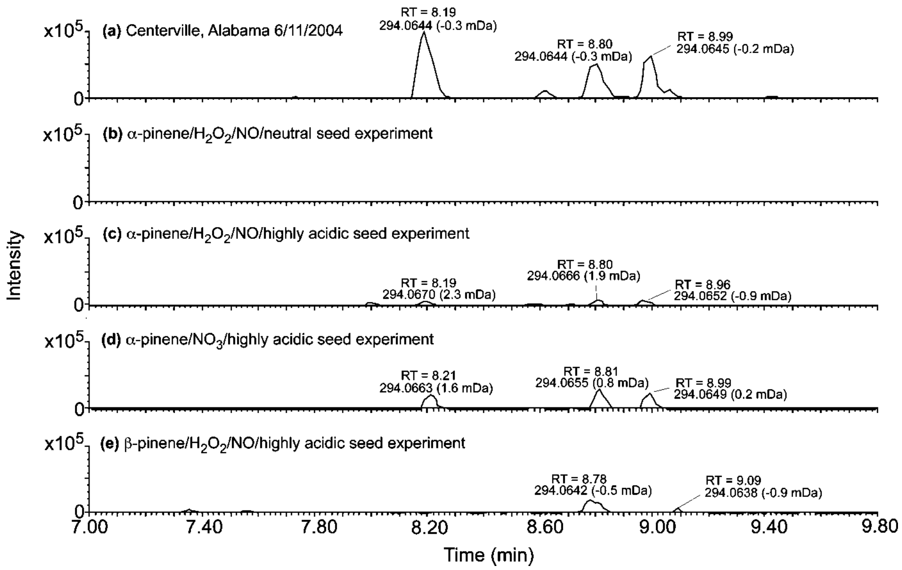


Figure 2. UPLC/(−)ESI-TOFMS extracted ion chromatograms (EICs) of *m/z* 294. The RTs, accurate masses, and mDa errors between the theoretical masses of the TOFMS suggested molecular formulas, and the accurate masses of the detected *m/z* 294 ions are listed above each chromatographic peak. All of the 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 2). Additionally, the *m/z* 294 nitrooxy organosulfates can form from the nighttime (NO_3-initiated) oxidation of α-pinene; however, the presence of highly acidified sulfate seed aerosol is also required (Table 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.

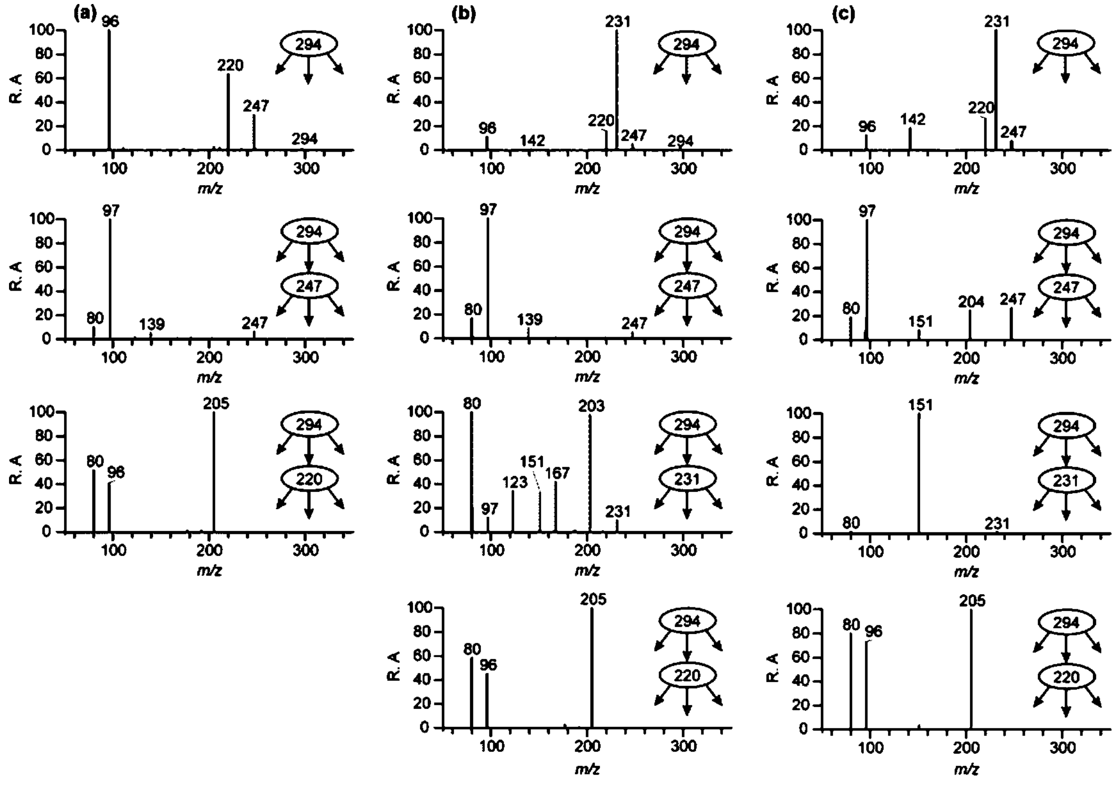


Figure 3. MS^2/MS^3 data obtained for *m/z* 294 compounds from an α-pinene/NO_3/highly acidic seed experiment with RTs of (a) 37.6, (b) 43.6, and (c) 45.3 min. These compounds are denoted in the text and Scheme 1 by **1**(295), **2**(295), and **3**(295), respectively.

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 tech-

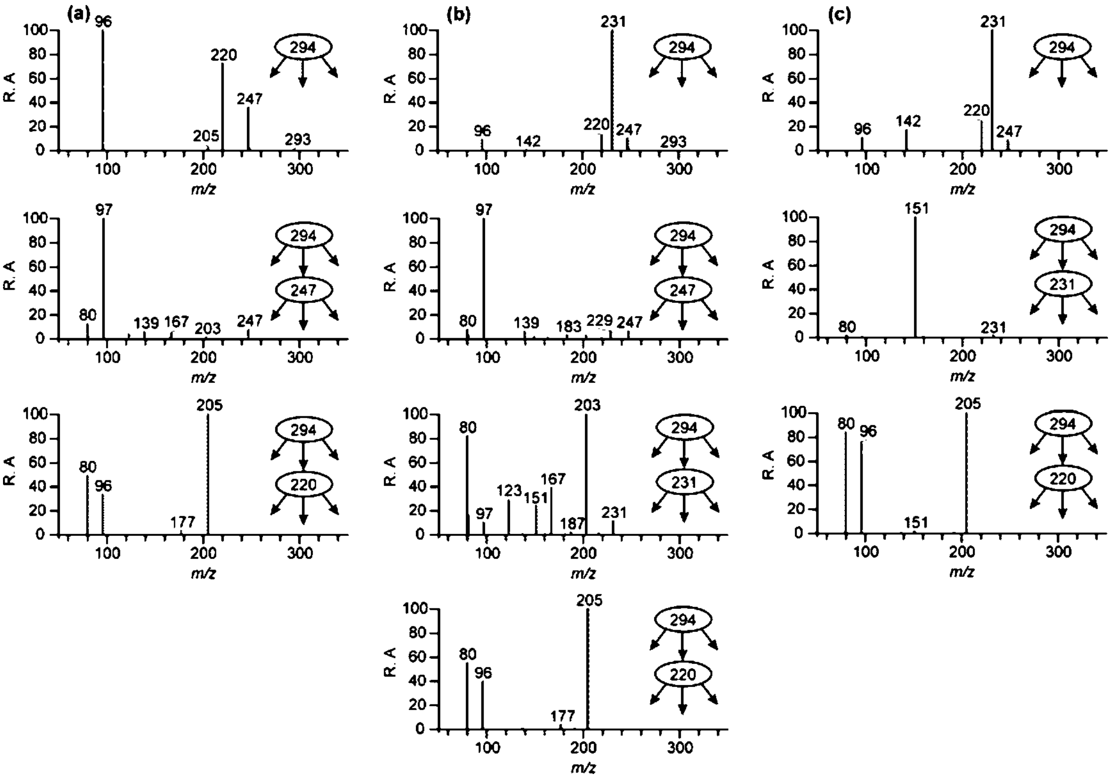


Figure 4. MS^2/MS^3 data obtained for m/z 294 compounds from a SEARCH sample (BHM 6/20/04) with RTs of (a) 37.4, (b) 43.4, and (c) 45.1 min. These compounds are denoted in the text and Scheme 1 by **1**(295), **2**(295), and **3**(295), respectively.

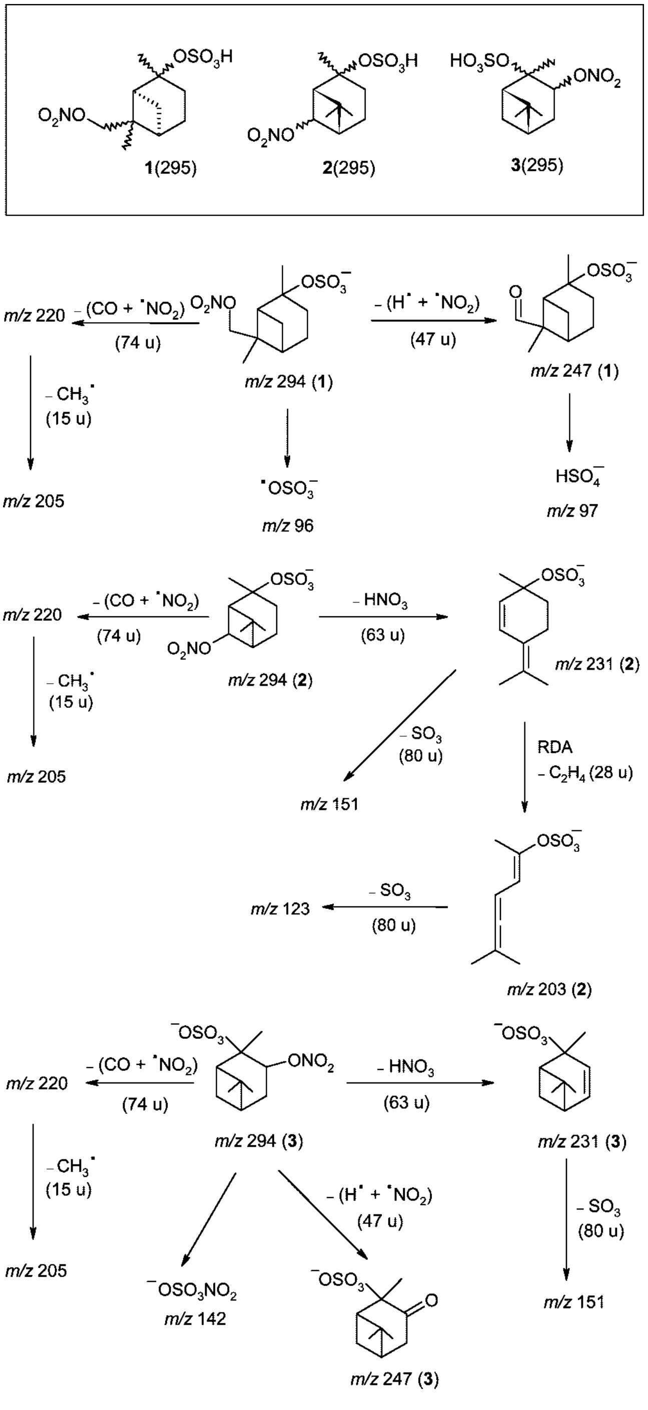
nique from these blank filters, consistent with the lack of observed aerosol growth under dark conditions. Additionally, it is worth mentioning that our initial study on organosulfate formation also included several quality control tests to ensure that organosulfate formation occurred only during SOA 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, filtered through a Teflon filter (0.45 μm), evaporated to dryness under a N_2 stream at ambient temperature, and reconstituted in 300 μL 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.

2.3. 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 campaign[47] 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 because of the risk of removing early eluting organosulfates of isoprene in C_{18} reversed phase LC, therefore preventing their detection by MS.

2.4. Ultra Performance Liquid Chromatography/Electrospray Ionization Time-of-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 h^{-1} cone gas flow rate, and 650 L h^{-1} desolvation gas flow rate. Data were collected from m/z 50 to 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 × 100 mm, 1.8 μm 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 was 0% for the first 2 min, increased to 90% from 2 to 10 min, held at 90%

SCHEME 1



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 μL, 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 C_{18} column. The latter column is essentially analogous to that of the C_{18} HPLC column previously employed by Surratt et al.[23,24] Both C_{18} 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 1, RT 0.79 min), and the organosulfates of the 2-methyltetrols previously identified by Surratt et al.[23,24] (Figure 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 coelution.

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 μL^{-1} 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 μL 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 α-pinene organosulfates previously characterized by Surratt et al.[23] was analyzed. The known elemental compositions (i.e., molecular formulas) of the previously characterized organosulfates[23] were in excellent agreement with their measured exact masses (i.e., within ±2 mDa or ±2 ppm, which is excellent for small molecules). In addition to accurate mass measurements, further insights into the 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 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.

2.5. 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 μm; 2.1 × 150 mm; 3 μm 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 C_{18} 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 μL 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 MS^2 and MS^3 experiments, an isolation width of 2 *m/z* units and a normalized collision energy

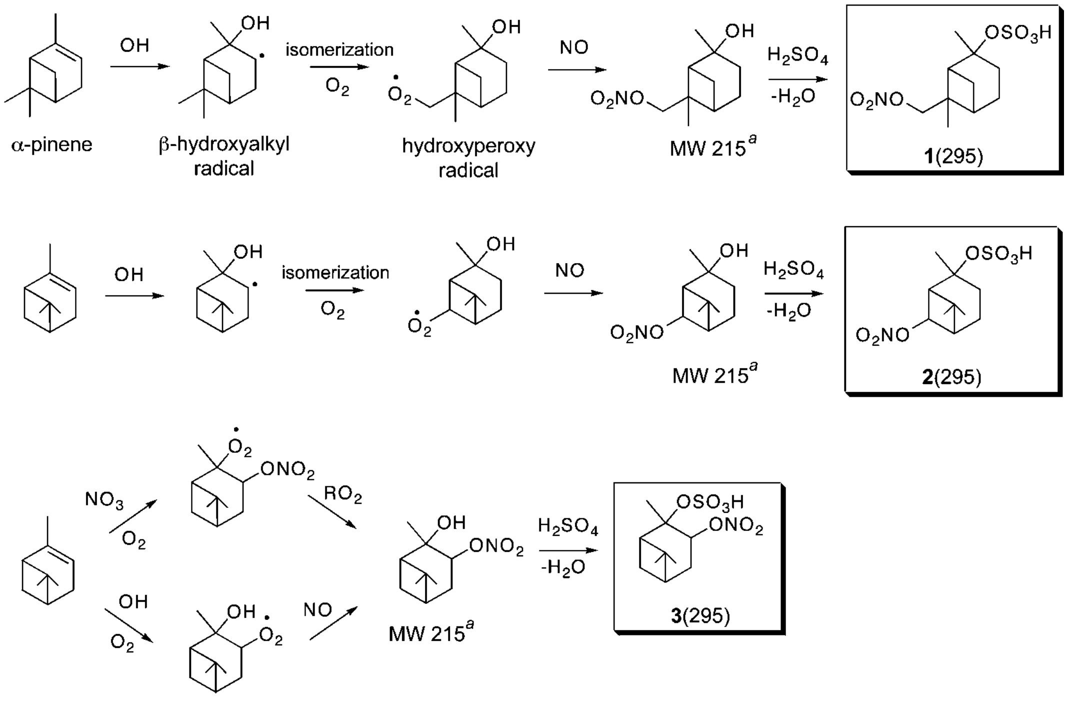


Figure 5. Proposed formation mechanism for the three major isomers of the *m/z* 294 nitrooxy organosulfates observed in ambient aerosol from the oxidation of α-pinene. Numerals **1**−**3**(295) correspond to the isomeric structural assignments based upon the explanations shown in Scheme 1 for the observed product ions formed in the tandem MS experiments. For isomers **1** and **2**(295), it remains unclear how the NO_3-initiated oxidation produces these compounds in the presence of highly acidified sulfate seed aerosol. Footnote *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.

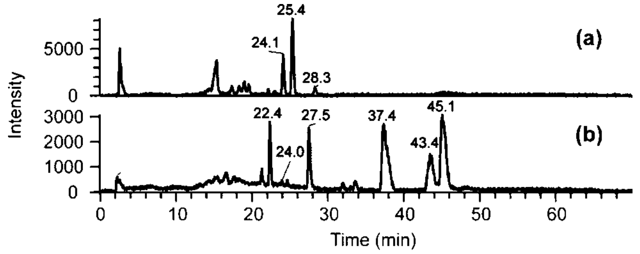


Figure 6. MS^2 (*m/z* 296) TICs obtained from (a) a *d*-limonene/H_2O_2/NO/highly acidic seed experiment and (b) a SEARCH sample (BHM 6/20/04).

level of 35% were applied. The $[M - H]^-$ signal optimization was done by introducing a 50 μg mL^{-1} malic acid standard solution.

3. 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 that 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 on the order of 5% or more; therefore, 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 PM_{10} 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 PM_{10} 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 μg m^{-3} of OM. The mass percentages of sulfur in some common BSOA organosulfates, that is, 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 nonsulfate sulfur mentioned above would correspond to 3.1 μg m^{-3} of OM for the 2003 summer campaign at K-puszta and thus represents about 30% of the total

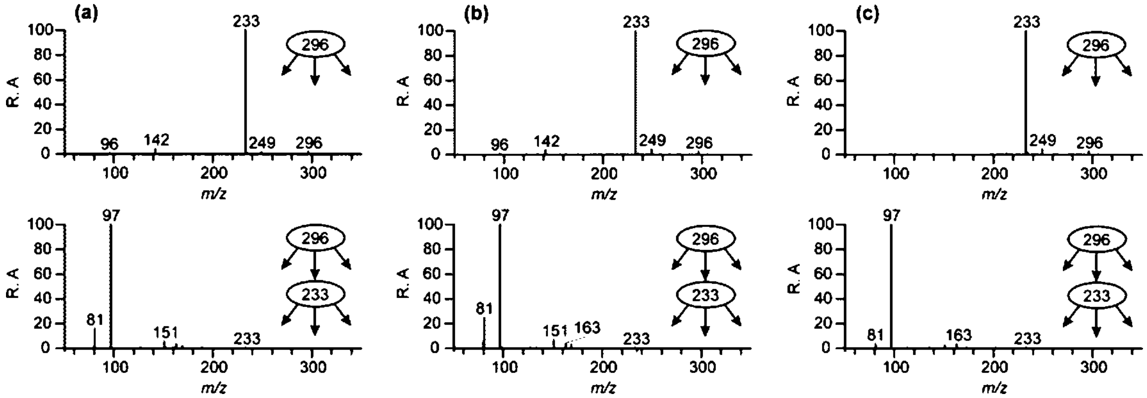
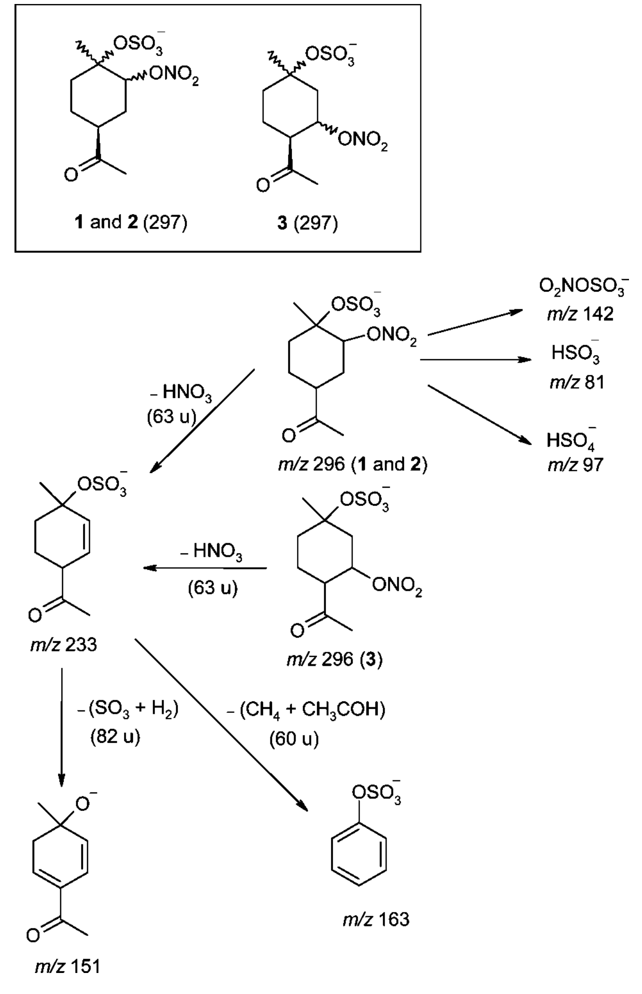


Figure 7. MS^2/MS^3 data obtained for the three *m/z* 296 compounds from a *d*-limonene/ H_2O_2/NO/highly acidic seed experiment with RTs of 24.1, 25.4, and 28.3 min. The compounds are denoted by **1**−**3**(297) in the text and Scheme 2.

SCHEME 2



PM_{10} OM. Despite the uncertainties associated with this estimate, it is clear that organosulfates may be responsible for a sizable 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.

4. Laboratory-Generated Organosulfates

4.1. Monoterpene Oxidation Experiments. Experimental conditions and results of the monoterpene oxidation experiments are summarized in Table 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 of the organosulfate ions listed in Table 2 are provided in Tables 1S-6S (Supporting Information); however, as noted in Table 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 formulas and the measured masses found in Tables 1S−6S (Supporting Information) 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 formulas containing at least one sulfur atom and, on the basis of the degree of oxidation indicated by their respective molecular formulas, 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 of the organosulfate ions listed in Table 2 showed prominent *m/z* 97 (HSO_4^-) product ions, as well as *m/z* 80 ($SO_3^{-\bullet}$) 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] MS^2 product ion spectra for all nitrooxy organosulfates yield a neutral loss of 63 u (HNO_3; nitric

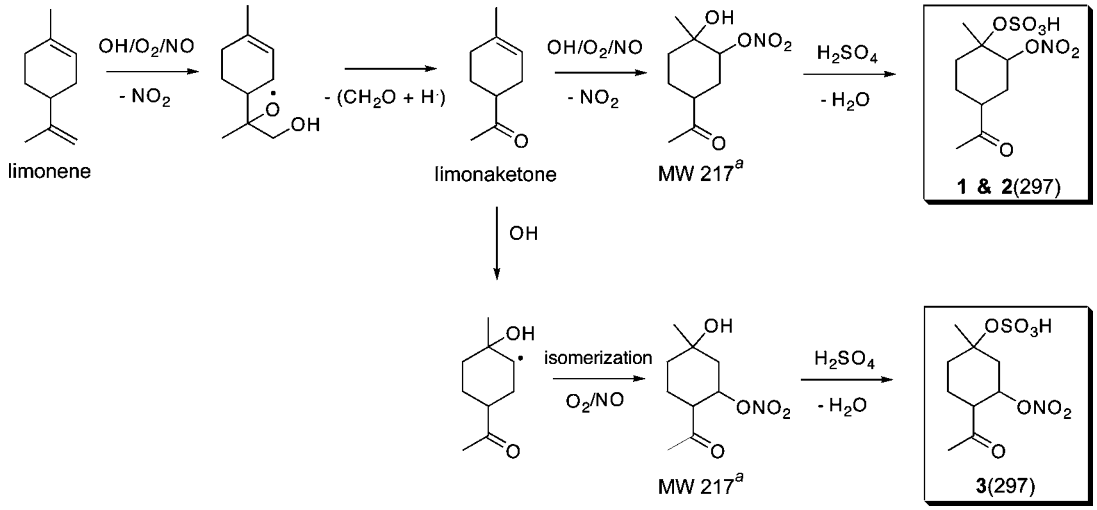


Figure 8. Proposed formation mechanism for the three major *m/z* 296 nitrooxy organosulfates observed from the photooxidation of limonene/limonaketone in the presence of NO_x and highly acidified sulfate seed aerosol. Numerals **1**−**3**(297) correspond to the isomeric structural assignments based upon the explanations shown in Scheme 2 for the observed product ions formed in the tandem MS experiments. Footnote *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.

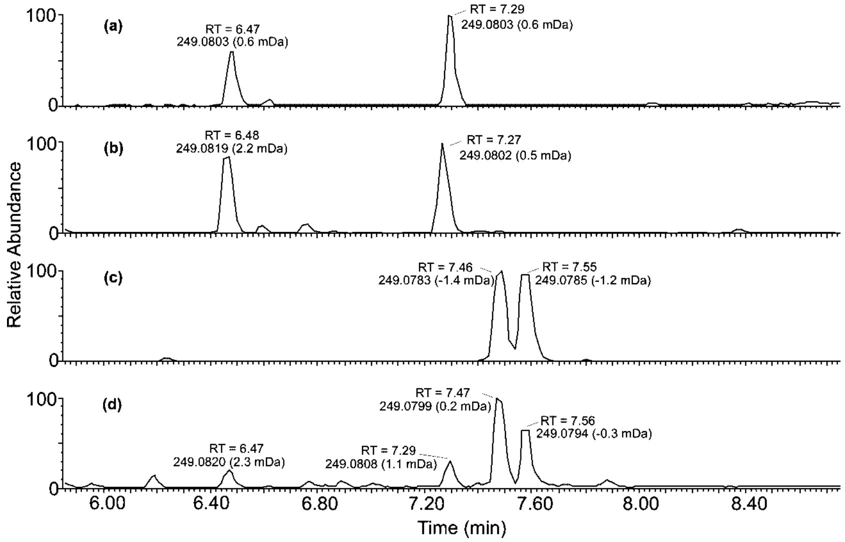


Figure 9. UPLC/(−)ESI-TOFMS extracted ion chromatograms (EICs) of *m/z* 249 for the following: (a) α-pinene/NO_3/highly acidic seed experiment; (b) α-pinene/ H_2O_2/NO/highly acidic seed experiment; (c) *β*-pinene/H_2O_2/NO/highly acidic seed experiment; (d) SEARCH sample collected from the CTR field 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 of the chromatographic peaks highlighted in the figure share the same elemental composition of $C_{10}H_{17}O_5S^-$. 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.

acid), further confirming the presence of a nitrooxy group. On the basis of these accurate mass and tandem MS results, all of the $[M - H]^-$ ions listed in Table 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., NO_3-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 SO_2.[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 SO_2. Organosulfates of α-pinene were observed in this prior study only when both α-pinene and SO_2 were present; particle-phase acidity was generated from the photochemical conversion of SO_2 to condensable H_2SO_4. 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 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

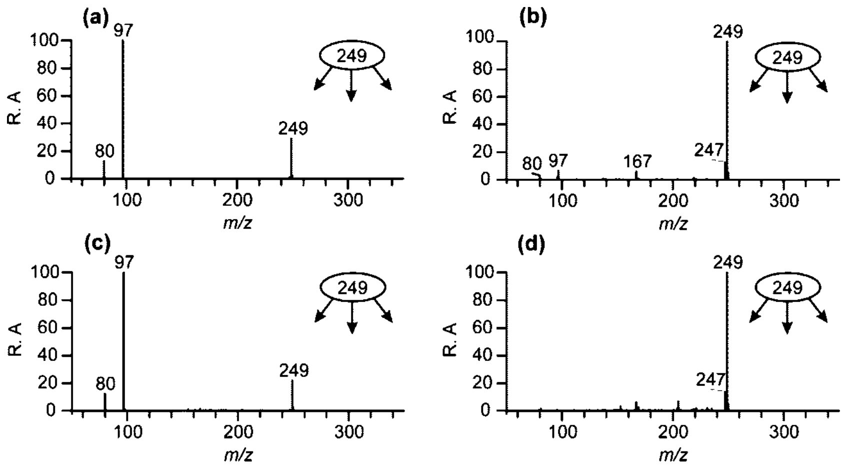


Figure 10. MS^2 spectra obtained for the two *m/z* 249 compounds with RTs of 31.2 and 32.2 min from (a, b) a β-pinene/H_2O_2/NO/highly acidic seed experiment and (c, d) a SEARCH sample (BHM 6/20/04). The compounds are denoted by **1**(250) and **2**(250) in the text, Figure 12, and Scheme 3.

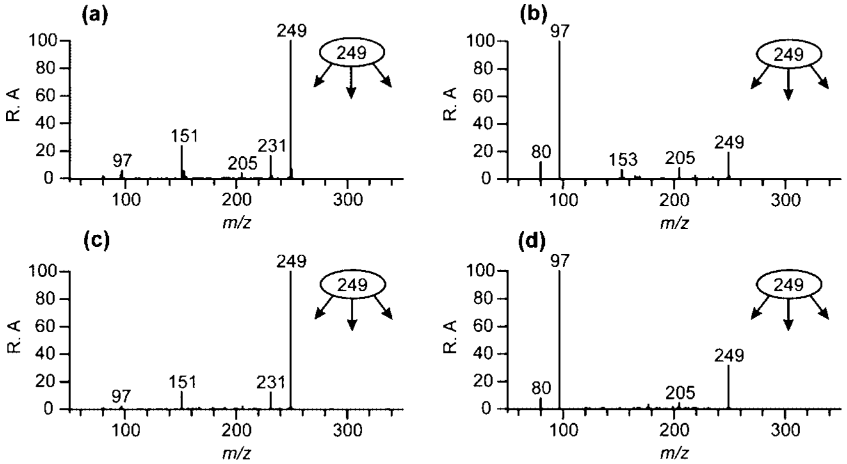


Figure 11. MS^2 spectra obtained for the two *m/z* 249 compounds with RTs of 24.4 and 29.3 min from (a, b) a α-pinene/H_2O_2/NO/highly acidic seed experiment and (c, d) a SEARCH sample (CTR 6/11/04). The compounds are denoted by **3**(250) and **4**(250) in the text, Figure 12, and Scheme 3. The ion at *m/z* 205 is due to an interference.

isoprene SOA.[23] Additionally, nitrooxy organosulfates were observed only under either intermediate- or high-NO_x conditions (denoted as H_2O_2/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 1S-6S (Supporting Information), 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 laboratory-generated and ambient aerosol.

4.2. 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 7S (Supporting Information) 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 formulas, 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

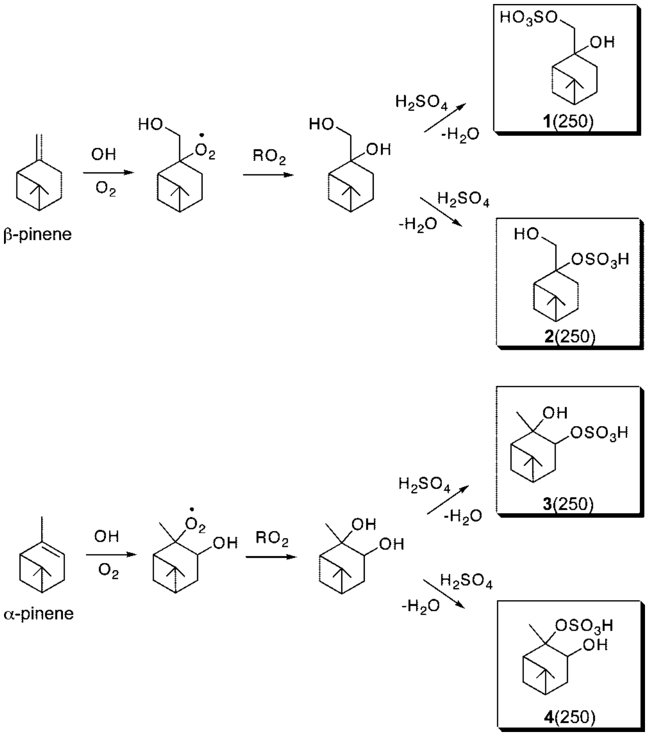


Figure 12. Proposed formation mechanism for the four *m/z* 249 organosulfates observed in ambient aerosol from the OH-initiated oxidation of *β*-pinene and α-pinene. Numerals **1**−**2**(250) correspond to the isomeric structural assignments for the *m/z* 249 *β*-pinene organosulfates, which are based upon the explanations for the observed product ions formed in the tandem MS experiments (Figure 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 11).

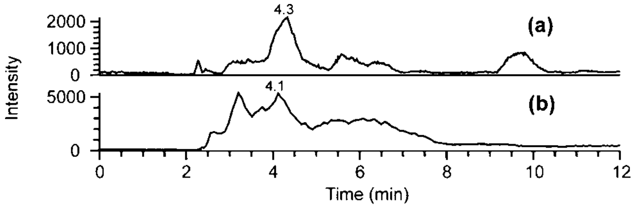


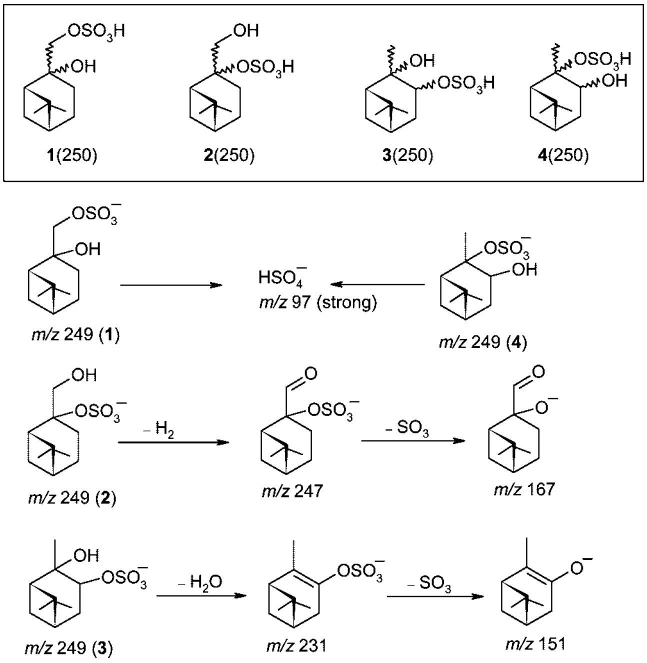
Figure 13. MS^2 (*m/z* 227) TICs obtained from (a) an α-pinene/H_2O_2/NO/highly acidic seed experiment and (b) a SEARCH sample (BHM 6/20/04).

subsequent sections; particular attention is focused on those ions detected for the first time in ambient aerosol.

5. Organosulfates in Ambient Aerosol

Figure 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 8S (Supporting Information) shows the accurate mass data for all organosulfates detected in each analyzed field sample.

SCHEME 3



In our previous study, the chemical composition of aerosol collected from this region was investigated; however, very few organic components identified in Figure 1 (and Table 8S, Supporting Information) were fully characterized, and in some cases, they were 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 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 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-methyltetrols 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 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.

5.1. Organosulfates of Monoterpenes in Ambient Aerosol.

5.1.1. 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

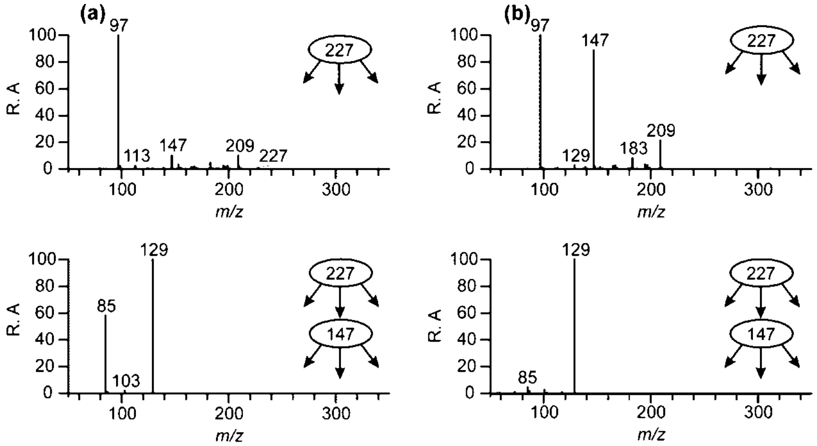
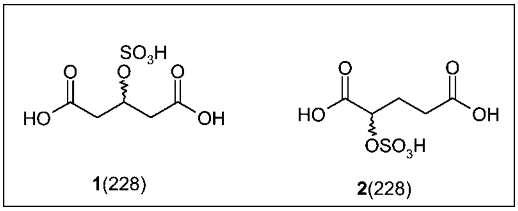


Figure 14. MS^2/MS^3 data for the *m/z* 227 compounds from (a) an α-pinene/H_2O_2/ NO/highly acidic seed experiment with a RT of 4.3 min and (b) a SEARCH sample (BHM 6/20/04) with a RT of 4.1 min.

SCHEME 4



1(228) **2**(228)

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 to 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 $C_{10}H_{16}NO_7S^-$,[26,47] consistent with the accurate mass data shown in Table 8S (Supporting Information). On the basis of these ion formulas, it was suggested that monoterpenes ($C_{10}H_{16}$) 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 SO_2 (i.e., acidified sulfate seed aerosol); however, it was noted in this prior study, as well as in that of 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 that an additional formation mechanism is possible (i.e., NO_3-initiated oxidation).[26,46] No such distinction between daytime and nighttime chemistry could be made in previous studies from the SEARCH campaign,[23,47] nor in the present study, owing to the fact that the samples were collected over a 24 h integrated period.

Figure 2 compares the UPLC/(−)ESI-TOFMS extracted ion chromatograms (EICs) of *m/z* 294 obtained from one representative SEARCH field sample (CTR 6/11/04) and four selected monoterpene oxidation experiments, including α-pinene/H_2O_2/NO/neutral seed, α-pinene/H_2O_2/NO/highly acidic seed, α-pinene/NO_3/highly acidic seed, and *β*-pinene/H_2O_2/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 8S, Supporting Information), 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 3S and 5S, Supporting Information), 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 2 to produce three *m/z* 294 nitrooxy organosulfates with the same RTs and accurate masses as those observed in the SEARCH samples (RTs of 8.19, 8.80, and 8.99 min; Figure 2a). As shown in Figure 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/NO_3/neutral seed experiment (Table 2). Additionally, Figure 2e shows that the *β*-pinene/H_2O_2/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 3 and 4 show MS^2/MS^3 data obtained with the HPLC/(−)ESI-LITMS technique for the three *m/z* 294 compounds formed in the α-pinene/NO_3/highly acidic seed experiment and MS^2/MS^3 data for the three *m/z* 294 compounds present from a selected SEARCH sample (CTR 6/20/04), respectively. MS^2 data similar to those for the α-pinene/NO_3/highly acidic seed

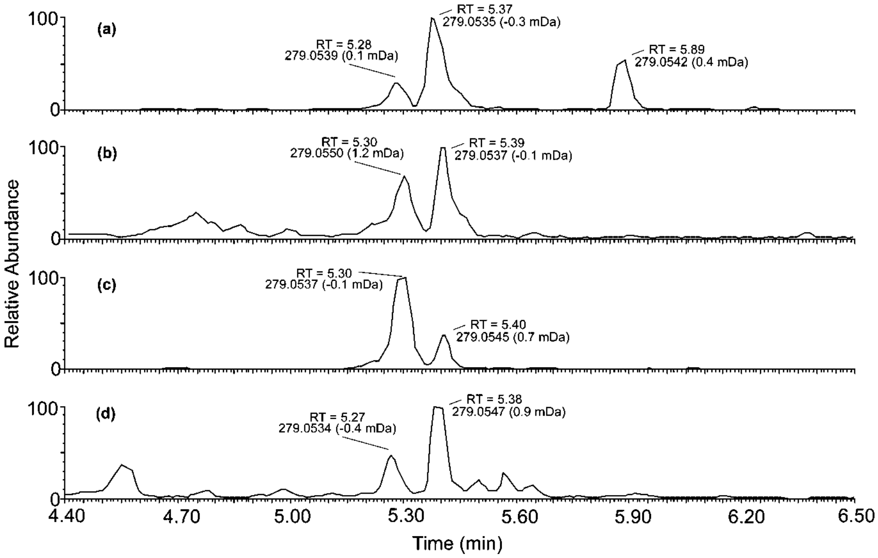


Figure 15. UPLC/(−)ESI-TOFMS extracted ion chromatograms (EICs) of *m/z* 279 for the following: (a) α-pinene/H_2O_2/NO/highly acidic seed experiment; (b) α-pinene/NO_3/highly acidic seed experiment; (c) *β*-pinene/H_2O_2/NO/highly acidic seed experiment; and (d) a SEARCH sample collected from the CTR 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* 279 ions are listed above each chromatographic peak. All of the chromatographic peaks highlighted in the figure share the same elemental composition of $C_{10}H_{15}O_7S^-$.

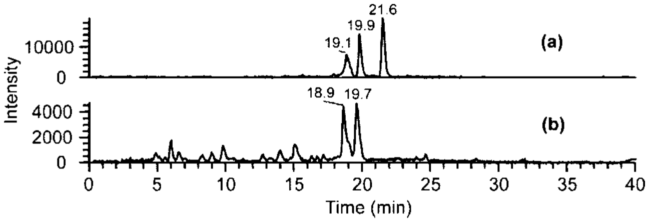


Figure 16. MS^2 (*m/z* 279) TICs obtained from (a) an α-pinene/H_2O_2/NO/highly acidic seed experiment and (b) a SEARCH sample (CTR 6/11/04). The compounds with RTs of 19.1 (or 18.9) and 19.9 min are denoted by **1**(280) and **2**(280) in the text and Scheme 5.

experiment were also obtained in the case of the α-pinene/H_2O_2/NO/highly acidic seed experiment (see Figure 1S, Supporting Information); in addition, similar MS^2 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 NO_3 and H_2O_2/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 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 MS^2 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 MS^2 spectra for compounds **2** and **3**(295) contain an abundant *m/z* 231 ion due to the loss of 63 u (HNO_3), which shows a different fragmentation behavior for the two compounds; in the case of compound **2**(295), multiple product ions are formed upon MS^3 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 → *m/z* 231 MS^3 spectrum of compound **2**(295) corresponds to the loss of 28 u ($CH_2{=}CH_2$). 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 MS^2 spectrum of compound **3**(295) points to neighboring OSO_3^- and ONO_2 groups and thus supports the proposed structure shown in Scheme 1. In regards to compound **1**(295), it is noted that the *m/z* 294 MS^2 spectrum is remarkably similar to those shown in Figure 2S (Supporting Information) 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 MS^3 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 HNO_2) in the *m/z* 294 MS^2 spectrum of compound **1**(295) is consistent with a primary nitrooxy group, while the base peak at *m/z* 96 ($SO_4^{-\bullet}$) 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 HNO_3 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 $NO_2^\bullet$ radical (74 u); however, a simple mechanism for this fragmentation could not be formulated.

On the basis of the interpretation of both the accurate mass and tandem MS data, Figure 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 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

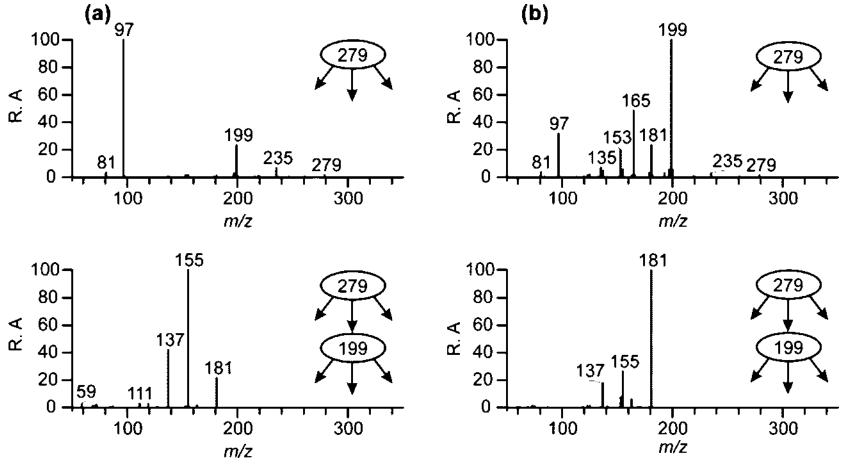


Figure 17. MS^2/MS^3 data for (a) the first- (19.1 min) and (b) second-eluting (19.9 min) m/z 279 compounds from the α-pinene/H_2O_2/NO/highly acidic seed experiment.

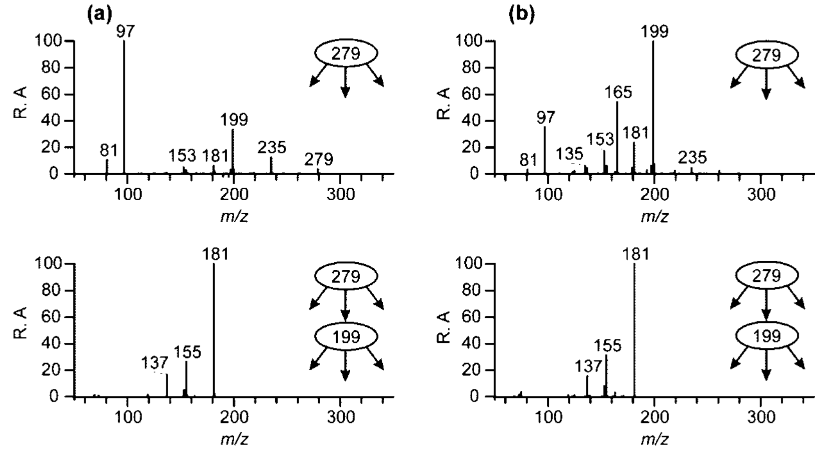
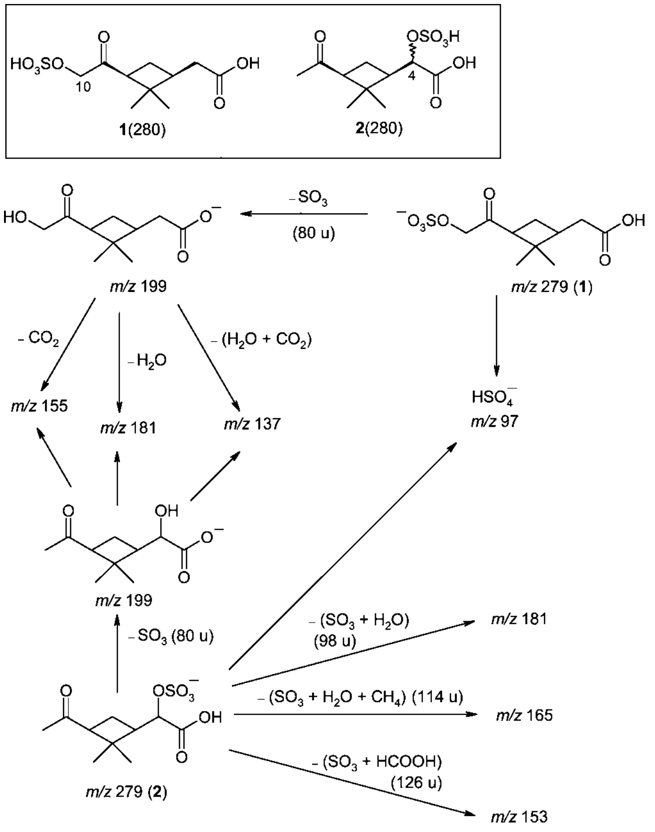


Figure 18. MS^2/MS^3 data for (a) the first- (19.1 min) and (b) second-eluting (19.9 min) m/z 279 compounds from the β-pinene/H_2O_2/NO/highly acidic seed experiment.

feasibility of our proposed reaction mechanism; in addition, Jay and Stieglitz[76] also observed hydroxynitrates from the NO_3-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 RO_2 chemistry, other structural isomers of the hydroxynitrate likely correspond to the detailed chemical structures shown in Scheme 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. Similar isomerization behavior has been proposed by Jay and Stieglitz[76] for β-nitrooxyalkyl radicals formed from the NO_3-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. Upon the formation of the hydroxyperoxy radicals from the isomerization of the initial β-hydroxyalkyl radical and subsequent addition of O_2, 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 RO_2 radical with NO, readily isomerize rather than fragment,[12,74,75] especially if the RO radical has at least four or more carbons and can form a six-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 dihydroxyalkyl radical. The latter radical immediately reacts with O_2 to form a dihydroxyperoxy radical, and in the presence of NO, it 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 that 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

SCHEME 5



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 nighttime-segregated filter samples collected from the SEARCH network to evaluate the importance of nighttime chemistry to the formation of the *m/z* 294 nitrooxy organosulfates.

5.1.2. 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 3S (Supporting Information) compares the UPLC/(−)ESI-TOFMS EICs of *m/z* 296 obtained from three selected monoterpene oxidation experiments, which includes the *d*-limonene/H_2O_2/NO/highly acidic seed, *β*-phellandrene + *d*-limonene mixture/H_2O_2/NO/highly acidic seed, and limonaketone/H_2O_2/NO/highly acidic seed experiments, to that of one representative SEARCH field sample (JST 6/26/04). Although not shown, it should be noted that the *l*-limonene/H_2O_2/NO/highly acidic seed experiment also produced three *m/z* 296 compounds with the same RTs and accurate masses as those highlighted in Figure 3S (Supporting Information) for the *d*-limonene experiments. From all of the monoterpene oxidation experiments conducted, *d*-/*l*-limonene and *β*-phellandrene, as well as limonaketone ($C_9H_{14}O$), 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 NO_x and highly acidified sulfate seed aerosol produced these compounds. Interestingly, no *m/z* 296 compounds formed in the NO_3/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 NO_3-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 3S (Supporting Information) indicate that the [M − H]$^-$ ion formulas for both the laboratory-generated (Figure 3Sa−c, Supporting Information) and ambient *m/z* 296 compounds (Figure 3Sd, Supporting Information) are $C_9H_{14}NO_8S^-$.

Figure 6 shows the *m/z* 296 MS^2 TICs obtained using the HPLC/(−)ESI-TOFMS technique for the *d*-limonene/H_2O_2/NO/highly acidic seed experiment and a SEARCH sample (BHM 6/20/04). As observed in the UPLC/(−)ESI-TOFMS EICs of *m/z* 296 (Figure 3S, Supporting Information), the RTs for the three *m/z* 296 compounds in *d*-limonene SOA were slightly shifted to longer times when compared to that for the ambient *m/z* 296 compounds. It is noted that the signals observed between 36 and 48 min in Figure 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 6a) eluting at 24.1, 25.4, and 28.3 min are given in Figure 7a−c, respectively. It can be seen that the *m/z* 296 MS^2 and *m/z* 296 → *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 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 2 [where numerals **1**−**3**(297) indicate the protonated compounds proposed]. The *m/z* 233 ion is explained by the loss of HNO_3 (63 u), indicating that a hydrogen is available for HNO_3 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 [HSO_4^-], it can be seen that the *m/z* 296 → *m/z* 233 MS^3 spectra show a *m/z* 81 ion corresponding to HSO_3^-. It is worth noting that this ion is not formed from the corresponding *m/z* 294 α-pinene derivatives, where instead *m/z* 80 [$SO_3^{-\bullet}$] is generated upon fragmentation of *m/z* 231.

In order to further support the proposed structures shown in Scheme 2 and gain insight into the formation mechanism of these compounds in *d*-limonene SOA, a limonaketone/H_2O_2/NO/highly acidic seed experiment was conducted. As shown in Figure 3S (Supporting Information), this experiment (Figure 3Sc, Supporting Information) 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 3Sa and 3Sb, respectively, Supporting Information). Additionally, comparison of the MS^2/MS^3 data collected for the three *m/z* 296 compounds observed in both the *d*-limonene (Figure 7) and limonaketone (Figure 4S, Supporting Information) H_2O_2/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. On the basis of the interpretation of both the accurate

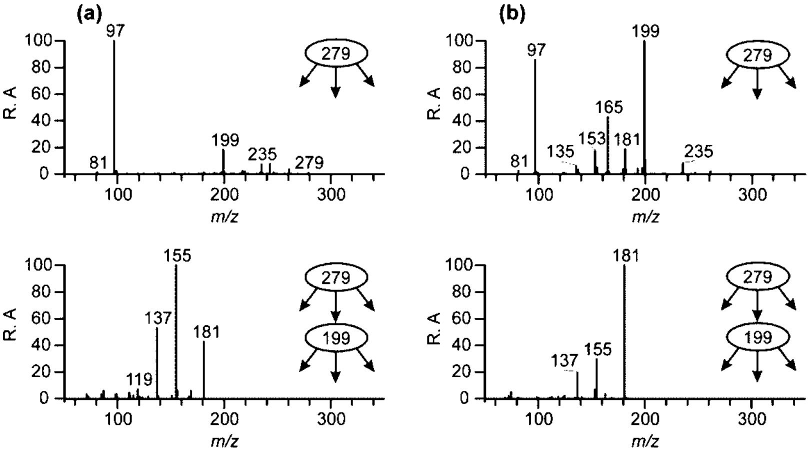


Figure 19. MS^2/MS^3 data for the first- (18.9 min) and second-eluting (19.7 min) *m/z* 279 compounds from the SEARCH sample (CTR 6/11/04).

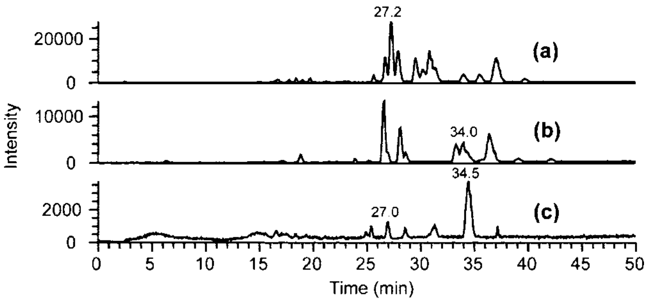


Figure 20. MS^2 (*m/z* 310) TICs obtained from (a) an α-pinene/H_2O_2/NO/highly acidic seed experiment, (b) a *β*-pinene/H_2O_2/NO/highly acidic seed experiment, and (c) a SEARCH sample (BHM 6/20/04). The compounds with RTs of 27.0 and 34.5 min from the ambient sample are denoted by **1** and **2**(311) in the text and Scheme 6.

mass and tandem MS data, Figure 8 shows the proposed formation mechanism for the three major *m/z* 296 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 RO_2 radical of limonaketone with NO; however, analogous to the proposed formation mechanism of compounds **1** and **2**(295) in α-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 3Sd, Supporting Information, and Figure 6b) were initially considered as *d*-limonene SOA products since their elemental compositions (i.e., $C_9H_{14}NO_8S^-$) were exactly the same as those observed in the limonene SOA experiments (Figure 3Sa−c, Supporting Information). Despite some differences in the RTs, careful inspection of the MS^2/MS^3 data shown in Figure 5S (Supporting Information) 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 7). The trace *m/z* 296 compound eluting at 24.0 min in Figure 6b corresponds with the second-eluting *m/z* 296 compound from *d*-limonene SOA [**2**(297)]. Comparison of their respective MS^2/MS^3 spectra (Figure 7b and Figure 5Sb, Supporting Information) supports this conclusion; the MS^2 spectrum obtained for the trace *m/z* 296 compound in the ambient sample reveals some additional interfering ions (i.e., at *m/z* 237, 179, and 137) compared to that of *d*-limonene SOA, but the *m/z* 296 → *m/z* 233 MS^3 spectra compare reasonably well, suggesting that the precursor of this compound is likely *d*-limonene. However, the two other major *m/z* 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 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- and *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 broadleaf 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]

5.1.3. m/z 249. Figure 9 compares the UPLC/(−)ESI-TOFMS EICs of *m/z* 249 obtained from three selected monoterpene oxidation experiments, which include α-pinene/NO_3/highly

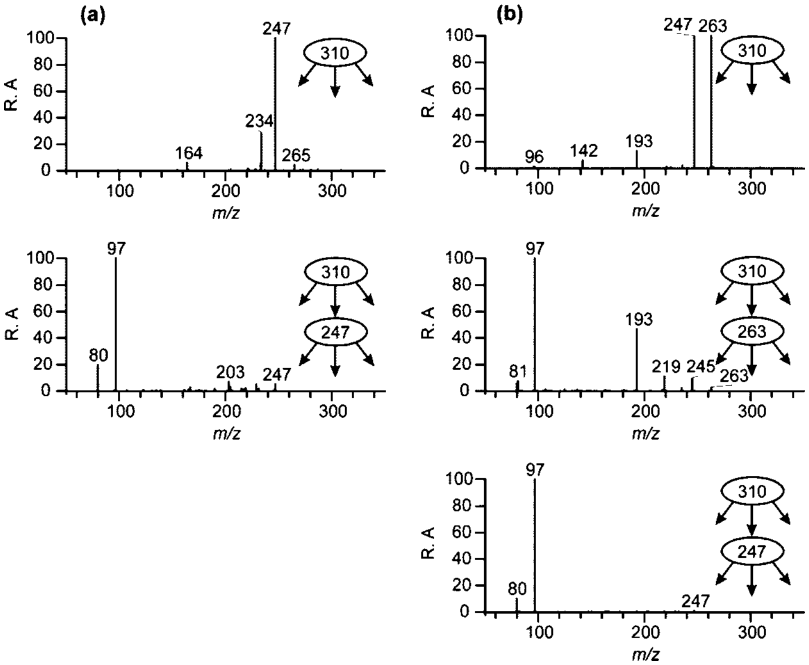
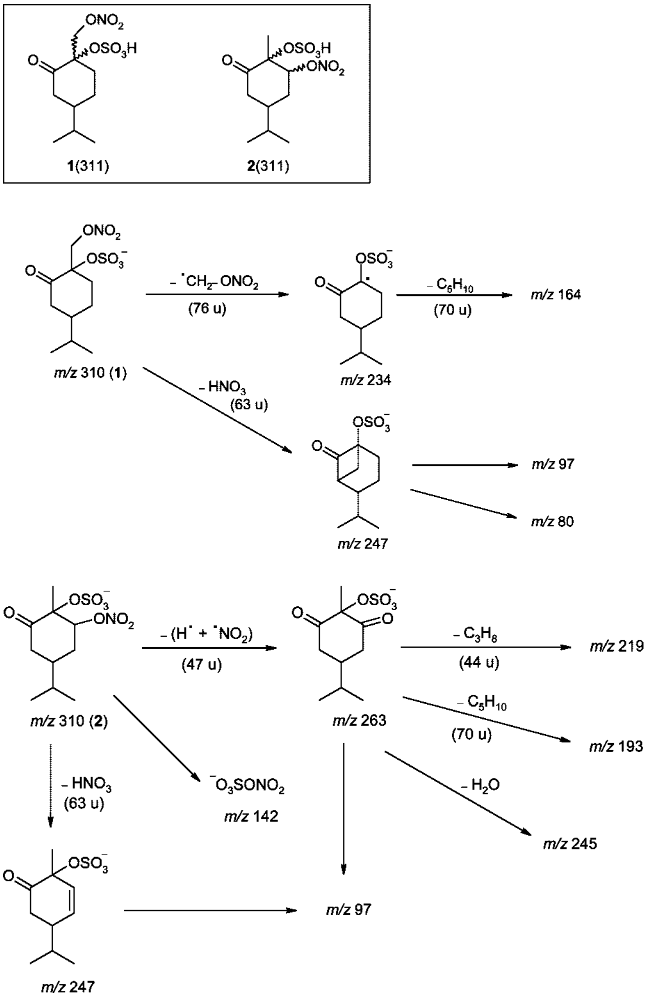


Figure 21. MS^2/MS^3 data for the m/z 310 compounds with RTs of (a) 27.0 min and (b) 34.5 min from the SEARCH sample (BHM 6/20/04).

SCHEME 6



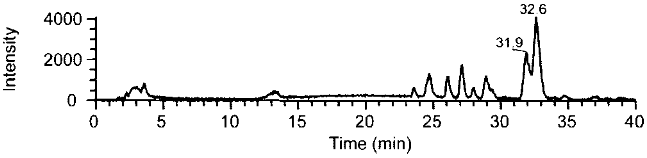


Figure 22. MS^2 (m/z 373) TIC obtained from a SEARCH sample (BHM 6/20/04). The compounds with RTs of 31.9 and 32.6 min are denoted by 1(374) and 2(374) in the text and Scheme 7.

acidic seed, α-pinene/H_2O_2/NO/highly acidic seed, and β-pinene/H_2O_2/NO/highly acidic seed experiments, to that of one representative SEARCH field sample (CTR 6/11/04). Accurate mass data for all chromatographic peaks highlighted in this figure indicate that the $[M - H]^-$ ion formula for both the laboratory-generated (Figure 9a–c) and ambient m/z 249 compounds (Figure 13d) is $C_{10}H_{17}O_5S^-$. Even though other monoterpenes shown in Tables 1S–6S (Supporting Information) 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 8S, Supporting Information), 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 10 shows the MS^2 spectra for the two m/z 249 compounds from the β-pinene/H_2O_2/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 11 shows the MS^2 spectra for the two m/z 249 compounds from the α-pinene/H_2O_2/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 8S, Supporting Information); 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 MS^2 spectra of the compounds from both the β-pinene and ambient samples with the same RTs perfectly

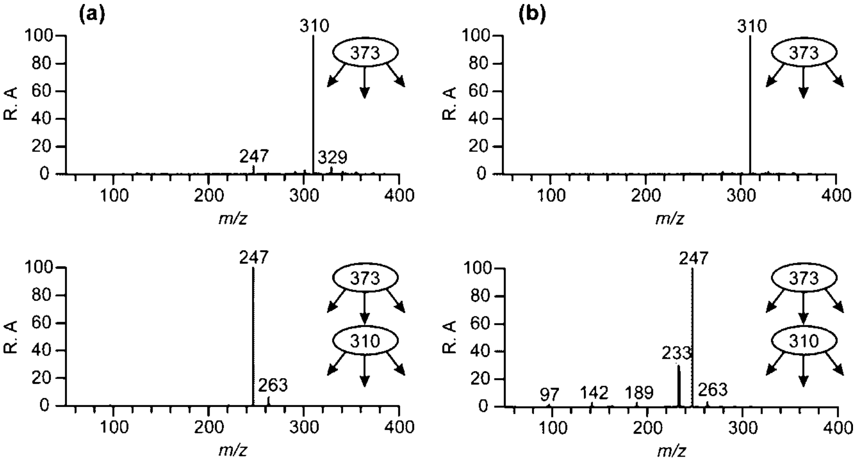
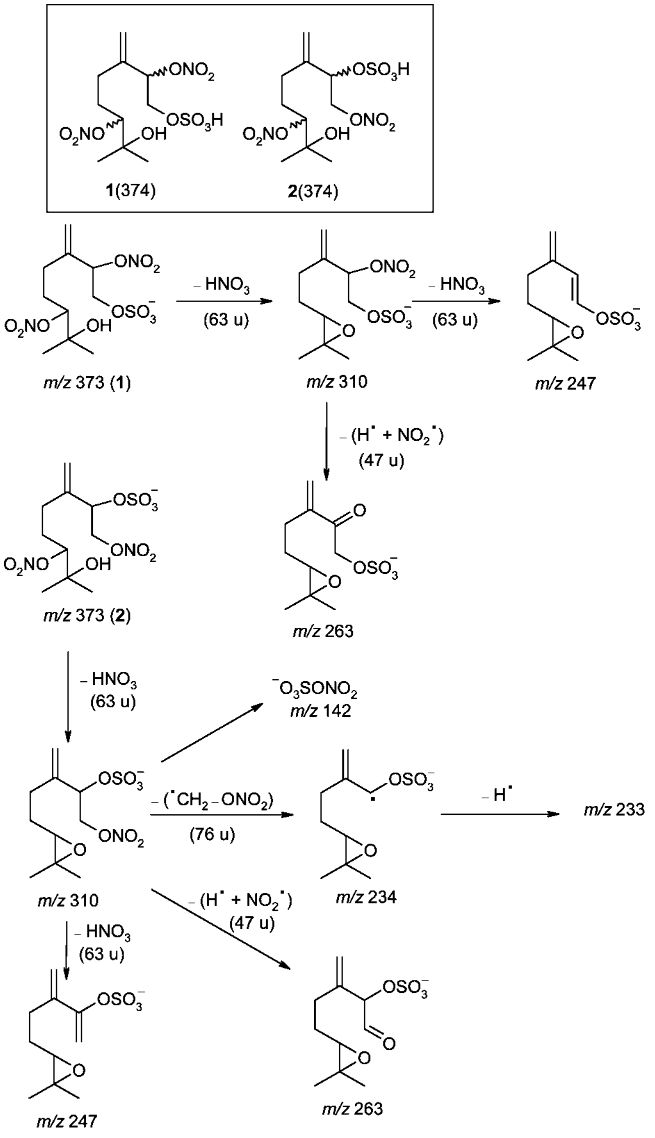


Figure 23. MS^2/MS^3 data for the *m/z* 373 compounds with RTs of (a) 31.9 min and (b) 32.6 min from a SEARCH sample (BHM 6/20/04).

SCHEME 7



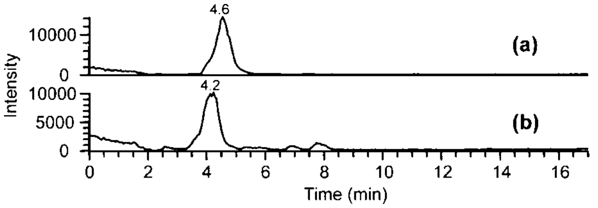


Figure 24. MS^2 (*m/z* 244) TICs obtained from (a) an isoprene/NO_x/SO_2 EPA photooxidation experiment and (b) a SEARCH sample (CTR 6/11/04).

agree. Plausible isomeric structures are given in Figure 12 and Scheme 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 SO_3 (80 u) yielding *m/z* 167 in its *m/z* 249 MS^2 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 [HSO_4^-]; while *m/z* 97 is virtually absent from the *m/z* 249 MS^2 spectrum of the second-eluting 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 MS^2 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 SO_3, respectively. As in the case of the β-pinene isomers, notable abundance differences are observed for *m/z* 97 [HSO_4^-]; while *m/z* 97 is virtually absent from the *m/z* 249 MS^2 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 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 H_2O_2 was employed as the OH radical source in both photooxidation experiments; however, as shown in Figure 9a, α-pinene + NO_3 cannot be ruled as a source for compounds **3** and **4**(250) until nighttime-segregated samples from the southeastern U.S. are analyzed. On the basis of the latter result, β-pinene + NO_3 may also contribute to the formation of compounds **1** and **2**(250); thus, this route cannot be excluded as a possible source at this time. Even though negligible amounts of O_3 were initially present at the start of each experiment, O_3 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 of O_3, which is the maximum mixing ratio of O_3 when β-pinene is still present, the reaction rate of β-pinene + OH is still nine times that of β-pinene + O_3. As previously observed in isoprene

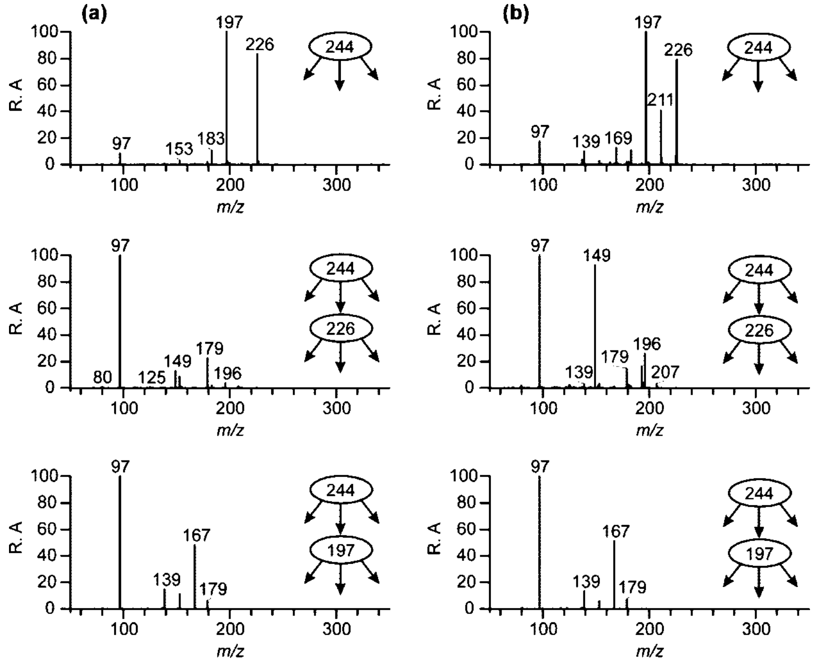


Figure 25. MS^2/MS^3 data for the *m/z* 244 compounds from (a) an isoprene/NO_x/SO_2 EPA photooxidation experiment and (b) a SEARCH sample (CTR 6/11/04).

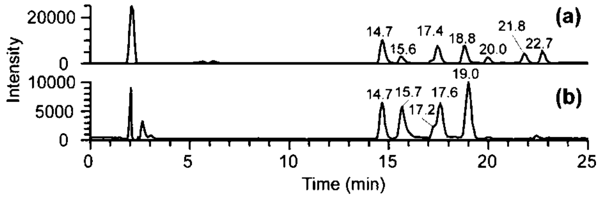


Figure 26. MS^2 (*m/z* 305) TICs obtained from (a) from an isoprene/NO_x/SO_2 EPA photooxidation experiment and (b) a SEARCH sample (CTR 6/11/04). The compounds with RTs of 15.7 and 19.0 min in the ambient sample are denoted by **2**(306) and **4**(306) in the text and Scheme 9.

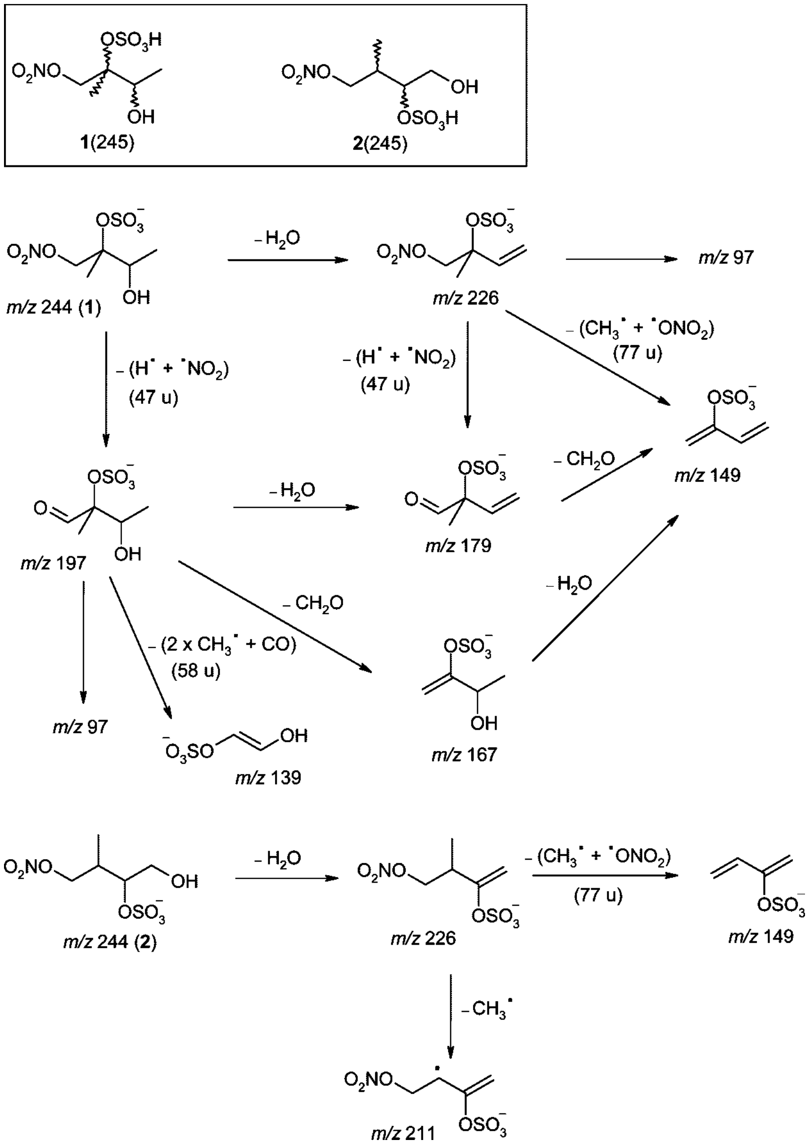
photooxidation experiments,[4,13,33] the NO mixing ratio needs to approach zero before significant levels of O_3 form; however, by this time, most of the hydrocarbon is typically reacted away by OH radicals.

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-spruce-dominated 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 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 O_3. 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 + O_3 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/NO_3/highly acidic seed experiment (Figure 9a) also produced the *m/z* 249 α-pinene organosulfates detected in ambient aerosol (Figure 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/NO_3/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 + NO_3 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.

5.1.4. m/z 227. Figures 13 and 14 show *m/z* 227 MS^2 TICs obtained from the α-pinene/H_2O_2/NO/highly acidic seed experiment and a SEARCH sample (BHM 6/20/04) and MS^2/MS^3 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 4 [where numerals **1** and **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 product[88] and 2-hydroxyglutaric acid was proposed to be an oxidation product of unsaturated fatty acids. It can be seen in the *m/z* 227 → *m/z* 147 MS^3 spectrum of the α-pinene SOA product (Figure 14a) that both *m/z* 129 and *m/z* 85 are produced, which are characteristic product ions of deprotonated 2- and 3-hydroxy-

SCHEME 8



glutaric 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 composition of both the laboratory-generated and ambient *m/z* 227 compounds is $C_5H_7O_8S^-$, confirming that these compounds are likely formed from either 2- or 3-hydroxyglutaric acids in ambient aerosol.

The *m/z* 227 MS^2/MS^3 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 → *m/z* 147 MS^3 spectrum (Figure 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/H_2O_2/NO/highly acidic seed experiment, none of the other monoterpenes studied in the present work produced laboratory-generated *m/z* 227 organosulfates (see Tables 2 and Tables 1S−6S, Supporting Information); 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]

5.1.5. m/z 279. Even though recent work identified a *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 15 compares the UPLC/(−)ESI-TOFMS EICs of *m/z* 279 obtained from three selected monoterpene oxidation experiments, which include α-pinene/H_2O_2/NO/highly acidic seed, α-pinene/NO_3/highly acidic seed, and *β*-pinene/H_2O_2/NO/highly acidic seed experiments, to that of one representative SEARCH field sample (CTR 6/11/04). Accurate mass data for all chromatographic peaks highlighted in this figure indicate that the $[M - H]^-$ ion formula for both the laboratory-generated (Figure 15a−c) and ambient *m/z* 279 compounds (Figure 15d) is $C_{10}H_{15}O_7S^-$. Although other monoterpene oxidation experiments (i.e., *d*-/*l*-limonene and α-/*γ*-

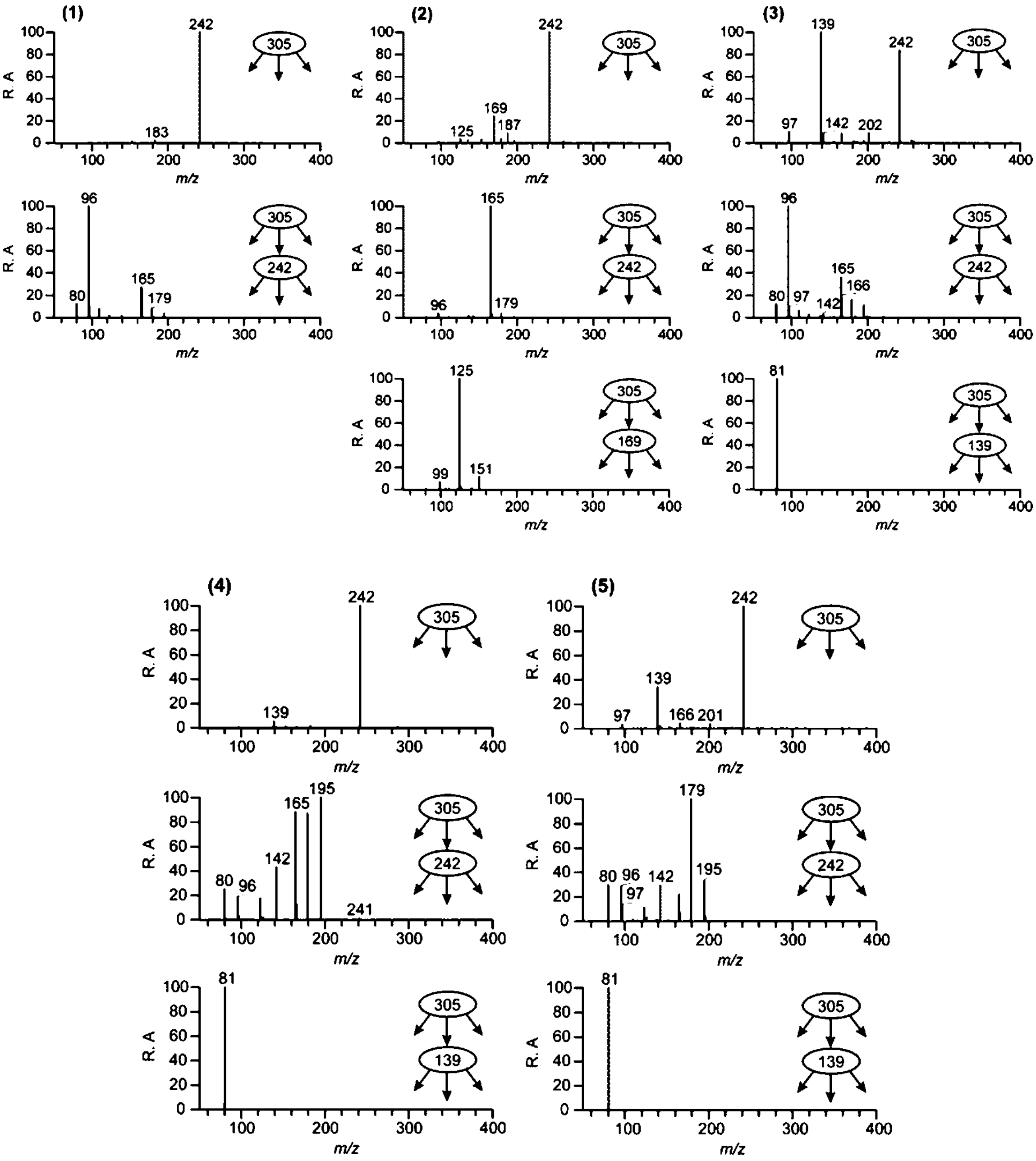


Figure 27. MS^2/MS^3 data obtained for the five first-eluting *m/z* 305 compounds from an isoprene/NO$_x$/SO$_2$ EPA photooxidation experiment. It is noted that MS^2/MS^3 data obtained for the three last-eluting *m/z* 305 compounds from the same isoprene experiment (Figure 26a) are shown in Figure 8S (Supporting Information).

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 8S, Supporting Information), 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 16−19 show *m/z* 279 MS^2 TICs from an α-pinene/H$_2$O$_2$/NO/highly acidic seed experiment and a SEARCH sample (CTR 6/11/04) and MS^2/MS^3 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 MS^2 spectra are distinctly different for the two first-eluting α-pinene SOA products (Figure 17); *m/z* 97 [HSO$_4^-$] is the base peak in the case of the first-eluting compound **1**(280), while *m/z* 199 due to loss of SO$_3$ dominates the *m/z* 279 MS^2 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 17) and those eluting at the same RTs of the ambient sample (Figure 19) are fairly similar. However, comparison of the MS^2/MS^3 data of the α-pinene SOA compounds (Figure 17) with those of the *β*-pinene SOA compounds with exactly

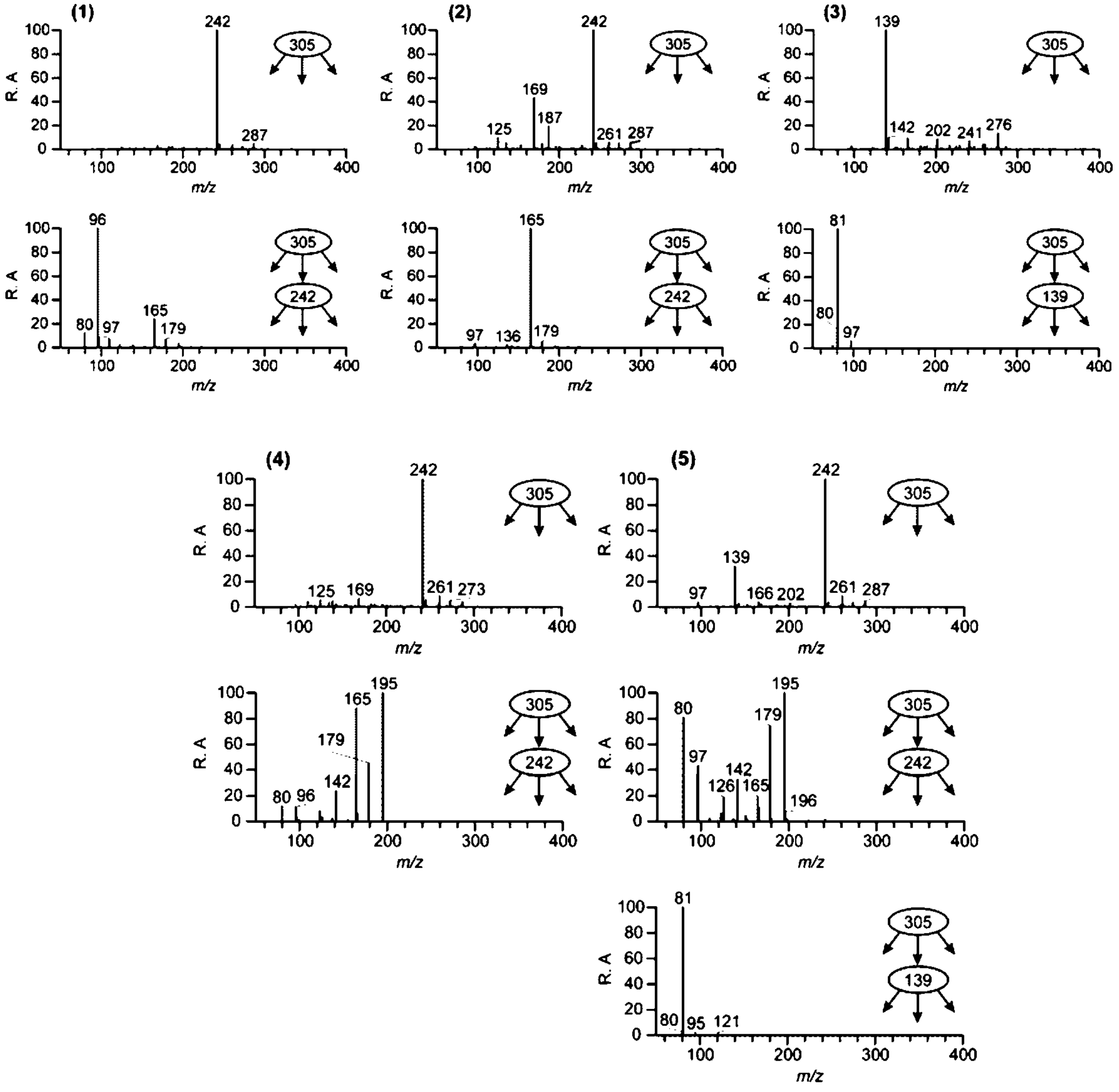
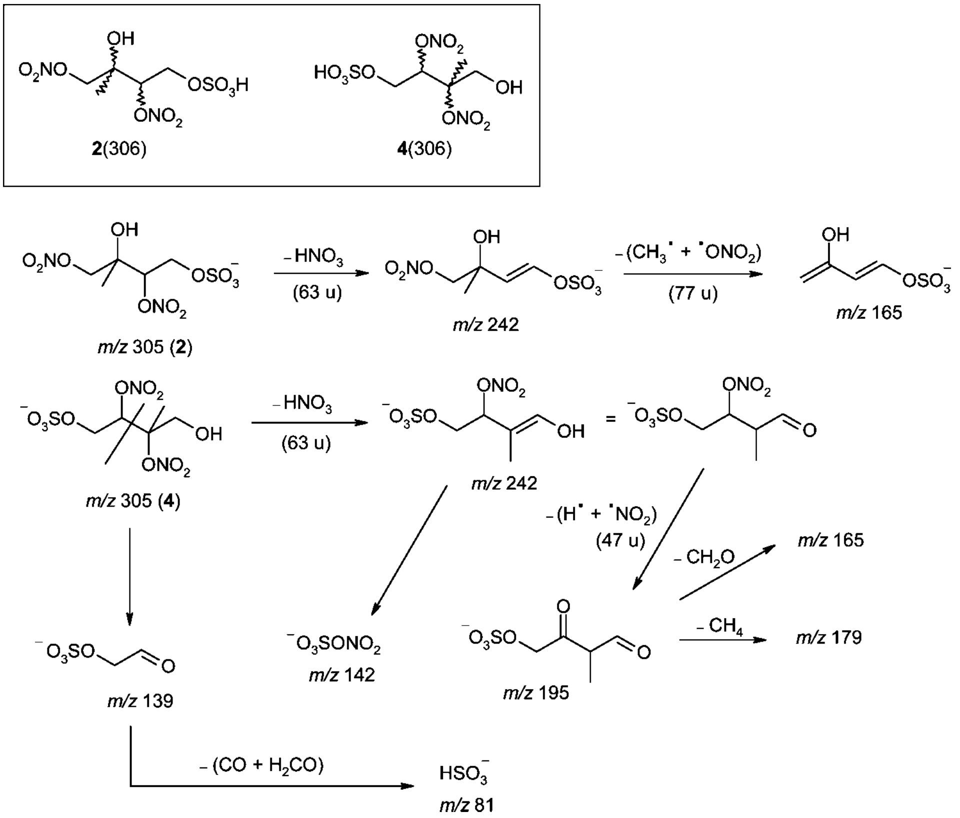


Figure 28. MS^2/MS^3 data obtained for the five *m/z* 305 compounds from a SEARCH sample (CTR 6/11/04).

the same RTs reveals some differences which are, at present, not understood; more specifically, the *m/z* 279 → *m/z* 199 MS^3 spectra are similar in the case of the β-pinene compounds, in contrast to those obtained for the α-pinene compounds. On the basis of the interpretation of the MS^2/MS^3 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 [where numerals **1** and **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.

5.1.6. m/z 310. Figures 20 and 21 show *m/z* 310 MS^2 TICs obtained from the α- and β-pinene/H_2O_2/NO/highly acidic seed experiments and a representative SEARCH sample (BHM 6/20/04) and MS^2/MS^3 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 6S (Supporting Information). Interestingly, in addition to α- and β-pinene, the α- and γ-terpinene/H_2O_2/NO/highly acidic seed experiments also produced *m/z* 310 compounds (Tables 3S and 4S, Supporting Information); 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 MS^2/MS^3 data for the selected compounds from the α- and β-pinene SOA, as well as those 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 $C_{10}H_{16}NO_8S^-$ (Tables 1S, 6S, and 8S, Supporting Information). In the following discussion, we will consider only the two *m/z* 310 compounds from the ambient sample. The *m/z* 310 MS^2 spectrum of the first-eluting compound **1**(311) contains *m/z* 247 due to loss of HNO_3, consistent with the presence of a nitrooxy group, while the *m/z* 310 → *m/z* 247 MS^3 spectrum reveals *m/z* 97 [HSO_4^-] and *m/z* 80 [$SO_3^{-\bullet}$], characteristic features of a sulfate group. Another characteristic fragmentation is the loss of 76 u (*m/z* 234), corresponding to a $CH_2{-}ONO_2$ radical and pointing to a terminal $CH_2{-}ONO_2$ group. The *m/z* 310 MS^2 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 NO_2 radicals, and *m/z* 245, 219, and 193 due to a subsequent loss of H_2O, C_3H_8, and C_5H_{10},

SCHEME 9



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 6 [where numerals **1** and **2**(311) indicate the protonated compounds proposed]. The major nitrooxy organosulfate 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]

5.1.7. m/z 373. Iinuma et al.[26] previously determined that the elemental composition of $[M - H]^-$ ions at *m/z* 373 detected in ambient aerosol collected from a forested site in Europe by (−)ESI-MS techniques is $C_{10}H_{17}N_2O_{11}S^-$. This prior study observed these compounds only in nighttime samples. On the basis of 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 7S (Supporting Information) 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/H_2O_2/NO/highly acidic seed and *β*-phellandrene + *d*-limonene/H_2O_2/highly acidic seed experiments, to that of one representative SEARCH field sample (BHM 6/20/04). Accurate mass data for all chromatographic peaks highlighted in this figure indicates that the $[M - H]^-$ ion formula for both the laboratory-generated (Figure 7Sa-b, Supporting Information) and ambient *m/z* 373 compounds (Figure 7Sc, Supporting Information) is $C_{10}H_{17}N_2O_{11}S^-$. 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 3S−5S, respectively, Supporting Information), also produced *m/z* 373 compounds with the same elemental compositions as those observed in the ambient samples (Table 8S, Supporting Information); 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 source. Unlike the photooxidation experiments, it is worth noting that the *d*-limonene/NO_3/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 2 and 1S−6S, Supporting Information), 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 22 and 23 show *m/z* 373 MS^2 TICs obtained from a representative SEARCH sample (BHM 6/20/04) and the MS^2/MS^3 data for the two major compounds **1** and **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 22 and 7Sc, Supporting Information). In agreement with the findings of Iinuma et al.,[26] the *m/z* 373 MS^2 spectra are very similar for the two compounds, revealing *m/z* 310 (loss of HNO_3) as the base peak. Subsequent fragmentation of *m/z* 310 proceeds through a second loss of HNO_3, affording *m/z* 247. In the case of compound **2**(373), the *m/z* 373 → *m/z* 310 MS^3 spectrum also shows an ion at *m/z* 234 due to the loss of a

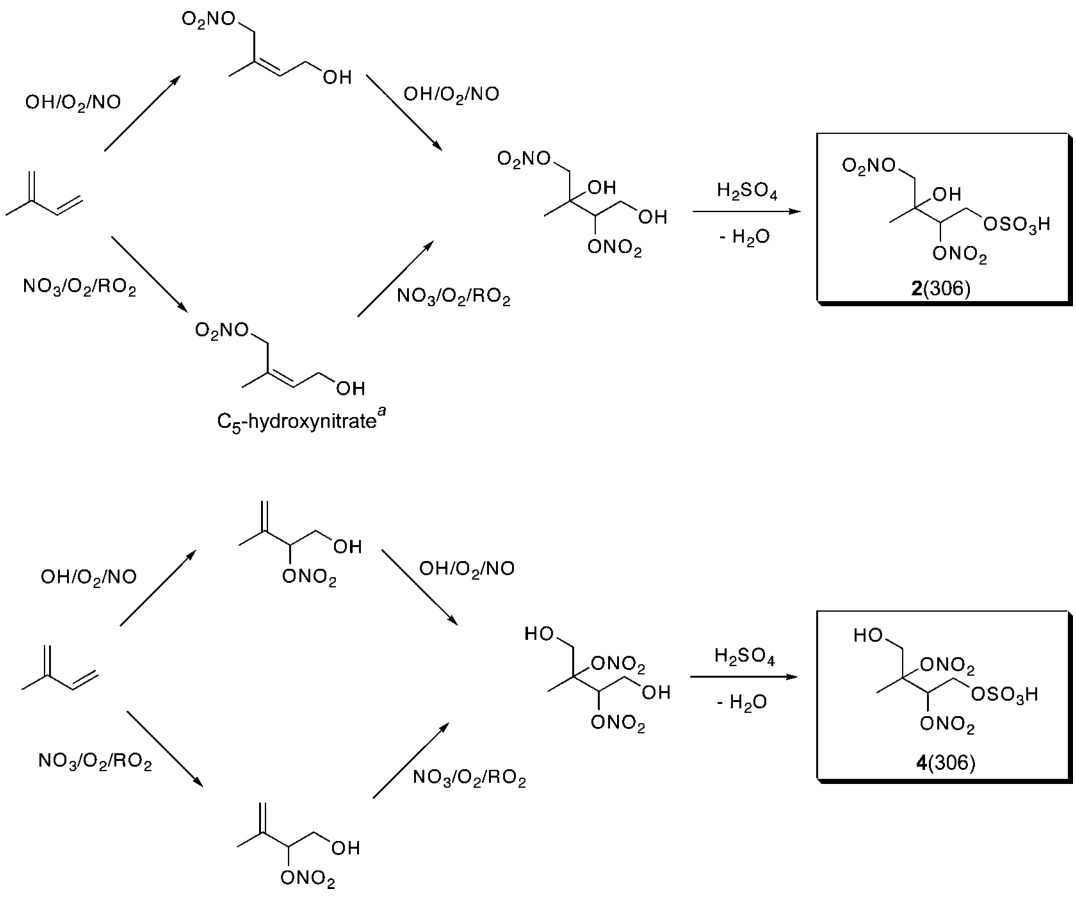


Figure 29. Proposed formation mechanism for the two major *m/z* 305 nitrooxy organosulfate isomers observed in ambient aerosol (Figure 26b) from either the photooxidation of isoprene in the presence of NO_x or the NO_3-initiated oxidation of isoprene under dark conditions, with both in the presence of acidified sulfate seed aerosol. Numerals **2** and **4**(306) correspond to the isomeric structural assignments based upon the explanations shown in Scheme 9 for the observed product ions formed in the tandem MS experiments. Footnote *a*: Ng et al.[93] observed a hydroxynitrate species of this MW in the gas phase from the NO_3-initiated oxidation of isoprene under dark conditions as the $[M + CF_3O^-]$ ion using chemical ionization MS.

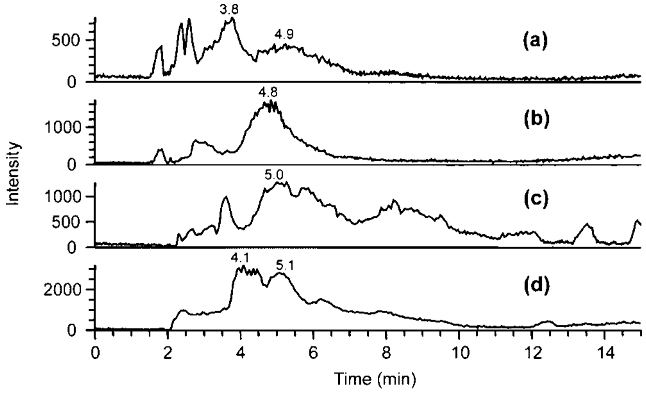


Figure 30. MS^2 (*m/z* 334 and 332) TICs obtained from (a, c) an isoprene/NO_x/SO_2 EPA photooxidation experiment and (b, d) a SEARCH sample (CTR 6/11/04), respectively.

$CH_2{-}ONO_2$ 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 8S, Supporting Information), a tentative structure with a myrcene skeleton is proposed in Scheme 7 [where numerals **1** and **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.

5.1.8. 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 8S (Supporting Information) 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 formulas 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

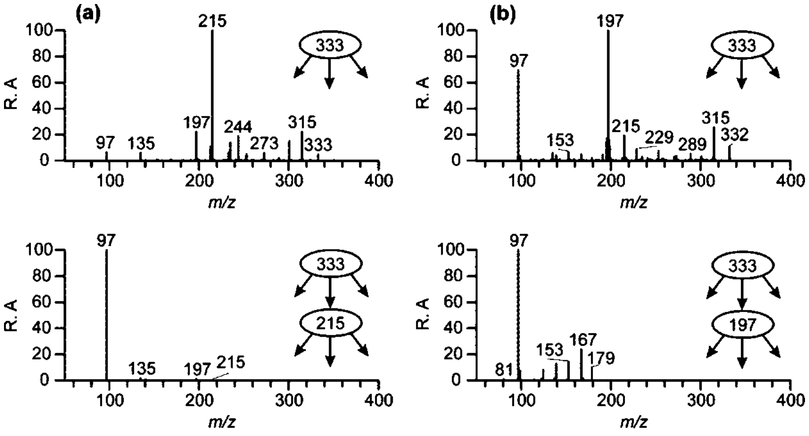


Figure 31. MS^2/MS^3 data obtained for the *m/z* 333 compounds from an isoprene/NO_x/SO_2 EPA photooxidation experiment eluting at (a) 3.8 and (b) 4.2 min.

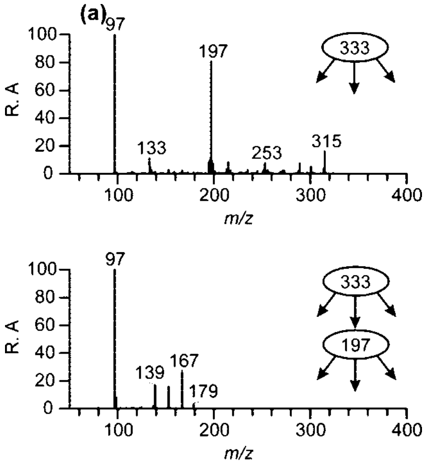


Figure 32. MS^2/MS^3 data obtained for *m/z* 333 compounds from a SEARCH sample (CTR 6/11/04) eluting at 4.8 min.

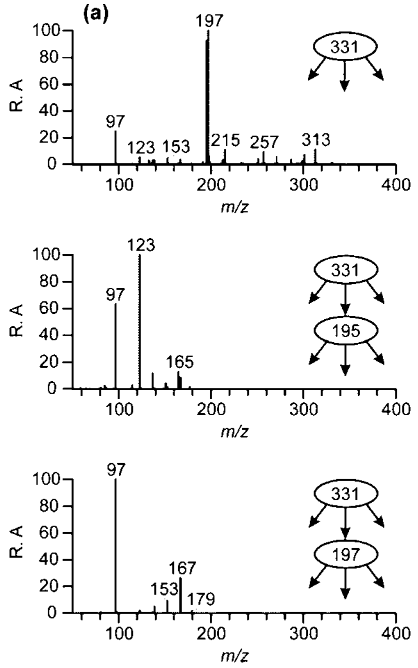


Figure 33. MS^2/MS^3 data obtained for *m/z* 331 compounds from an isoprene/NO_x/SO_2 EPA photooxidation experiment eluting at 5.0 min.

to a C_7-diketone aldehyde. As indicated in Table 2S (Supporting Information), 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 2S, Supporting Information) do not have the same RTs as those in the ambient samples (Table 8S, Supporting Information). 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 H_2O_2/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 8S, Supporting Information). Although the α-terpinene/H_2O_2/NO/highly acidic seed experiment produced one *m/z* 283 compound with the same elemental composition (i.e., $C_9H_{15}O_8S^-$) 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. On the basis of the current laboratory findings (Tables 1S−6S, Supporting Information), 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 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 of these laboratory-generated *m/z* 326 compounds indicate that these ions have an elemental composition of $C_{10}H_{16}NO_9S^-$, consistent with the ambient compounds (Table 8S, Supporting Information); 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.

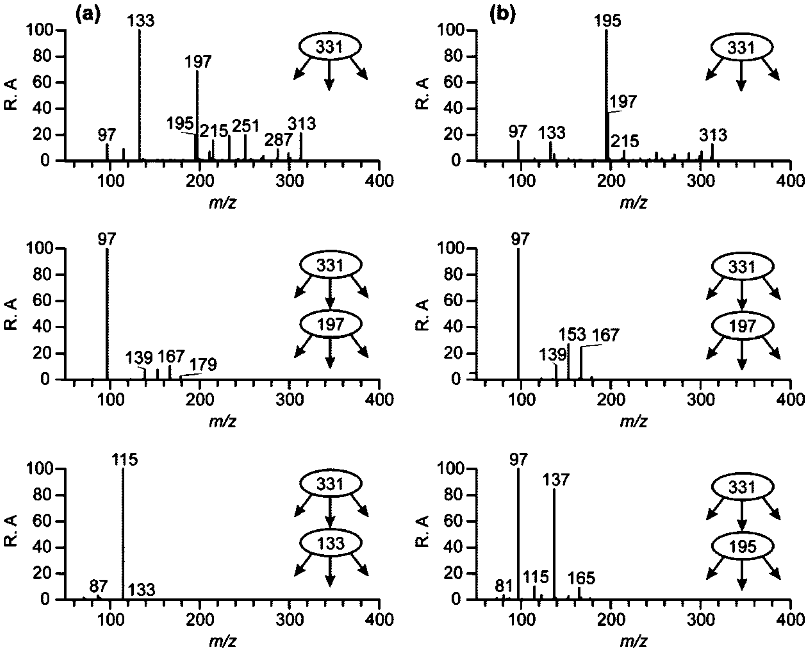
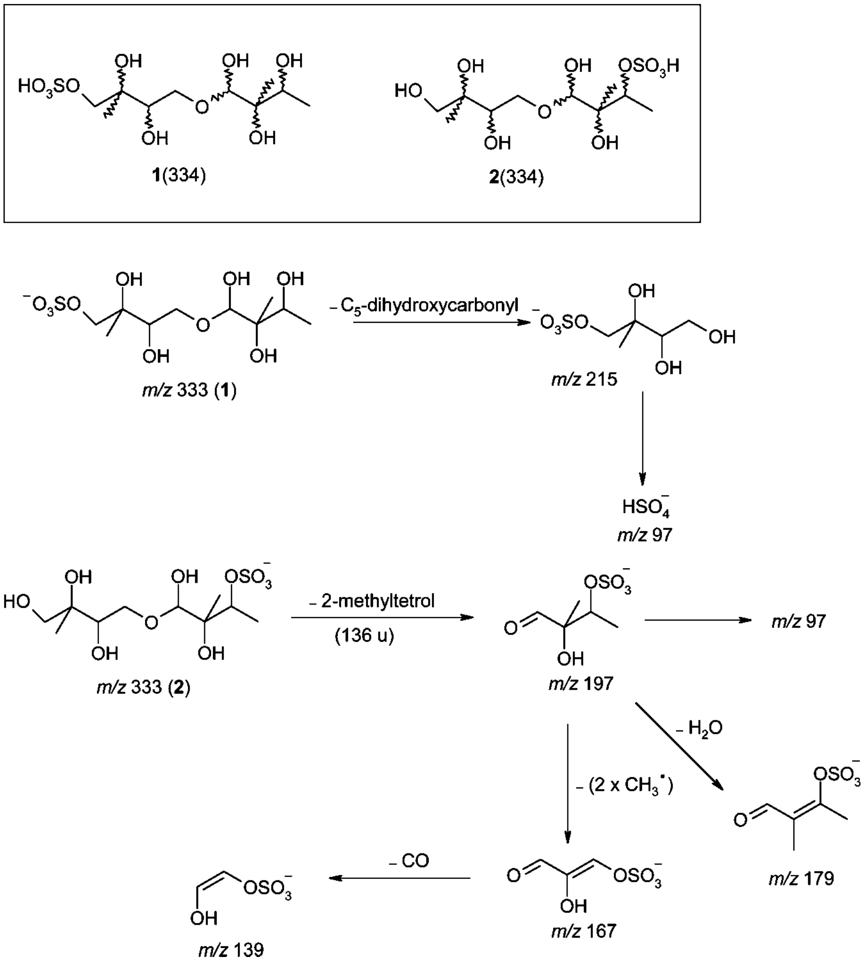


Figure 34. MS^2/MS^3 data obtained for *m/z* 331 compounds from a SEARCH sample (CTR 6/11/04) eluting at (a) 4.1 and (b) 5.1 min.

SCHEME 10



Iinuma 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., $C_{10}H_{16}NO_{10}S^-$) 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 were also not determined. As shown in Figure 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., $C_{10}H_{15}N_2O_{12}S^-$) determined from the accurate mass measurements (Table 8S, Supporting Information) suggests a monoterpene part.

5.2. Organosulfates of Isoprene in Ambient Aerosol. ***5.2.1. m/z 244.*** Figures 24 and 25 show *m/z* 244 MS^2 TICs obtained from an isoprene/NO_x/SO_2 EPA photooxidation experiment and a SEARCH sample (CTR 6/11/04) and MS^2/MS^3 data for the *m/z* 244 compounds from both samples, respectively. As shown in Tables 7S and 8S (Supporting Information), both the Caltech isoprene/H_2O_2/NO/acidic seed and isoprene/HONO/neutral seed experiments also produced *m/z* 244 compounds with the same RTs and elemental compositions (i.e., $C_5H_{10}NO_8S^-$) 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 7S and 8S, Supporting Information) as well as the MS^2/MS^3 data not supporting such a structure.

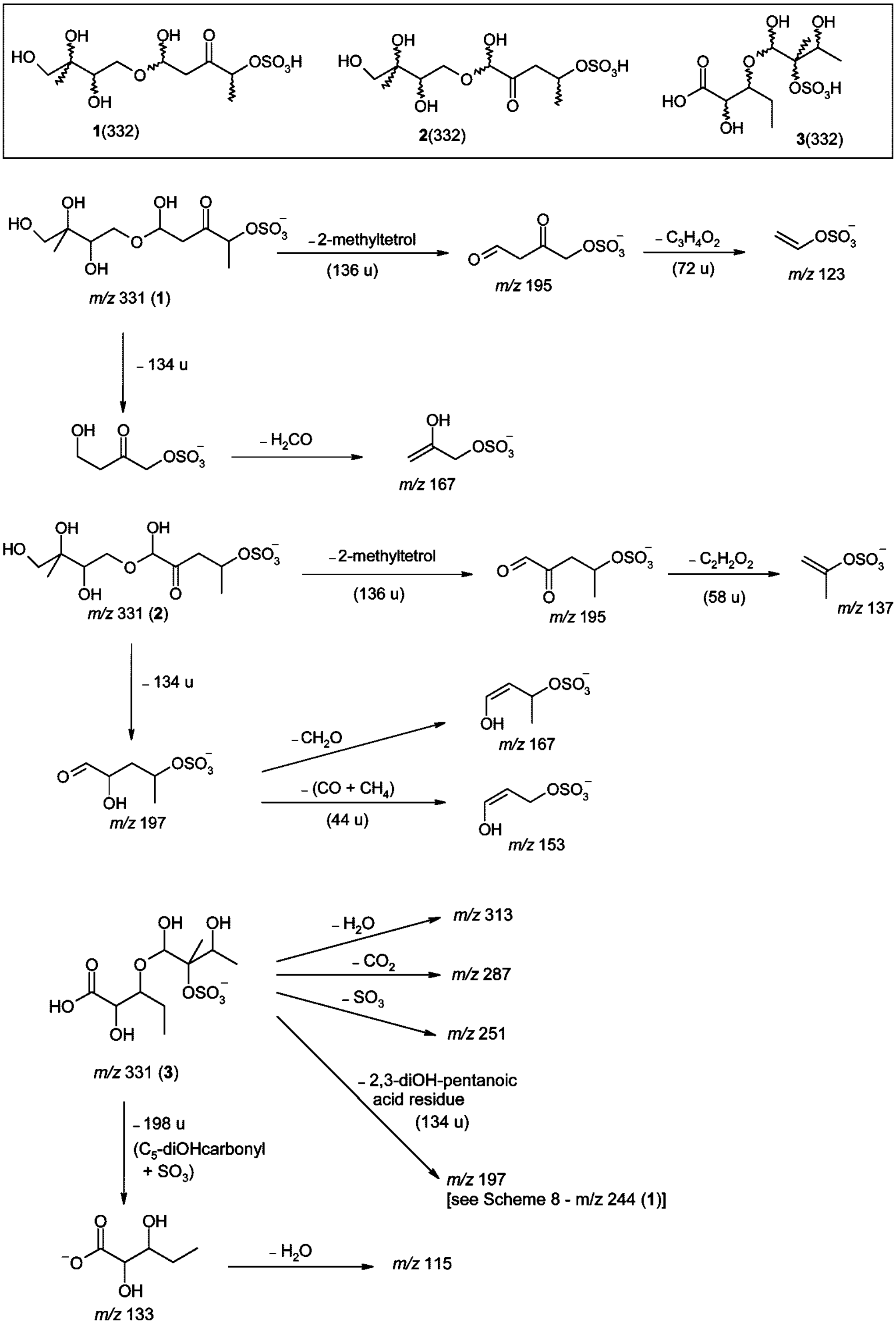
It can be seen that the *m/z* 244 MS^2 spectra shown in Figure 25 reveal some differences; the spectrum obtained for the ambient sample is more complex, however. In both cases, *m/z* 226 and 197, due to the loss of water and the combined loss of hydrogen and NO_2 radicals, respectively, are the most abundant product ions. Furthermore, it can be noted that the *m/z* 244 → *m/z* 197 MS^3 spectra are similar and, moreover, show the same product ions as the *m/z* 260 → *m/z* 197 MS^3 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 C_5-alkane triols for the *m/z* 244 compounds. On the basis of the interpretation of the MS^2/MS^3 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 8 [where numerals **1** and **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 MS^2 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 MS^2 spectrum, as well as the abundant *m/z* 149 ion in the *m/z* 244 → *m/z* 226 MS^3 spectrum. The formation of C_5-alkane triols through photooxidation of isoprene has, to our knowledge, not yet been documented in the literature.

5.2.2. m/z 305. Figures 26−28show *m/z* 305 MS^2 TICs obtained from an isoprene/NO_x/SO_2 EPA photooxidation experiment and a SEARCH sample (CTR 6/11/04) and MS^2/MS^3 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 26. Recent work of the Caltech laboratory has shown that the NO_3-initiated oxidation of isoprene under dark conditions, in the presence of either nonacidified or highly acidified sulfate seed aerosol, also produces *m/z* 305 compounds.[93] The further oxidation of a C_5-hydroxynitrate, a known first-generation gas-phase product, by NO_3 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 8S, Supporting Information) and Caltech isoprene SOA samples (Table 7S, Supporting Information), 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 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 five major *m/z* 305 isomers from the ambient sample, namely, those with RTs of 15.7 min [**2**(306)] and 19.0 min [**4**(306)]. Possible structures for these compounds are proposed and supported in Scheme 9 [where numerals **2** and **4**(306) indicate the protonated compounds proposed]; insufficient MS structural information was available in the case of the three other isomers. Four of the major *m/z* 305 compounds from the ambient sample have *m/z* 242 as the base peak in their respective MS^2 spectra (Figure 28), corresponding to the loss of HNO_3 (63 u). In regards to compound **2**(306), the ion at *m/z* 165 due to the combined loss of CH_3 and ONO_2 radicals (77 u) in the *m/z* 305 → *m/z* 242 MS^3 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 MS^2 spectrum of compound **4**(306) points to a sulfated nitrooxy diol part and a terminal sulfate group. Furthermore, the *m/z* 305 → *m/z* 242 MS^3 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 NO_2 radical (47 u), and, at *m/z* 179 and 165, which can be attributed to further loss of CH_4 and CH_2O, respectively, from *m/z* 195.

On the basis of the interpretation of both the accurate mass and tandem MS data, Figure 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 NO_3-initiated oxidation of isoprene

SCHEME 11



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, nighttime-segregated 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.

5.2.3. m/z 333 and 331. Figures 30−34 show *m/z* 333 and 331 MS^2 TICs obtained from an isoprene/NO_x/SO_2 EPA photooxidation experiment and a SEARCH sample (CTR 6/11/04) and MS^2/MS^3 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 C_5-dihydroxycarbonyl, that is, 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 MS^2 spectra for the middle sections of the peaks with RTs of 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 C_5-dihydroxycarbonyl part for the isomeric mixtures with RTs of 3.8 and 4.9 min, respectively. Possible structures for *m/z* 333 compounds are given and supported in Scheme 10 [where numerals **1** and **2**(334) indicate the protonated compounds proposed]; accurate mass measurements of both the Caltech laboratory-generated and SEARCH *m/z* 333 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 → *m/z* 215 MS^3 spectrum obtained for the *m/z* 333 isomeric mixture eluting at 3.8 min is exactly the same as the *m/z* 215 MS^2 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/z* 333 compounds is located in the 2-methyltetrol part. It is noted that the *m/z* 333 → *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 → *m/z* 197 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 C_5-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 nonsulfated products with MW 254. It was verified here that the latter MS data are also consistent with the new revised C_5-dihydroxycarbonyl structure. The *m/z* 333 → *m/z* 197 MS^3 spectrum reveals *m/z* 97 [HSO_4^-] as base peak and product ions at *m/z* 179, 167, 153, and 139, which are all readily explained with the revised sulfated C_5-dihydroxycarbonyl structure.

In regards to the *m/z* 331 compounds, it can be seen that the *m/z* 331 MS^2 spectra (Figures 33 and 34) show features that are similar to those of the *m/z* 333 compounds, that is, the presence of *m/z* 215 and 197, of which the latter ion shows exactly the same fragmentation behavior as that for the *m/z* 333 compounds. In addition, a product ion at *m/z* 195 can be observed in the *m/z* 331 MS^2 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 33), fragmentation to *m/z* 137 occurs for the ambient sample (Figure 34b). Possible structures for the *m/z* 331 compounds from isoprene SOA (RT of 5 min) [**1**(332)] and the ambient sample (RT of 5.1 min) [**2**(332)], taking into account their fragmentation behaviors, are given in Scheme 11 [where numerals **1**−**3**(332) indicate the protonated compounds proposed]. The proposed C_5-hydroxydicarbonyl part in the *m/z* 331 compound from the ambient sample likely has a precursor that is different from isoprene. The *m/z* 331 compound with a RT of 4.1 min [**3**(332)] from the ambient sample shows *m/z* 133 as a base peak in its MS^2 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 → *m/z* 133 MS^3 spectrum perfectly agrees with the *m/z* 133 MS^2 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 11.

5.2.4. 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/SO_2 EPA photooxidation experiment,[46] the [M − H]$^-$ ions at *m/z* 155 and 169 detected in the SEARCH (Table 8S, Supporting Information) and the Caltech laboratory-generated isoprene SOA samples (Table 7S, Supporting Information) 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. MS^2 product ion spectra (not shown) for both of these organosulfates show a major product ion at *m/z* 97 [HSO_4^-], consistent with prior work[46] and the neutral nature of the nonsulfated 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 coeluted 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 noncovalent adduct formed between glyoxal and sulfuric acid; theoretical calculations indicate that the organosulfate of glyoxal exists in the α-hydroxysulfate ester (i.e., sulfate derivative) form rather than the noncovalent adduct form. As shown in Figure 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 noncovalent 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 2 and Tables 1S−7S, Supporting Information), 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 7S (Supporting Information), only the photooxidation of isoprene under intermediate (H_2O_2/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 of 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/H_2O_2/acidic seed photooxidation experiment and the SEARCH samples contain *m*/*z* 213 organosulfates (Tables 7S and 8S, respectively, Supporting Information) with the same elemental composition (i.e., $C_5H_9O_7S^-$) 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/H_2O_2/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/H_2O_2/acidic seed experiment (Table 7S, Supporting Information) produced a *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 8S, Supporting Information). 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 aerosol[46] 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 7S and 8S (Supporting Information), the accurate mass measurements indicate that these compounds have an elemental composition of $C_5H_{10}NO_9S^-$, confirming the initial characterization of these compounds in SOA as well as identifying isoprene as the VOC precursor.

6. 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 SO_2, 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 nonacidified 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 the 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 semivolatile 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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Supporting Information Available: Tables containing the detailed accurate mass measurements for all experiments conducted in Table 2, MS^2 data for the three *m/z* 294 nitrooxy organosulfates formed in the α-pinene/H_2O_2/NO/highly acidic seed experiment, MS^2/MS^3 data for the *m/z* 294 nitrooxy organosulfates formed in the β-pinene/H_2O_2/NO/highly acidic seed experiment, UPLC/(−)ESI-TOFMS EICs of *m/z* 296 for three selected limonene experiments and one SEARCH field site, MS^2/MS^3 data for the three *m/z* 296 nitrooxy organosulfates formed in the limonaketone/H_2O_2/NO/highly acidic seed experiment, MS^2/MS^3 data for the three *m/z* 296 nitrooxy organosulfates found in the BHM field site, MS^2/MS^3 data for the *m/z* 310 nitrooxy organosulfates from an α-pinene/H_2O_2/NO/highly acidic seed experiment and a β-pinene/H_2O_2/NO/highly acidic seed experiment, UPLC/(−)ESI-TOFMS EICs of *m/z* 373 for two selected limonene experiments and one SEARCH field site, and MS^2/MS^3 data for the three last-eluting *m/z* 305 compounds from an isoprene/NO_x/SO_2 EPA photooxidation experiment. This material is available free of charge via the Internet at http://pubs.acs.org.

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