

Role of Multiphase Chemistry on the Formation of Aerosol from the
Reactions of Monoterpenes with NO₃ Radicals and O₃

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Thesis directed by Professor Paul Ziemann

Abstract

Secondary organic aerosols (SOA) have been shown to influence regional and global air quality, climate, and human health. To predict and mitigate the impacts of SOA formation, it is essential to better understand the detailed mechanisms of formation, atmospheric processing, and physical properties of SOA. In this thesis, the gas- and particle-phase reaction products and mechanisms involved in the formation of SOA from the oxidation of monoterpenes in an environmental chamber were studied in an extensive series of laboratory experiments that employed a variety of online and offline analytical methods. In addition, a limited selection of laboratory-generated samples and ambient aerosol samples collected from the Southeast US were analyzed to compare the utility of two different methods of functional group analysis.

The research included four major studies. 1) Identification and quantification of the products that form SOA from the reaction of β -pinene with NO₃ radicals. The results highlight the importance of ring-opening, alkoxy radical decomposition, and oligomerization reactions, and were used to develop gas- and particle-phase reaction mechanisms. 2) A detailed study of the thermal desorption characteristics of hemiacetal and acetal oligomers for use in understanding mass spectra obtained from the analysis of SOA containing these components. Oligomers formed by a single hemiacetal linkage, when subjected to thermal desorption analysis, will decompose to their precursor aldehyde and alcohol monomers prior to desorption and detection. Oligomers

formed by more than one of these linkages, or an acetal or ester linkage, will desorb and be detected intact. 3) Quantification of the functional group composition of SOA formed from α -pinene ozonolysis over a range of α -pinene concentrations and humidities, including autoxidation conditions. The SOA analyses, when combined with results of modeling, provide insight into the effects of $\text{RO}_2^{\bullet}$ radical reaction regime, humidity, and particle-phase reactions in determining SOA composition. 4) Comparison of two methods for quantifying the functional group composition of organic aerosol: the Fourier Transform Infrared spectroscopy method developed by the Russell group at the Scripps Institute of Oceanography and a derivatization-spectrophotometric method developed by the Ziemann group at the University of Colorado, Boulder. Results for laboratory-generated SOA and ambient aerosol samples show that the two methods agree quite well when results for certain functional groups are combined, and that either is adequate for measuring SOA functional group composition. This study also demonstrates that the functional group composition of SOA can help in elucidating the sources and environmental conditions under which the SOA was formed.

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Chapter 1

Introduction

1.1 Atmospheric Aerosols

Aerosols, which are defined as suspensions of liquid or solid particles in air, can enter the atmosphere directly as primary emissions from processes such as biomass burning, combustion of fossil fuels by vehicles or industry, cooking, sea spray, volcanic eruptions, and wind-blown mineral dust or biological matter.¹ They are also formed in the atmosphere through oxidation reactions involving volatile organic compounds (VOCs), nitrogen and sulfur oxides, and sunlight, in which case they are referred to as secondary aerosols. All of these various types of aerosols are known to influence regional and global air quality, climate, and human health.^{2,3} A major component of atmospheric aerosols in both urban and rural environments is organic matter,^{4,5} a large fraction of which is secondary material formed from the oxidation of VOCs by OH radicals, O₃, and NO₃ radicals.^{6,7} These oxidation reactions can lower the volatility of the VOC precursor through the addition of functional groups to the molecule, and when the volatility is sufficiently low, the oxidized compound can partition onto pre-existing particulate matter in the atmosphere or nucleate with other species to form secondary organic aerosol (SOA).⁸ Despite the ubiquity of SOA and the large research effort that has been expended by scientists to investigate the formation and effects of SOA in the atmosphere, there are still many unanswered questions that need to be addressed to better understand the detailed mechanisms of formation,

atmospheric processing, and physical properties of SOA in support of efforts to predict and mitigate its impacts.^{5,9,10}

The VOC precursors that are emitted to the atmosphere and can be subsequently oxidized to form SOA are usually classified as either anthropogenic or biogenic. According to global estimates, annual total emissions of non-methane VOCs are approximately 1000 Tg, with biogenic VOCs (BVOCs) accounting for more than two thirds of these emissions.¹¹ The major BVOCs are isoprene (C_5H_8) and monoterpenes ($C_{10}H_{16}$), both of which are alkenes that react rapidly in the atmosphere with OH radicals, NO_3 radicals, and O_3 due to their unsaturated structures.^{6,7} The reactions of monoterpenes have been of particular interest to the SOA research community because they have been shown to form SOA very efficiently and are estimated to account for a substantial amount of the global SOA budget.¹⁰

SOA formation in the atmosphere is an incredibly complex and dynamic process, due in part to the wide variety of biogenic and anthropogenic VOC precursors, the complexity of VOC oxidation mechanisms, and the large variation of oxidation regimes that depend on location, season, and environmental factors such as proximity to anthropogenic pollutants such as NO_x ($NO + NO_2$).⁸ In general, however, atmospheric VOC oxidation leads to the formation of peroxy radicals (RO_2^*), which, depending on the environment can subsequently react with other RO_2^* radicals, HO_2 , NO , or NO_3 radicals.¹² And in environments with sufficiently low concentrations of these reaction partners, RO_2^* radical isomerization (autooxidation) can also become competitive.¹³ As will be discussed throughout this thesis, the stable gas-phase products that are eventually formed depend on the structure of the VOC precursor, the oxidant that initiated the reaction (OH, NO_3 radicals or O_3), and the subsequent reactions of RO_2^* radicals. An important facet of RO_2^* radical reactions is the formation of alkoxy radical (RO^*) products, species whose

chemistry is less influenced by the oxidation regime they are formed under, these radicals have important ramifications as the formation of RO[•] radicals is followed by either isomerization or decomposition which can greatly impact the volatility of the resulting products.⁸

The gas-phase products of VOC oxidation can either remain in the gas phase and possibly undergo further oxidation, or they can partition into particles. Once a compound has partitioned into the particle phase, it is susceptible to particle-phase reactions that can transform the structure of the molecule and in some cases result in oligomer formation through accretion reactions. These particle-phase reactions can result in changes to the aerosol composition and have large impacts on the physical properties of the aerosol such as volatility, viscosity, hygroscopicity, and phase.^{8,14-16}

1.2 Thesis Overview

The primary objective of this thesis was to advance the state of knowledge concerning the gas-and particle-phase reaction products and mechanisms involved in the formation of SOA from the oxidation of monoterpenes. This goal was achieved through an extensive series of laboratory studies that employed a variety of online and offline analytical methods to characterize the molecular and functional group composition of SOA formed in selected monoterpene reaction systems, as well as more limited analysis of aerosol samples collected from the Southeast US. The results provide new insights into monoterpene oxidation mechanisms and highlight the importance of particle-phase reactions in SOA formation, and they demonstrate the utility of bulk functional group composition measurements for constraining the mechanisms of SOA formation in complex SOA systems when detailed molecular analysis is not feasible. The measurements made in this work offers characteristic aerosol compositions that can be applied to ambient samples in an effort to identify SOA sources and evidence of particle-phase processing.

In Chapter 2, the reaction of β -pinene with NO_3 radicals was studied in an environmental chamber and the molecular and functional group composition of the resulting SOA was determined using a variety of methods. Eight products, which comprised ~95% of the SOA mass, were identified and quantified. More than 90% (by mass) of these consisted of acetal heterodimers and heterotrimers that were apparently formed through acid-catalyzed reactions in phase-separated particles. Molar yields of both the oligomers and their monomer building blocks were reported. The identification of the particle-phase products led to the elucidation of gas- and particle-phase reaction mechanisms for this system. The results demonstrate the importance of ring opening, alkoxy radical decomposition, and acid-catalyzed oligomerization reactions in the NO_3 radical-initiated oxidation of β -pinene and subsequent formation of SOA. These results are useful for understanding reactions of other monoterpenes and for developing models for the laboratory and atmosphere.

In Chapter 3, the thermal desorption properties of hemiacetal, and acetal/ether compounds, two types of oligomers commonly found in atmospheric aerosols, were studied. For this work, synthesized standards and authentic SOA were investigated. The thermal desorption behavior was studied using a thermal desorption particle beam mass spectrometer with either rapid, real-time desorption or slow, temperature-programmed desorption of sampled aerosol particles. The combination of mass spectral information and thermal desorption behavior was used to determine conditions under which compounds desorbed intact as oligomers or decomposed to monomers prior to ionization and mass analysis. The results show that when hemiacetals are analyzed in real time they are ionized as the intact oligomer. When they are slowly heated, however, they reversibly decompose on the vaporizer and are instead ionized as monomers. This effect was not seen for acetals, which were ionized as the intact oligomer in

both real-time and temperature-programmed thermal desorption analyses due to the irreversible nature of the decomposition reaction. Our observations on the response of these important classes of oligomers to different methods of thermal desorption analysis will be useful to others seeking to interpret data on the thermal properties of aerosols that may contain hemiacetal and acetal/ether structures.

In Chapter 4, the composition of SOA formed from the ozonolysis of α -pinene was characterized using derivatization-spectrophotometric methods that provide quantitative information on peroxide, carbonyl, carboxyl, ester, and hydroxyl groups. Experiments were conducted over a range of α -pinene concentrations and humidities, including regimes in which gas-phase highly oxygenated multifunctional compounds (HOMs), presumably formed through autoxidation, were observed using NO_3^- chemical ionization mass spectrometry. Results for experiments conducted with high concentrations of α -pinene were compared with predictions of a model that employed the Master Chemical Mechanism and gas-particle partitioning theory. The aerosol analyses, along with the results of the modeling, provide insight into shifts in gas-phase chemistry that occur as a function of $\text{RO}_2^\bullet$ radical reaction regime and humidity, and demonstrate an important role for particle-phase Baeyer-Villager reactions in determining SOA composition. The measurements also provide constraints for future studies conducting comprehensive molecular characterization of this SOA as well as attempts to develop improved models of monoterpene oxidation and SOA formation using this popular reaction system.

In Chapter 5, two very different, but complementary methods for quantifying the bulk functional group composition of organic aerosol were compared: 1) a Fourier Transform Infrared (FTIR) spectroscopy method developed by the Russell group at the Scripps Institute of Oceanography and 2) a derivatization-spectrophotometric method developed by the Ziemann

group at the University of Colorado, Boulder. The methods were compared using filter samples of SOA formed in a suite of environmental chamber experiments and with ambient samples collected during the 2013 Southern Oxidant and Aerosol Study (SOAS) field campaign. The environmental chamber experiments allowed the two methods to be compared using several types of SOA formed from reactions of different VOCs and oxidants. In addition, the results of analyses of the well-defined chamber-generated SOA were used to interpret the composition of ambient SOA samples collected during SOAS in order to identify possible sources, processes, and environmental conditions that influenced the formation of SOA.

Chapter 2

Identification and Quantitation of Aerosol Products of the Reaction of β -Pinene with NO_3 Radicals and Implications for Gas- and Particle-Phase Reaction Mechanisms

2.1 Introduction

According to global estimates, emissions of biogenic volatile organic compounds (BVOCs) account for more than half of non-methane VOCs emitted into the atmosphere each year.¹¹ These BVOC emissions are primarily isoprene (C_5H_8) and monoterpenes ($\text{C}_{10}\text{H}_{16}$), which due to their unsaturated structures react rapidly in the atmosphere with OH radicals, NO_3 radicals, and O_3 .^{6,7} The oxygenated products of these reactions, if formed with low-enough volatility, can condense onto particles to form secondary organic aerosol (SOA)^{8,17} that can influence regional and global air quality, climate, and human health.^{2,3} Monoterpenes have been shown to dominate nighttime BVOC emissions, with approximately 30–40% of their total emissions occurring at night.¹⁸ This makes their reaction with NO_3 radicals, a major nighttime oxidant, especially competitive.¹⁹ The reaction of monoterpenes with NO_3 radicals usually results in the formation of organic nitrates, which can serve as a reservoir or sink for NO_x ($\text{NO} + \text{NO}_2$)^{20,21} and also participate in SOA formation.^{21–23} For example, results from the Southern Oxidant and Aerosol Study (SOAS) indicate that organic nitrates accounted for 5–12% of the total organic aerosol mass,²⁴ and estimate a 23–44% molar yield of organic nitrate aerosol from

the reaction of monoterpenes with NO_3 radicals in the Southeast US, which can explain about half of the total nighttime SOA observed.^{25,26}

Laboratory studies have identified the reaction of NO_3 radicals with β -pinene, a major monoterpene emission, as a particularly efficient source of SOA, with mass yields of 27–104%.^{22,27–30} And results from a recent modeling study indicate that this reaction may account for up to 20% of the total nighttime SOA formed in Southeast Texas.³¹ Despite the potential atmospheric importance of this reaction, however, the gas- and particle-phase products and reaction mechanisms remain poorly understood. Like most atmospheric VOC reactions, this is due in part to the inherent complexity of VOC oxidation mechanisms as well as uncertainties about the oxidation regime that determines the fate of organic peroxy radical ($\text{RO}_2^\bullet$) intermediates.^{6–8,17} For the NO_3 radical-initiated oxidation of monoterpenes, potential $\text{RO}_2^\bullet$ reaction partners include $\text{RO}_2^\bullet$, HO_2 , and NO_3 radicals,^{21,29,32} and for sufficiently low concentrations of these radicals $\text{RO}_2^\bullet$ isomerization can also become competitive.^{12,13} In general, the relative importance of each of these pathways is unknown, probably highly variable, and dependent on location and environmental factors such as proximity to anthropogenic emissions.²³ For example, a modeling study by Pye et al.³³ estimated that $\text{RO}_2^\bullet + \text{HO}_2$ and $\text{RO}_2^\bullet + \text{RO}_2^\bullet$ reactions accounted for 60% and 40%, respectively, of the nighttime fate of $\text{RO}_2^\bullet$ radicals in the Southeast US, while one conducted by Kirchner and Stockwell³⁴ for a few different scenarios predicted that $\text{RO}_2^\bullet + \text{NO}_3$ reactions are most important, followed by $\text{RO}_2^\bullet + \text{RO}_2^\bullet$ reactions. Nonetheless, while the relative importance of different oxidation regimes is not well established, it has been shown that SOA formed from the reaction of β -pinene with NO_3 radicals over a range of oxidation conditions has similar yields and composition.²⁹ It thus appears that an improved

understanding of the products and mechanism of the reaction of β -pinene with NO_3 radicals in any of these regimes will be of significant value.

In the work presented here, the NO_3 radical-initiated reaction of β -pinene was investigated in an environmental chamber and the oxidation products that contributed to the formation of SOA were identified and quantified using a variety of mass spectrometric, spectroscopic, and chromatographic methods. The results of the experiments were then used to create mechanisms for gas-phase oxidation and the particle-phase reactions that occurred upon partitioning of the products into the aerosol.

2.2 Experimental Section

2.2.1 Chemicals. The following chemicals, with purities/grades and suppliers were used: (1s)-(-)- β -pinene (99%), tridecanoic acid (98%), 1,2-tetradecanediol (90%), benzoyl peroxide (98%), 1,10-decanediol (98%), decanal (98%), 1-nonanol (98%), acetaldehyde di-isoamyl acetal (98%) (Sigma-Aldrich); bis(2-ethylhexyl) sebacate (97%) (Fluka); 3-hexadecanone (99%) (ChemSampCo); ethyl acetate (99.5%) (EMD Millipore); $(\text{NH}_4)_2\text{SO}_4$ (99.5%, ACS), acetonitrile (HPLC grade, ACS), water (HPLC grade) (Fisher); methanol (HPLC grade) (Honeywell); 18 M Ω water purified using Milli-Q Advantage A10 water system. N_2O_5 was synthesized according to the procedures of Atkinson et al.³⁵ and was stored in a glass vacuum bulb in dry ice until used. Chemicals used for derivatization-spectrophotometric functional group analyses have been reported previously.^{36,37}

2.2.2 Environmental Chamber Experiments. Experiments were conducted in an 8.0 m³ Teflon FEP environmental chamber filled with clean, dry air supplied by two AADCO Model 737-14A clean air generators (<5 ppbv hydrocarbons, <0.1% RH) at room temperature (~23°C)

and pressure (~ 630 Torr). Water was evaporated from a heated glass bulb into a stream of ultra-high purity (UHP) N_2 to achieve a chamber RH of $\sim 55\%$ for each experiment. Ammonium sulfate particles were then formed using a Collison atomizer and flushed into the humidified chamber to attain $\sim 200 \mu\text{g m}^{-3}$ of deliquesced seed particles that according to E-AIM^{38,39} (<http://www.aim.env.uea.ac.uk/aim/aim.php>) calculations were comprised of an $\sim 2:1$ mixture of ammonium sulfate and water by mass. β -pinene was then added to the chamber by evaporation from a heated glass bulb into a flow of UHP N_2 to achieve a concentration of 1 ppm, followed by sufficient N_2O_5 (added similarly but without heating) to achieve of concentration of 0.33 ppm in the absence of reaction. Upon dilution of N_2O_5 in the chamber, NO_3 radicals were generated by thermal decomposition according to the reaction $N_2O_5 \leftrightarrow NO_3 + NO_2$. They then reacted rapidly and completely with β -pinene ($k = 2.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)⁷ within ~ 1 min at a rate controlled by decomposition of N_2O_5 ($k = 5.2 \times 10^{-2} \text{ s}^{-1}$).⁴⁰ A Teflon-coated fan was run for 30 s after adding each chemical to fully mix the chemicals inside the chamber within ~ 20 s.

Gas Analysis. Concentrations of β -pinene in the chamber were measured before and after the reaction by collecting samples onto Tenax adsorbent for gas chromatography-flame ionization detection (GC-FID) analysis. For each sampling period, chamber air was first drawn through the 30 cm stainless steel sampling line for 20 min at $250 \text{ cm}^3 \text{ min}^{-1}$ to passivate the walls of the tube. Chamber air was then sampled through an attached Tenax cartridge at the same flow rate for 4 min, with 3 replicate samples taken immediately before and after reaction. Tenax cartridges were inserted into an Agilent 6890 GC and compounds were thermally desorbed onto a $30 \text{ m} \times 0.32 \text{ mm}$ Agilent DB-1701 column with $1 \mu\text{m}$ film thickness by ramping the inlet to 250°C in 7 min while the column was held at 40°C . The column temperature was then ramped at $10^\circ\text{C min}^{-1}$ to 280°C and eluted compounds were quantified with the FID. NO_x concentrations in

the chamber were monitored throughout the reaction using a Thermo Scientific Model 42C NO-NO₂-NO_x Analyzer.

Particle Analysis. Particle composition was monitored in real time using a thermal desorption particle beam mass spectrometer (TDPBMS).⁴¹ The TDPBMS samples chamber air through an aerodynamic lens that focuses the particles into a narrow beam for efficient transport into a high vacuum detection region where they are impacted on a polymer-coated copper rod that is resistively heated to 160°C. Particles are instantly vaporized and molecules are ionized by 70 eV electrons for analysis in an Extrel triple-quadrupole mass spectrometer. In order to make the ionization method explicit in the upcoming discussion, we will hereafter refer to this instrument as the EI-TDPBMS. Throughout each chamber reaction, particle mass concentrations and size distributions were measured continuously using a scanning mobility particle sizer (SMPS) comprised of a long differential mobility analyzer and a TSI Model 3010 condensation particle counter.

After the aerosol stopped growing (~15 min), two replicate aerosol samples were collected onto pre-weighed filters (Millipore Fluoropore PTFE, 0.45 µm) for 120 min at a flow rate of 14 L min⁻¹. Immediately after sampling, the filters were reweighed to determine the mass of aerosol collected. All filter masses were measured to within ±0.5 µg using a Mettler Toledo XS3DU Microbalance. Filters were then extracted twice, each time in 5 mL of ethyl acetate. The extracts were combined in a pre-weighed vial and dried in a stream of UHP N₂, after which the vial was reweighed to determine the extracted aerosol mass. Extracted masses were ~10% less than the mass collected on filters, consistent with the ~10% contribution of non-extractable ammonium sulfate seed particles to the aerosol mass. The extraction efficiencies for SOA were

therefore ~100%, similar to previous studies.⁴² The dried SOA was then reconstituted in acetonitrile for subsequent off-line analyses.

The SOA mass yield was quantified as the mass of SOA formed divided by the mass of β -pinene reacted.⁴³ The mass of SOA formed was calculated from the mass collected on filters with correction for the contribution of ammonium sulfate seed particles and from the mass of SOA extracted, with both values corrected for wall loss of particles using SMPS measurements and the method of Yeh et al.³² The mass of β -pinene reacted was determined from the difference in GC-FID signals per volume of air sampled before and after the reaction, the amount of β -pinene added to the chamber, and the chamber volume.

The SOA components were fractionated using reversed-phase high performance liquid chromatography (HPLC) with a Shimadzu Prominence HPLC equipped with a Nexera X2 SPD-M30A UV-Vis photodiode array detector (PDA) and a Zorbax Eclipse XDB-C18 column (250 $\times$ 4.6 mm with 5 μ m particle size). The method of separation employed a binary mobile-phase gradient with a flow rate of 0.5 mL min⁻¹, where mobile phase A was water and mobile phase B was methanol. The method was as follows: begin with 20% B and hold for 2 min, increase to 50% B at 1% min⁻¹, increase to 80% B at 3% min⁻¹, increase to 95% B at 1.5% min⁻¹ and hold for 28 min, then increase to 100% B at 2.5% min⁻¹ and hold for 8 min. Absorbance was measured at 210 nm, where the molar absorptivity of nitrate groups is ≥ 20 times that of alcohols, ketones, carboxylic acids, or alkenes,⁴⁴ indicating that peaks in the chromatogram are solely due to nitrate-containing products. The calibration factor (absorbance mole⁻¹ of C₁₀ organic nitrate monomer) used for HPLC analysis of nitrate groups was determined by first summing the absorbance measured for all peaks and then dividing this sum by the mass of SOA injected to obtain the total absorbance per SOA mass. This value was then divided by the mean molecular

weight of each C₁₀ organic nitrate monomer determined from its mass spectrometric identification, with the contribution of each product being weighted according to the absorbance of its HPLC peak. In the case of C₂₀ dimers and C₃₀ trimers, which constituted >90% of the SOA mass, the C₁₀ monomer molecular weight used in the calculation was obtained by dividing by factors of 2 and 3, respectively. A C₁₀ hydroxynitrate standard was also synthesized and used for HPLC analysis to compare with the retention times of the SOA components. The nitrate standard was synthesized through the condensed-phase reaction of 1,10-decanediol with N₂O₅,⁴⁵ which converts hydroxyl groups to nitrate groups, and then purified by HPLC-UV.

Compounds associated with each chromatographic peak were analyzed using electron-ionization (EI), chemical-ionization (CI), and electrospray ionization (ESI) mass spectrometry for product identification. EI mass spectra were obtained by atomizing the HPLC eluent using a Collison atomizer located downstream of the PDA detector, removing the solvent from the resulting aerosol using a Nafion drier, and then sampling the dried aerosol into the EI-TDPBMS for real-time analysis.^{42,46,47} To obtain CI and ESI mass spectra the compounds associated with each chromatographic peak were manually collected as fractions, dried using UHP N₂, and then analyzed. CI mass spectra were acquired using a Finnigan PolarisQ ion trap mass spectrometer (CI-ITMS) equipped with isobutane reagent gas.⁴⁸ Dried samples were introduced into the ITMS in a glass cup placed in the tip of a direct insertion probe, and then vaporized into the ion source by ramping the probe temperature from 30°C to 300°C at 10°C min⁻¹. The ion source was operated at 250°C to reduce loss of low volatility compounds to the walls of the ionization region. ESI mass spectra of compounds associated with HPLC-UV peaks 2–6 were obtained using a Waters Synapt G2 mass spectrometer equipped with an ESI interface and operated by the Central Analytical Mass Spectrometry Facility at the University of Colorado Boulder. An ESI

mass spectrum of the compound associated with HPLC-UV peak 1 was obtained using an Agilent 6220A ESI-ToF-MS that is recently available in our laboratory. Fractions collected from HPLC analysis were reconstituted into methanol and directly infused into the mass spectrometer.

The functional group composition of the bulk SOA was quantified using derivatization-spectrophotometric methods we developed previously.^{36,37} Briefly, carbonyl (aldehyde and ketone), carboxyl, hydroxyl, and ester groups were converted to UV-Vis absorbing forms by derivatizing with 2,4-DNPH, 2-NPH.HCl, 4-NBC, and hydroxamic acid, respectively; peroxides (hydroperoxides, dialkyl and diacyl peroxides, peroxy acids, and peroxy nitrates) were reacted with I^- to form an absorbing I_3^- solution; and nitrate groups were quantified directly using their naturally strong absorbance at 210 nm. 3-Hexadecanone, tridecanoic acid, 1,2-tetradecanediol, bis(2-ethylhexyl) sebacate, and benzoyl peroxide were used as surrogate standards for carbonyl, carboxyl, hydroxyl, ester, and peroxide groups, respectively, and because we previously reported that the presence of a nitrate group adjacent to the carbonyl group decreased the molar absorptivity of carbonyl-derivatized compounds by ~35%,³⁷ and most of the products formed in this study have this structure, a factor of 1.35 was applied to the carbonyl measurements. A molar absorptivity of $2230\text{ M}^{-1}\text{ cm}^{-1}$ was used to quantify SOA nitrate groups. This value was determined by multiplying the ratio of the molar absorbance (absorbance mole^{-1}) of SOA organic nitrates and ethylhexyl nitrate by the molar absorptivity of $3000\text{ M}^{-1}\text{ cm}^{-1}$ measured for an ethylhexyl nitrate standard. A commercially available acetal standard, acetaldehyde di-isoamyl acetal, was analyzed to determine its response to the derivatization-spectrophotometric analyses of hydroxyl and carbonyl groups. This standard was also analyzed by EI-TDPBMS and CI-ITMS to determine its mass spectral fragmentation pattern, and an Agilent Cary 630 ATR-FTIR was employed to qualitatively analyze the extracted SOA functional group composition.

The reported uncertainties for the derivatization-spectrophotometric functional group analyses are standard deviations calculated from two replicate measurements for each functional group analysis. In addition, there are inherent uncertainties in the analyses that stem from differences in the molar absorptivity of derivatized SOA compounds and the surrogate standards used for quantification. A previous study conducted with a large variety of monofunctional and multifunctional compounds indicate that these uncertainties are approximately ($\pm$) 10%, 30%, 10%, 20%, and 20% for peroxide, ester, carbonyl, carboxyl, and hydroxyl groups.^{37,49} The approximate uncertainty for nitrate groups measured by this study was estimated at $\pm 5\%$, due to uncertainties in the approach used to determine the molar absorptivity from the HPLC analyses of SOA and ethylhexyl nitrate.

2.3 Results and Discussion

3.2.1 Mechanism of Reaction of β -Pinene with NO_3 Radicals. A proposed mechanism for the reaction of β -pinene with NO_3 radicals is shown in Figure 2.1.^{7,32} As with all alkenes, reaction occurs almost exclusively by addition of the NO_3 radical to the C=C double bond, with structure-activity calculations predicting that for β -pinene >99% of the reaction occurs by addition and the remainder by H-atom abstraction.⁵⁰ It is also expected that the NO_3 radical will predominantly add to form the most substituted alkyl radical, which for β -pinene means that most addition occurs at the primary carbon atom located outside the ring to form a tertiary β -nitrooxyalkyl radical. Since ~90% of the addition reaction occurs at the primary carbon atom in 1-pentadecene to form a secondary β -nitrooxyalkyl radical,³² it is expected that addition to form a tertiary β - nitrooxyalkyl radical is even more favorable.

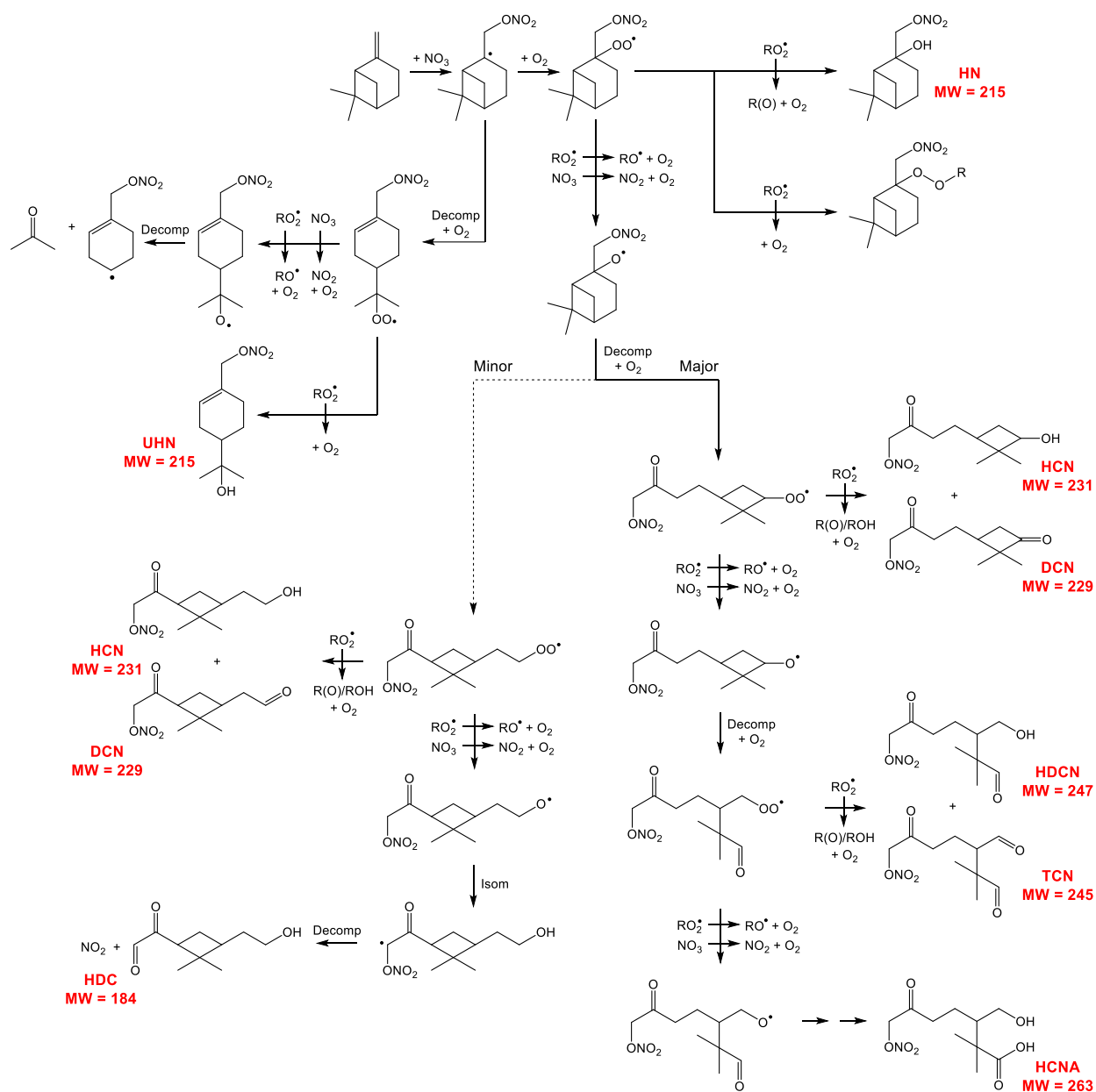


Figure 2.1. Proposed mechanism for the formation of first-generation products in the reaction of β -pinene with NO_3 radicals.

In air at atmospheric pressure the tertiary β -nitrooxyalkyl radical can add O_2 to form a tertiary β -nitrooxyperoxy radical ($RO_2^\bullet$), or it might first undergo an alkyl radical shift through decomposition of the 4-membered ring and then add O_2 to form an unsaturated tertiary nitrooxyperoxy radical. This type of alkyl radical shift has been proposed for the β -hydroxyalkyl radical formed through the reaction of α -pinene with an OH radical, which has a similar structure to the tertiary β -nitrooxyalkyl radical formed here.^{51,52} The fate of the tertiary β -nitrooxyperoxy radical, unsaturated nitrooxyperoxy radical, and other organic peroxy radicals, and the types of products formed in subsequent reactions depends on the oxidation regime, with possible reactions including $RO_2^\bullet + RO_2^\bullet$, $RO_2^\bullet + HO_2$, $RO_2^\bullet + NO_3$, $RO_2^\bullet + NO_2$, $RO_2^\bullet + NO$, and $RO_2^\bullet$ isomerization.¹² The reaction with NO is not relevant in our experiments since NO was not added and NO_3 radicals would quickly react with any background NO to form NO_2 . Reaction with HO_2 and isomerization are also not significant, since these would form hydroperoxides, and only trace amounts of peroxide were detected in the derivatization-spectrophotometric functional group analysis. It is possible that a small yield of hydroperoxides were formed and that these were then lost by oxidizing aldehyde groups to carboxyl groups through a particle-phase Baeyer-Villiger reaction.^{53,54} This could account for the small amount of carboxyl groups detected in the SOA (discussed below). And although it is expected that some reaction occurred with NO_2 to form peroxy nitrates (RO_2NO_2), these compounds reversibly decompose on time scales of a few seconds.¹² Kinetic modeling results that will be presented in a future publication indicate that <10% of $RO_2^\bullet$ radicals were present as peroxy nitrates ~15 min after the start of reaction, when filter sampling was begun, and that essentially all had decomposed by the end of the 2 h sampling period. This is again consistent with the absence of peroxide groups in the SOA. Furthermore, since the difference between the measured amount of β -pinene that reacted (0.31

ppm) and the amount of N_2O_5 added (0.33 ppm, all of which either reacted with β -pinene or was hydrolyzed to HNO_3), was only 20 ppb, the fraction of $\text{RO}_2^\bullet$ radicals that reacted with NO_3 radicals must have been small. It thus appears that the chamber reactions were dominated by $\text{RO}_2^\bullet + \text{RO}_2^\bullet$ reactions with a small fraction of $\text{RO}_2^\bullet + \text{NO}_3$ and $\text{RO}_2^\bullet + \text{HO}_2$ reactions, and since the observed products are consistent with those fates and for the sake of clarity, other possible reactions of $\text{RO}_2^\bullet$ radicals are not shown in Figure 2.1.

The initially-formed tertiary β -nitrooxyperoxy radical can react with an $\text{RO}_2^\bullet$ radical to form either a β -hydroxynitrate (HN) via the Russell mechanism⁵⁵ or a tertiary β -nitrooxyalkoxy radical ($\text{RO}^\bullet$),³² whereas reaction with NO_3 produces only a tertiary β -nitrooxyalkoxy radical. These tertiary β -nitrooxyalkoxy radicals can either isomerize or decompose, but because of ring strain caused by the bicyclic structure and the lack of favorable sites for H-atom abstraction, structure-activity calculations^{56,57} indicate that rates of decomposition are many orders of magnitude faster than isomerization. Because of ring strain the maximum rate of isomerization for this tertiary β -nitrooxyalkoxy radical is predicted to be $<1 \text{ s}^{-1}$, whereas the rates of decomposition resulting in ring opening are approximately 1×10^{10} and $2 \times 10^{13} \text{ s}^{-1}$ for the left- and right-hand pathways shown in Figure 2.1.⁵⁶ These calculations thus predict that $>99\%$ of the tertiary β -nitrooxyalkoxy radicals decompose by the right-hand pathway. The primary and secondary $\text{RO}_2^\bullet$ radicals formed by ring-opening of the tertiary β -nitrooxyalkoxy radical and then addition of O_2 can either react with $\text{RO}_2^\bullet$ radicals through the Russell mechanism⁵⁵ to form a hydroxycarbonyl nitrate (HCN) or a dicarbonyl nitrate (DCN), or they can react with $\text{RO}_2^\bullet$ or NO_3 radicals to form alkoxy radicals. These alkoxy radicals either decompose or isomerize and then react further by similar pathways to those described above to form a hydroxydicarbonyl nitrate (HDCN), tricarbonyl nitrate (TCN), hydroxycarbonyl nitrate acid (HCNA), or

hydroxydicarbonyl (HDC). Although our analyses of HCN and DCN products cannot distinguish between the two possible pairs of isomers shown in Figure 2.1, the branching ratios estimated above for tertiary β -nitrooxyalkoxy radical decomposition and the detection of HDCN, TCN, and HCNA products indicate that the dominant HCN and DCN isomers are those shown on the right-hand side of Figure 2.1.

The initially-formed unsaturated tertiary nitrooxyperoxy radical can react with an $\text{RO}_2^\bullet$ radical to form either an unsaturated hydroxynitrate (UHN) or an unsaturated tertiary nitrooxyalkoxy radical, whereas reaction with NO_3 produces only an unsaturated tertiary nitrooxyalkoxy radical. The unsaturated tertiary nitrooxyalkoxy radicals can either isomerize or decompose, but because of ring strain the rate of decomposition to form a C_7 unsaturated nitrooxyalkyl radical and acetone ($2 \times 10^{13} \text{ s}^{-1}$) is many orders of magnitude faster than isomerization (0.2 s^{-1}) and thus leads to only volatile products.^{56,57} The UHN formation pathway apparently also does not contribute to SOA formation in this experiment, since under these conditions the UHN should react with NO_3 radicals either in the gas-phase ($k \sim 6.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, similar to α -pinene)⁹ or in particles^{32,58} to form condensable dihydroxy dinitrate and hydroxycarbony dinitrate monomers, none of which were detected in the SOA.

We also note that Hallquist et al.³⁰ measured a yield of nopinone of $\leq 2\%$ from this reaction, which was most likely formed through decomposition of the primary β -nitrooxyalkoxy radical (not shown in Figure 2.1) formed following addition of an NO_3 radical to the tertiary carbon atom located in the ring. Although the fraction of the addition reaction that occurs at this site is only a few percent,^{32,50} the primary β -nitrooxyalkoxy radical that is subsequently formed should exclusively decompose to nopinone, CH_2O , and NO_2 . This compound is also too volatile to form SOA.

The gas-phase reaction mechanism that is proposed in Figure 2.1, which is consistent with the experimental results presented below, indicates that the majority of the reaction products were formed following ring opening of β -nitrooxyalkoxy radicals. Wängberg⁵⁹ reached a similar conclusion in his studies of the reactions of NO_3 radicals with cyclopentene, cyclohexene, and 1-methyl-1-cyclohexene, but since the identification of gas-phase products was based on infrared spectroscopy he could only speculate that the ring-opened products were aldehydes. Conversely, Boyd et al.²⁹ observed gas-phase products with MW 215, 229, 231, and 245 for this reaction using CIMS, but assigned them to a variety of ring-retaining compounds formed by first- and multi-generation reaction mechanisms that included pathways such as tertiary β -nitrooxyalkoxy radical isomerization, methyl shifts, and bimolecular H-atom abstraction by alkoxy, RO_2^* , and NO_3 radicals. As can be easily shown from calculations conducted using structure-activity relationships and available bimolecular rate constants, these reaction pathways are much too slow to compete with the pathways that occur in Figure 2.1. This is highlighted in Figure 2.2, which provides a comparison of reaction pathways shown in Figure 2.1 versus those purposed by Boyd et al.²⁹ The purpose of this comparison is to demonstrate that although current knowledge of VOC oxidation reactions is very limited, there is often sufficient information available from experimental and computational studies of fundamental reaction pathways to identify the likely dominant reaction pathways.

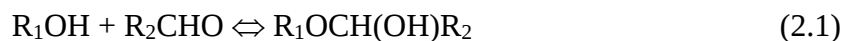
Figure 2.2 and the associated discussion is divided into three parts, A, B, and C that highlight three important branching points in the mechanism. Section A) the unsaturated tertiary nitrooxyalkoxy radical is shown to decompose to form acetone and a new alkyl radical in Figure 2.1, this reaction is predicted to occur on a timescale of $\sim 10^{-13}$ s.⁵⁶ Whereas in the mechanism proposed by Boyd et al.,²⁹ this unsaturated tertiary nitrooxyalkoxy radical is shown to either

hydroxynitrate, which they then show undergoing an H-atom abstraction. The timescale of ~ 10 h (shown in Figure 2.2) for this set of reactions was calculated using rate constants for H-atom abstraction by NO_3 or $\text{RO}_2^\bullet$ radicals of 5×10^{-17} and $10^{-21} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,^{50,60} respectively, and an assumed upper limit concentration of NO_3 and $\text{RO}_2^\bullet$ radicals of 30 ppb (the maximum value obtained immediately after 1 ppm of N_2O_5 reaches equilibrium with NO_2 and NO_3 radicals, with $K_{\text{eq}} = 3.4 \times 10^{10}$),⁴⁰ which give timescales of ~ 10 h and ~ 1 yr for the NO_3 and $\text{RO}_2^\bullet$ radical reactions, respectively. Section C) the tertiary β -nitrooxyalkoxy radical is shown to decompose to form a ring-opened carbonylnitrate alkyl radical in Figure 2.1, this reaction is predicted to occur on a timescale of $\sim 10^{-13}$ s.⁵⁶ The pathways proposed by Boyd et al.²⁹ include, alkoxy radical isomerization and the formation of a hydroxynitrate. The timescale of >1 min for alkoxy radical isomerization was calculated as that of a 1,5- 1° -alkyl H-shift. Because of the ring strain correction it is predicted to have the same isomerization rate as that for a 1,3- 1° -alkyl H-shift with $k_{\text{isom}} < 2 \times 10^{-2} \text{ s}^{-1}$. The timescale of ~ 10 d for formation of the hydroxynitrate by the proposed mechanism was calculated the same way as the timescale for formation of the unsaturated hydroxynitrate in section A.

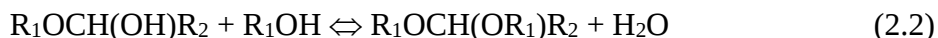
This comparison shows that for these three key sections of the reaction mechanism the estimated timescales of $\sim 10^{-13}$ s for the reaction pathways proposed in Figure 2.1 are many orders of magnitude smaller than the ~ 1 min to ~ 10 d timescales for those proposed by Boyd et al.²⁹ Two other pathways in the Boyd et al.²⁹ mechanism that are not shown in Figure 2.2 also involve formation of multi-generation products through H-atom abstraction by NO_3 or $\text{RO}_2^\bullet$ radicals that have been shown in Section B to be too slow to be significant. We thus feel that Figure 2.1 provides a more plausible mechanism for forming the reaction products observed in our study.

2.3.2 Mechanisms of Particle-Phase Reactions. The gas-phase products of VOC oxidation have the potential to undergo particle-phase reactions that alter their functionality and cause changes to the SOA composition.^{8,17} For the products shown in Figure 2.1, which contain nitrate, carbonyl, hydroxyl, and carboxylic acid groups, these reactions are expected to primarily involve carbonyl and hydroxyl groups in the formation of hemiacetals and acetals. While nitrate groups can undergo hydrolysis, this is likely to only be important for tertiary nitrates that are not formed in this reaction.^{62,63}

Hemiacetal formation involves a reversible reaction between a carbonyl and a hydroxyl group, as shown in Reaction 2.1 for an intermolecular reaction.



These hemiacetals can then further react reversibly with hydroxyl groups to form acetals through H₂O elimination as shown in Reaction 2.2.



The equilibrium constants for these reactions depend to some degree on the structure of the molecules involved. Most importantly, the presence of an electron-withdrawing group, such as a hydroxyl or nitrate group, adjacent to the carbonyl group usually enhances the extent of hemiacetal formation and reduces that of acetal formation,^{64,66} while its presence adjacent to the hydroxyl group has relatively little effect.⁶⁶ The rate constants of hemiacetal and acetal formation are less consistently affected by electron-withdrawing groups, but are known to be sensitive to the structure of the alcohols, increasing in the order primary < secondary < tertiary.⁶⁷ As shown in Figure 2.1, the gas-phase products formed in the β -pinene reaction with NO₃ radicals have structures with a nitrate group adjacent to a carbonyl group (β -carbonylnitrates), making these

compounds especially prone to hemiacetal formation, and the tertiary β -hydroxynitrate (HN) product should be especially reactive. It is also important to note that acetal formation is catalyzed by protons,^{8,65–67} which in these experiments were provided by HNO_3 formed by hydrolysis of N_2O_5 on particles and the environmental chamber walls according to Reaction 2.3.⁴⁰



Previous studies have shown that hemiacetal and acetal formation can occur in aerosols either through intramolecular cyclization or by intermolecular accretion reactions that form oligomers on timescales that range from seconds to a few hours.^{68–72} These studies involved OH oxidation of VOCs in the presence of NO_x , where HNO_3 was formed from the reaction of OH radicals with NO_2 , and at elevated humidity water reduced the formation of hemiacetals and acetals by competing with alcohols and shifting the equilibrium away from dehydration.^{70–72} Because of the relatively low hygroscopicity of SOA⁷³ and possibility of organic-aqueous phase separation,⁷⁴ it is not necessarily the case that these reactions will be eliminated at high humidity.

2.3.3 SOA Product Identification. An HPLC-UV chromatogram of the SOA is shown in Figure 2.3. Since all the oxidation products are expected to contain a nitrate group, we were able to use 210 nm, where nitrate groups have a strong characteristic absorbance, as the detection wavelength. Subsequent analysis of the fractionated components of the SOA by EI-TDPMS, CI-ITMS, and ESI-MS analysis allowed identification of 8 products (some of which may have multiple structural isomers), which accounted for ~95% of the total HPLC-UV peak area

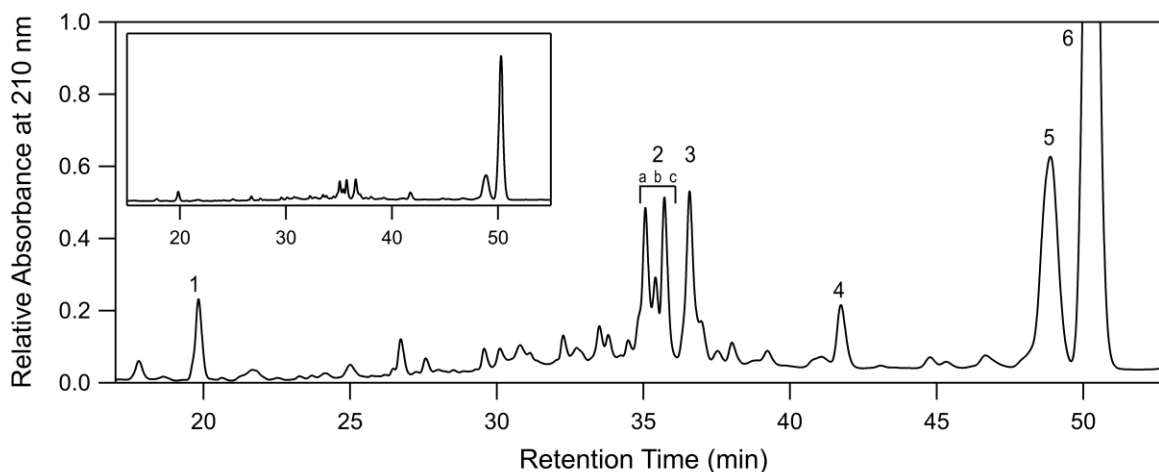
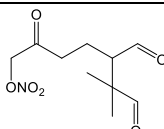
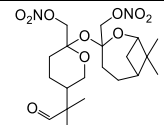
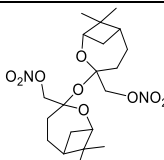
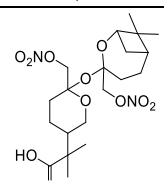
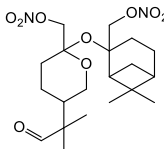
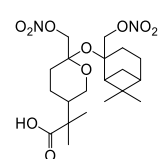
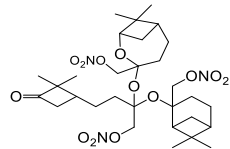
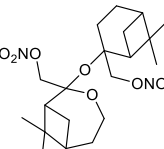


Figure 2.3. HPLC-UV chromatogram of SOA formed from reaction of β -pinene with NO_3 radicals. The insert is provided in order to fully observe peak 6.

measured at 210 nm. For the remainder of this discussion the identified products will be referred to by their peak number in the chromatogram, labeled 1–6 in Figure 2.3, with each peak corresponding to a different compound except for peak 2, which is a cluster of 3 peaks that were not fully resolved and are labeled a, b, c. The structures of the identified products, their contributions to the total HPLC-UV peak area, and the ions observed in their ESI mass spectra are presented in Table 2.1. Approximately 92% of the total peak area in the chromatogram is due to oligomers consisting of heterodimer and heterotrimer acetals formed in the particles from gas-phase products according to the reactions proposed in Figure 2.4. It is important to note that because all the oligomers were either heterodimers or heterotrimers it is not possible that they were formed during ESI-MS analysis, since this would require that the different monomers that formed an oligomer had the same retention times. EI-TDPBMS and CI-ITMS mass spectral data that support the assignments of products based on ESI-MS are presented in Table 2.2. Unlike ESI-MS analysis, these methods induce fragmentation of the products and thus provide structural information beyond that of the molecular ion. The EI-TDPBMS analyses also support the claim

Table 2.1. ESI-MS identification and relative amounts of monomer and oligomer products in SOA formed from the reaction of β -pinene with NO_3 radicals.

Peak Number	% PA ^a	Structure	MW	Formula	Observed Mass (Da)	Exact Mass (Da)	Mass Accuracy (ppm)
1	3.0		245	[M + H] ⁺	246.0968	246.0977	3.6
				[M + Na] ⁺	268.0787	268.0797	3.7
				[M + K] ⁺	284.0527	284.0536	3.2
2a	15.7		460	[M + Na] ⁺	483.1951	483.1955	0.8
2b			444	[M + Na - HNO ₃] ⁺	404.2044	404.2050	1.5
2c			476	[M + Na] ⁺	499.1889	499.1904	3.0
	[M + Na - HNO ₂ - CH ₂ O] ⁺			422.2150	422.2156	1.4	
3	7.8		444	[M + Na] ⁺	467.1982	467.2006	5.1
				[2M + Na] ⁺	911.4096	911.4114	2.0
4	4.1		460	[M + Na] ⁺	483.1962	483.1955	1.4
				[M + K] ⁺	499.1709	499.1694	3.0
				[2M + Na] ⁺	943.3987	943.4012	2.6
				[2M + K] ⁺	959.3740	959.3751	1.1
5	13.3		657	[M + Na] ⁺	680.3011	680.3007	0.6
6	50.8		428	[M + Na] ⁺	451.2058	451.2056	0.4
				[M + K] ⁺	467.1803	467.1795	1.7
				[2M + Na] ⁺	879.4196	879.4214	2.0

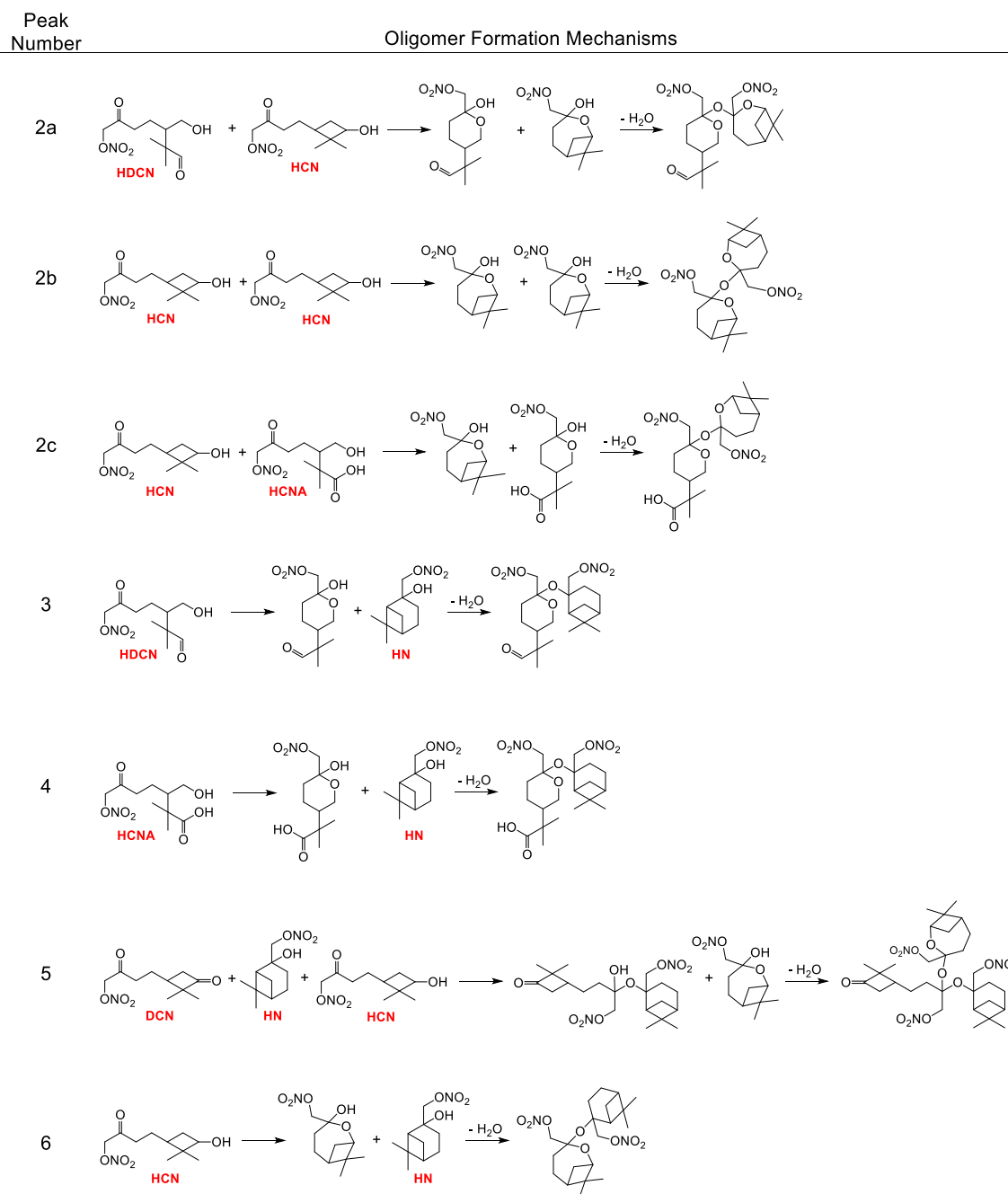
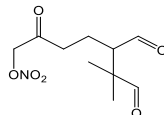
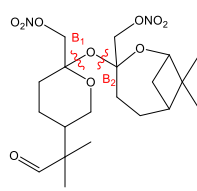
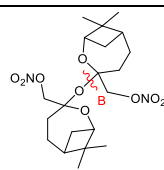
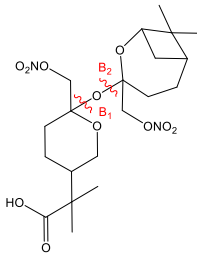
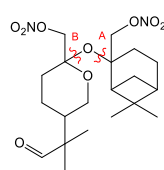
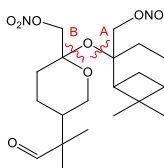
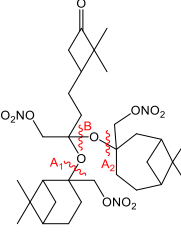
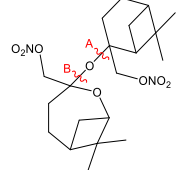


Figure 2.4. Proposed mechanisms of formation of oligomers identified in SOA formed from the reaction of β -pinene with NO_3 radicals.

Table 2.2. EI and CI fragmentation pathways of products identified in SOA formed from reaction of β -pinene + NO_3 .

EI-TDPBMS						CI-ITMS			
Peak #	% PA ^a	MW	M ⁺⁺ Pathway	Neutral Loss	m/z	[M + H] ⁺ Pathway	Neutral Loss	m/z	
1	3.0		245				HNO ₂	199	
							HNO ₂ + H ₂ O	181	
							HNO ₂ + 2H ₂ O	163	
							CH ₂ O + HNO ₃	153	
							CH ₂ O + HNO ₃ + H ₂ O	135	
2a			460	Acetal-B ₁	230	Acetal-B ₁ ^b	NO ₂	185	
				Acetal-B ₂	214	Acetal-B ₁ ^b	NO ₂ + H ₂ O	167	
						Acetal-B ₁ ^b	NO ₂ + 2H ₂ O	149	
2b	15.7		444	Acetal-B	214	Acetal-B	HNO ₂	167	
				Acetal-B	NO ₂	168	Acetal-B	HNO ₂ + H ₂ O	149
2c			476	Acetal-B ₁ ^c	H + HNO ₂	198	Acetal-B ₂	HNO ₃	152
				Acetal-B ₂	NO ₃	152	Acetal-B ₂	NO ₃ + CH ₃ ^d	137
				Acetal-B ₂	NO ₃ + CH ₃ ^d	137			
3	7.8		444	Acetal-B	H ₂ O	212	Acetal-B	HNO ₂	183
				Acetal-A		198	Acetal-B	HNO ₂ + H ₂ O	165
				Acetal-B	HNO ₂	183			
				Acetal-B	H ₂ O + NO ₂	166			
				Acetal-A	C ₃ H ₅ + H ₂ ^e	155			
				Acetal-A	NO ₂	152			
4	4.1		460	Acetal-A		198	Acetal-B	H ₂ O + HNO ₃	165
				Acetal-B	H ₂ O + C ₃ H ₅ + H ₂ ^e	185	Acetal-A	NO ₂	152
				Acetal-A	NO ₂	152	Acetal-A	NO ₂ + CH ₃ ^d	137
				Acetal-A	NO ₂ + CHO	123	Acetal-A	NO ₂ + CHO	123
				Acetal-A	NO ₂ + C ₃ H ₅ + H ₂ ^e	109			

Peak #	% PA ^a	Structure	MW	EI-TDPBMS			CI-ITMS		
				M ⁺ Pathway	Neutral Loss	m/z	[M + H] ⁺ Pathway	Neutral Loss	m/z
5	13.3		657	Acetal-A ₁		198	Acetal-B ^b	NO ₂	185
				Acetal-A ₁ ^c	H	197	Acetal-A ₁	NO ₂	152
				Acetal-A ₂	NO ₂	168	Acetal-A ₁	NO ₂ + CH ₃ ^d	137
				Acetal-A ₁	NO ₂	152	Acetal-A ₁	NO ₂ + CHO	123
				Acetal-A ₁	NO ₂ + CH ₃ ^d	137			
				Acetal-A ₁	NO ₂ + CHO	123			
				Acetal-A ₁	NO ₂ + C ₃ H ₅ + H ₂ ^e	109			
6	50.8		428	Acetal-A		198	Acetal-B		214
				Acetal-A ^c	H	197	Acetal-A		198
				Acetal-A ^c	H + NO ₂	185	Acetal-A ^b	NO ₂	185
				Acetal-B	NO ₂	168	Acetal-B	NO ₂	168
				Acetal-A	NO ₂	152	Acetal-A	NO ₂	152
				Acetal-A	NO ₂ + CH ₃ ^d	137	Acetal-A	NO ₂ + CH ₃ ^d	137
				Acetal-A	NO ₂ + CHO	123	Acetal-A	NO ₂ + CHO	123
				Acetal-A	NO ₂ + C ₃ H ₅ + H ₂ ^e	109			

^a Percent of total peak area in HPLC chromatogram measured at 210 nm.

^b Acetal-A pathway for [M + H]⁺ ion to form stable cyclic hemiacetal ion.

^c Acetal-A pathway following H-atom shift to form stable alkene ion.

^d Loss of CH₃ common for gem-dimethyl groups.⁷⁶

^e Loss of C₃H₅ + H₂ specific to the pinene structure.⁷⁶

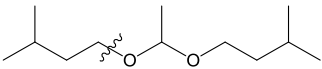
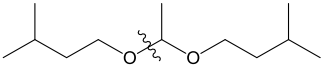
Fragmentation Site	Pathway
	Acetal-A
	Acetal-B

Figure 2.5. Fragmentation sites observed for an acetal standard, acetaldehyde di-isoamyl acetal, in EI-TDPBMS and CI-ITMS.

that oligomers were formed in the chamber and not during sample processing, since the EI-TDPBMS mass spectra taken during the chamber reaction and offline by coupling the HPLC-UV to the EI-TDPBMS show similar peaks. In order to more accurately interpret the EI-TDPBMS and CI-ITMS mass spectra, an acetal standard was analyzed to determine the characteristic EI and CI fragmentation pathways. These pathways are shown in Figure 2.5 (and more explicitly with the associated mass spectra in Figure 2.6) and are consistent with expected fragmentation mechanisms for these structures.^{75,76} They are referred to throughout Table 2.2 to explain the mass spectral peaks observed for each product. Although the mass spectra obtained for peaks 2b and 3 could also be explained by hemiacetal structures, we have assigned these as acetals because the derivatization-spectrophotometric and FTIR analyses of functional groups detected only trace amounts of hydroxyl groups in the SOA.

Peak 6 in the chromatogram is by far the dominant product in the SOA (accounting for >50% of the total peak area), and so is employed here to demonstrate the approach used to identify products based on ESI, EI, and CI mass spectra. This product is identified as a C₂₀ dinitrate acetal heterodimer (MW 428) that is proposed to form when a hydroxycarbonyl nitrate (HCN) cyclizes to form a cyclic hemiacetal,^{8,32} which then reacts with a hydroxynitrate (HN) to

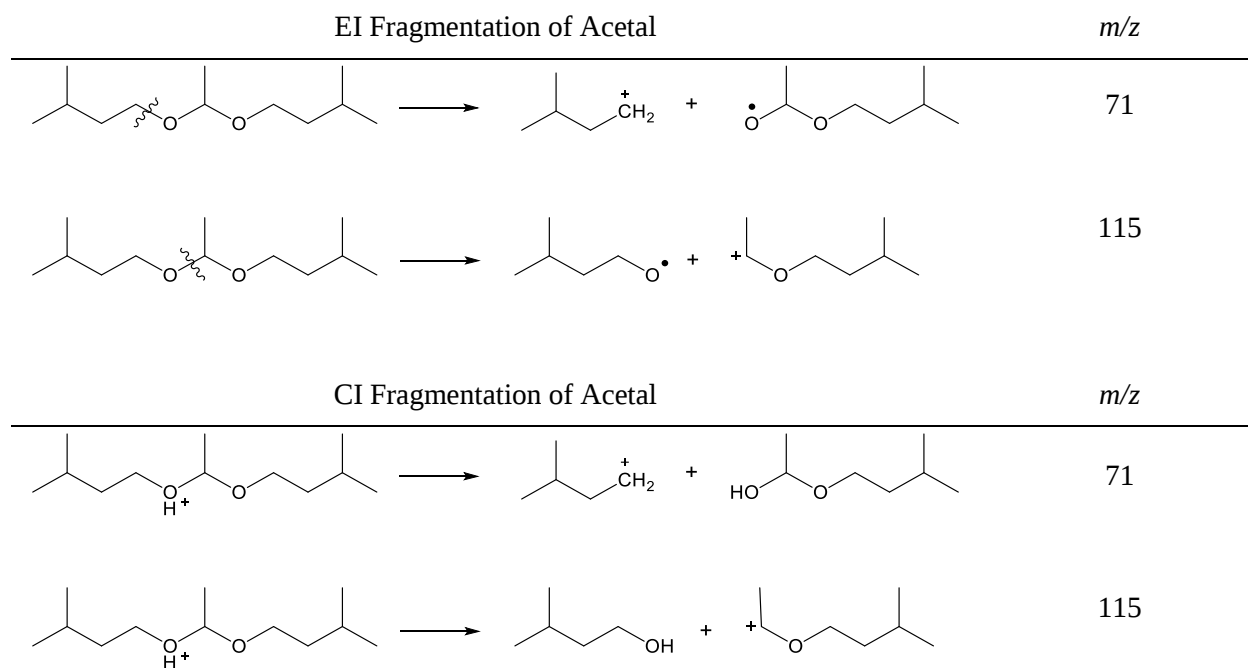
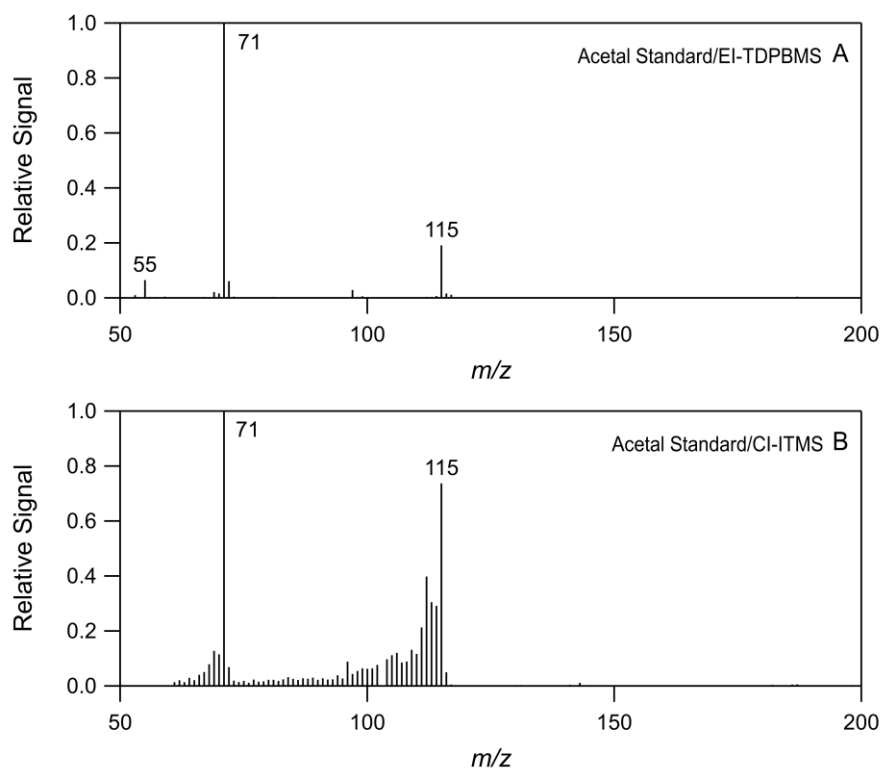


Figure 2.6. The electron and chemical ionization mass spectra and fragmentation pathways of an acetal standard, acetaldehyde di-isoamyl acetal (MW = 202 g mol⁻¹).

form the acetal product through H₂O elimination. This reaction is shown in Figure 2.4 for one of the two HCN isomers formed in Figure 2.1, but the other could react similarly. Note also that no other combination of monomers in Figure 2.1 could form a hemiacetal or acetal with the same molecular weight. The ESI, EI, and CI mass spectra of this product are shown in Figure 2.7. The three peaks in the ESI spectrum (Figure 2.7A) are assigned to the Na⁺ adduct (*m/z* 451), the K⁺ adduct (*m/z* 467), and the Na⁺ adduct of a non-covalently bound dimer (*m/z* 879).

The EI mass spectrum (Figure 2.7B) shows peaks at *m/z* 198 and 197 that are due to fragmentation of the parent M⁺⁺ ion by the Acetal-A pathway (Figure 2.5), with formation of the *m/z* 197 ion being preceded by an H-atom shift that results in a stable alkene ion and neutral cyclic hemiacetal. If this cyclic hemiacetal instead retained the charge in this process and then fragmented by loss of NO₂, it would also explain the presence of an *m/z* 185 peak in the mass spectrum. The peaks at *m/z* 168 and 152 are due to loss of NO₂ from *m/z* 214 and 198 ions formed by the Acetal-B and Acetal-A pathways, respectively, probably followed by an H-atom shift from the –CH₂O group to the ring in order to form a more stable cyclic aldehyde ion. The peaks at *m/z* 137, 123, and 109 are then explained by loss of CH₃ and CHO from the *m/z* 152 ion and C₃H₅ + H₂ from the *m/z* 168 ion, since loss of CHO is expected for cyclic aldehydes and losses of CH₃ and C₃H₅ + H₂ are common for terpenes.^{75,76} The pathway by which the *m/z* 142 ion is formed is unclear.

The CI mass spectrum (Figure 2.7C) has many of the same peaks as the EI mass spectrum, since similar fragmentation pathways are favored by the M⁺⁺ and [M + H]⁺ parent ions formed in EI and CI, respectively. Whereas in EI the R₁O⁺⁺R₂ parent ion fragments to form R₁⁺ + •OR₂ or R₂⁺ + •OR₁, in CI the R₁(OH)⁺R₂ parent ion fragments to form R₁⁺ + R₂OH or R₂⁺ + R₁OH (Figure 2.6). Thus, the same ions are formed but in EI the neutral fragment is an alkoxyl

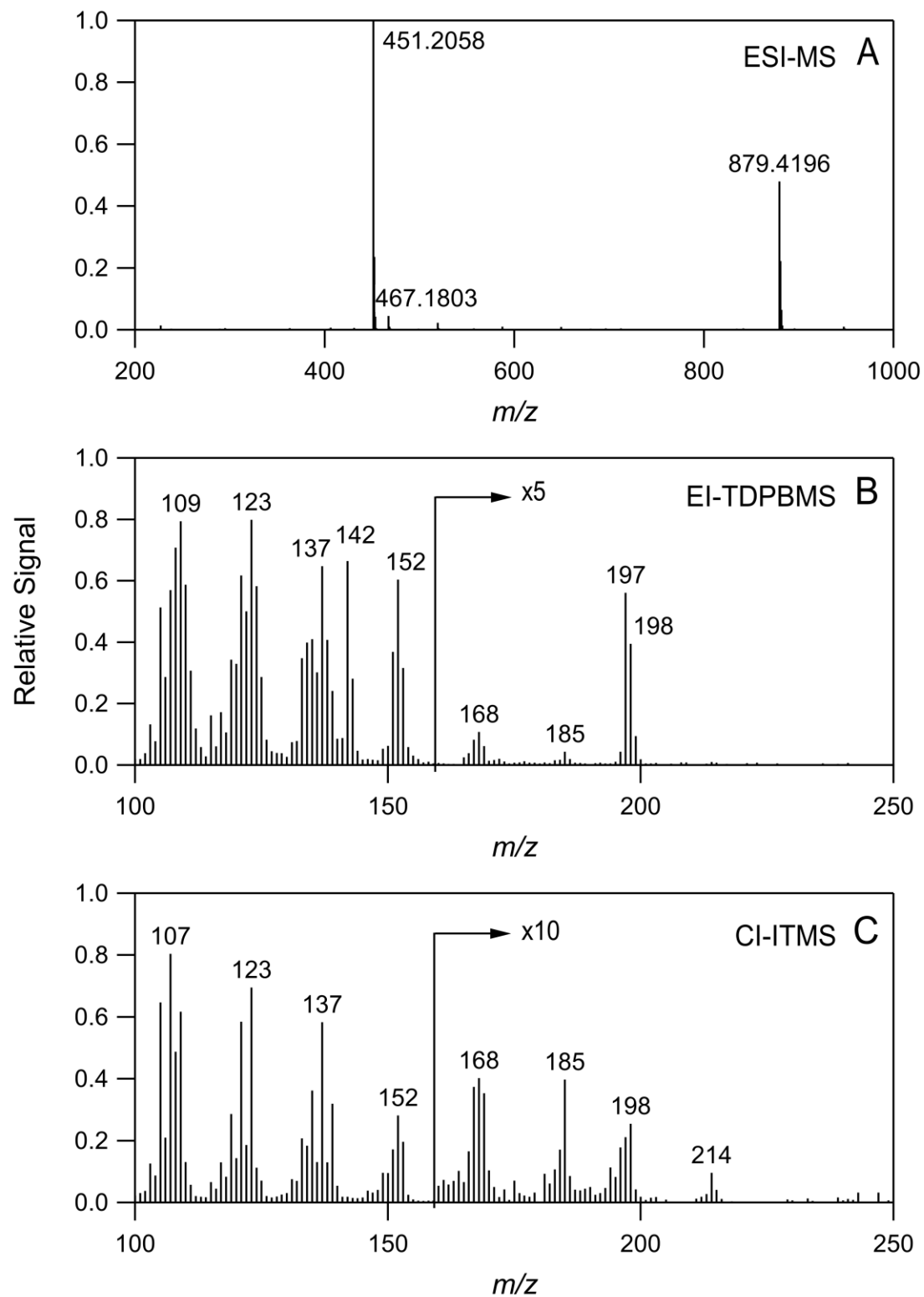


Figure 2.7. Mass spectra of HPLC-UV peak 6 obtained by (A) ESI-MS, (B) EI-TDPBMS, and (C) CI-ITMS analysis of SOA formed from reaction of β -pinene with NO_3 radicals.

radical while in CI it is an alcohol. The peaks at m/z 214 and 198 are then due to fragmentation of the parent ion by the Acetal-B and Acetal-A pathways with corresponding losses of a neutral β -hydroxynitrate and cyclic hemiacetal, respectively, with loss of NO_2 from a cyclic hemiacetal ion leading to a peak at m/z 185. Fragmentation of the m/z 214 and 198 ions by the same pathways described above for EI can then explain the presence of peaks at m/z 168, 152, 137, and 123.

For the remainder of the products identified in Table 2.1, all peaks in the ESI mass spectra were due to Na^+ or K^+ adducts of the product or its non-covalently bonded dimer with neutral losses of H_2O or HNO_3 observed in a few cases. The EI and CI mass spectral data are also presented in Table 2.2. In all cases, the oligomers fragmented according to the patterns observed for the acetal standard, as shown in Figure 2.5, followed by neutral losses of HNO_3 , HNO_2 , NO_2 , H_2O , CH_2O , CHO , $\text{C}_3\text{H}_5 + \text{H}_2$, and CH_3 . In the case of peak 2 (Figure 2.3), which contained the unresolved peaks labeled a, b, and c, all 3 peaks were collected as a single sample for ESI and CI analysis. From the ESI and CI spectra the three products were assigned as acetals with MW 444, 460, and 476, with structures shown in Table 2.1 and proposed formation mechanisms in Figure 2.4. In order to assign each product to a peak in the chromatogram, which was necessary for quantification, the HPLC-UV was directly coupled to the EI-TDPBMS using an atomizer so that EI mass spectra could be obtained after each compound had passed through the UV-Vis detector. Figure 2.8 shows the overlay of the HPLC-UV chromatogram with time profiles of the total ion signal and selected ions. Note that in the chromatogram in Figure 2.8 only peaks 2a and 2c are clearly distinguished, apparently because the SOA sample used for that HPLC-UV analysis contained less of the product responsible for the small peak 2b observed in Figure 2.3. Nonetheless, this analysis still allowed us to identify the two major products that

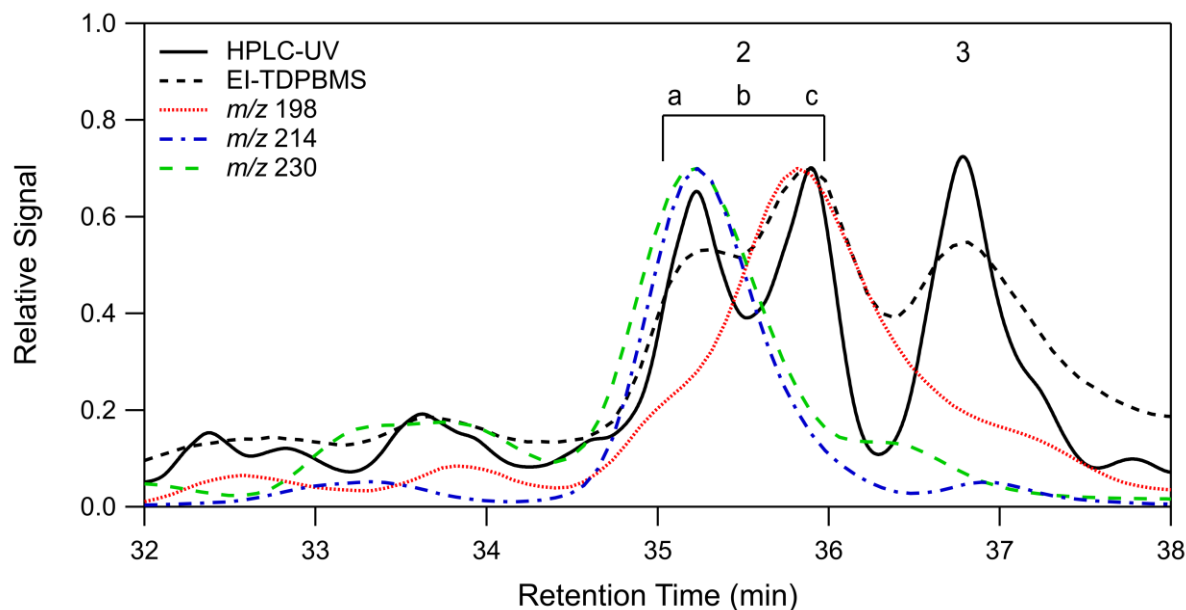


Figure 2.8. Overlay of HPLC-UV chromatogram with time profiles of total ion signal and selected ions measured in SOA formed from reaction of β -pinene with NO_3 radicals by EI-TDPBMS.

dominate peak 2. As can be seen in Figure 2.8, the m/z 230 and 214 profiles overlap with peak 2a, while the m/z 198 profile overlaps with peak 2c. The m/z 214 and 230 ions associated with peak 2a are formed by fragmentation of the acetal with MW 460, and the m/z 198 ion associated with peak 2c is formed by fragmentation of the acetal with MW 476, meaning that the acetal with MW 444 is responsible for peak 2b in Figure 2.3.

The only peak in the HPLC-UV chromatogram that was due to a monomer was peak 1. This product was identified as a tricarboxynitrate (TCN) based on its ESI (Table 2.1) and CI (Table 2.2) mass spectra. The ESI mass spectrum has peaks at m/z 246, 268, and 284 due to H^+ , Na^+ , and K^+ adducts, whereas the CI mass spectrum has peaks at m/z 199, 181, 163, 153, and 135 due to losses of HNO_3 , HNO_2 , CH_2O , and H_2O from the $[\text{M} + \text{H}]^+$ ion. Comparison of the retention time of this product with that of the synthesized C_{10} hydroxynitrate standard provides

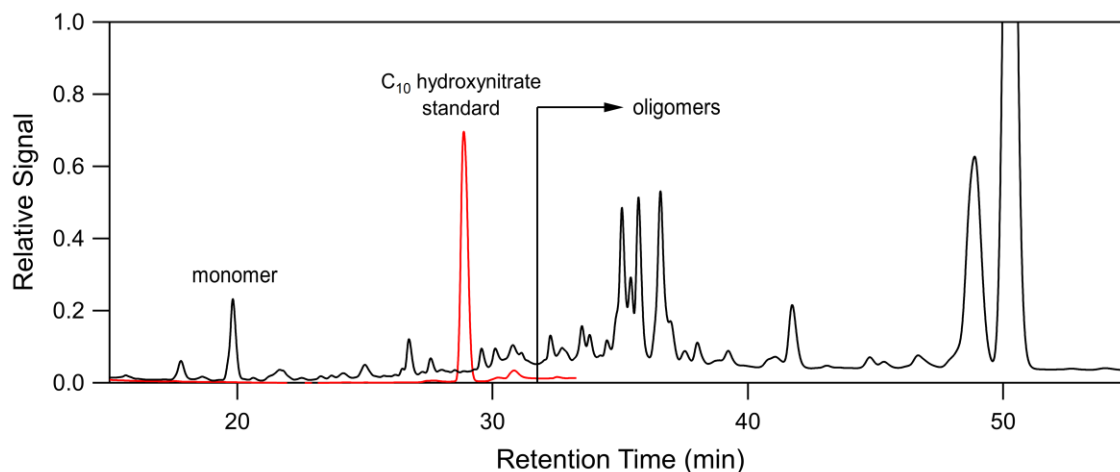


Figure 2.9. Overlay of the HPLC-UV chromatogram for the SOA formed from reaction of β -pinene with NO_3 radicals (black), and the chromatogram of a synthesized C_{10} hydroxynitrate standard (red).

additional evidence that it is a monomer. As shown in Figure 2.9, whereas all the oligomers elute after the standard, because of their much larger size and thus lower polarity, the monomer elutes before the standard because of its additional functional groups and thus higher polarity.

2.3.4 Measured Yields of SOA Products. Two types of molar yields of SOA products are reported in Table 2.3: yields of the identified monomer and oligomers responsible for peaks 1–6 in the HPLC-UV chromatogram (Figure 2.3), and yields of the monomer building blocks that reacted to form the oligomers. The yield of the tricarbonylnitrate (TCN) monomer identified in SOA was 2.0%, the yield of the major oligomer was 16.7%, and the yields of the other 6 oligomers ranged from 1.1% to 2.9%, for a total yield of 30.7%. The yields of the 2 major monomer building blocks, the hydroxynitrate (HN) and hydroxycarbonyl nitrate (HCN), were 23.6% and 25.9%, respectively, while the yields of the other 4 (including the tricarbonyl nitrate (TCN) that existed in SOA as a monomer) ranged from 2.0% to 4.8%, for a total yield of 62.4%.

Table 2.3. Molar yields of monomers and oligomers identified in SOA formed from the reaction of β -pinene with NO_3 radicals, and the corresponding molar yields of the monomer building blocks of the oligomers.

Monomer and Oligomers				Monomer Building Blocks			
Peak Number	MW of Product	Mole Fraction (%)	Molar Yield (%)	Monomer ID	MW of Monomer	Mole Fraction (%)	Molar Yield (%)
1	245	6.5	2.0	HN	215	37.8	23.6
2a	460	7.3	2.2	DCN	229	4.7	2.9
2b	444	3.6	1.1	HCN	231	41.5	25.9
2c	476	5.9	1.8	TCN	245	3.2	2.0
3	444	8.4	2.6	HDCN	247	7.7	4.8
4	460	4.4	1.4	HCNA	263	5.1	3.2
5	657	9.5	2.9				
6	428	54.4	16.7				

2.3.5 SOA Yields and Functional Group Composition. Results of the derivatization-spectrophotometric analysis of SOA functional group composition, as well as O/C, N/C, and H/C ratios, molecular weight, and density calculated from the functional group composition are shown in Table 2.4. Although the SOA is composed mainly of oligomers, for simplicity the functional group composition is reported as the average number of each functional group per C_{10} molecule, the carbon number of β -pinene and the monomers. The numbers of peroxide, ester, carbonyl, carboxyl, hydroxyl, nitrate, and methylene groups (CH_2) per C_{10} SOA molecule were 0.02, 0.01, 0.43, 0.06, 0.00, 1.12, and 8.37, respectively, with the number of methylene groups determined from the difference in mass of measured functional groups and total SOA mass.³⁷ These values can be compared to the corresponding values of 0.00, 0.00, 0.78/0.30, 0.05, 0.00, 1.00, and 8.20/8.68 estimated from the molecular structures (Table 2.1) and molar yields (Table

Table 2.4. Functional group composition of SOA formed from the reaction of β -pinene with NO_3 radicals, determined by derivatization-spectrophotometry of bulk SOA and estimated from results of molecular (HPLC-UV-MS) analysis.

	Derivatization- Spectrophotometry	HPLC-UV-MS
Functional Group	FG/ C_{10} Molecule	
Peroxide [CHOOR]	0.02 ± 0.01	0.00
Ester [C(O)OR]	0.01 ± 0.02	0.00
Carbonyl [C(O)]	0.43 ± 0.02	0.78/0.30 ^a
Carboxyl [C(O)OH]	0.06 ± 0.05	0.05
Hydroxyl [CHOH]	0.00 ± 0.01	0.00
Nitrate [CHONO ₂]	1.12 ± 0.21	1.00
Methylene [CH ₂]	8.37 ± 0.14	8.20/8.68 ^a
O/C	0.40	0.34
N/C	0.11	0.10
H/C	1.79	1.84
MW (g mol ⁻¹)	217	207
Density (g cm ⁻³)	1.21	1.16

^aValues correspond to those predicted assuming the following behavior during carbonyl analysis: all oligomers are converted to original ring-opened monomers/none are converted to original monomers.

2.3) determined by HPLC-UV-MS analysis, where two possible values, 0.78 and 0.30, are listed for the carbonyl groups. The first of these assumes that all oligomers are converted to the original ring-opened monomers under the acidic conditions of the analysis, whereas the second assumes that only initially-free carbonyl groups are detected. We know from previous analysis of a C_5 cyclic hemiacetal that these compounds are converted to the corresponding C_5 1,4-

hydroxycarbonyl during analysis, so that the carbonyl groups are measured.³⁷ The extent to which the acetals formed here are predicted to hydrolyze is more of an open question, although the relatively good agreement between the results of the derivatization-spectrophotometric functional group analysis (0.42) and estimates based on the molecular HPLC-UV-MS analysis (0.30) suggests that they do not. This would be consistent with studies of the acid-catalyzed hydrolysis of sucrose, which is formed from the dehydration reaction between the cyclic hemiacetal forms of glucose and fructose and also has electron withdrawing hydroxyl groups in some of the same locations where nitrooxy groups are present on the SOA oligomers. Kinetics studies^{77,78} indicate that the lifetime for hydrolysis of sucrose at the same pH (~1.5) used in the carbonyl analysis is ~50 h, which would correspond to hydrolysis of ~20% of the acetals in SOA during the ~10 h reaction period. If this were then case, then using the HPLC results given in Table 2.4 for the number of initially-free carbonyl groups (0.30) and the initially-free carbonyl groups + carbonyl groups formed by acetal hydrolysis ($0.78 - 0.30$), the number of carbonyl groups predicted to be determined by carbonyl analysis would be $0.30 + (0.2 \times (0.78 - 0.30)) = 0.40$. This value agrees very well with the value of 0.43 determined from the derivatization-spectrophotometric carbonyl analysis. We also note that in the comparison of the results of the hydroxyl group composition determined by derivatization-spectrophotometry and HPLC-UV-MS analysis it was necessary to account for the fact that acetals do not hydrolyze under the basic conditions of the hydroxyl analysis,³⁷ so the corresponding monomer hydroxyl groups are not detected. As a qualitative check on the results of our derivatization-spectrophotometric analysis of functional groups an ATR-FTIR spectra was taken of the extracted SOA, as shown in Figure 2.10. The ATR-FTIR spectra qualitatively confirms the functional group analysis, showing

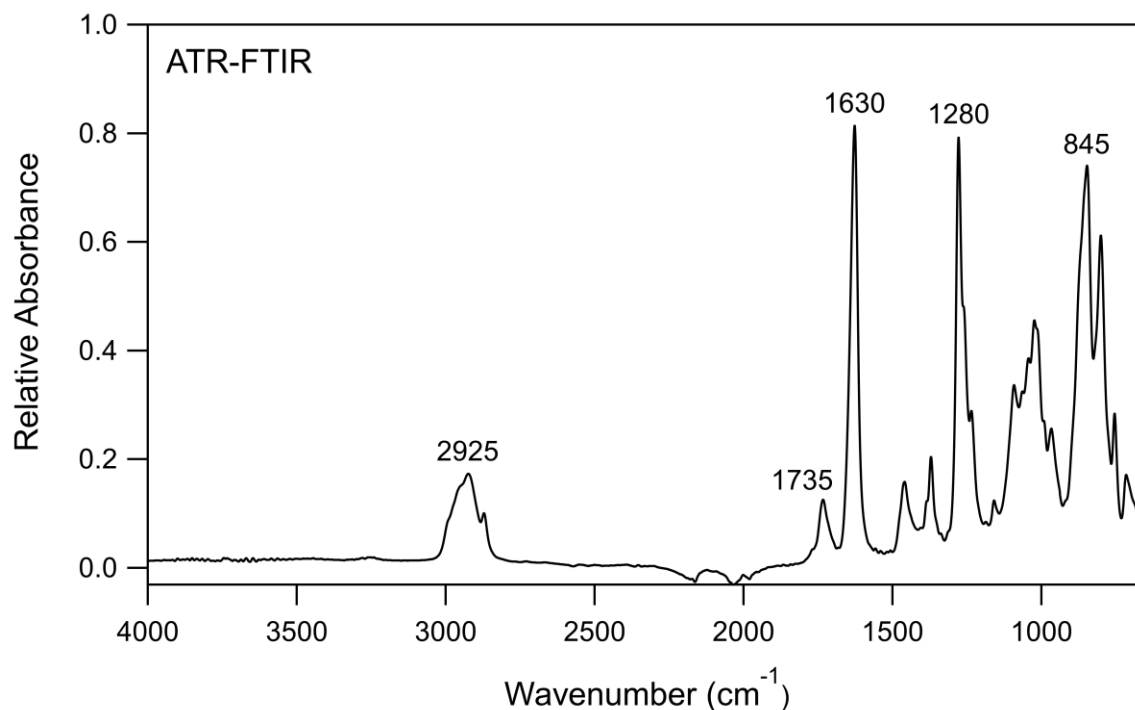


Figure 2.10. ATR-FTIR spectrum of extracted SOA formed from reaction of β -pinene with NO_3 radicals. Peaks at 1630, 1280, and 845 cm^{-1} correspond to absorbance by nitrate groups, while the peaks at 2925 and 1735 cm^{-1} are due to methylene and carbonyl groups, respectively. The absence of a significant broad peak between 3200-3600 cm^{-1} indicates that hydroxyl groups were negligible.

significant peaks from nitrate, methylene, and carbonyl groups, but no detectable contribution from hydroxyl groups.⁷⁹

The O/C, N/C, and H/C ratios, molecular weight, and density of the SOA calculated from the results of the derivatization-spectrophotometric analysis of functional group composition were 0.40, 0.11, 1.79, 217 g mol^{-1} , and 1.21 g cm^{-3} , which are in excellent agreement with the values of 0.34, 0.10, 1.84, 207, and 1.16 calculated from the results of the molecular HPLC-UV-MS analysis. The SOA density was calculated from the O/C, N/C, and H/C ratios using the equation of Kuwata et al.⁸⁰ and assuming that an N atom contributed the same amount to the

density as an O atom. The SOA mass yields determined using the filter mass (corrected for ammonium sulfate) and the extracted SOA mass were 90.6% and 87.1%, which is essentially the same as the value of 90% measured by Griffin et al.²⁴ for a similarly high mass loading of $450 \mu\text{g m}^{-3}$. Multiplying the mass yields measured here by the ratio of the molecular weights of β -pinene and the SOA (136/217) determined from the results of the derivatization-spectrophotometric functional group analysis give SOA molar yields of 56.8% and 54.6%. These values agree well with the SOA molar yield of 62.4% calculated from the sum of the molar yields of individual SOA products, and indicate that ~60% of the reacted β -pinene molecules reacted to form SOA products.

2.4 Conclusions

In this study a variety of analytical methods were used to identify and quantify products that make up ~95% of the SOA mass formed from the reaction of β -pinene with NO_3 radicals in an environmental chamber. The methods included liquid chromatography and mass spectrometry with electron, chemical, and electrospray ionization for molecular analysis, and derivatization-spectrophotometry and attenuated total reflectance-Fourier transform infrared spectroscopy for bulk functional group analysis. Of the eight identified SOA products, more than 90% by mass consisted of acetal heterodimers and heterotrimers that were formed in the particles through acid-catalyzed reactions involving hydroxyl and carbonyl functional groups and protons derived from HNO_3 generated by hydrolysis of N_2O_5 . The oligomerization reactions were promoted by the particular structures of the monomers, which usually contained carbonyl groups that were activated by the presence of an adjacent electron-withdrawing nitrate group, and highly reactive tertiary hydroxyl groups. The reactions also likely occurred in a relatively hydrophobic organic phase⁸¹ of a phase-separated SOA/aqueous ammonium sulfate aerosol,⁷⁴ since hemiacetal

formation competes with hydration and acetal formation involves dehydration. The absence of peroxide groups in the SOA is also consistent with the conclusion that these oligomers were not dialkyl peroxides formed through gas-phase reactions, as has been observed for the reaction of isoprene with NO_3 radicals.⁸²

The molar yield of the major oligomer product (C_{20} dinitrate acetal) was 16.7%, the yields of the other 6 oligomers ranged from 1.1% to 2.9%, and the yield of the only monomer identified in the SOA (tricarboxylnitrate) was 2.0%, for a total yield of 30.7%. Since the identities of each of the oligomers was known, yields of the monomer building blocks could also be determined and were 23.6% and 25.9% for the 2 major monomer building blocks (hydroxynitrate and hydroxycarbonyl nitrate), while the yields of the other 4 ranged from 2.0% to 4.8%, for a total monomer yield of 62.4%. This value was in good agreement with the total monomer yield of 55.7% obtained from the SOA mass yield (88.9%) and ratio of the molecular weights of the SOA and β -pinene. The O/C, N/C, and H/C ratios, molecular weight, and density of the SOA calculated from results of the results of the derivatization-spectrophotometric functional group analysis were 0.40, 0.11, 1.79, 217 g mol^{-1} , and 1.21 g cm^{-3} , respectively, nearly identical to those calculated from the molecular HPLC-UV-MS analysis.

The results of this study demonstrate the importance of ring-opening, alkoxy radical decomposition, and oligomerization reactions in the NO_3 radical-initiated oxidation of β -pinene and the subsequent formation of SOA, and should be applicable to other monoterpene reactions, especially those that form radical intermediates and oxidation products with similar structures to those identified here. Although the experiments were conducted under conditions in which $\text{RO}_2^\bullet$ radicals reacted primarily with other $\text{RO}_2^\bullet$ radicals, it is quite possible that reactions with NO_3 or HO_2 radicals can also produce alkoxy radicals (although these reactions have not been

investigated specifically for β -nitrooxyperoxy radicals),¹² thus making the results potentially relevant for a wider range of oxidation regimes and atmospheric conditions. The results also suggest that hydroxycarbonyl compounds (which are formed in many types of VOC oxidation reactions)⁸ rapidly react in particles to form acetals, and that these reactions can occur in the presence of an aqueous phase and atmospheric concentrations of HNO_3 . It seems quite reasonable to expect then that similar reactions are highly favored in the atmosphere and play a role in SOA formation. We have recently used the monomer and oligomer yields measured here to develop a quantitative kinetic model for this system that includes gas-phase and acid-catalyzed particle-phase reactions, and which should be useful for modeling this and similar reactions in the laboratory and atmosphere.

Chapter 3

Thermal Desorption Characteristics of Hemiacetal and Acetal Oligomers

3.1 Introduction

The oxidation of volatile organic compounds (VOCs) in the atmosphere by O_3 , OH radicals, or NO_3 radicals can lead to the production of low-volatility products that can partition onto particles to create secondary organic aerosol (SOA).⁸ Although it has been shown that SOA can play an important role in climate forcing and be detrimental to human health,² there are large uncertainties associated with these effects. Additional studies are therefore needed in order to better understand the formation mechanisms, atmospheric processing, and physical properties of SOA, information that is essential for improving model predictions and possibly mitigating SOA impacts.^{5,10}

An important property of SOA is its volatility, since this affects the partitioning of organic compounds between the gas and particle phases, and thus the composition and physical properties of SOA as well as the atmospheric fate and transport of organic compounds. In recent years a variety of thermal desorption methods, some of which are coupled with chemical analysis, have been developed to measure the volatility of SOA.⁸³⁻⁸⁷ In general, as the SOA is heated its various components desorb according to their vapor pressures, which in turn depend on compound carbon number and functional group composition.⁸⁸ A key component of SOA is oligomers, the presence of which affects not only SOA volatility but also other physical and

chemical properties.⁸ The existence of oligomers in SOA has been demonstrated in laboratory experiments and from field measurements,^{68–70,89,90} with their formation being attributed most often to particle-phase accretion reactions that occur on timescales of seconds to hours.^{68–70,90} Some common types of oligomers that are formed in SOA include hemiacetals, acetals, and peroxyhemiacetals.⁸ Although oligomers can be detected using offline and online electrospray mass spectrometric methods,^{91–93} this approach gives no direct information on volatility. For this reason studies are often conducted instead using instruments that combine thermal desorption of the SOA with mass spectrometric analysis of the particles and/or vapor to determine the volatility-resolved composition.^{86,94,95} Unfortunately, one of the unknowns in this approach is how oligomers, especially those that form via reversible reactions, respond to thermal desorption. In particular, it is not yet established which oligomers will desorb intact and which will decompose, and whether those that decompose do so by a reversible pathway to reform the monomers from which they were formed or if they do so by some other pathway.

Previous studies conducted in our laboratory that employed temperature-programmed thermal desorption (TPTD) to analyze SOA showed that peroxyhemiacetal oligomers formed by the reaction of hydroperoxides and aldehydes remained intact through the thermal desorption process prior to electron ionization and mass analysis.⁸⁴ Conversely, using the same method to analyze SOA formed from the OH radical-initiated reaction of 3-methyl-furan, Strollo and Ziemann⁷² obtained evidence that suggested hemiacetals decomposed to their monomer building blocks while ester and acetal oligomers formed by dehydration reactions remained intact throughout the analysis.

A relatively new instrument called the Filter Inlet for Gases and AEROsols coupled to a chemical ionization mass spectrometer (FIGAERO-CIMS) analyzes the volatility and

composition of an aerosol sample collected on a Teflon filter by thermally desorbing the components using a flow of heated N₂ prior to analysis by chemical ionization mass spectrometry. Multiple studies have observed thermally induced decomposition and fragmentation of aerosol components using this method.^{87,95} In one study conducted using the FIGAERO-CIMS, small, highly volatile products were detected during the desorption process and it was suggested that these were an artifact of oligomer fragmentation by pathways other than the one leading to the original monomer building blocks.⁹⁶ In another FIGAERO-CIMS study, however, Lopez-Hilfiker et al.⁹⁴ suggested that multimodal thermal desorption profiles observed for some ions were due to thermal decomposition of oligomers (likely to the monomer building blocks) or weakly bound complexes.

Another thermal desorption technique that has been widely used to investigate aerosol volatility is the thermal denuder. In this approach the aerosol is passed through a heated tube and any gases that evaporate are collected onto a charcoal adsorbent. As the temperature in the denuder is increased, the mass fraction of aerosol remaining after heating is measured to obtain information about the volatility of the aerosol. In one study conducted using this device, An et al.⁸⁵ observed that the evaporation of SOA formed by ozonolysis of α -pinene was similar to that of a pinic acid standard. Although if taken at face value this indicated that only a small fraction of the SOA consisted of oligomers, because this contradicted a previous study³⁶ they instead suggested that the oligomers reverted to their volatile monomer precursors when heated for only a few seconds at an elevated temperature. Based on the results of a related study, Cappa and Jimenez⁸⁶ note that the high temperatures used in a thermal denuder could accelerate either particle-phase accretion or decomposition reactions, thus enhancing the formation of lower-volatility or higher-volatility products, respectively. Although they suggest that this type of

chemistry would only occur at temperatures above 150°C, they recommended a more detailed, speciated chemical analyses to clarify the effect of heating on aerosol chemistry.⁸⁶

In light of the persistent questions regarding the interpretation of thermal desorption data on SOA, the objective of this work was to investigate the thermal desorption properties of selected oligomers with linkages typical of those identified in laboratory studies and expected to be present in atmospheric SOA. By conducting studies on oligomers with known structures it should then be possible to better predict the thermal behavior of oligomers and identify those that are most likely to behave unpredictably during thermal analysis. The classes of oligomers studied were those containing hemiacetal and acetal linkages; either created by benchtop synthetic methods or in an environmental chamber as a component of SOA formed from the reaction of β -pinene with NO₃ radicals. We have shown previously that ~94% of the SOA formed in this reaction consists of acetal and diacetal oligomers,⁹⁰ thus providing an opportunity to investigate the thermal desorption properties of authentic SOA that has been carefully characterized and is made almost entirely of a small number of known oligomers. The thermal desorption behavior was studied using a thermal desorption particle beam mass spectrometer (TDPBMS) for both real-time analysis with rapid desorption and slow temperature-programmed thermal desorption (TPTD). The results provide new information on the thermal desorption behavior of two important classes of oligomers that are known to be present in SOA, and should be useful for interpreting measurements made using many of the available thermal desorption methods.

3.2 Experimental Section

3.2.1 Chemicals. The following chemicals, with purities/grades and suppliers were used: (1s)-(-)- β -pinene (99%), decanal (98%), 1-nonanol (98%), acetaldehyde di-isoamyl acetal (98%), 1,10-decanediol (98%) (Sigma-Aldrich); methanol (HPLC grade) (Honeywell); (NH₄)₂SO₄

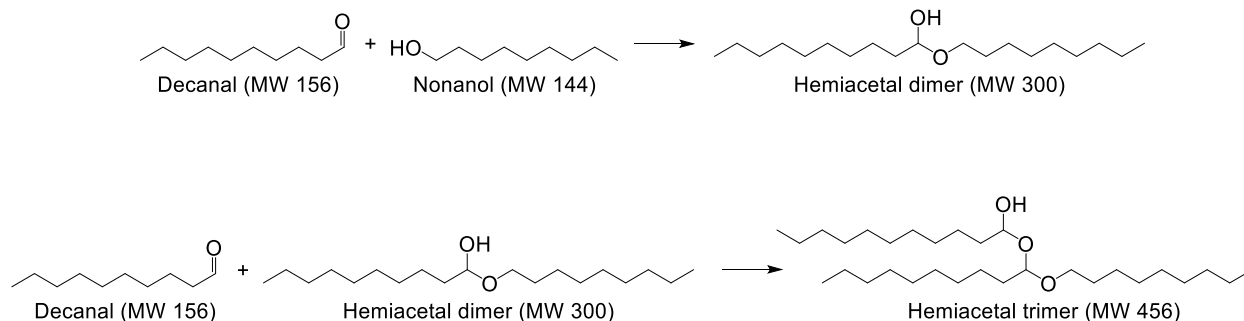


Figure 3.1. Reaction of decanal with 1-nonanol to form hemiacetal standard used in this study. And subsequent reaction of the hemiacetal with decanal to form the hemiacetal trimer observed in the TPTD profile of the hemiacetal solution.

(99.5%, ACS), acetonitrile (HPLC grade, ACS) (Fisher); 18 M Ω water purified using Milli-Q Advantage A10 water system. N₂O₅ was synthesized according to the procedures of Atkinson et al.³⁵ and was stored in a glass vacuum bulb in dry ice until used.

3.2.2 Synthesis of Hemiacetal Standard. The hemiacetal was synthesized using a method adapted from Erickson and Campbell.⁹⁷ Equimolar amounts of decanal and 1-nonanol were mixed and heated in a 50°C water bath for 30 min to produce a hemiacetal with MW 300 g mol⁻¹ according to the reactions shown in Figure 3.1. Extent of hemiacetal formation was measured by comparing the FTIR spectrum of each of the reactants to that of the mixture after 30 min of reaction. The existence of the hemiacetal was apparent due to the decay of absorbance at 1725 and 2715 cm⁻¹ from the C=O group in the decanal precursor, and growth of absorbance at 1110 cm⁻¹ due to the C–O–C group in the hemiacetal, as shown in Figure 3.2.^{79,97}

3.2.3 Synthesis of C₁₀ Monomer Standards. A C₁₀ hydroxynitrate (1-hydroxy-10-nitrooxydecane) and C₁₀ dinitrate (1,10-dintrooxydecane) were synthesized according to the method of Kames et al.⁴⁵ via the condensed phase reaction of the corresponding C₁₀ diol (1,10-decanediol) with N₂O₅, which converts hydroxyl groups to nitrate groups. The resulting mixture

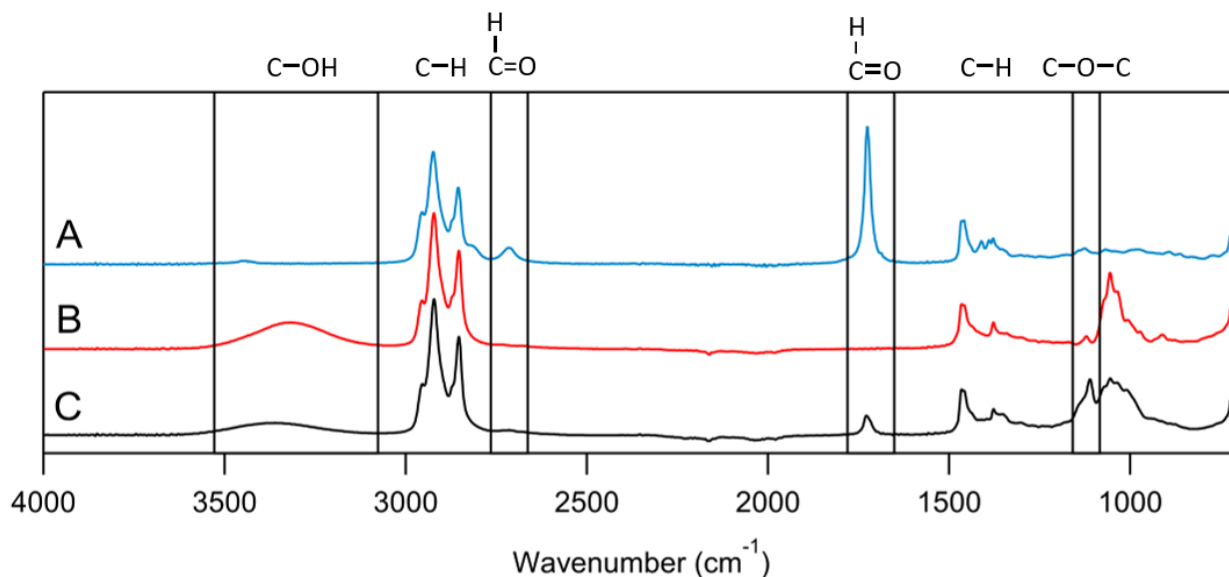
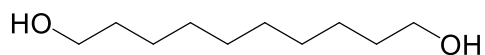


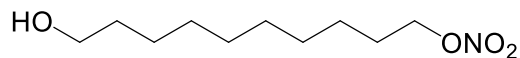
Figure 3.2. ATR-FTIR spectrum of (A) decanal standard, (B) 1-nonanol standard, and (C) hemiacetal mixture after reaction period. Peaks at 1725 and 2715 cm^{-1} represent the C=O stretch and aldehydic C-H stretch, respectively, for an aldehyde functional group. Broad absorbance at $\sim 3300 \text{ cm}^{-1}$ is due to O-H stretching, from the hydroxyl group present in both 1-nonanol and the hemiacetal. Absorbance at 1110 cm^{-1} is associated with the C-O-C stretching of an ether linkage, in this case associated with the hemiacetal structure.

of the C_{10} hydroxynitrate, dinitrate, and unreacted diol, whose structures are shown in Figure 3.3, was used for TPTD analysis as described below.

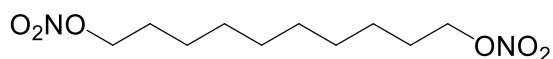
3.2.4 Environmental Chamber Experiment. It has been shown previously that $\sim 94\%$ mole fraction of the SOA formed from the reaction of β -pinene with NO_3 radicals consists of acetal and diacetal oligomers (7 heterodimers and 1 heterotrimer) whose structures are shown in Table 3.1. Because these oligomers were formed through dehydration reactions such as that shown in Figure 3.4, this aerosol was chosen as a model system for comparing with the thermal desorption behavior of hemiacetal oligomers formed through simple association reactions (Figure 3.1). The aerosol was formed in an 8 m^3 environmental Teflon FEP chamber filled with



C₁₀ Diol (MW 174)



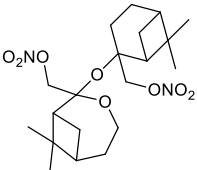
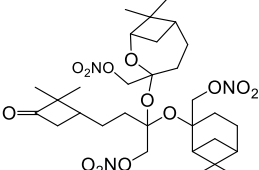
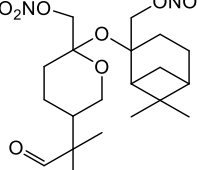
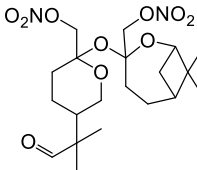
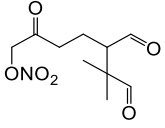
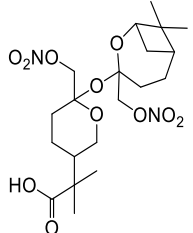
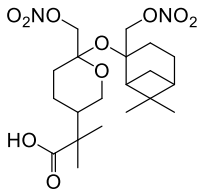
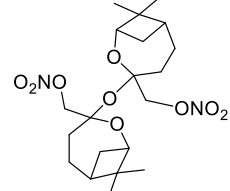
C₁₀ Hydroxynitrate (MW 219)



C₁₀ Dinitrate (MW 264)

Figure 3.3. Structures of C₁₀ monomers used for temperature programmed thermal desorption (TPTD) profile. Monomer solution contained a mixture of C₁₀ diol, hydroxynitrate (HN), and dinitrate (DN) compounds.

Table 3.1. Composition of SOA formed from the oxidation of β-pinene with NO₃ radicals

Structure of Particle-Phase Compounds ^a			
			
1 (54.4%)	2 (9.5%)	3 (8.4%)	4 (7.3%)
			
5 (6.5%)	6 (5.9%)	7 (4.4%)	8 (3.6%)

^a Numbers in prentices are the aerosol mole fraction of each compound.

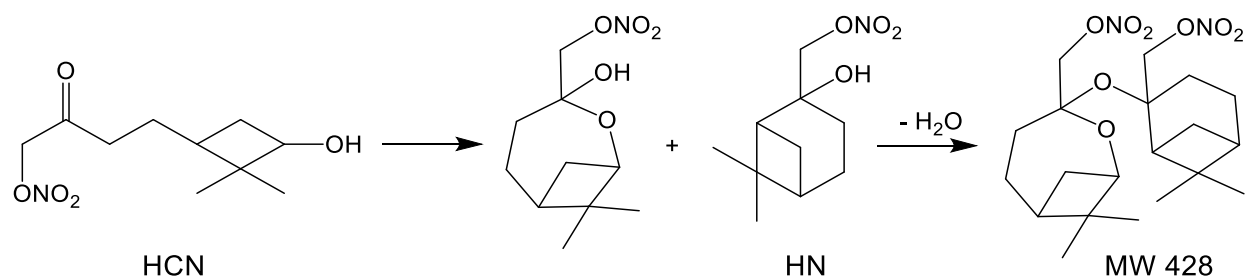


Figure 3.4. Proposed mechanism of formation of the dominate SOA product through the dehydration reaction of the cyclic HCN hemiacetal and HN monomers.

clean, dry air supplied by two AADCO Model 737-14A clean air generators (<5 ppbv hydrocarbons, <0.1% RH) at room temperature ($\sim 23^{\circ}\text{C}$) and pressure (~ 630 Torr). The chamber was humidified to 55% RH by evaporating water from a heated glass bulb into a stream of N_2 flowing into the chamber. Ammonium sulfate particles were formed using a Collison atomizer and flushed into the humidified chamber to obtain $\sim 200 \mu\text{g m}^{-3}$ of deliquesced seed particles. β -pinene was then added by evaporation from a heated glass bulb into a flow of N_2 to achieve a concentration of 1 ppm in the chamber. This was followed by addition of N_2O_5 , added similarly but without heating, to achieve a chamber concentration of 0.33 ppm in absence of reaction. Upon dilution of N_2O_5 in the chamber, NO_3 radicals were generated by thermal decomposition of N_2O_5 according to the reaction $\text{N}_2\text{O}_5 \leftrightarrow \text{NO}_3 + \text{NO}_2$ and reacted completely with β -pinene within a few minutes. A Teflon-coated fan was run for 30 s after adding each chemical to ensure a well-mixed chamber.

3.2.5 Real-Time TDPBMS Analysis. Chamber aerosol composition was monitored in real time by sampling air directly from the chamber into a thermal desorption particle beam mass

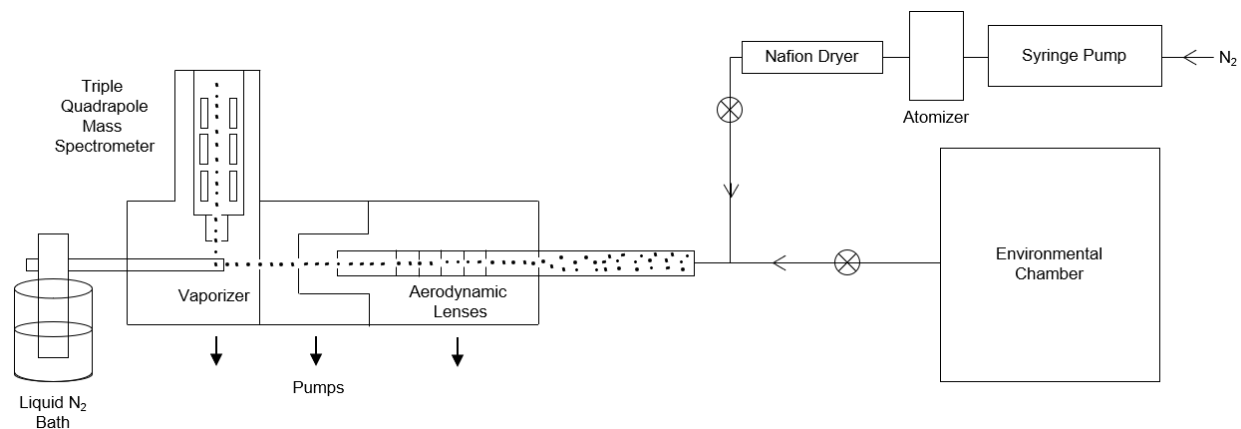


Figure 3.5. Schematic of the experimental setup used for both real-time TDPBMS and for temperature-programmed TDPBMS.

spectrometer (TDPBMS).⁴¹ A hemiacetal standard was analyzed similarly by using a syringe pump to supply a solution of the analyte to an atomizer, drying solvent from the atomized sample with a Nafion dryer, and then sampling the residual hemiacetal aerosol directly into the TDPBMS. The TDPBMS samples aerosol into an aerodynamic lens that focuses particles into a narrow beam for efficient transport into a high vacuum detection region where they impact on a polymer-coated copper rod that is resistively heated to 160°C. Particles are instantly vaporized and molecules are ionized by 70 eV electrons for analysis in an Extrel triple-quadrupole mass spectrometer (Figure 3.5).

3.2.6 Temperature-Programmed TDPBMS Analysis. The chamber SOA, hemiacetal standard, and mixture of C₁₀ monomers were also analyzed by temperature-programmed thermal desorption (TPTD) using the TDPBMS.⁸³ For TPTD analysis, the vaporizer rod was cooled to –40°C using liquid nitrogen and then an aerosol sample was cryogenically collected onto the cooled rod (Figure 3.5). The chamber SOA was collected by sampling directly from the chamber for 30 min, and the hemiacetal and mixture of C₁₀ monomers were each collected by atomizing

the standards into a stream of N₂ and collecting for 4 min. It should be noted that the solution of C₁₀ monomers (mixture of C₁₀ hydroxynitrate, dinitrate, and diol) was doped with dioctyl sebecate (MW 426) to provide a non-volatile organic solvent to reduce evaporation during transit to the TDPBMS. Once the sample was collected on the cooled vaporizer, the rod was allowed to warm to -5°C before being heated to 200°C at 2°C min⁻¹. During this slow thermal ramp the components of the sample desorb according to their volatility prior to mass spectral analysis.

3.3 Results and Discussion

3.3.1 Real-Time TDPBMS and TPTD Analysis of the Hemiacetal Standard. The real-time mass spectrum of the synthesized C₁₉ hemiacetal standard is shown in Figure 3.6A. This mass spectrum was acquired by keeping the vaporizer at 160°C, so that upon impaction in the vaporizer the hemiacetal aerosol was vaporized into the ionization region of the TDPBMS on a sub-second timescale. Since this hemiacetal (MW 300) was synthesized from decanal and 1-nonanol, which have molecular weights of 156 and 144, and electron ionization only generates ions with masses equal to or less than that of the molecular ion, the presence of peaks in the mass spectrum at m/z 157 and 173 indicates that the hemiacetal was ionized as the intact oligomer. As shown in Table 3.2, the peaks at m/z 127, 157, and 173 are all characteristic ions formed by fragmentation of the intact hemiacetal dimer ion around the hemiacetal linkage, similar to those predicted for ethers.⁹⁸ If the hemiacetal had thermally decomposed back to its monomers prior to ionization, then the mass spectrum should have instead been a combination of the mass spectra of decanal and 1-nonanol shown in Figures 3.6B and 3.6C (obtained from the NIST database, <https://webbook.nist.gov/chemistry/>,⁹⁹ because decanal and 1-nonanol are too volatile to form aerosol that can be sampled into the TDPBMS). The peaks at m/z 112, 128, and 138 are characteristic ions of decanal formed by losses of CH₂=CHOH, H₂C=CH₂, and H₂O, while the

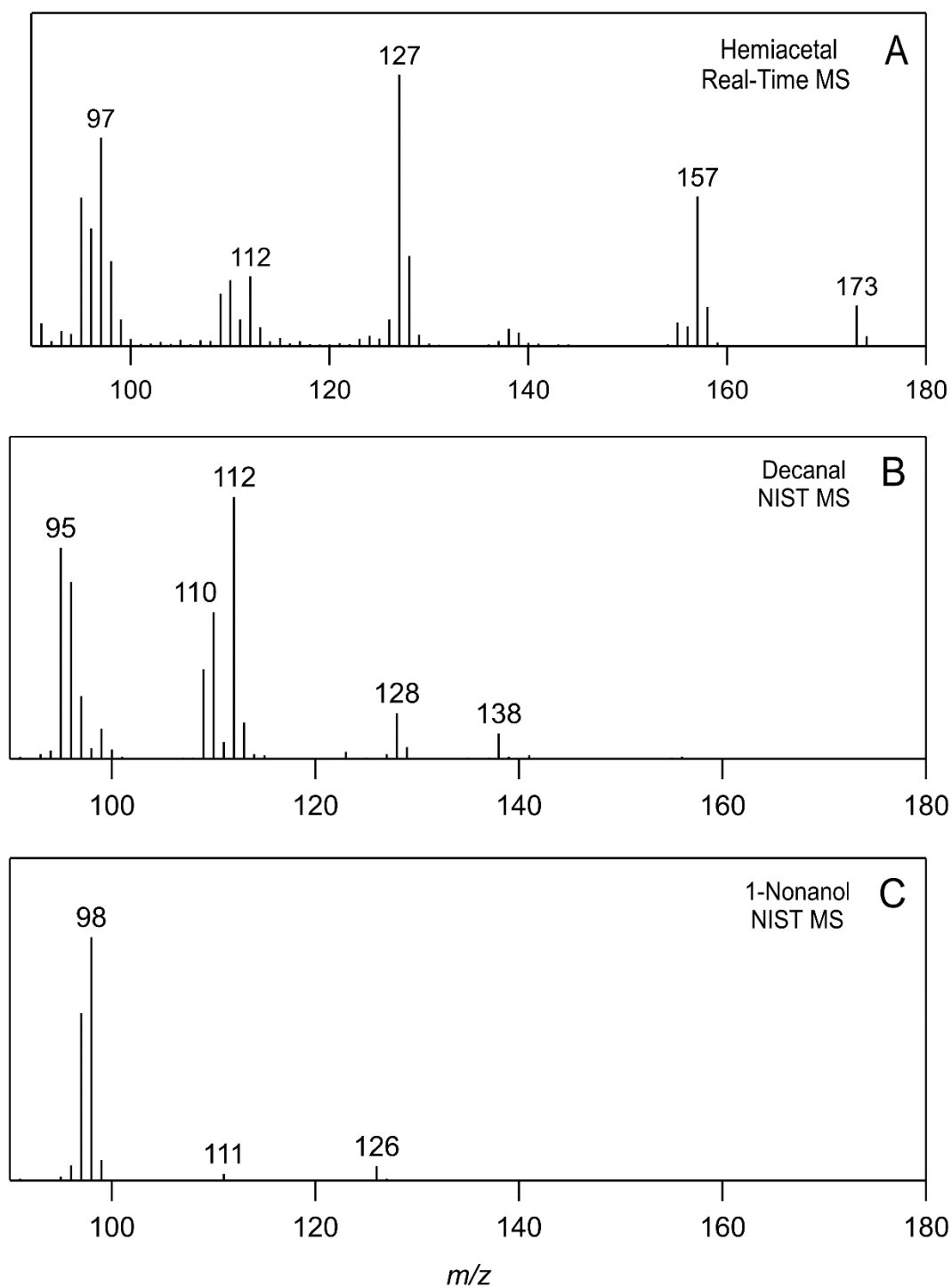


Figure 3.6. (A) Real-time electron-ionization mass spectra for a hemiacetal (MW 300) synthesized from nonanol (MW 144) and decanal (MW 156). And standard NIST electron-ionization mass spectra for (B) decanal and (C) 1-nonanol.

Table 3.2. Electron-ionization fragmentation pathways for hemiacetal standard that has been ionized in real-time. The hemiacetal was synthesized from nonanol and decanal, resulting in a hemiacetal with MW = 300 g mol⁻¹, R = C₈H₁₇.

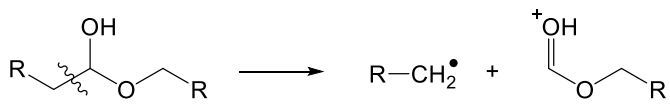
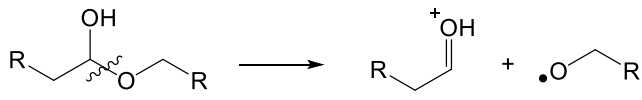
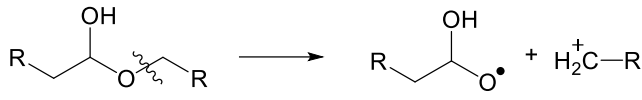
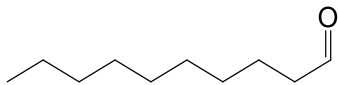
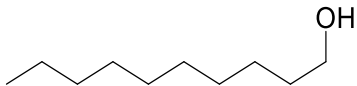
EI Fragmentation Pathways		<i>m/z</i>
		173
		157
		127

Table 3.3. Electron-ionization fragmentation pathways for decanal (MW 156) and 1-nonanol (MW 144) monomers.

Structure	Neutral Loss	<i>m/z</i>
	H ₂ O	138
	H ₂ C=CH ₂	128
	H ₂ C=CHOH	112
	H ₂ O	126
	H ₂ O + H ₂ C=CH ₂	98

peaks at m/z 98 and 126 are characteristic ions of 1-nonanol formed by losses of $\text{H}_2\text{O} + \text{H}_2\text{C}=\text{CH}_2$ and H_2O (Table 3.3).

TPTD profiles and associated mass spectra measured for the hemiacetal standard are shown in Figure 3.7. As described above, for this analysis the sample was collected onto the cooled vaporizer and then slowly desorbed into the ionization region using a temperature ramp of 2°C min^{-1} . The TPTD profiles of total ion signal (TIS) (Figure 3.7A), which is proportional to mass, and of selected characteristic ions (Figure 3.7B) are all bimodal with peaks at 20 and 77°C , indicating the presence of more than one component. The mass spectra associated with the two peaks differ significantly from each other and from the real-time mass spectrum of the hemiacetal standard (Figure 3.6A). The mass spectrum obtained for the 20°C peak has peaks at m/z 110, 112, 126, 128, and 138 that are a combination of those present in the mass spectra of decanal (m/z 110, 112, 128, 138) and 1-nonanol (m/z 98, 126), which indicates that at 20°C the hemiacetal decomposed reversibly back to decanal and 1-nonanol prior to desorption and ionization. This reaction is promoted at higher temperature, which shifts the equilibrium towards monomers,¹⁰⁰ and also by the rapid desorption of volatile monomers that drives further decomposition in an attempt to maintain reaction equilibrium. Since decanal and 1-nonanol are too volatile to even be sampled into the TDPBMS as an aerosol, and a previous study¹⁰¹ has shown that C_{15} alkyl nitrates with vapor pressures much lower than decanal and 1-nonanol⁸⁸ desorb at $\sim 12^\circ\text{C}$, it is clear that decanal and 1-nonanol desorbed at $\sim 20^\circ\text{C}$ because of decomposition of the hemiacetal at that temperature.

The mass spectrum associated with the TPTD peak at 77°C (Figure 3.7D) also differs significantly from the real-time mass spectrum (Figure 3.6A), showing substantial signal at m/z 313, a mass larger than that of the hemiacetal dimer (MW 300). As shown in Figure 3.1, during

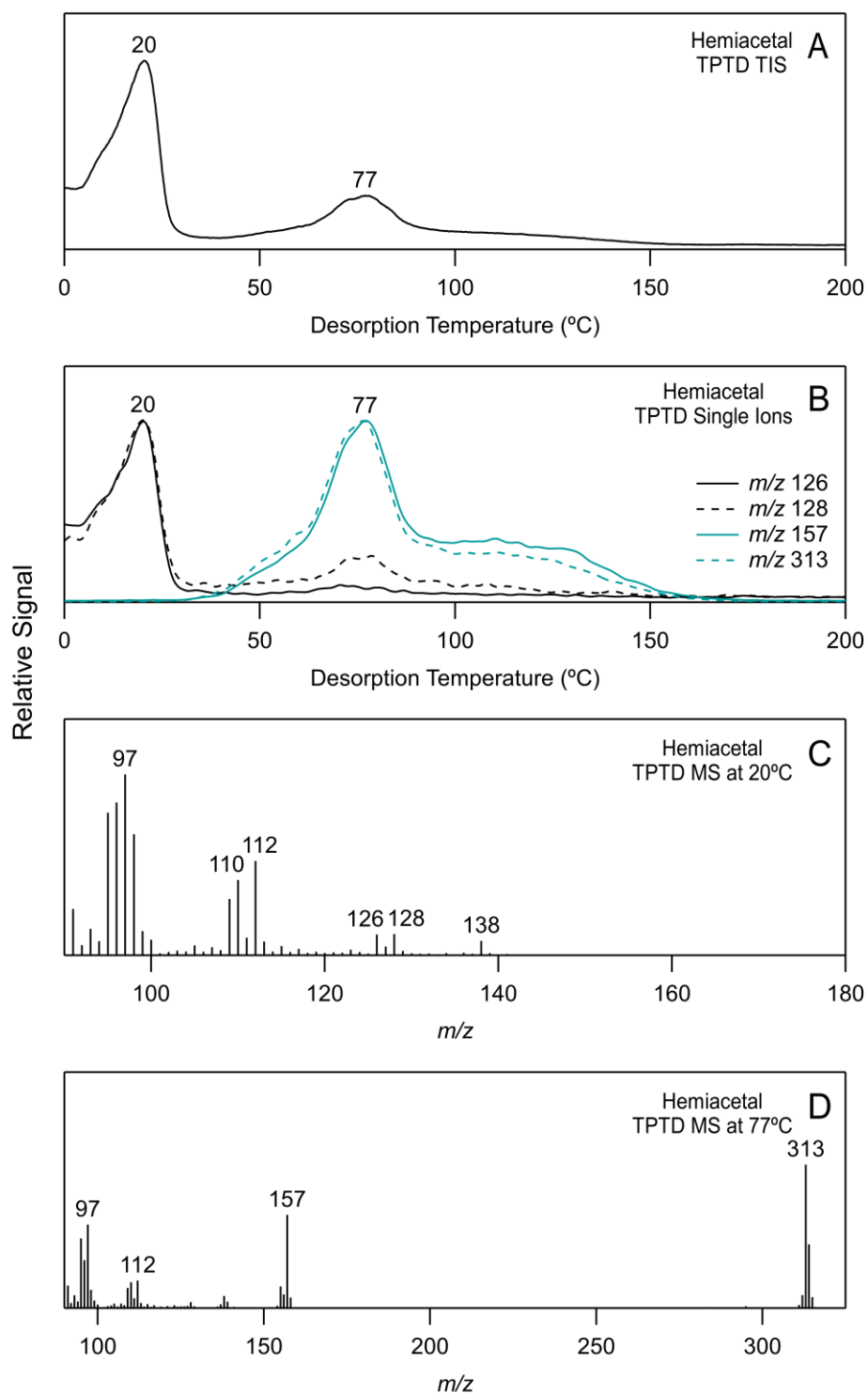


Figure 3.7. (A) Total ion signal (TIS) of temperature programmed thermal desorption (TPTD), (B) selected normalized TPTD single ion traces, and corresponding mass spectra for thermal desorption peaks at (C) 20°C and (D) 77°C for a hemiacetal (MW 300) synthesized from nonanol (MW 144) and decanal (MW 156).

Table 3.4. Electron-ionization fragmentation pathways for trimer formed during hemiacetal synthesis. The hemiacetal trimer formed has MW = 456 g mol⁻¹, R = C₈H₁₇.

EI Fragmentation Pathways	<i>m/z</i>
The reaction shows a hemiacetal trimer molecule with a central acetal linkage and a terminal hemiacetal group. An arrow indicates the cleavage of the C-O bond in the terminal hemiacetal group, resulting in a cyclic hemiacetal cation (a six-membered ring with an oxygen atom and a positive charge on the ring carbon) and an alkoxyl radical (R-O•).	313
The reaction shows the same hemiacetal trimer molecule. An arrow indicates the cleavage of the C-O bond in the central acetal linkage, resulting in an aldehyde cation (R-CHO⁺) and an acetal radical (R-O-C(R)-O-R).	157

hemiacetal synthesis it is possible for the hemiacetal dimer to react with decanal to form a hemiacetal trimer (MW 456), which contains both a hemiacetal and acetal linkage in its structure. This trimer is expected to undergo electron ionization fragmentation similar to the dimer, leading to *m/z* 157 and 313 ions as shown in Table 3.4. Thus, it appears that the TPTD peak at 77°C is due to this hemiacetal trimer, which, unlike the dimer, does not decompose during the heating process. Instead, the trimer stays intact during heating and is desorbed and ionized as a C₂₉ oligomer. One reason the hemiacetal trimer stays intact while the dimer does not, could be that the trimer contains an acetal linkage that provides added stability during the heating process.

3.3.2 Real-Time TDPBMS and TPTD Analysis of SOA formed from the Reaction of β -Pinene + NO₃ Radicals. As mentioned above, we have previously shown that ~94% mole fraction of the SOA formed from the reaction of β -pinene with NO₃ radicals consists of oligomers containing acetal linkages that are formed through particle-phase cyclization and dehydration reactions.⁹⁰ Because this aerosol is overwhelmingly comprised of heterodimers with

known structures of this type, it was chosen as a model system to study the thermal desorption characteristics of acetals and ethers. The real-time mass spectrum of the SOA is shown in Figure 3.8A. Although the SOA consists of a complex mixture of products, as shown in Table 3.1, there is a dominant product (product 1) that accounts for over 50% of the aerosol. As shown in Figure 3.4, this oligomer is formed through a dehydration reaction involving a cyclic hemiacetal (formed by cyclization of a hydroxycarbonyl) and an alcohol. The peak in the real-time mass spectrum (Figure 3.8A) at m/z 352 can be attributed to the ionization of this oligomer (MW 428) followed by neutral losses of NO_2 and CH_2O . From this example, it is apparent that when the oligomers formed through acetal linkages are analyzed in real time they are ionized as intact oligomers, similar to the hemiacetal standard.

The TPTD TIS profile of the SOA is shown in Figure 3.8B, and contains two unresolved peaks at 48 and 64°C. The mass spectra associated with the peaks at 48 and 64°C are shown in Figures 3.8C and 3.8D. Unlike the hemiacetal standard, the mass spectra of the thermally desorbed SOA components (Figures 3.8C and 3.8D) are similar to the real-time mass spectrum of the SOA (Figure 3.8A), with all three spectra showing significant signal at m/z 152, 168, 197, 214, 230, and 352. Whereas the hemiacetal dimer clearly decomposed during the TPTD analysis, in the case of the SOA the similarities between the real-time and TPTD mass spectra show that during the slow TPTD analysis the components of the SOA do not decompose and instead are thermally desorbed and ionized as intact oligomers. This difference in thermal desorption behavior between oligomers formed through acetal and linkages (SOA) versus the hemiacetal dimer can be attributed to differences in their formation reactions. Unlike hemiacetals, which are formed by reactions that only involve atomic rearrangements, these oligomers are formed through dehydration reactions. Since the reverse hydrolysis reactions that re-form monomers

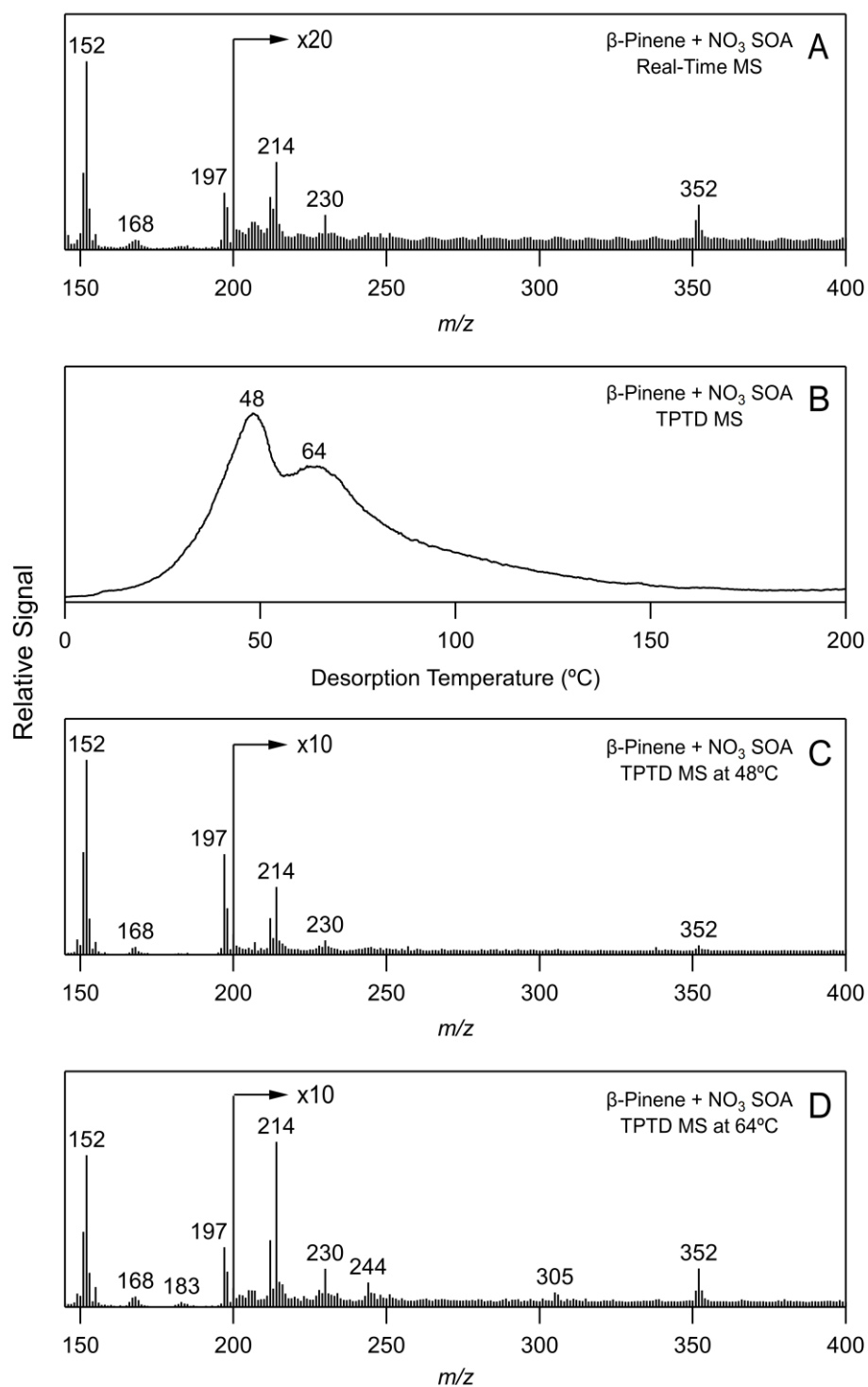


Figure 3.8. (A) Real-time electron-ionization mass spectra (B) temperature programmed thermal desorption (TPTD) total ion signal (TIS) profile and corresponding mass spectra for thermal desorption peaks at (C) 48 $^{\circ}\text{C}$ and (D) 64 $^{\circ}\text{C}$ for SOA formed from the reaction of β -pinene with NO_3 radicals.

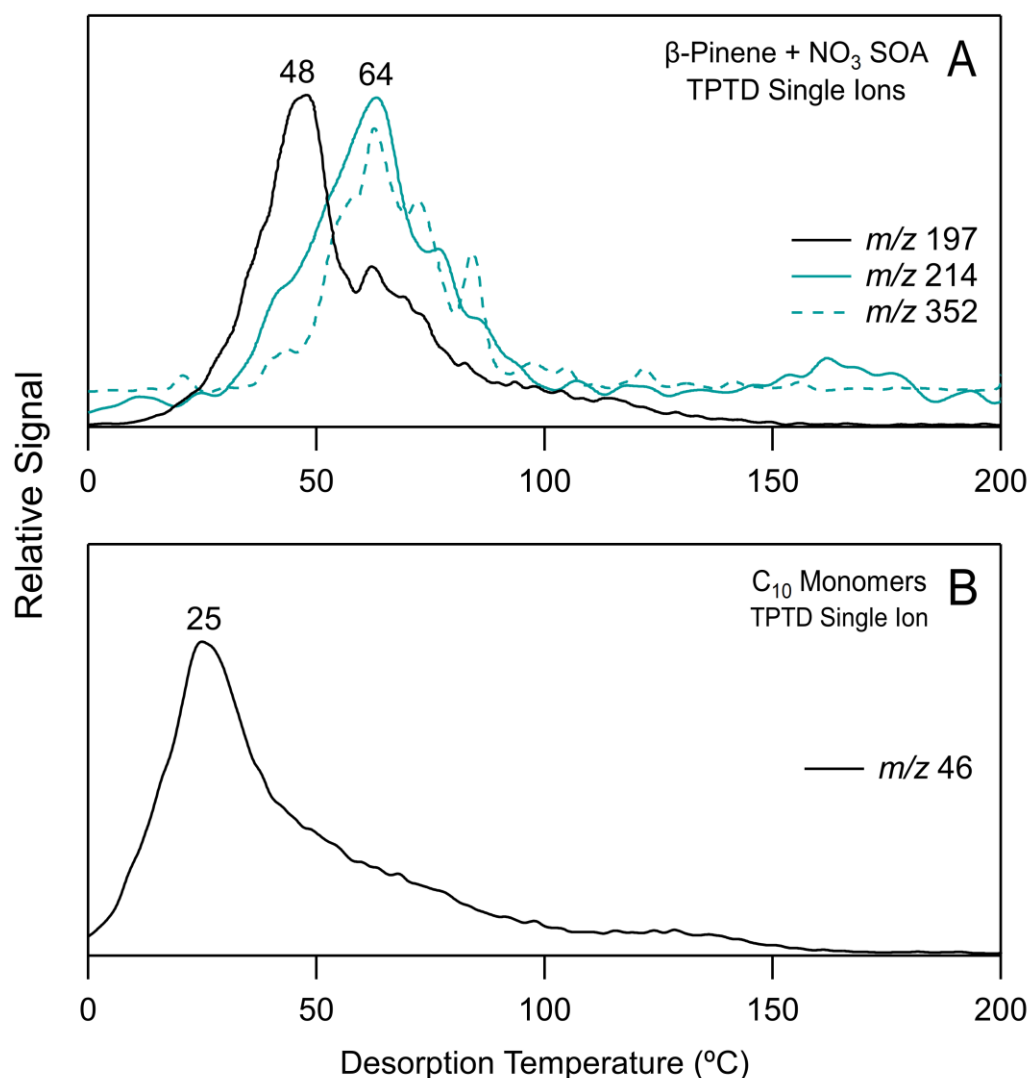


Figure 3.9. Normalized temperature programmed thermal desorption profiles of (A) SOA formed from the reaction of β -pinene with NO₃ and (C) a mixture of C₁₀ hydroxynitrate, dinitrate, and diol monomers.

require the presence of water, which is lost during sampling into the vacuum chamber and during the heating that occurs prior to compound desorption, these oligomers will not decompose to monomers. Furthermore, since in the absence of water acetals must be heated to temperatures above 400°C in order to decompose on timescales of minutes,¹⁰² the oligomers will not

decompose by other pathways prior to desorption at the much lower temperatures employed for TPTD analysis.

To further validate that the oligomer components of the SOA were not decomposing back to their monomer building blocks during TPTD analysis, a mixture of C₁₀ monomers were synthesized and analyzed by TPTD. This mixture of C₁₀ monomers consisting of a hydroxynitrate, dinitrate, and diol was chosen because the monomer building blocks in the SOA are also C₁₀ multifunctional compounds and so should have similar vapor pressures. The desorption temperature of the synthesized C₁₀ monomers was 25°C, as shown in Figure 3.9B. In this figure the m/z 46 NO₂⁺ ion was used to track desorption of the hydroxynitrate and dinitrate standards because the total ion profile was excessively noisy. Although no characteristic diol peaks could be found in the mass spectrum, because its vapor pressure is similar to that of the other two standards it should have desorbed similarly. The 25°C desorption temperature was significantly lower than those of the components of the SOA shown in Figure 3.9A, where the earliest desorption occurred at 48°C. This again suggests that the compounds in the SOA were in fact desorbing as the intact lower-volatility oligomers rather than as monomers.

3.4 Conclusions

The results of our experiments show that when hemiacetal dimers are analyzed by thermal desorption particle beam mass spectrometry in real time they are rapidly desorbed, ionized, and detected as the intact oligomer. When they are analyzed using slow thermal desorption, however, they decompose to their precursor alcohol and aldehyde before these monomers are desorbed into the ionization region. The different outcome of these analyses is clearly due to differences in desorption timescales, with only the slow thermal desorption process allowing sufficient time for the hemiacetal dimer to decompose prior to desorption. But another

factor that promotes decomposition is that the reaction that forms the monomers is simply the reverse of the reaction by which the hemiacetal dimer was formed, involving only the rearrangement of a few atoms and no additional reactants. Furthermore, because the monomers are much more volatile than the hemiacetal dimer they quickly desorb into the gas phase, thus promoting further decomposition in an attempt to maintain reaction equilibrium. In our experiments it was also observed that thermally-induced decomposition reactions of hemiacetals were highly dependent on hemiacetal structure. For although the hemiacetal dimer decomposed when it was slowly heated, the hemiacetal trimer that was formed through two hemiacetal reactions did not. This behavior indicates that the acetal linkage that is added when the trimer is formed stabilizes this oligomer against decomposition to the extent that it was desorbed and ionized as the intact trimer. This may also explain the results of our previous thermal desorption analysis of peroxyhemiacetals⁸⁴ that had an acetal linkage similar to that of the hemiacetal trimer (since they were formed from reactions of hydroperoxides that contained an α -alkoxy group) and were observed to desorb and ionize as the intact oligomer. It seems quite likely then that peroxyhemiacetals present in atmospheric SOA, which are usually formed from reactions of hydroperoxides that do not contain an α -alkoxy group, would decompose to monomers prior to desorption and ionization.

In contrast to the behavior of hemiacetal dimers, thermal decomposition was not observed when dimers or trimers containing acetal linkages were analyzed using the same methods. This is likely because the reaction by which acetals are formed involves dehydration. The reverse hydrolysis reaction to form monomers thus requires the presence of water that is not available, even when present in the sampled aerosol, since it should be rapidly lost by evaporation at low temperatures as the sample is slowly heated. Although oligomers containing

ester linkages were not studied here, because they are also formed through dehydration reactions (involving an alcohol and carboxylic acid) and have high thermal stability in the absence of water,¹⁰³ their thermal desorption behavior should be similar to that of acetals.

It appears, therefore, that if the aerosol being analyzed by thermal desorption methods contains oligomers bound by a single hemiacetal or peroxyhemiacetal linkage they will decompose to their precursors before being desorbed, and thus be detected as the original monomers. Conversely, oligomers containing more than one of these linkages, or acetal or ester linkages, will desorb intact and be detected as the oligomer. By using these insights when interpreting the results of thermal desorption analyses it may be possible to extract information about the types of linkages that bind oligomers in atmospheric SOA and the types of accretion reactions by which they were formed.

Chapter 4

Functional Group Composition of Secondary Organic Aerosol Formed from Ozonolysis of α -Pinene Under High VOC and Autoxidation Conditions

4.1 Introduction

According to global estimates approximately 1000 Tg of non-methane volatile organic compounds are emitted into the atmosphere each year, with biogenic VOCs accounting for more than two thirds of these emissions.¹¹ In the atmosphere, these VOCs can react with OH radicals, NO₃ radicals, and O₃ to form oxygenated products that can either remain in the gas phase or participate in secondary organic aerosol (SOA) growth.⁸ This SOA material contributes significantly to the mass of atmospheric fine particles,⁴ and has the potential to impact regional and global air quality, climate, and human health.² The oxidation of monoterpenes, which comprise ~15% of biogenic VOCs,¹¹ has been estimated to account for a substantial fraction of the global SOA budget.¹⁰ As a result, numerous laboratory and modeling studies have been conducted to better understand the products and mechanisms of these reactions and the chemical and physical properties of the SOA that is formed.^{10,52,104–107} Many of these studies have focused on the dominant monoterpene, α -pinene, which accounts for over 40% of global monoterpene emissions.¹¹ In particular, α -pinene ozonolysis has received the most attention, since this reaction is the major atmospheric sink for α -pinene⁷ and forms SOA in large yields.^{10,22,36} Laboratory

studies of this reaction have identified and quantified a number of gas- and particle-phase products,^{10,104,106,107} and models such as the Master Chemical Mechanism (MCM)¹⁰⁵ and Biogenic hydrocarbon Oxidation and Related Aerosol formation Model (BOREAM)⁵² have been used to simulate the reactions that lead to SOA formation for comparison with measurements of SOA yields and molecular composition. As a result of this large body of work, and in spite of the chemical complexity and general lack of knowledge of the composition of the SOA formed from α -pinene ozonolysis, this material has to a large extent become the de facto “standard SOA” for the aerosol community.

More recently, α -pinene ozonolysis has returned to the forefront of SOA research because of the detection of highly-oxygenated multifunctional compounds (HOMs) among its gas-phase products, and the demonstrated significance of these to new particle formation and growth, particularly in pristine, forested areas.^{108–112} In 2012, Ehn et al.¹⁰⁸ first reported elemental formulas for HOMs and demonstrated the use of nitrate ion chemical ionization mass spectrometry (NO₃-CIMS) as an effective method for HOM detection. In a later study of α -pinene ozonolysis, Ehn et al.¹⁰⁹ detected HOMs in the gas-phase with O/C atomic ratios > 0.7, with corresponding HOM aerosol mass yields of 14–18%, and attributed the observed rapid formation of HOMs to autoxidation reactions in which organic peroxy radicals (RO₂•) are propagated by intramolecular H-shifts that rapidly add functional groups to the molecule. The proposed role of autoxidation in HOM formation has been supported by other experimental studies as well as quantum chemical calculations that have been used to develop detailed mechanisms of HOM formation from ozonolysis of a variety of biogenic VOCs and other cyclic alkenes.^{110,113} There remains considerable uncertainty surrounding these mechanisms, however, as theory has shown that proposed RO₂• isomerization reactions would be too slow to explain the

observed rates of HOM formation from α -pinene ozonolysis because of constraints imposed by the bicyclic structure of the parent VOC.¹¹⁴ Nonetheless, these studies have provided useful guidelines in attempts to develop gas-phase mechanisms of HOM formation.^{110,113} In addition, other studies have focused on the fate of HOMs in aerosol particles,^{110,115} since they are thought to contain functional groups including peroxy-carboxyl, hydroperoxide, carbonyl, and hydroxyl,^{110,113,115} all of which make HOMs vulnerable to particle-phase reactions.^{8,36} For example, Mutzel et al.¹¹¹ investigated the effects of seed particle composition on the composition of SOA formed from α -pinene ozonolysis under conditions in which gas-phase HOMs were present. They observed carboxylic acids and short-chain carbonyls, presumably formed through decomposition of ketohydroperoxides, as well as intact HOMs, all in the particle phase. In experiments conducted under similar conditions, Krapf et al.¹¹⁵ observed significant loss of peroxides from SOA and associated decreases in SOA mass and increases in SOA oxidation state on timescales of tens of minutes.

Although considerable progress has been made in determining the products and mechanism of α -pinene ozonolysis and in identifying reactions that may lead to the formation of HOMs and SOA, detailed information on the chemical constituents, reactions, and processes that determine the composition of this SOA is still very limited. In light of these deficiencies, we have conducted a series of environmental chamber experiments to investigate the effects of VOC concentration, humidity, and particle-phase reactions on the functional group composition of SOA formed from α -pinene ozonolysis over a range of conditions, including those in which HOMs are formed. The study employs methods we have recently developed for quantifying the contributions of peroxide, ester, carbonyl, carboxyl, and hydroxyl groups to SOA formed at high³⁷ and low¹¹⁶ VOC concentrations, which helps to constrain currently available gas-phase,

autoxidation, and particle-phase reaction products and mechanisms, as well as proposed molecular structures of HOMs. This study was conducted in collaboration with Jordan Krechmer, Weiwei Hu, and Jose Jimenez at CU, Boulder.

4.2 Experimental Section

4.2.1 Chemicals. The following chemicals, with purities/grades and suppliers were used: (1S)-(-)- α -pinene (99%), tridecanoic acid (98%), 1,2-tetradecanediol (90%), benzoyl peroxide (98%), cyclohexane (99%, ACS grade) (Sigma-Aldrich); bis(2-ethylhexyl) sebecate (97%) (Fluka); 3-hexadecanone (99%) (ChemSampCo); ethyl acetate (99.5%) (EMD Millipore); 18 M Ω water purified using Milli-Q Advantage A10 water system. O₃ was generated using a BMT 802N O₃ generator with ultra-high purity (UHP) O₂ (Airgas). Chemicals used for functional group analyses have been reported previously.^{36,37,116}

4.2.2 Environmental Chamber Experiments. Two sets of α -pinene ozonolysis experiments were conducted: a set of low-VOC concentration experiments (Low-VOC) and a set of high-VOC concentration experiments (High-VOC). The Low-VOC experiments were conducted with 10 ppb α -pinene and 300 ppb O₃ in dry (<1% RH) and humid (65% RH) air, whereas the High-VOC experiments were conducted with 1 ppm α -pinene and 2 ppm O₃ in dry (<1% RH) and humid (50% and 85% RH) air. The Low-VOC experiments were conducted in one of two 20 m³ Teflon FEP chambers that are part of the recently constructed CU Chamber facility. These two chambers are fully and separately enclosed with computer-regulated temperature and humidity controls. The High-VOC experiments were conducted in an 8.0 m³ Teflon FEP chamber at room temperature. Both chambers were filled with clean, dry air (<5 ppb hydrocarbons, <1% RH) from AADCO clean air generators at room temperature (~25°C) and

pressure (~630 Torr for Boulder, CO). Chemicals were added to the chamber by evaporation from a heated glass bulb into a stream of UHP N₂ and a Teflon-coated fan was run for ~1 min after each addition to mix the chemicals. Water was added to adjust the humidity when needed, and no seed aerosol was used in the experiments. For the Low-VOC experiments 100 ppb of cyclohexane was added as an OH scavenger, and then 300 ppb of O₃ followed by 10 ppb of α -pinene to initiate the reaction. Using a simple kinetic model and published rate constants it was estimated that ~80% of the α -pinene reacted with O₃ and ~20% with OH radicals, and that only ~5% of the first-generation products reacted further with OH radicals.^{6,52,117–119} For the High-VOC experiments 1200 ppm of cyclohexane (sufficient to scavenge >99% of the OH radicals formed during the reaction)³⁶ was added, and then 1 ppm of α -pinene followed by 2 ppm of O₃ to initiate the reaction.

4.2.3 Gas Analysis. Highly oxidized gas-phase reaction products were detected in the Low-VOC experiments using an Aerodyne high-resolution time-of-flight mass spectrometer employing a nitrate-ion chemical ionization source (NO₃-CIMS). The instrument, source, and experimental configuration have been described in previous publications.^{120–123} The NO₃-CIMS was placed inside the environmental chamber enclosure so that only a short, 0.7 m $\times$ 15 mm inner diameter electropolished stainless steel inlet was needed to continuously sample 10 standard L min⁻¹ of air. The short inlet helped reduce the loss of HOMs to the inlet walls (estimated ~70% transmission). The O₃ concentration was monitored during the reaction using a Thermo Scientific 49i O₃ monitor.

4.2.4 Particle Analysis. Particle size distributions and volume concentrations were measured during each experiment using a TSI model 3080 scanning mobility particle sizer (SMPS) with a TSI model 3775 condensation particle counter. Submicron non-refractory organic

aerosol (OA) was measured using an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS)¹²⁴ with a newly designed capture vaporizer.^{125,126} Elemental O/C and H/C atomic ratios of total OA were calculated according to the laboratory calibration for a standard vaporizer.^{127,128} Differences between the standard and capture vaporizers were accounted for using results from a comparison of measurements made with collocated AMSs with both vaporizers during the 2013 SOAS field study, which was dominated by biogenic SOA.^{129,130} The uncertainty of elemental ratios is estimated as $\pm 28\%$ for O/C and $\pm 14\%$ for H/C.¹²⁸

Two replicate SOA samples were collected after each experiment onto pre-weighed filters (Millipore Fluoropore PTFE, 0.45 μm) for 120 min at a flow rate of 14 L min⁻¹. Immediately after sampling the filters were reweighed to determine the mass of SOA collected. Filters were weighed to $\pm 0.5 \mu\text{g}$ using a Mettler Toledo XS3DU Microbalance. Filter samples were extracted twice into 5 mL of ethyl acetate each time within 10 min after sampling. Extracts were then combined in a pre-weighed vial and dried in a stream of UHP N₂ and the vial was reweighed to determine the extracted SOA mass. Comparison of collected and extracted SOA masses indicated extraction efficiencies were $>95\%$. The dried SOA was reconstituted in ethyl acetate to achieve a sample concentration of 1 $\mu\text{g } \mu\text{L}^{-1}$ for subsequent functional group analysis and stored at -20°C between analyses. SOA functional group composition was quantified using the micro-methods described by Ranney and Ziemann¹¹⁶ for the Low-VOC experiments and using the macro-methods described by Aimanant and Ziemann³⁷ and Docherty et al.³⁶ for the High-VOC experiments. These two methods differ primarily in the amounts of reagents and sample used and have been previously compared for standards and SOA and give similar results.¹¹⁶ Benzoyl peroxide, bis(2-ethylhexyl) sebacate, 3-hexadecanone, tridecanoic acid, and

1,2-tetradecanediol were employed as surrogate standards for peroxide, ester, carbonyl, carboxyl, and hydroxyl groups, respectively.

The SOA mass yield was quantified as the mass of SOA formed divided by the mass of α -pinene reacted. The mass of SOA formed was calculated from the filter mass measurements with correction for particle wall loss using SMPS measurements and the method described in Yeh et al.³² No attempt was made to correct yields for loss of gas-phase products to the chamber walls.^{112,131} Although such losses may have been significant in the Low-VOC experiments where SOA mass concentrations were small, no modeling was conducted for those experiments (for reasons described below) that could have attempted to account for these losses. And although modeling was conducted in the High-VOC experiments, the online version of the Master Chemical Mechanism that was used does not include gas-wall partitioning. This is unlikely to have had a major impact on the results, since most semivolatile products should have quickly partitioned to the SOA that was present at very high mass concentrations before they could partition to the walls.¹²³ Because of the concentrations of O₃ used in these experiments and the large excess relative to α -pinene, the lifetime of α -pinene was sufficiently short (about 5 and 25 min for the High-VOC and Low-VOC experiments) that essentially all α -pinene reacted prior to filter sampling. For this reason the concentration of α -pinene reacted was assumed to be equal to the initial added concentration.

4.2.5 Description of Functional Group Composition and Other Properties of SOA.

The functional group composition of SOA was expressed as the average number of each measured functional group per parent VOC molecule,³⁷ assuming that the SOA contained only peroxide [CHOOH], ester [C(O)O], carbonyl [C(O)], carboxyl [C(O)OH], hydroxyl [CHOH], and methylene [CH₂] groups. This composition was determined by first summing the masses of

measured functional groups, calculated as the measured moles $\times$ molecular weight (g mol^{-1}) of each group: peroxide = 46, ester = 44, carbonyl = 28, carboxyl = 45, hydroxyl = 30. The moles of methylene groups were then obtained by subtracting this sum from the measured SOA mass and dividing by 14, the molecular weight of CH_2 . Molar concentrations of functional groups were used to calculate mole fractions, which were then multiplied by 10, the carbon number of α -pinene, to obtain the number of functional groups per C_{10} molecule in SOA.

The uncertainties in the functional group measurements were estimated as standard deviations calculated from analyses conducted for each of four replicate dry (0% RH) Low-VOC experiments, three replicate humid (65% RH) Low-VOC experiments, and the single experiments conducted for each of the High-VOC conditions (0%, 50%, and 85% RH) where two replicate samples from each experiment were analyzed. In addition, there are inherent uncertainties in the analyses that stem from differences in the molar absorptivity of derivatized SOA compounds and the surrogate standards used for quantification. Previous studies conducted with a large variety of monofunctional and multifunctional compounds indicate that these uncertainties are approximately ($\pm$) 10%, 30%, 10%, 20%, and 20% for peroxide, ester, carbonyl, carboxyl, and hydroxyl groups.^{37,49}

The measured functional group composition was used to calculate the O/C and H/C ratios, molecular weight, and the saturation concentration of the SOA, with the latter calculation employing SIMPOL.1⁸⁸ to estimate effects of functional groups on compound vapor pressure. The density of the SOA was estimated using O/C and H/C ratios and the parameterization of Kuwata et al.⁸⁰ The SOA molar yield (moles of SOA formed/moles of α -pinene reacted) was calculated by dividing the mass yield (mass of SOA formed/mass of α -pinene reacted) by the molecular weight of the SOA calculated from the functional group composition.

4.2.6 Modeling Functional Group Composition and Other SOA Properties. Our experimental results for the High-VOC experiments were compared with results of simulations conducted using the Master Chemical Mechanism (MCM, <http://mcm.leeds.ac.uk/MCM>),^{132,133} which is widely used for atmospheric chemistry modeling. The MCM was not used to simulate the results of the Low-VOC experiments because it does not include autoxidation reactions and gas-wall partitioning that are expected to have major effects on the SOA composition due to the lower RO₂^{*} radical and SOA mass concentrations. The model predicts an array of gas-phase products that contain hydroperoxide, peroxy-carboxyl, carbonyl, carboxyl, ester, and hydroxyl groups. While all products produced in the model were tracked, only products that had molar yields above 1% were used to estimate SOA composition. These compounds accounted for 96% of the total carbon reacted in the High-VOC modeled system.

We note that one modification was made to the model with regard to the fate of stabilized Criegee intermediates (SCI). In the MCM it is always assumed that SCI react with water vapor (their most common fate in the atmosphere) to form a hydroxy hydroperoxide that then decomposes to pinonaldehyde or pinonic acid, even though under dry conditions SCI will react with aldehydes to form secondary ozonides and with carboxylic acids to form hydroperoxy esters.^{6,134} The major small aldehydes formed in the ozonolysis of α -pinene are formaldehyde and acetaldehyde, and the major small carboxylic acids are formic and acetic acid, with reported measured molar yields of 30%, 3%, 8%, and 8%, respectively.¹⁰⁶ In addition, the MCM predicts that under High-VOC conditions pinonic acid, pinic acid, hydroxy pinonic acid, and a C₉ aldo-acid are formed with molar yields of 10%, 3%, 2%, and 6%, respectively. These larger carboxylic acids are important for modeling the fate of SCI in the dry High-VOC reaction, since it has been shown that large carboxylic acids (heptanoic acid) react ~2.5 times faster than small

carboxylic acids (formic acid) and ~6 times faster than small aldehydes (formaldehyde).¹³⁴ In our modeling the yields given above were used with relative rate constants¹³⁴ for reactions of SCI to estimate the yields of products formed in the dry reaction, whereas under humid conditions the SCI were assumed to react with water vapor to form hydroxy hydroperoxides that did not decompose to pinonaldehyde and water, consistent with our previous studies of these types of compounds.¹³⁵ We also added the “hot-acid” decomposition of ECIs for both dry and humid conditions, which has been shown to result in an ~8% yield of pinonic acid⁵² but is not included in the MCM.

Once the molar yields of all the gas-phase products were calculated at the end of the reaction, particle-phase molar yields were calculated using an iterative procedure¹³⁶ in which the fraction of each compound that partitioned into particles was estimated using gas-particle partitioning theory¹³⁷ with vapor pressures calculated using the SIMPOL.1 group contribution method⁸⁸ and activity coefficients were assumed to be unity (since the partitioning medium was formed from all partitioned molecules and thus was similar in chemical character). The SOA mass concentration and mean molecular weight were initially taken to be the measured values, though subsequent tests verified that the calculation converges to the same equilibrium yields regardless of the initial values. The particle-phase molar yields were used to calculate SOA molar yields of peroxide, carbonyl (aldehydes + ketones), carboxyl, hydroxyl, ester, and methylene groups; and the total SOA molar and mass yields. The calculated functional group composition was then used in the same way as the measured values to calculate SOA O/C and H/C ratios, molecular weight, saturation concentration, and density.

4.3 Results and Discussion

4.3.1 Mechanism of Formation of SOA from the Reaction of α -Pinene with O_3 . To interpret the functional group composition of SOA formed in these experiments, it is necessary to first understand the major gas- and particle-phase reactions by which each of the quantified functional groups can be added to products. Although the full mechanism of the reaction of α -pinene with O_3 is not yet understood, most of the basic reaction pathways that can lead to the addition of specific groups are reasonably well known.⁸ In Figures 4.1 and 4.2 we show examples of pathways that can lead to the addition of peroxide (hydroperoxide, dialkyl peroxide, peroxy-carboxyl, secondary ozonide), carbonyl (aldehyde, ketone), hydroxyl, carboxyl, and ester groups. It is also important to remember that the functional group composition of the SOA depends not only on gas- and particle-phase reactions, but also gas-particle partitioning and therefore compound vapor pressure. According to the SIMPOL.1 group contribution method,⁸⁸ hydroperoxide, dialkyl peroxide, aldehyde, ketone, hydroxyl, carboxyl, and ester groups reduce compound vapor pressures by factors of about 300, 2, 20, 10, 200, 4000, and 20, respectively.

4.3.1.1 Gas-Phase Reactions. The proposed initial steps in the reaction of α -pinene with O_3 (with estimated branching ratios) are shown in Figure 4.1.^{6,52} The reaction is initiated by the addition of O_3 to the C=C double bond to form an unstable primary ozonide, which rapidly decomposes equally to form two excited Criegee intermediates (ECI 1 and 2) that contain both a carbonyl and carbonyl oxide group. The ECI can be collisionally stabilized to form stabilized Criegee intermediates (SCI 1 and 2), or they can undergo isomerization or decomposition reactions through the vinyl hydroperoxide (VHP) pathway to produce organoperoxy radicals (RO_2^* 1, 2, and 3) + OH radicals.⁵² It is estimated that ~77% of ECI undergo isomerization or decomposition through the VHP pathway to yield RO_2^* radicals, while the rest are stabilized to

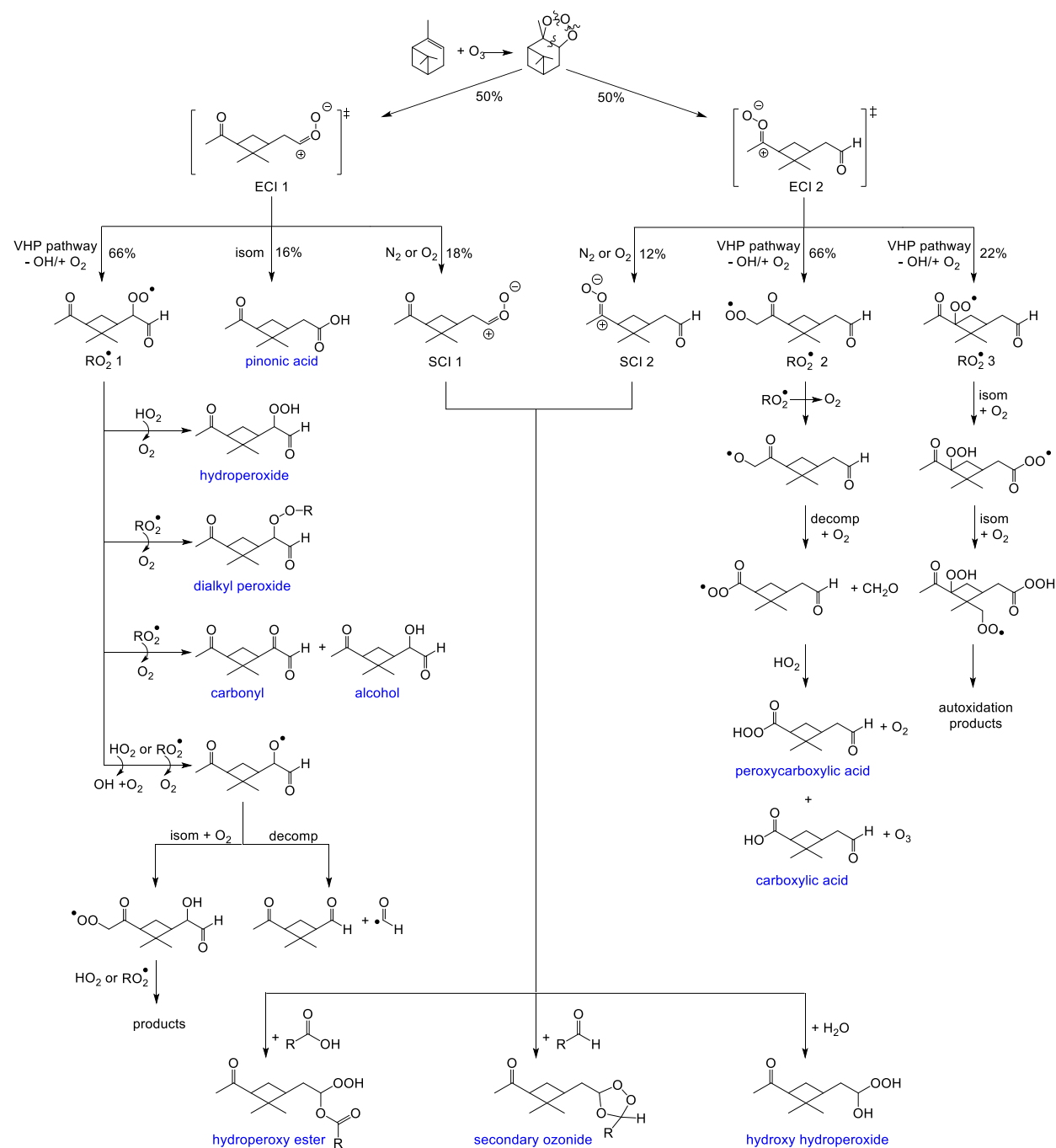


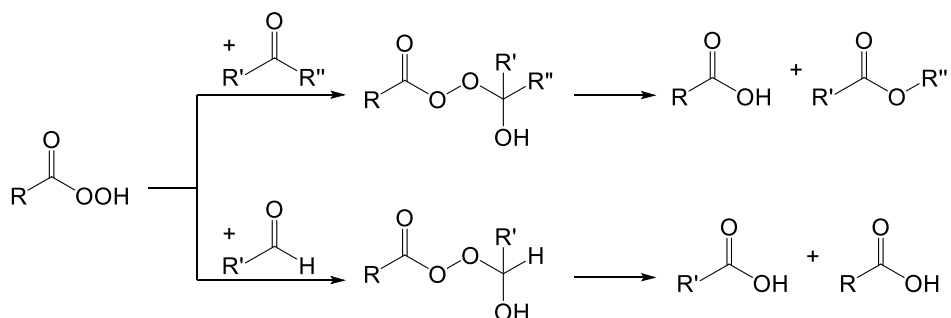
Figure 4.1. The formation mechanism of the SCI and $RO_2^{\bullet}$ radicals from the ozonolysis of α -pinene. Only syn ECI and SCI isomers are shown, and labeled branching ratios are from Capouet et al.⁵² The generation of the different functional groups are shown through subsequent reactions of the SCI and $RO_2^{\bullet}$ radicals.

SCI (~15%) or isomerize to pinonic acid (~8%).^{6,52,118,119} As noted above, in the High-VOC experiments all of the α -pinene reacted with O_3 , whereas in the Low-VOC experiments ~80% reacted with O_3 and ~20% with OH radicals formed in the reaction. Thus in the Low-VOC experiments ~25% of the $RO_2^{\bullet}$ radicals would have somewhat different structures from those shown in Figure 4.1, although many of the subsequent reaction pathways should be similar. Furthermore, as was also discussed above, in the dry experiments the SCI react with carboxylic acids and aldehydes to form hydroperoxy esters and secondary ozonides, whereas under humid conditions they react with water vapor to form hydroxy hydroperoxides.

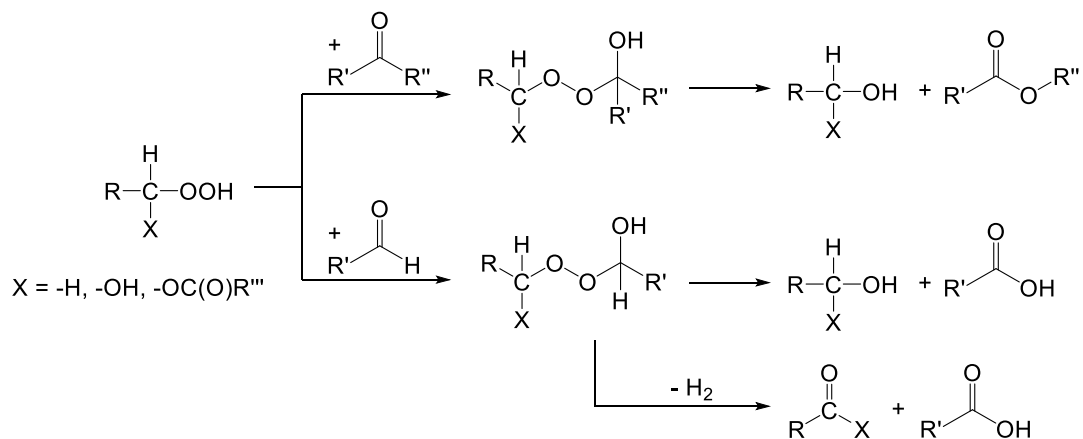
The reactions of $RO_2^{\bullet}$ radicals and resulting products depend on the VOC and NO_x concentration regimes. When NO_x concentrations are sufficiently low (as in these experiments), $RO_2^{\bullet}$ radicals react with HO_2 or $RO_2^{\bullet}$ radicals or they undergo intramolecular H-shift isomerization reactions. Reactions with HO_2 can form hydroperoxides, peroxy-carboxylic acids, or carboxylic acids, whereas reactions with $RO_2^{\bullet}$ radicals can form dialkyl (or diacyl or mixed alkyl-acyl) peroxides, carbonyls, or alcohols.⁸ Reactions with HO_2 or $RO_2^{\bullet}$ radicals can also form alkoxy radicals ($RO^{\bullet}$), which will either decompose to form carbonyls + alkyl (or acyl) radicals, or isomerize and add O_2 to form hydroxyperoxy radicals, depending on the structure of the molecule.^{56,57} Isomerization of $RO_2^{\bullet}$ radicals leads to the addition of hydroperoxide or peroxy-carboxyl groups by chain propagation and carbonyl groups by chain termination, and are presumed to be the route by which HOMs are formed. These so-called autoxidation pathways propagate the radical species and rapidly add multiple functional groups to the molecule.^{13,110,113}

4.3.1.2 Particle-Phase Reactions. The mechanisms of the major particle-phase reactions expected to contribute to SOA formation are shown in Figure 4.2. These include Baeyer-Villager reactions in which peroxy-carboxylic acids and hydroperoxides react with carbonyls to form

peroxycarboxyl acid + carbonyl $\longrightarrow$ acylperoxy hemiacetal $\longrightarrow$ carboxylic acid + ester



hydroperoxide + carbonyl $\longrightarrow$ peroxyhemiacetal $\longrightarrow$ alcohol + carboxylic acid + ester + aldehyde



alcohol + carbonyl $\longrightarrow$ hemiacetal $\longrightarrow$ acetal

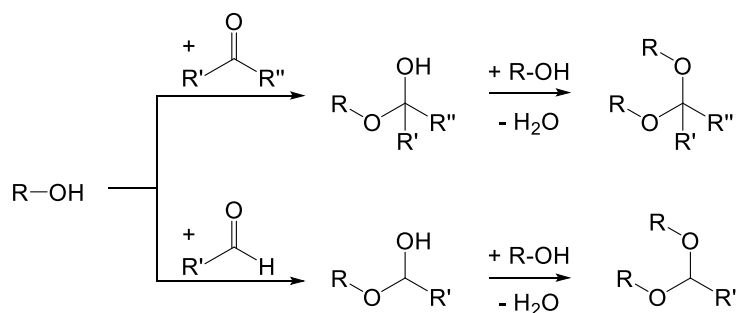


Figure 4.2. Particle-phase reactions of peroxycarboxyl, hydroperoxy, and hydroxyl groups with aldehydes and ketones resulting in the formation of carboxyl, ester, and hydroxyl groups along with acylperoxy hemiacetal, peroxyhemiacetal, hemiacetal, and acetal oligomers.

acylperoxy hemiacetals and peroxy hemiacetals that decompose to carboxylic acids, esters, and alcohols; and reactions of alcohols and carbonyls to form hemiacetals and acetals.^{8,53,54,138} As discussed above, when hydroperoxy esters and hydroxy hydroperoxides (formed from reactions of SCI with carboxylic acids or with water, respectively), undergo these particle-phase reactions they are converted to hydroxy esters and gem-diols, with the latter decomposing to water and pinonaldehyde that should evaporate from the SOA either in the chamber or during filter sampling. On the basis of a number of studies that have employed mass spectrometry to show that oligomers contribute significantly to the SOA formed from α -pinene ozonolysis,^{36,91,94} particle-phase reactions are expected to be important in the experiments conducted here.

4.3.2 Interpretation of Functional Group Composition of SOA. The SOA is composed of compounds with a range of carbon numbers, which is not determined in our analyses. For presentation purposes the composition is therefore reported as the average number of each functional group per C₁₀ molecule, the carbon number of α -pinene. Using this approach, our analysis of the functional group composition provided the following information about the SOA: (1) number of each functional group per C₁₀ molecule, (2) total number of functional groups per C₁₀ molecule, (3) total number of oxygen atoms per C₁₀ molecule, and (4) O/C and H/C atomic ratios.

It is important to note here, since it may not be immediately apparent, that the total number of functional groups in a molecule is determined predominantly by gas-phase reactions (Figure 4.1), with particle-phase reactions mostly serving to convert one type of functional group to another, usually through H-atom and/or O-atom transfer (Figure 4.2). This is always the case when reactions of peroxy-carboxylic acids or hydroperoxides with carbonyls go to completion (Baeyer-Villiger reactions), thereby forming the same number of products as reactants (Figure

4.2), but it does not necessarily hold when stable oligomers are formed that do not decompose to a pair of products. In the latter case the outcome depends on the type of oligomer formed, since they can affect the analysis of functional groups in different ways. We can summarize possible effects or non-effects of the oligomers shown in Figure 4.2 on functional group analyses^{37,116} as follows: (1) ester and carboxyl groups are accurately quantified since they do not participate in the oligomer formation/dissociation equilibria; (2) peroxide groups are accurately quantified regardless of oligomer formation/dissociation equilibria; (3) secondary ozonides, hemiacetals, and acetals (other than those formed from cyclic hemiacetals) are hydrolyzed to the original monomers during carbonyl analysis, so the carbonyl groups in the monomers are quantified; (4) hydroxyl groups are accurately quantified in hemiacetals regardless of the formation/dissociation equilibrium, but are not quantified if peroxy or acylperoxy hemiacetals dissociate to the original monomers; and (5) acylperoxy groups are accurately quantified in both carboxyl and peroxide analysis, but because of the short lifetime of acylperoxy hemiacetals¹³⁸ they likely decompose irreversibly prior to analysis. Furthermore, we note that although the measured functional group composition of SOA is affected by particle-phase reactions that occur in the chamber and during filter sampling, the types of reactions and products should be similar regardless of where they occur. This should be the case for reactions that might occur during filter extraction and functional group analysis as well, with the most likely changes being due to dissociation of oligomers to the original monomers upon dilution in solvents.

4.3.3 High-VOC Experiments. These experiments were conducted with a high concentration of α -pinene (1 ppm) and excess O₃ (2 ppm) in order to achieve a lifetime for α -pinene of ~5 min and thus reduce the loss of products by gas-wall partitioning that would occur on a similar timescale in the absence of particles¹²² but on a much longer timescale at the high

SOA mass concentrations achieved here.¹²³ Under these conditions products formed through $\text{RO}_2^\bullet + \text{RO}_2^\bullet$ or $\text{RO}_2^\bullet + \text{HO}_2$ reactions should be enhanced relative to Low-VOC conditions because of the shorter bimolecular reaction timescales, and the autoxidation reactions (which are not included in the MCM model) that lead to HOMs are expected to be less important. Nonetheless, one should keep in mind that although the SOA composition simulated using the MCM model provides a useful starting point for interpreting the measurements, the comparison has a number of limitations: (1) the α -pinene + O_3 reaction mechanism is based on poorly constrained reaction rate constants and branching ratios; (2) estimated vapor pressures used to calculate gas-particle partitioning of multifunctional compounds can be in error by 1–2 orders of magnitude; (3) the model does not include multiphase chemistry; and (4) the model predicts the SOA composition at the end of the reaction (~ 10 min), whereas the SOA composition was measured on filter samples collected over 120 min and during which time particles in the chamber were subject to losses of semivolatile products due to gas-particle-wall partitioning.

The results of measurements and MCM modeling of the functional group composition and other properties of SOA formed in the High-VOC experiments conducted in dry ($\sim 0\%$ RH) and humid (50% and 85% RH) air are shown in Figure 4.3 and listed in Table 4.1. Model results are reported for dry/humid conditions, since results for 50% and 85% RH were essentially the same. Similarly, since measured values for all functional groups except esters showed no clear trend with RH, in the following discussion average measured values are also presented for dry/humid conditions, where the humid values are the average for 50% and 85% RH. Results for all experiments are given in Table 4.2.

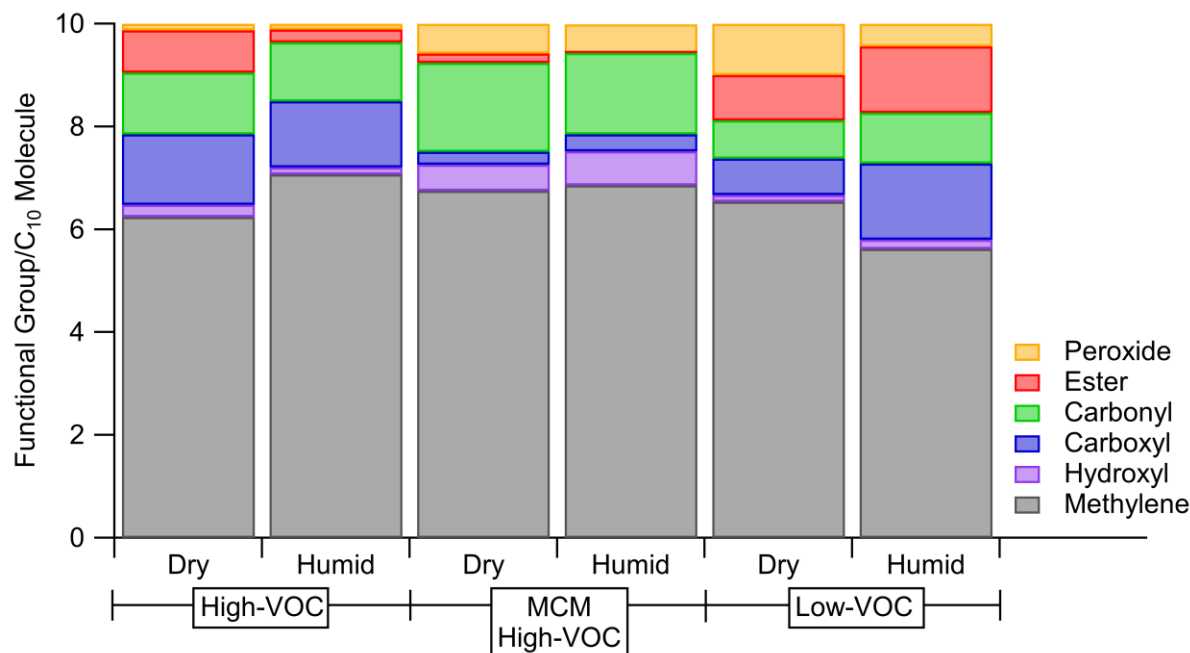


Figure 4.3. Results of measurements and MCM modeling of the functional group composition of SOA formed from reactions of α -pinene with O_3 under a variety of conditions.

4.3.3.1 SOA Functional Group Composition. The number of functional groups per C_{10} molecule measured for dry/humid conditions were as follows: 0.13/0.11 peroxide, 0.82/0.25 ester, 1.20/1.15 carbonyl, 1.37/1.28 carboxyl, and 0.24/0.14 hydroxyl, for a total of 3.76/2.93 and thus 6.24/7.07 methylene groups, whereas the number obtained from the MCM model was in general quite different: 0.58/0.56 peroxide, 0.18/0.00 ester, 1.73/1.58 carbonyl, 0.25/0.33 carboxyl, and 0.51/0.66 hydroxyl, but with similar totals of 3.25/3.14 and thus 6.75/6.86 methylene groups. The measurements show that the SOA composition was dominated by carbonyl and carboxyl groups, with far fewer peroxide, ester, and hydroxyl groups; and that except for esters humidity had little effect on the functional group composition. The measured 3.76/2.93 functional groups is consistent with the 3.25/3.14 functional groups predicted by the MCM model for products of $RO_2^\bullet + RO_2^\bullet$ and $RO_2^\bullet + HO_2$ reactions, with the presence of more

Table 4.1. Results of measurements and MCM modeling of the functional group composition and other properties of SOA formed from reactions of α -pinene with O_3 under a variety of conditions.

Functional Group	High-VOC			Low-VOC	
	Measurement		Model	Measurement	
	Dry	Humid	Dry/Humid	Dry	Humid
Functional Group	Functional Group/ C_{10} Molecule ^a				
Peroxide [HCOOH]	0.13 ± 0.04	0.11 ± 0.02	0.58/0.56	1.00 ± 0.01	0.44 ± 0.2
Ester [O=COR]	0.82 ± 0.04	0.25 ± 0.06	0.18/0.00	0.88 ± 0.1	1.29 ± 0.1
Carbonyl [C=O]	1.20 ± 0.04	1.15 ± 0.2	1.73/1.58	0.74 ± 0.1	0.99 ± 0.2
Carboxyl [O=COH]	1.37 ± 0.1	1.28 ± 0.1	0.25/0.33	0.71 ± 0.03	1.48 ± 0.4
Hydroxyl [HCOH]	0.24 ± 0.02	0.14 ± 0.1	0.51/0.66	0.13 ± 0.04	0.18 ± 0.1
Total FG	3.76 ± 0.1	2.93 ± 0.3	3.25/3.14	3.46 ± 0.1	4.38 ± 0.5
Methylene [CH ₂]	6.24 ± 0.1	7.07 ± 0.3	6.75/6.86	6.54 ± 0.1	5.62 ± 0.5
O/C	0.61 ± 0.05	0.46 ± 0.09	0.43/0.40	0.61 ± 0.06	0.76 ± 0.23
H/C	1.46 ± 0.13	1.59 ± 0.22	1.59/1.65	1.60 ± 0.08	1.40 ± 0.56
MW	232 ± 1	209 ± 3	204/201	233 ± 1	255 ± 14
C* ($\mu\text{g m}^{-3}$)	1 ± 0.2	6 ± 2	70/40	2 ± 0.5	0.02 ± 0.01
Density (g/mL)	1.38 ± 0.03	1.24 ± 0.05	1.22/1.19	1.33 ± 0.02	1.49 ± 0.13
SOA Mass Yield	0.78 ± 0.04	0.45 ± 0.05	1.1/1.1	0.22 ± 0.03	0.24 ± 0.03
SOA Molar Yield	0.45 ± 0.02	0.30 ± 0.03	0.77/0.78	0.13 ± 0.01	0.13 ± 0.02

^aUncertainties are standard deviations calculated from replicate experiments.

Table 4.2. Functional group composition of SOA formed from reactions of α -pinene with O_3 under High-VOC conditions.

	Dry	High-VOC	
		Humid 50%	Humid 85%
Functional Group	Functional Group/ C_{10} Molecule ^a		
Peroxide [HCOOH]	0.13	0.09	0.12
Ester [O=COR]	0.82	0.27	0.23
Carbonyl [C=O]	1.20	0.95	1.34
Carboxyl [O=COH]	1.37	1.22	1.33
Hydroxyl [HCOH]	0.24	0.06	0.21
Total FG	3.76	2.59	3.22
Methylene [CH ₂]	6.24	7.41	6.78
O/C	0.61	0.42	0.49
H/C	1.46	1.63	1.55
MW ^a	232	203	214
C* ($\mu\text{g m}^{-3}$)	1	20	2
Density ^b (g/mL)	1.38	1.20	1.27
SOA Mass Yield ^c	0.78	0.41	0.48
SOA Molar Yield ^d	0.45	0.27	0.31

^a Average MW (g mol^{-1}) per C_{10} molecule calculated using the FG data.

^b Density of the SOA calculated using the methods of Kuwata et al.⁸⁰

^c SOA mass yield calculated by combining filter mass data with SMPS volume data to correct for wall loss.

^d SOA molar yield calculated using the SOA mass yield (e) and reported average MW of products.

Table 4.3. Functional group composition of SOA formed from reactions of α -pinene with O₃ under Low-VOC conditions.

	Low-VOC						
	Dry I	Dry II	Dry III	Dry IV	Humid I	Humid II 65%	Humid III
Functional Group	Functional Group/C ₁₀ Molecule						
Peroxide [HCOOH]	1.00	1.00	1.00	1.01	0.64	0.36	0.32
Ester [O=COR]	0.77	0.87	1.01	0.89	1.37	1.19	1.32
Carbonyl [C=O]	0.73	0.67	0.64	0.91	1.21	0.71	1.06
Carboxyl [O=COH]	0.69	0.70	0.74	0.71	2.01	1.18	1.24
Hydroxyl [HCOH]	0.13	0.18	0.08	0.13	0.13	0.15	0.26
Total FG	3.32	3.43	3.47	3.65	5.36	3.59	4.20
Methylene [CH ₂]	6.68	6.57	6.53	6.35	4.64	6.41	5.80
O/C	0.58	0.60	0.61 0.58 ^a	0.63	0.94	0.63 0.58 ^a	0.71 0.50 ^a
H/C	1.63	1.62	1.60 1.60 ^a	1.57	1.28	1.50 1.70 ^a	1.40 1.67 ^a
MW ^b	229	232	236	236	283	236	247
C* ($\mu\text{g m}^{-3}$)	30	20	20	10	2×10^{-5}	1	0.1
Density ^c (g/mL)	1.30	1.32	1.34	1.35	1.64	1.38	1.46
SOA Mass Yield ^d	0.26	0.20	0.23	0.20	0.25	0.26	0.21
SOA Molar Yield ^e	0.15	0.12	0.13	0.12	0.12	0.15	0.12

^a O/C and H/C ratios measured by online HR-ToF-AMS.

^b Average MW (g mol⁻¹) per C₁₀ molecule calculated using the FG data.

^c Density of the SOA calculated using the methods of Kuwata et al.⁸⁰

^d SOA mass yield calculated by combining filter mass data with SMPS volume data to correct for wall loss.

^e SOA molar yield calculated using the SOA mass yield (e) and reported average MW of products.

than 3 functional groups in a product indicating the occurrence of either alkoxy or $\text{RO}_2^\bullet$ radical isomerization by a pathway other than abstraction of an aldehydic H atom, which does not add a functional group (Figure 4.1).

As can be seen in Figure 4.1 and in the MCM results for carbonyls (1.73/1.58), the products are generally predicted to contain 1–3 carbonyl groups per molecule, on average significantly more than the measured values of 1.20/1.15. This discrepancy can be explained by the occurrence of particle-phase reactions in which aldehyde and ketone groups are oxidized to carboxyl and ester groups, respectively, by Baeyer-Villiger reactions involving hydroperoxide or peroxy-carboxyl groups (Figure 4.2) formed by $\text{RO}_2^\bullet + \text{HO}_2$ or $\text{RO}_2^\bullet$ radical isomerization reactions. Such reactions also help to explain the presence of 1.37/1.28 carboxyl groups and 0.82/0.25 ester groups per C_{10} molecule. Although carboxyl groups can be formed in the gas-phase through the “hot-acid” decomposition channel to form pinonic acid, and through reactions of acylperoxy radicals with HO_2 , the contribution of carboxyl groups to SOA predicted by the MCM model is only 0.25/0.33 per C_{10} molecule. Furthermore, the only known gas-phase mechanism for forming esters in these experiments is the reaction of SCI with carboxylic acids under dry conditions (which we added to the MCM model used here), although they can be formed by ozonolysis of dihydrofurans formed from cyclization and dehydration of hydroxycarbonyls in the presence of strong acid,⁸ and Müller et al.¹³⁹ have suggested that the esters they identified by mass spectrometry in SOA formed by α -pinene ozonolysis might be formed by an unknown gas-phase radical mechanism. The MCM model thus under-predicts the number of ester groups measured per C_{10} molecule for both dry (0.18 compared to 0.82) and humid (0.00 compared to 0.25) conditions, although the predicted value of 0.18 due the reaction of SCI with carboxylic acids does account for some of the increase in measured ester groups

from humid (0.25) to dry (0.82) conditions and could be more if the SCI yield is closer to 0.30 rather than the value of 0.15 used in the MCM.¹⁴⁰ We also note that esters could not have been formed via particle-phase decarboxylation of diacyl peroxides, as proposed by Zhang et al.,¹⁴¹ since this requires an ionic aerosol matrix such as aqueous ammonium sulfate that was not present in our experiments. It thus appears that particle-phase oxidation of carbonyl groups contributes significantly to the formation of both carboxyl and ester groups in the SOA.

The peroxides that are formed in the gas phase and can subsequently oxidize carbonyl groups include peroxydicarboxylic acids, hydroperoxides, hydroperoxy esters, and hydroxy hydroperoxides (Figures 4.1 and 4.2). The low peroxide content of the SOA of 0.13/0.11 peroxide groups per C₁₀ molecule compared to the MCM predictions of 0.58/0.56 is consistent with significant loss of these compounds due to particle-phase reactions, which can occur on timescales of a few hours or less.^{115,138} The peroxides detected in the SOA may thus be residuals of these compounds or they may be relatively non-reactive dialkyl (or diacyl) peroxides formed with low yields (Figure 4.1) that are not included in the MCM. These peroxides are known to be stable against thermal decomposition below ~100°C, and were not exposed to strong acid that could catalyze decomposition.^{84,135,142,143}

The number of hydroxyl groups measured in SOA was also small, 0.24/0.14 per C₁₀ molecule compared to 0.51/0.66 for the MCM model, indicating that the role of RO₂• + RO₂• or alkoxy radical isomerization reaction pathways by which they could have been formed (Figure 4.1) was less than that predicted by the MCM model. It is also possible, however, that particle-phase formation of acetals acted as a sink for hydroxyl groups (two hydroxyl groups are lost per one acetal formed in Figure 4.2), since acetals are not hydrolyzed back to alcohols under the basic conditions of the hydroxyl group analysis.³⁷

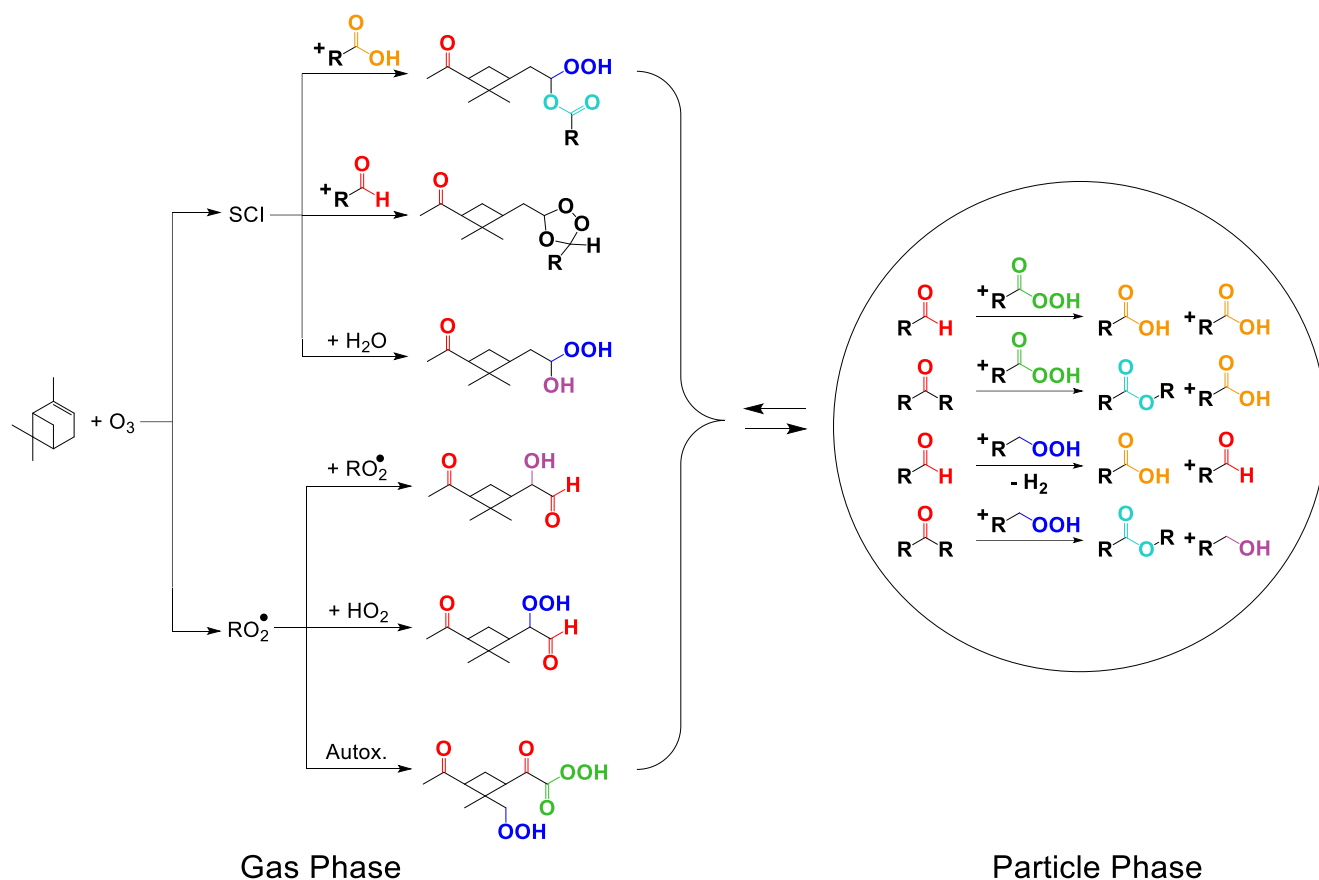


Figure 4.4. A simplified schematic showing the formation of functional groups through gas-phase chemistry, and their possible fate once they partition into the aerosol and are vulnerable to particle-phase reactions that alter their functionality.

The general gas- and particle-phase reactions that lead to formation and loss of the functional groups measured here are summarized in Figure 4.4. This scheme is relevant for both the High-VOC and Low-VOC reaction regimes, the latter of which will be discussed below.

4.3.3.2 Other SOA Properties and Yields. The O/C and H/C ratios, molecular weight, saturation concentration, and density calculated from the measured functional group composition for the dry/humid reactions were 0.61/0.46 and 1.46/1.59, 232/209 g mol⁻¹, 1/6 µg m⁻³, and 1.38/1.24 g cm⁻³, whereas the corresponding values obtained from the MCM model were 0.43/0.40 and 1.59/1.65, 204/201 g mol⁻¹, 70/40 µg m⁻³, and 1.22/1.19 g cm⁻³. The differences in

the measured values for dry and humid reactions are in general a reflection of the larger number of functional groups in SOA formed in the dry (3.76) compared to humid (2.93) experiments, which led to higher O/C and lower H/C ratios, higher molecular weight and density, and lower saturation concentration. Differences in the MCM model predictions are small for the dry and humid experiments, due to the similar functional group compositions. For comparison, after correcting for AMS calibration¹²⁸ the O/C and H/C ratios extrapolated to high mass loadings reported by Kuwata et al.⁸⁰ for this reaction under dry conditions were 0.48 and 1.63, and their measured particle density was 1.25 g cm⁻³.

The measured SOA mass and molar yields for the dry/humid reactions were 0.78/0.45 and 0.45/0.30, whereas those obtained from the MCM model were 1.1/1.1 and 0.77/0.78. The measured SOA molar yields mean that 45% and 30% of the α -pinene molecules that reacted formed SOA products under dry and humid conditions, with the rest either remaining in the gas phase or partitioning to the Teflon chamber walls.^{122,123,131} The significantly higher SOA yield measured for the dry (0.78) compared to humid (0.45) conditions is probably due to the differences in the fates of the hydroperoxy esters and hydroxy hydroperoxides formed from the reactions of SCI under dry and humid conditions, respectively. Although both of these products will partition to the particle phase and apparently undergo Baeyer-Villiger reactions as described above (Figure 4.2), the hydroxyesters formed under dry conditions from hydroperoxyesters are expected to be stable and have sufficiently low vapor pressure to remain in the SOA,¹⁴⁴ whereas the gem-diol formed under humid conditions from the hydroxy hydroperoxide is expected (in the presence of carboxylic acids)¹⁴⁵ to rapidly decompose to water and pinonaldehyde, which are sufficiently volatile to evaporate. The additional particulate mass from hydroxyesters should not

only increase the SOA yield directly, but also indirectly by enhancing the partitioning of semivolatile products due to the larger SOA mass concentration.

The measured and modeled SOA mass yields agree to within a factor of ~ 2 , which is quite good, considering that the model does not account for particle-phase reactions and gas-wall partitioning that are clearly important. In particular, gas-wall partitioning will reduce the SOA yield, partially explaining the higher model yields. In a previous comparison for this reaction Jenkin¹⁰⁵ found that in order to achieve reasonable agreement between the measurements and MCM model predictions the estimated vapor pressures of all products had to be reduced by a factor of ~ 120 . Although it was thought that this adjustment was needed to account for the effects of oligomer formation on product volatility, it may also have been due to inaccuracies in estimated vapor pressures that were orders of magnitude higher than those used here. For example, the sub-cooled liquid vapor pressures used by Jenkin¹⁰⁵ for pinonic acid, pinic acid, and 1-hydroxypinonic acid, three of the major low volatility products, were 4.3×10^{-3} , 4.7×10^{-4} , and 3.3×10^{-4} Torr, whereas the corresponding values used here (estimated using the SIMPOL.1 group contribution method of Pankow and Asher)⁸⁸ rather than the empirical method used by Jenkin¹⁰⁵ were 5.9×10^{-5} , 3.6×10^{-7} , and 3.4×10^{-7} Torr.

4.3.4 Low-VOC Experiments. These experiments were conducted with a low concentration of α -pinene (10 ppb) and excess O_3 (300 ppb) in order to increase timescales for $RO_2^* + RO_2^*$ and $RO_2^* + HO_2$ reactions compared to High-VOC conditions, thus allowing enhanced RO_2^* radical isomerization and addition of hydroperoxide and peroxy-carboxyl groups that are characteristic of autoxidation (Figure 4.1) and HOM formation.^{53,109} These conditions also reduced the SOA mass loading, thus unfortunately enhancing the loss of products by gas-wall partitioning that occurs on a timescale of ~ 18 min in this chamber.^{122,123,131} The experiments

were conducted under dry (~0% RH) and humid (65% RH) conditions to probe the possible effects of water vapor on autoxidation reactions.

The results of measurements of the functional group composition and other properties of SOA formed in the Low-VOC experiments conducted in dry (~0% RH) and humid (65% RH) air are shown in Figure 4.3 and listed in Table 4.1. Since the functional group composition showed a clear effect of RH, in the following discussion measured average values are discussed for dry and humid conditions. Results for all experiments are given in Table 4.3. The proposed explanations for the results of these experiments are certainly speculative, given the current limited state of knowledge concerning the products of autoxidation reactions for this system, which is limited to molecular formulas,^{108–111} and the failure of theory to explain the observed rates of these reactions for α -pinene ozonolysis using plausible mechanisms.¹¹⁴ Nonetheless, it is possible to show that the functional group composition of the SOA is roughly consistent with expectations when $\text{RO}_2^\bullet$ radicals formed are allowed to undergo autoxidation reactions comparable to those identified for simpler cycloalkenes,^{118,146} and the subsequent products then react further in particles by Baeyer-Villager reactions that appear to occur under High-VOC conditions.

4.3.4.1 Evidence for HOMs. In all dry and humid Low-VOC experiments, gas-phase HOMs with elemental formulas identical to those measured under dry conditions by Ehn et al. were detected using the NO_3 -CIMS.^{108,109} As illustrated in Figure 4.5, the mass spectra for the dry and humid reactions are similar and contain peaks that are indicative of HOM monomers and dimers previously identified by Ehn et al.^{108,109} under dry conditions, along with a few other high-mass products not assigned to HOMs in previous studies. These other compounds, while not considered to be HOMs, were relevant here since they likely contributed to the SOA composition measured with our functional group methods. For dry conditions the O/C and H/C

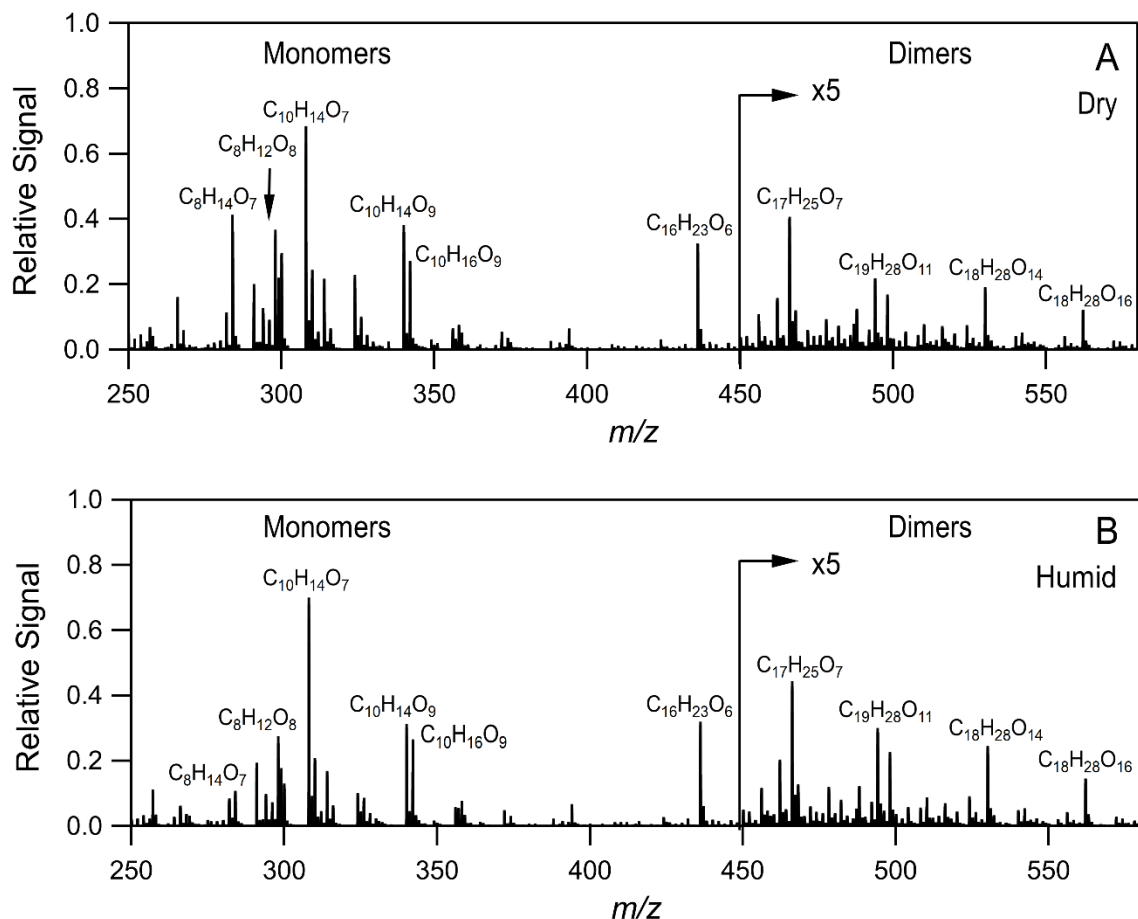


Figure 4.5. Mass spectra of gas-phase reaction products measured with the NO_3 -CIMS during the (A) dry and (B) humid Low-VOC experiments. Compounds were detected as $C_xH_yO_z \cdot NO_3^-$ adducts, except for peaks identified as $C_{16}H_{23}O_6$ and $C_{17}H_{25}O_7$, which were $C_xH_yO_z \cdot HNO_3 \cdot NO_3^-$ adducts.

ratios calculated from the NO_3 -CIMS spectra were 0.8 and 1.5, similar to the values of 0.7 and 1.5 reported by Ehn et al.,^{108,109} and the O/C and H/C ratios of the SOA measured using a HR-ToF-AMS were 0.58 and 1.6, also in good agreement with the ratios of 0.7 and 1.5 reported by Ehn et al.¹⁰⁹ From this comparison it is apparent that we were able to replicate the experimental conditions of earlier HOM studies, and that the SOA analyzed here and results discussed below should also apply to SOA produced in that work.

4.3.4.2 SOA Functional Group Composition. The number of functional groups per C₁₀ SOA molecule measured in the dry Low-VOC experiment were as follows: 1.00 peroxide, 0.88 ester, 0.74 carbonyl, 0.71 carboxyl, and 0.13 hydroxyl, for a total of 3.46, with 6.54 methylene groups. The measured number of functional groups in the dry Low-VOC SOA (3.46) was only slightly lower than the in the dry High-VOC SOA (3.76), but the amounts of specific functional groups differed significantly between these experiments. The larger number of peroxide groups in dry Low-VOC SOA (1.00) compared to dry High-VOC SOA (0.13) is indicative of a larger contribution from dialkyl and diacyl peroxides, which are relatively unreactive and thus able to persist in the SOA without undergoing decomposition reactions. This seems reasonable, given the much smaller mass of Low-VOC SOA ($\sim 5 \mu\text{g m}^{-3}$ compared to $\sim 2000 \mu\text{g m}^{-3}$ for the High-VOC SOA), which leads to preferential partitioning by low volatility dimers rather than the monomers that appear to dominate the High-VOC SOA (at least prior to particle-phase oligomer formation). An example of diacyl peroxide formation followed by a Baeyer-Villiger reaction (shown here to be intramolecular for simplicity) is shown in Figure 4.6, where the RO₂[•] radical involved in the self-reaction is one that is proposed to lead to autoxidation products in Figure 4.1. For this compound the number of peroxide, ester, carbonyl, carboxyl, and hydroxyl groups per C₁₀ molecule that would be reported from functional group analysis are 1.0, 0.5, 0.5, 1.0, and 0.5, for a total of 3.5, since the diacyl peroxide group would be measured as 1 peroxide and 2 carboxyl groups. These values agree reasonably well with the measured SOA composition (1.0, 0.71, 0.88, 0.74, and 0.13 for a total of 3.46). As noted above, the lower-than-expected measured number of hydroxyl groups may be due to formation of acetals in the particles, which are not hydrolyzed back to monomers in the analysis.

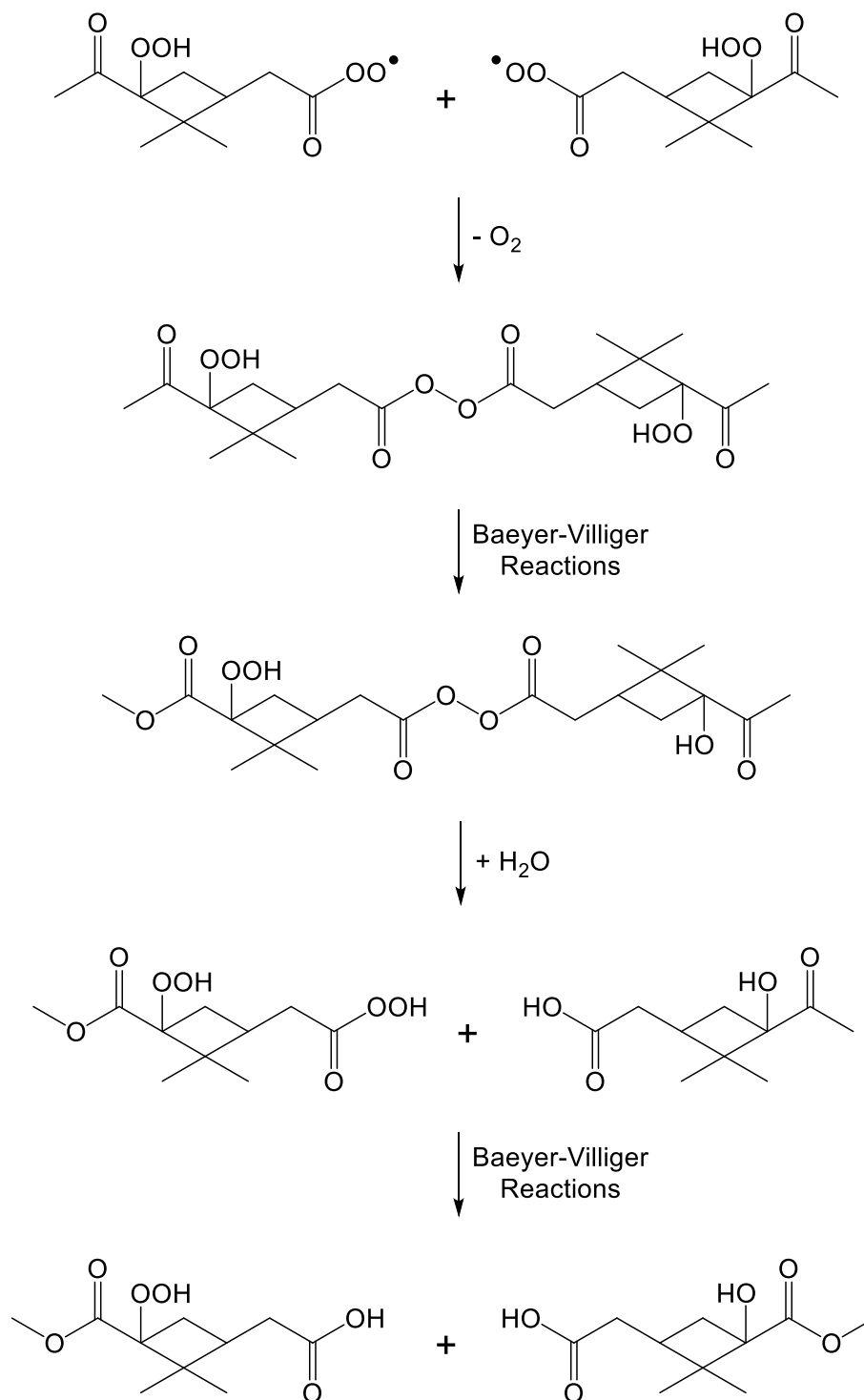


Figure 4.6. Schematic showing an example of the formation of a diacyl peroxide from the gas-phase self-reaction of $\text{RO}_2^\bullet$ radicals, and subsequent particle-phase hydrolysis and Baeyer-Villiger reactions leading to the formation of peroxycarboxylic acid, carboxylic acid, and ester groups.

The number of functional groups per C₁₀ SOA molecule measured in the humid Low-VOC experiment were as follows: 0.44 peroxide, 1.29 ester, 0.99 carbonyl, 1.48 carboxyl, and 0.18 hydroxyl, for a total of 4.38, with 5.62 methylene groups. The 4.38 functional groups are significantly higher than the 3.46 measured in the dry Low-VOC SOA, with the number of peroxide groups decreasing from 1.00 to 0.44; the number of ester, carbonyl, and carboxyl groups increasing from 0.88, 0.74, and 0.71 to 1.29, 0.99, and 1.48; and the number of hydroxyl groups remaining about the same at 0.13 and 0.18. The simplest explanation for the increased number of functional groups measured under humid conditions is that water somehow enhanced the fraction of RO₂[•] radicals that isomerized, which would increase the number of functional groups per C₁₀ molecule and the O/C ratio. This could occur if water either increased the rate of isomerization or reduced the rate of chain termination. However, quantum chemical calculations predict, for example, that at 50% RH and 298K only ~1% of CH₂(OH)CH₂O₂[•] and CH₃C(O)CH₂O₂[•] radicals are complexed with water,¹⁴⁷ so the extent to which water might impact RO₂[•] radical isomerization or termination reactions seems limited. It may be that these effects are enhanced for larger multifunctional compounds, but additional studies are clearly needed to understand the effect of humidity on autoxidation reactions.

An alternative explanation for the effect of humidity on functional group composition is that diacyl peroxides are hydrolyzed by water taken up by the particles, even though the amount absorbed is expected to be small at 65% RH.⁷³ Kinetics studies¹⁴⁸ have shown that diacyl peroxides can be hydrolyzed to a peroxy-carboxylic acid and carboxylic acid in water (although sulfuric acid was used as a catalyst in the reactions studied), which as shown in Figure 4.6 would affect the functional group composition by eliminating 1 peroxide group and forming 1 ester group via a Baeyer-Villager reaction. For these products the number of peroxide, ester, carbonyl,

carboxyl, and hydroxyl groups per C₁₀ molecule that would be reported from functional group analysis are 0.50, 1.0, 1.0, 0.0, and 0.5, for a total of 3.0. With the exception of the carbonyl groups, this composition compares reasonably well with the measured SOA composition (0.44, 1.48, 1.29, 0.99, and 0.18 for a total of 4.38). It may be that small carbonyl compounds such as formaldehyde were taken up by the SOA during filter sampling, forming peroxyhemiacetals that can then dissociate back to the hydroperoxide and aldehyde during analysis. We have previously observed this reaction when SOA containing hydroperoxides (formed from the ozonolysis of 1-tetradecene in the presence of an alcohol) were exposed to formaldehyde.⁸⁴ It would also be consistent with measurements made by Mutzel et al.,¹¹¹ who detected large amounts of particle-phase C₁ – C₄ carbonyl compounds, including formaldehyde, acetaldehyde, acetone, and methyl glyoxal, while studying HOM formation under conditions similar to the Low-VOC experiments conducted here. Such uptake would also increase the number of functional groups per C₁₀ molecule, possibly explaining the increase observed for humid conditions.

4.3.4.3 Other SOA Properties and Yields. The average O/C and H/C ratios calculated for the dry Low-VOC experiments from the functional group composition were 0.61 and 1.60, the average molecular weight and density were 233 g mol⁻¹ and 1.33 g cm⁻³, and the average SOA mass and molar yields were 0.22 and 0.13, whereas the corresponding values calculated for the humid experiments were 0.76 and 1.40, 255 g mol⁻¹ and 1.49 g cm⁻³, and 0.24 and 0.13. The differences in O/C and H/C ratios and molecular weight and density are in general a reflection of the larger number of functional groups in SOA formed in the humid compared to dry experiments, but this appears to have had no significant effect on SOA yields. Also for comparison, the O/C and H/C ratios of the SOA measured using a HR-ToF-AMS were 0.58 and 1.6 in one dry experiment and the average values measured in two humid experiments were 0.54

and 1.69. The values measured with the HR-ToF-AMS and from functional group analysis agree very well for the dry experiment (0.58 and 1.60 compared to 0.61 and 1.60) but less well for the humid experiments (0.54 and 1.69 compared to 0.67 and 1.45). One possible explanation for the discrepancy in the humid experiments is that the previously proposed uptake of small carbonyl-containing compounds during filter sampling altered the SOA composition from what it was in the chamber when the HR-ToF-AMS measurements were made.

4.4 Conclusions

It is shown here that functional group analysis of SOA formed from the ozonolysis of α -pinene over a range of α -pinene concentrations and humidities can provide information on the products and mechanisms of both the gas- and particle-phase reactions involved in SOA formation. These methods, which employ derivatization and spectrophotometry, quantify the contributions of peroxide, carbonyl, carboxyl, hydroxyl, and ester groups and are especially useful by providing top-down constraints on studies of SOA formation from VOC oxidation reactions such as this one, where reaction mechanisms are still not well understood and the SOA composition is extremely complex (in this case containing many hundreds of compounds). When the functional group composition is normalized to the carbon number of the parent VOC (in this case C_{10}), the results can be used to estimate the number of each functional group per C_{10} molecule, the total number of functional groups per C_{10} molecule, the total number of oxygen atoms per C_{10} molecule, and the O/C and H/C ratios. In general, the total number of functional groups in a molecule is determined predominantly by gas-phase reactions, with subsequent particle-phase reactions converting one type of functional group to another (usually through H-atom and/or O-atom transfer) and in some cases reducing the number of functional groups via oligomer formation. All of this information can be very useful for developing and evaluating

models of VOC oxidation and SOA formation, for which comparisons are usually limited to SOA yields and O/C ratios and perhaps a few molecular products. Here we compared the results of experiments conducted with high VOC concentrations to simulations conducted using the Master Chemical Mechanism and gas-particle partitioning theory, since most of the products formed SOA and thus artifacts due to gas-wall partitioning (which was not included in the model) were minimized.

In the high concentration experiments the gas-phase products that contributed to SOA formation appeared to be similar under dry and humid conditions and consist primarily of monomers containing on average a total of 3–4 peroxide, carbonyl, carboxyl, or hydroxyl groups per C₁₀ molecule formed through $\text{RO}_2^\bullet + \text{RO}_2^\bullet$ and $\text{RO}_2^\bullet + \text{HO}_2$ reactions, with a minor contribution from ester group-containing dimers that were formed under dry conditions from reactions of stabilized Criegee intermediates with carboxylic acids. Although the total number of functional groups per C₁₀ molecule determined from SOA measurements was similar to that predicted by the model, the distribution of functional groups differed considerably. In particular, measured amounts of carboxyl and ester groups were significantly larger than those predicted by the model, whereas peroxide, carbonyl, and hydroxyl groups were significantly smaller. A plausible explanation for this discrepancy is that aldehyde and ketone groups were converted to carboxyl and ester groups, respectively, through particle-phase Baeyer-Villager reactions with hydroperoxides and peroxy-carboxylic acids, thus adding carboxyl and ester groups while removing peroxide groups. The small measured amounts of hydroxyl groups indicates that alkoxy radical isomerization was less important than predicted by the model, and may also have been due to particle-phase formation of acetals, which converts these groups (but not the carbonyl groups in the reaction partners) to a form that is not detected in the functional group

analysis. Also noteworthy, is that despite the similar functional group composition measured in the dry and humid experiments, the SOA yield was significantly larger under dry conditions. This may have been due to formation of low-volatility ester group-containing dimers from reactions of stabilized Criegee intermediates with carboxylic acids under dry conditions, and subsequent enhanced partitioning of other semivolatile products due to the larger SOA mass concentration. Furthermore, although the measured and simulated functional group composition of the SOA differed significantly, the SOA yields agreed to within a factor of ~ 2 . This was probably due in large part to the similar total number of measured and simulated functional groups and the high SOA mass concentrations formed under these conditions, which resulted in gas-to-particle partitioning of a large fraction of the products and thus reduced the sensitivity of the SOA yield prediction to errors in gas-phase composition and the absence of particle-phase chemistry. It is also likely that the absence of gas-wall partitioning in the model contributed to the higher simulated SOA yield.

In the low concentration experiments conditions were achieved that resulted in the formation of gas-phase HOMs, apparently due to increased timescales for $\text{RO}_2^\bullet + \text{RO}_2^\bullet$ and $\text{RO}_2^\bullet + \text{HO}_2$ reactions that enhanced competition with $\text{RO}_2^\bullet$ radical isomerization and the formation of ROOR dimers from $\text{RO}_2^\bullet$ self reactions. Because of the absence of $\text{RO}_2^\bullet$ radical isomerization pathways in the Master Chemical Mechanism and much greater expected loss of products by gas-wall partitioning, no attempt was made to model these experiments. The total number of functional groups per C_{10} molecule measured in these experiments ranged from about 3–5, and was higher for humid than dry conditions. In addition, the distribution of functional groups varied significantly: more peroxide groups for dry conditions; more carbonyl, carboxyl, and ester groups for humid conditions; and similarly low amounts of hydroxyl groups for both conditions.

Although explanations for these results are more speculative than for the high VOC experiments, the functional group composition of the SOA can be plausibly explained based on the same gas- and particle-phase reactions that appear to occur under high VOC conditions, but with the addition of autoxidation reactions, gas-phase dimer formation, particle-phase hydrolysis reactions, and gas-to-particle partitioning of small carbonyl compounds. In particular, it appears that the larger number of peroxide groups is due to enhanced $\text{RO}_2^\bullet$ isomerization and contributions from dimers containing dialkyl and diacyl peroxide groups, which are unreactive under dry conditions. Under humid conditions, however, diacyl peroxide groups are apparently hydrolyzed to carboxylic acids and peroxy-carboxylic acids, with the latter then undergoing Baeyer-Villiger reactions that convert aldehyde and ketone groups to carboxylic acid and ester groups. Although this proposed mechanism should lead to fewer carbonyl groups under humid conditions, the slight increase that is observed may be due to enhanced gas-to-particle partitioning of small carbonyl compounds that subsequently react with hydroperoxides to form peroxyhemiacetals.

Chapter 5

Comparison of Methods of Functional Group Analysis Using Results from Laboratory and Field Measurements Aerosol

5.1 Introduction

Atmospheric aerosols are derived from a variety of natural and anthropogenic sources and are known to impact human and ecosystem health, visibility, atmospheric chemistry, and climate.² Whereas primary aerosols are directly emitted from processes such as combustion, or as wind-blown dust or sea spray,¹ secondary aerosols are formed in the atmosphere through the photo-oxidation of volatile organic compounds (VOCs) and nitrogen and sulfur oxides.⁸ Biogenic VOCs (BVOCs) are the most abundant class of VOCs emitted into the atmosphere, with isoprene and monoterpenes accounting for ~70% of global emissions.¹¹ BVOCs have been shown to be dominant precursors of secondary organic aerosol (SOA) formation, due to their large emissions and high reactivity with respect to atmospheric oxidants (Atkinson and Arey, 2003; Hallquist, et al., 2009).^{7,10} Understanding the factors that influence the formation of SOA from BVOCs, such as oxidation regime, temperature, humidity, particle acidity, and interactions with anthropogenic emissions of nitrogen and sulfur oxides, is vital to understanding how current and future regulations will impact regional and global air.^{8,12}

Measurements of organic aerosol composition have most often been made using online or offline mass spectrometry.^{10,149} The chemical information obtained varies widely in specificity,

ranging from molecular characterization (typically involving some degree of component separation achieved by coupling gas or liquid chromatography or temperature-programmed thermal desorption with mass spectrometry) to quantifying bulk aerosol properties like O/C ratios. While characterization of the individual molecules in the aerosol is ideal, this type of measurement is time consuming and rarely comprehensive due to the complexity of the sample. An alternative approach is to characterize the composition of the organic aerosol by its functional groups, which yields a level of chemical detail that falls between molecular identification and elemental ratios. The benefit of this type of analysis is that the measurements are specific enough to allow inferences to be made about the type of chemistry that caused the aerosol to form as well as the environmental conditions under which it happened.¹⁵⁰

The most commonly used method for quantifying the functional group composition of SOA is Fourier Transform Infrared (FTIR) spectroscopy, which has been developed and employed for field applications primarily by the Russell group at the Scripps Institute of Oceanography (SIO),^{151,152} and the Dillner group at UC-Davis.^{153–155} More recently, the Ziemann group at the University of Colorado, Boulder (CU) has developed an alternative approach that employs derivatization-spectrophotometry (Deriv-Spec)^{37,116} and applied it in a number of laboratory studies (and thesis Chapters 2 and 4).^{48,72,90,156,157} Each of these methods have benefits and draw-backs, but both aim to characterize SOA through the quantification of a suite of functional groups (though not necessarily the same ones) that are commonly present in atmospheric aerosol.

The SIO FTIR method, which was employed in the study reported here, determines the aerosol functional group composition from the FTIR absorption spectrum (measured directly by transmission) of filter samples. The spectrum is then used to quantify groups classified as acid-

carbonyl, non-acid carbonyl, alcohol, organonitrate, sulfate, amine, alkane, alkene, and aromatic. While this technique provides relative ease of sampling, automated analysis, and the ability to work with small amounts of aerosol mass ($\sim 10 \mu\text{g}$), all of which are critical for field studies, it has the potential for significant interferences in identification and quantification due to overlapping absorbance by functional groups in some regions in the FTIR spectrum. The method also has problems distinguishing between some functional groups with similar structures.

The CU Deriv-Spec method measures carbonyl (ketone + aldehyde), carboxyl, hydroxyl, ester, peroxide, and nitrate groups in the aerosol (and estimates methylene groups by difference compared to the total mass). These methods are specific for each functional group because of the use of derivatizing agents, targeted iodometric reactions, and characteristic wavelengths for detection, and the methods have been developed to avoid a range of potential interferences.³⁷ Compared to the SIO method, however, the CU analyses require more time (about 3 days) for complete sample analysis, and more aerosol mass ($\sim 50 \mu\text{g}$).

In the study presented here, the SIO and CU methods for quantifying the functional group composition of SOA were compared using aerosol formed in a suite of environmental chamber experiments and ambient samples collected during the Southern Oxidant and Aerosol (SOAS) field campaign. In addition, the results of the environmental chamber experiments were used to aid in the interpretation of the ambient SOA collected during SOAS, in order to identify possible sources, environmental conditions, and processes that caused the aerosol to form. This study was conducted in collaboration with Jun Liu and Lynn Russell from SIO.

The SOAS campaign took place during the summer of 2013 in the Southeast US, an environment dominated by isoprene and monoterpene emissions.¹²⁹ An overarching goal was to

identify and quantify the effects of anthropogenic inorganic and organic emissions on SOA formed from BVOCs. In this regard, observations made during the campaign indicated the presence of organic nitrates in SOA^{24,25,158–160} and an impact of sulfate on SOA formation,^{24,159,161,162} with Xu et al.¹⁵⁹ estimating that the formation of 43–70% of the total organic aerosol in the Southeast US was mediated by the presence of anthropogenic sulfate and NO_x. Several studies reported correlations between isoprene SOA formed through IEPOX pathways and the presence of particle-phase sulfate. Liu et al.¹⁶¹ reported evidence of selective uptake of isoprene SOA onto sulfate particles, indicative of heterogeneous reactions, and it was shown that the formation of isoprene SOA was directly mediated by the abundance of sulfate, not by the aerosol water content or particle acidity.^{24,159} This was presumably because the aerosol was so acidic (pH < 2) and the air so humid, that these were not limiting factors during the campaign. Furthermore, it was reported that organic nitrates accounted for 5–12% of the total organic aerosol,²⁴ and that organic nitrates formed from the reaction of monoterpenes with NO₃ radicals accounted for 50% of the total nighttime SOA.¹⁵⁹ Because the ambient samples analyzed in the present study were collected during SOAS, the chamber experiments were designed to target the VOCs, oxidation regimes, humidity, and particle acidity that were observed during the campaign.

5.2 Experimental Section

5.2.1 Chemicals. The following chemicals with purities/grades and suppliers were used: pentadecane (99%), (-)- α -pinene (99%), (1s)-(-)- β -pinene (99%), (R)-(+)-limonene (97%), camphene (95%), isoprene (99%), paraformaldehyde (95%), tridecanoic acid (98%), 1,2-tetradecanediol (90%), benzoyl peroxide (98%), cyclohexane (99%, ACS grade), 2 M trimethylsilyldiazomethane in diethyl ether, toluene (99.8%), 3,5-dinitrobenzoyl chloride (98%),

pyridine (99.5%) (Sigma-Aldrich); bis(2-ethylhexyl) sebacate (97%) (Fluka); 3-hexadecanone (99%) (ChemSampCo); methanol (HPLC grade) (Honeywell); (NH₄)₂SO₄ (99.5%, ACS grade), H₂SO₄ (ACS grade), acetonitrile (HPLC grade, ACS grade), NaHCO₃ (ACS grade), water (HPLC grade), HCl (ACS grade), NaCl (ACS grade) (Fisher); ethyl acetate (99.5%, ACS grade), hexanes (ACS grade), dichloromethane (ACS grade) (EMD Millipore); NO (CP grade, 99%) (Matheson); 18 MΩ water purified using Milli-Q Advantage A10 water system. O₃ was generated using a BMT 802N O₃ generator with ultra-high purity (UHP) O₂ (Airgas). N₂O₅ was synthesized according to the procedures of Atkinson et al.³⁵ and was stored in a glass vacuum bulb in dry ice until used. Methyl nitrite was synthesized¹⁶³ and stored in a lecture bottle at room temperature until used. Chemicals used for the derivatization-spectrophotometric functional group analyses have been reported previously.^{36,37,116}

5.2.2 Environmental Chamber Experiments. The following observations made during the SOAS campaign were used as a guide in selecting the conditions for the experiments: 1) the dominant VOCs were isoprene, α -pinene, β -pinene, and limonene; 2) VOC reactions with OH radicals, O₃, and NO₃ radicals were all important; 3) the humidity ranged from ~35–100%; and 4) the average aerosol acidity was ~1. Presented in Table 5.1 is a full list of the laboratory chamber experiments conducted at CU for this study. In each experiment, SOA was formed in an 8 m³ environmental Teflon FEP chamber filled with clean, dry air supplied by two AADCO Model 737-14A clean air generators (<5 ppbv hydrocarbons, < 0.1% RH) at room temperature (~23°C) and pressure (~630 Torr). Experiments 1–3 were conducted under dry conditions (< 1% RH) and without the presence of seed aerosol. The remaining experiments, 4–14, were conducted under humid conditions (50% RH) by evaporating water into the chamber from a heated glass bulb in a stream of N₂. For these experiments (4–14) ammonium sulfate particles

were flushed into the humidified chamber after being formed with a Collison atomizer to obtain a concentration of $\sim 200 \mu\text{g m}^{-3}$ of deliquesced seed particles. In the case of experiments 12 and 13, the ammonium sulfate seed solution was doped with sulfuric acid to form seed particles in the chamber with a pH of ~ 1 , as determined from E-AIM calculations (<http://www.aim.env.uea.ac.uk/aim/aim.php>).^{38,39} For experiments 1 and 4 (ozonolysis oxidation), 1200 ppm of cyclohexane was added to the chamber in a flow of N_2 from a heated glass bulb. The cyclohexane acts as an OH scavenger and, at this concentration, is sufficient to scavenge $>99\%$ of the OH radicals formed during the reaction.³⁶ To promote the formation of HO_2 in experiments 8–11 and 13, 1500 ppm of formaldehyde was added to the chamber by heating paraformaldehyde from a glass bulb into a stream of N_2 , the heating process decomposes the paraformaldehyde back to its formaldehyde precursor. For all experiments, the VOC of interest was then added to the chamber from a heated glass bulb into a flow of N_2 to achieve the desired concentration (Table 5.1) in the chamber. This was followed by the addition of oxidant, either O_3 , N_2O_5 , or $\text{CH}_3\text{ONO/NO}$. The oxidant was added to the chamber by a similar method to the VOC but without heating. A Teflon-coated fan was run for 30 s after each addition to ensure a well-mixed chamber. For experiments with O_3 or N_2O_5 the addition of the oxidant initiated the reaction and subsequent SOA formation. When $\text{CH}_3\text{ONO/NO}$ was used (for OH/high NO_x reactions) blacklights that cover two walls of the chamber were turned on for a certain amount of time (Table 5.1) to generate OH radicals through the photolysis of CH_3ONO .

5.2.3 Gas Analysis. Throughout the chamber reactions, O_3 concentrations were monitored using a Thermo Scientific 49i O_3 monitor, NO_x concentrations were monitored using a Thermo Scientific Model 42C $\text{NO-NO}_2\text{-NO}_x$ Analyzer, and humidity was monitored using a Vaisala HMP110 RH probe. The concentration of parent VOC in the chamber was measured

Table 5.1. List of experiments and conditions used where the SOA formed was collected and analyzed for its bulk functional group composition both by the derivatization-spectrophotometric methods (CU) and by the FTIR method (SIO).

Exp.	VOC	Oxidant	Seed	RH (%)	hv	Concentration (ppm)		
						VOC	Oxidant	CH ₂ O
1	α -pinene	O ₃	---	0	---	1	2	---
2	Pentadecane	CH ₃ ONO/NO	---	0	60 min at 50%	1	10/10	---
3	Isoprene	CH ₃ ONO/NO	---	0	40 min at 100%	5	10/10	---
4	α -pinene	O ₃	(NH ₄) ₂ SO ₄	50	---	1	2	---
5	Limonene	N ₂ O ₅	(NH ₄) ₂ SO ₄	50	---	1	0.33	---
6	β -pinene	N ₂ O ₅	(NH ₄) ₂ SO ₄	50	---	1	0.33	---
7	α -pinene	N ₂ O ₅	(NH ₄) ₂ SO ₄	50	---	1	0.33	---
8	Limonene	N ₂ O ₅	(NH ₄) ₂ SO ₄	50	---	0.3	0.6	1500
9	β -pinene	N ₂ O ₅	(NH ₄) ₂ SO ₄	50	---	0.3	0.6	1500
10	α -pinene	N ₂ O ₅	(NH ₄) ₂ SO ₄	50	---	0.3	0.6	1500
11	Camphene	N ₂ O ₅	(NH ₄) ₂ SO ₄	50	---	0.3	0.6	1500
12	β -pinene	N ₂ O ₅	(NH ₄) ₂ SO ₄ /H ₂ SO ₄	50	---	1	0.33	---
13	β -pinene	N ₂ O ₅	(NH ₄) ₂ SO ₄ /H ₂ SO ₄	50	---	0.3	0.6	1500
14	α -pinene	CH ₃ ONO/NO	(NH ₄) ₂ SO ₄	50	12 min at 50%	1	10/10	---

before and after the reaction by collecting samples onto Tenax adsorbent for gas chromatography-flame ionization detection (GC-FID) analysis. For each sampling period, chamber air was first drawn through the 30 cm stainless steel sampling line for 20 min at 250 cm³ min⁻¹ to passivate the walls of the tube. Chamber air was then sampled through an attached Tenax cartridge at the same flow rate for 4 min, with samples taken 30 and 90 min before and after the reaction. Tenax cartridges were inserted into an Agilent 6890 GC and compounds were

thermally desorbed onto a 30 m $\times$ 0.32 mm Agilent DB-1701 column with 1 μ m film thickness by ramping the inlet to 250°C in 7 min while the column was held at 40°C. The column temperature was then ramped at 10°C min⁻¹ to 280°C and eluted compounds were quantified with the FID.

5.2.4 Particle Analysis. Particle size distributions and mass concentrations were measured during each chamber reaction using a scanning mobility particle sizer (SMPS) composed of a long differential mobility analyzer and a TSI Model 3010 condensation particle counter. After each reaction four SOA samples were collected, two for the CU Deriv-Spec analyses and two for the SIO FTIR analysis. The two replicate CU samples were collected onto pre-weighed filters (Millipore Fluoropore PTFE, 0.45 μ m) for 120 min at a flow rate of 14 L min⁻¹. The filters were reweighed after sampling to determine the mass of SOA collected. Filters were weighed using a Mettler Toledo XS3DU Microbalance. Filter samples were separately extracted into 10 mL of ethyl acetate, the extracts were then combined in a pre-weighed vial and dried in a stream of N₂, and the vial was reweighed to determine the extracted SOA mass. The dried SOA was reconstituted in ethyl acetate to achieve a sample concentration of 1 mg mL⁻¹ for subsequent Deriv-Spec functional group analysis and stored at -20°C between analyses. The two SIO samples were collected onto 37 mm stretched Teflon filters for 5 min at a flow rate of 12 L min⁻¹ (SIO samples). The SIO samples were immediately sealed in a container and stored at -20°C until mailed to SIO for FTIR analysis.

Deriv-Spec Analysis of Chamber Samples (CU). The chamber SOA functional group composition was quantified using the macro-methods we developed previously.^{36,37} Briefly, these methods measure carbonyl (aldehyde and ketone), carboxyl, hydroxyl, and ester groups by converting them to UV-Vis absorbing forms by derivatizing with 2,4-DNPH, 2-NPH.HCl, 4-

NBC, and hydroxamic acid, respectively; peroxides (hydroperoxides, dialkyl and diacyl peroxides, peroxy acids, and peroxy nitrates) are reacted with I^- to form an absorbing I_3^- solution; and nitrate groups are directly quantified using their characteristic strong absorbance at 210 nm. Surrogate standards used for carbonyl, carboxyl, hydroxyl, ester, peroxide, and nitrate groups were 3-hexadecanone, tridecanoic acid, 1,2-tetradecanediol, bis(2-ethylhexyl) sebacate, benzoyl peroxide, and 2-ethylhexyl nitrate, respectively. Absorbance was measured using an Ocean Optics USB4000-UV-Vis Miniature Fiber Optic spectrophotometer with a 1 cm quartz cell, for each analysis a five-point calibration curve, a standard blank, a filter blank, and two duplicate SOA samples were analyzed.

5.2.5 FTIR Analysis of Chamber Samples (SIO). An automated algorithm was used to quantify the mass of organic functional groups.^{151,152} In short, FTIR spectroscopy quantifies organic functional groups by their absorbance, which is associated with the frequency of particular bonds within the molecule. An algorithm is then used to quantify the mass of each functional group, which is then summed to get a total SOA mass, and then mass fractions are calculated by dividing the mass of each functional group category by the total mass. The types of functional groups quantified with the FTIR technique reported here were: alkane (saturated aliphatic CH_2), non-acid carbonyl ($C=O$ group contribution from non-specified aldehydes, ketones, and esters), acid-carbonyl (absorbance of $C-OH$ also associated with $C=O$ from carboxyl groups $O=C-OH$), alcohol ($C-OH$), and organonitrate ($R-ONO_2$) groups. The filters collected for FTIR analysis were scanned before and after chamber sampling using a Bruker Tensor 27 FTIR spectrometer with a deuterated triglycine sulfate (DTGS) detector.

5.2.6 Collection of Field Samples (SIO). During the SOAS field campaign, samples of the ambient aerosol were collected onto pre-scanned Teflon filters (Teflon, Pall Life Science

Inc., 37 mm diameter, 1.0 μm pore size) at both the Centerville, AL (CTR) and Look Rock, TN (LRK) field sites. After collection, samples were frozen and transported to the SIO laboratory for FTIR analysis and then re-frozen and sent to CU for Deriv-Spec analysis. The field samples were pooled and put into four groups as follows: 1) combined daytime and nighttime samples from LRK during low- NO_x conditions; 2) combined daytime and nighttime samples from LRK during high- NO_x conditions; 3) nighttime samples from CTR during low- NO_x conditions; and 4) daytime samples from CTR during high- NO_x conditions. Each group contained between three and seven filter samples. These groupings were chosen to provide enough mass for all CU analyses (described below) once the samples were pooled, and to provide samples from both high- and low- NO_x conditions at both field sites.

5.2.7 Deriv-Spec Analysis of Field Samples (CU). Each filter was initially extracted into 8 mL of ethyl acetate, and the filter extracts were combined into a pre-weighed vial for each of the four groups (described above). The extracts were dried down with N_2 and then reweighed to obtain the mass of aerosol extracted. In order to ensure that all organic mass was extracted from the filters, each pool of filters was then placed in 20 mL of methanol and sonicated for 30 min. This extract was transferred to a pre-weighed vial, separate from that of the first extraction, dried down with N_2 and reweighed to obtain the mass extracted. Filter blanks for each of the sample pools were also extracted using these same methods.

Because the CU Deriv-Spec analyses use UV-Vis absorbance measurements for quantification, the presence of inorganic components, especially black carbon, present potential interferences for the field samples. In particular, during the methanol extraction phase of the sample preparation inorganic components that would not have dissolved during the ethyl acetate extraction phase could dissolve in methanol during the subsequent sonication period. To check

for this artifact, each sample group, and its associated blank, was reconstituted in ethyl acetate and its UV-Vis spectrum was measured using an IMPLEN NanoPhotometer NP80. By comparing the spectra from the ethyl acetate and methanol/sonication extracts, it was apparent that this artifact was negligible since the spectra from the two extraction methods were similar. So to obtain as much mass as possible for the subsequent Deriv-Spec analyses the samples from each extraction method were combined for each of the four groups into a pre-weighed vial. The samples were again dried with N₂ and reweighed to obtain a final mass of aerosol sample, and then reconstituted into ethyl acetate to obtain a 1 µg µL⁻¹ solution for the subsequent functional group analyses.

The functional group composition of each of the four field samples was quantified using micro-methods we developed previously,¹¹⁶ which are similar to the macro-methods described above for the chamber sample analyses. Although the micro-methods were developed to measure carbonyl, carboxyl, ester, hydroxyl, peroxide, and nitrate groups, two exceptions were made for the field samples. The first was that the method for measuring nitrate groups was not used because it does not include a derivatization reaction that leads to high specificity, and instead quantifies nitrate groups through the absorbance at 210 nm. While this approach has been shown to work well for laboratory aerosol,⁴² in ambient samples there is sufficient absorbance from other species, like aromatics, to confound this approach. The second exception was that the peroxide analysis was not attempted because it requires more mass than was available, and it was expected that any peroxides present had already decomposed after the long storage period.¹¹⁵

Another important note about the CU field sample analysis is that the micro-method for hydroxyl quantification was slightly modified from the procedure that was previously reported¹¹⁶ to avoid interferences that were present in the previous method. The modified hydroxyl analysis

used the following reagents: 1) toluene/methanol solution: [3:2] toluene:methanol, 2) trimethylsilyldiazomethane (TMSDM) solution: 0.04 M TMSDM (in diethyl ether) in toluene/methanol solution, 3) 3,5-dinitrobenzoyl chloride (3,5-DNBC) solution: 0.2 M 3,5-DNBC in pyridine, 4) NaHCO₃ solution: 0.6 M NaHCO₃ in water, 5) HCl solution: 0.24 N HCl and 0.9 M NaCl in water, 6) hexane/dichloromethane (DCM) solution: [23:2] hexane:DCM. The procedure was as follows: a sample or standard solution containing at least 0.07 nmol of hydroxyl groups dissolved in 5 µL of toluene/methanol solution is added to a 0.5 mL conical glass reaction vial with 10 µL of TMSDM solution. The solution is kept at room temperature for 1 h to convert any carboxyl groups to methyl esters,³⁷ and is then dried using a stream of N₂. The sample is then reconstituted into 5 µL pyridine and 7.5 µL of 3,5-DNBC solution and left at room temperature for 15 min to allow time for derivatization. To hydrolyze any excess 3,5-DNBC, 25 µL of water is added to the sample and the solution is kept at room temperature for 10 min. The sample is then dried using a stream of N₂. Once dried, each sample is reconstituted in 250 µL of hexane/DCM solution. The sample is then washed with 100 µL of NaCO₃ solution followed by 250 µL of HCl solution, after each washing the aqueous layer is discarded. The remaining organic layer is then dried down with N₂ and is reconstituted into 25 µL of acetonitrile and the absorbance is measured at 231 nm.

To summarize, the field samples were quantified for their carbonyl (ketone + aldehyde), carboxyl, and ester content using the Deriv-Spec micro-methods and the hydroxyl content was quantified using the modified procedure described above. Surrogate standards used for carbonyl, carboxyl, ester, and hydroxyl groups were 3-hexadecanone, tridecanoic acid, bis(2-ethylhexyl) sebecate, and 1,2-tetradecanediol, respectively. For each analysis absorbance was measured on an 2 µL drop using an IMPLEN NanoPhotometer NP80, and a five-point calibration curve, a

standard blank, a filter blank, and duplicate SOA samples (two from each of the four sample groups) were analyzed.

5.2.8 FTIR Analysis of Field Samples (SIO). The filters were scanned and spectral peaks integrated and quantified following the same procedure used for the chamber samples described above.^{151,152} The field samples were quantified by FTIR for the functional groups listed above for the chamber samples (alkane, non-acid carbonyl, acid-carbonyl, and alcohol groups) and in some cases the contributions from primary amine (CNH₂), alkene (unsaturated aliphatic CH), and aromatic (CH) groups are also reported. Because the measurements found that organonitrate groups were below the limit of quantification at both sites they were excluded.¹⁶⁴

5.2.9 Description of Reported Functional Group Composition and Properties of SOA. The functional group composition of SOA measured with the CU Deriv-Spec methods is reported in Tables 5.2 – 5.4 as the average number of each measured functional group per parent VOC molecule,³⁷ assuming that the SOA only contained peroxide [CHOOH], ester [C(O)O], carbonyl [C(O)], carboxyl [C(O)OH], hydroxyl [CHOH], nitrate [CHONO₂] and methylene [CH₂] groups. This composition was determined by summing the masses of measured functional groups, calculated as the measured moles $\times$ molecular weight (g mol⁻¹) of each group: peroxide = 46, ester = 44, carbonyl = 28, carboxyl = 45, hydroxyl = 30, nitrate = 75. The moles of methylene groups were then obtained by subtracting this sum from the measured SOA mass and dividing by the molecular weight of the methylene group, 14 g mol⁻¹. Molar concentrations of functional groups in the SOA were used to calculate mole fractions, which were then multiplied by the carbon number of the parent VOC to obtain the number of functional groups per molecule in the SOA. To further describe the properties of the bulk SOA, the measured functional group composition was then used to calculate the average O/C, H/C, and N/C ratios, molecular weight,

and the saturation concentration of the SOA, with the latter calculation employing SIMPOL.1⁸⁸ to estimate effects of functional groups on compound vapor pressure. The density of the SOA was calculated from the O/C, H/C, and N/C ratios using the equation of Kuwata et al.⁸⁰ and assuming that an N atom contributed the same amount to the density as an O atom. These bulk aerosol properties for each SOA system are also reported in Tables 5.2 – 5.4.

As described above, the results of Deriv-Spec analyses of functional group composition are typically reported as the number of functional groups per molecule (essentially a mole fraction), which in laboratory studies can be helpful for understanding the reaction mechanisms by which SOA was formed from the oxidation of a parent VOC. Because field analyses of SOA (including those made using the SIO FTIR method) are almost always reported as mass fractions, however, the results of the derivatization-spectrophotometric analyses are also reported in these units for comparison with the results of the FTIR analyses. This was done by multiplying the moles of each functional group in the aerosol sample by the molecular weight of each functional group given above and then dividing by the total mass. Furthermore, because FTIR and derivatization-spectrophotometric methods use different terms to describe the same type of functional group, for this discussion the following terms were used for both methods, where the terms normally used for FTIR/ Deriv-Spec analyses are given in parentheses: carbonyl (non-acid carbonyl/carbonyl), carboxyl (acid carbonyl/carboxyl), alcohol (alcohol/hydroxyl), ester (non-acid carbonyl/ester), peroxide (NA/peroxide), nitrate (nitrate/nitrate), amine (amine/NA), aromatic (aromatic/NA), alkene (alkene/NA), and alkane (alkane/methylene).

5.3 Results and Discussion

5.3.1 Comparison of Methods: Environmental Chamber Studies. Results of functional group analysis of SOA formed in environmental chamber reactions of isoprene, α -

pinene, β -pinene, limonene, and pentadecane with OH radicals in the presence of NO_x, O₃, or NO₃ radicals (reaction conditions are reported in Table 5.1) are shown in Figure 5.1 and 5.2, and explicitly reported in Table 5.2, 5.3, and 5.4. Compositions shown were measured using both the Deriv-Spec methods and the FTIR methods. The results obtained with the two methods agree well when the measurements are grouped into four categories, which we refer to as groups 1–4 defined according to the following criteria. 1) Functional groups that contain an O–H bond (for the FTIR method this is alcohol + carboxyl (non-acid carbonyl) groups, and for the Deriv-Spec method this is alcohol + carboxyl + peroxide groups). 2) Non-acid functional groups containing a C=O moiety (for the FTIR method this includes the non-acid carbonyl groups calculated as the difference between mass of carbonyl C=O and mass of C=O associated with carboxyl C–OH, and for the Deriv-Spec methods this is carbonyl (ketone + aldehyde) + ester groups). 3) The nitrate group, which is a direct comparison between the FTIR and Deriv-Spec measurements of this group. 4) The alkane group, which is a direct comparison between the FTIR alkane and Deriv-Spec methylene measurements. These groupings are shown in Figures 5.1 and 5.2 for the different types of SOA as carboxyl + alcohol + peroxide (group 1), ketone/aldehyde + ester (group 2), nitrate (group 3), and alkane (group 4).

While the agreement between the methods is quite good when the results are grouped in this way, it does appear that there are two discrepancies observed within groups 1 and 2. In group 1, the FTIR method appears to be biased high. This could be due to a couple of reasons, including: the carboxyl and alcohol C–OH peaks are not well resolved in an FTIR spectrum, and this area of the spectrum also includes absorbance from hydroperoxide groups that are not accounted for in the FTIR method. This bias could also be due to absorbance from the ammonium sulfate seed present in the aerosol, since N–H bonds also absorb in the C–OH

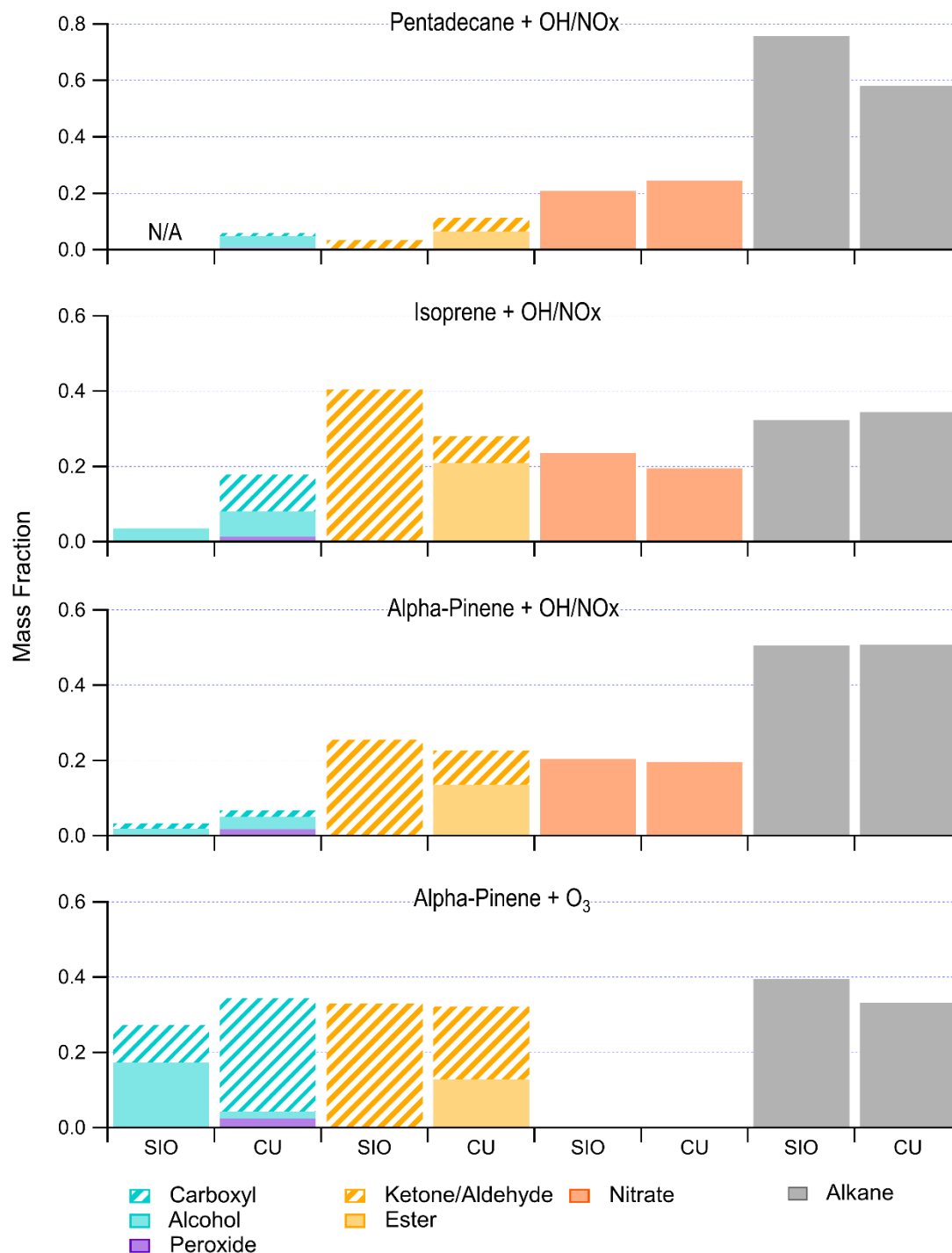


Figure 5.1. Functional group composition of SOA formed in environmental chamber experiments designed to mimic daytime reaction conditions observed during the SOAS field campaign and analyzed by derivatization-spectrophotometric (CU) and FTIR methods (SIO). SOA formed in all OH/NO_x reactions has nitric acid in the particles because it is formed by the OH + NO₂ reaction.

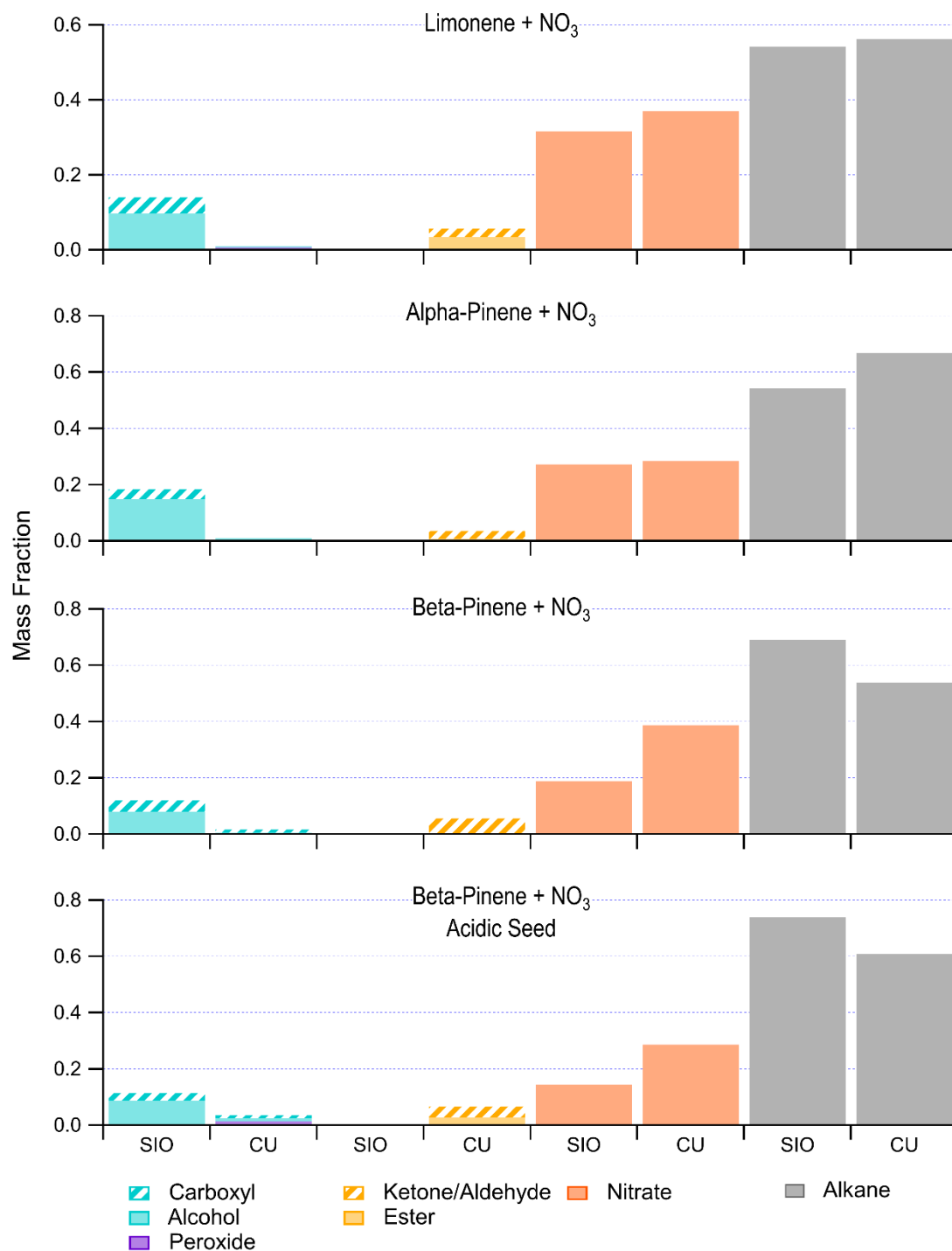


Figure 5.2. Functional group composition of SOA formed in environmental chamber experiments designed to mimic nighttime reaction conditions observed during the SOAS field campaign and analyzed by derivatization-spectrophotometric (CU) and FTIR methods (SIO). SOA formed in all reactions has nitric acid in particles since it is formed by N₂O₅ hydrolysis in the NO₃ reaction.

Table 5.2. Functional group composition of the SOA formed from the reaction of a variety of monoterpenes with NO₃ radicals.

	Limonene	α -Pinene	β -Pinene	β -Pinene ^a
Functional Group	Functional Group / C ₁₀ Molecule			
Peroxide [HCOOH]	0.03	0.01	0.02	0.06
Ester [O=COR]	0.17	0.04	0.01	0.12
Carbonyl [C=O]	0.17	0.18	0.43	0.28
Carboxyl [O=COH]	0.00	0.00	0.06	0.04
Nitrate [HCONO ₂]	1.05	0.71	1.12	0.76
Hydroxyl [HCOH]	0.02	0.05	0.00	0.08
Methylene [CH ₂]	8.56	9.00	8.37	8.65
O/C	0.37	0.25	0.40	0.31
H/C	1.83	1.88	1.80	1.84
N/C	0.10	0.07	0.11	0.08
MW ^c	213	188	217	199
C* ($\mu\text{g m}^{-3}$)	5×10^4	1×10^5	1×10^4	5×10^4
Density (g/mL)	1.19	1.07	1.21	1.12

^a SOA formed with (NH₄)₂SO₄/H₂SO₄ seed.

Table 5.3. Functional group composition of the SOA formed from the reaction of a variety of monoterpenes with NO₃ radicals in the presence of CH₂O.

	Limonene	α -Pinene	Camphene	β -Pinene	β -Pinene ^a
Functional Group	Functional Group / C ₁₀ Molecule				
Peroxide [HCOOH]	0.05	0.01	0.17	0.05	0.14
Ester [O=COR]	0.18	0.48	0.70	0.21	1.29
Carbonyl [C=O]	0.33	0.37	1.74	1.38	0.80
Carboxyl [O=COH]	0.01	0.14	0.43	0.32	0.19
Nitrate [HCONO ₂]	0.64	0.63	0.65	0.75	0.52
Hydroxyl [HCOH]	0.06	0.01	0.15	0.07	0.04
Methylene [CH ₂]	8.74	8.35	6.17	7.22	7.02
O/C	0.28	0.35	0.64	0.49	0.57
H/C	1.83	1.75	1.41	1.57	1.51
N/C	0.06	0.06	0.06	0.07	0.05
MW ^c	192	203	246	224	233
C* ($\mu\text{g m}^{-3}$)	1×10^5	5×10^4	6	1×10^3	1×10^3
Density (g/mL)	1.10	1.17	1.46	1.31	1.37

^a SOA formed with (NH₄)₂SO₄/H₂SO₄ seed.

Table 5.4. Functional group composition of the SOA formed from the reaction of a variety of VOCs either with OH radicals in the presence of NO_x or with O₃.

	Pentadecane	Isoprene	α -Pinene	α -Pinene ^a	α -Pinene
	OH/NO _x			O ₃	
Functional Group	Functional Group / Molecule				
Peroxide [HCOOH]	0.06	0.04	0.08	0.13	0.09
Ester [O=COR]	0.45	0.61	0.65	0.71	0.27
Carbonyl [C=O]	0.52	0.32	0.69	1.66	0.95
Carboxyl [O=COH]	0.07	0.28	0.08	1.62	1.22
Nitrate [HCONO ₂]	0.99	0.33	0.55	0.00	0.00
Hydroxyl [HCOH]	0.40	0.28	0.23	0.14	0.06
Methylene [CH ₂]	12.52	3.14	7.07	5.74	7.41
O/C	0.34	0.69	0.42	0.67	0.42
H/C	1.80	1.51	1.54	1.36	1.63
N/C	0.07	0.07	0.06	0.00	0.00
MW ^c	301	127	203	241	203
C* (μg m ⁻³)	10	1 x 10 ⁶	1 x 10 ⁴	0.1	50
Density (g/mL)	1.14	1.45	1.27	1.45	1.20

^a SOA formed without the presence of seed.

stretching region and in every ammonium sulfate molecule there are eight N–H bonds contributing to absorbance in that area of the FTIR spectrum. This could account for the especially high bias in the SOA generated in the reaction of VOCs with NO₃ radicals, where the Deriv-Spec methods measured very little contribution for group 1 while the FTIR methods had large contributions. The second discrepancy is associated with group 2, where it appears that the FTIR analysis is biased low. This could either be because the measurements are close to the FTIR method limit of quantification (5–10% of the SOA), or because the non-acid carbonyl group measurement is calculated by subtracting the acid carbonyl content associated with C–OH from the total carbonyl, and the low bias is an artifact of that approach. Nonetheless, these discrepancies do not significantly change any of the conclusions drawn from the analyses of the environmental chamber or the SOAS field samples.

While groups 1 (carboxyl + alcohol + peroxide) and 2 (ketone/aldehyde + ester) appear to be subject to the above discrepancies, the agreement for groups 3 (nitrate) and 4 (alkane) is quite good. Overall, the agreement for group 3 is between 4–15% for the two methods. And even though the nitrate measurements for the β -pinene + NO₃ SOA fall outside this range, for that case the methods still agree within a factor of two. The agreement for group 4 is within ~20%, with a range of 1–23% and an average of 14% for the two methods.

5.3.2 Environmental Chamber Studies: Characteristic Observations. A number of valuable observations were made by comparing the measured functional group composition for the chamber SOA generated by the different VOC + oxidant systems (Figure 5.1 and 5.2, Tables 5.2, 5.3, and 5.4). In theory, by recognizing features of the composition that are characteristic of particular oxidation system these results could be used to interpret and identify SOA sources in ambient samples. These results are as follows. 1) SOA formed from reactions of the four

monoterpenes with NO_3 radicals under the same reaction conditions always had a large contribution from nitrate groups. While this was expected because the reaction is initiated by the addition of NO_3 to the $\text{C}=\text{C}$ double bond in the monoterpene precursor, primarily at the least substituted carbon,⁵⁰ the large contribution of nitrate groups in the SOA shows that the nitrates that are formed in the reaction are stable and not susceptible to particle-phase reactions such as hydrolysis. It thus appears that the nitrate groups formed in these reactions are a mixture of primary and secondary nitrates, consistent with expectations based on monoterpene structure and the absence of obvious loss of nitrates by hydrolysis, since it has been shown that tertiary nitrates hydrolyze on timescales relevant to these chamber reactions and sample processing.^{62,63}

2) The SOA formed from the reaction of monoterpenes with NO_3 radicals contains a surprisingly small fraction of alcohol and peroxide groups. Although the carbonyl contribution also appears to be small compared to the nitrate contribution, this difference is significantly reduced if composition is reported as number of functional groups per molecule (essentially by mole fraction) rather than mass fraction (Table 5.2). The lack of peroxide groups in the aerosol is indicative of an absence of $\text{RO}_2^\bullet + \text{HO}_2$ reactions occurring in the chamber experiments, since these reactions lead to the production of hydroperoxides.⁸ The small fraction of peroxides in the SOA also indicates that the $\text{RO}_2^\bullet + \text{RO}_2^\bullet$ reaction resulting in the formation of dialkyl peroxide dimers is likely negligible. The absence of a significant contribution from alcohols to the SOA produced from these reactions is likely a sign of particle-phase reactions occurring in the aerosol to form acetals. This has been shown to be the case for the reaction of β -pinene with NO_3 radicals (Chapter 2),⁹⁰ when either a hemiacetal or an alcohol reacts with another alcohol through a dehydration reaction to form an acetal, respectively. Both of these reactions result in the loss of two alcohol groups for every acetal formed.

3) The SOA formed from the reaction of isoprene or monoterpenes (in this

case α -pinene) with OH radicals in the presence of NO_x contains similar amounts of nitrate groups to the SOA formed from the reaction of monoterpenes with NO₃ radicals, but the SOA formed from the OH/NO_x reaction also contains significant amounts of carboxyl, carbonyl, and ester groups. This difference in aerosol composition might make it possible to distinguish contributions to SOA from daytime OH/high-NO_x reactions and nighttime NO₃ reactions. 4) The SOA formed from the reaction of isoprene with OH radicals in the presence of NO_x and from the ozonolysis of monoterpenes (α -pinene) in the absence of NO_x (both systems are considered to be important ambient daytime SOA sources) contains significant fractions of carboxyl groups. Therefore, the presence of a significant amount of carboxyl and nitrate groups in ambient samples could indicate the reaction of isoprene with OH/NO_x as an SOA source, but if there is a significant amount of carboxyl groups and little nitrate then monoterpene ozonolysis is the more likely source of the SOA. It is important to note that the reaction of monoterpenes with OH radicals under low-NO_x conditions could also contribute to the latter case (high carboxyl, low nitrate content), but these could not be studied in the lab because of the loss of oxidation products to the chamber walls during the slow reaction. 5) The presence of ester groups in the SOA is a clear indicator of either Baeyer-Villiger type reactions between peroxides and carbonyls (Chapter 4)^{53,54} or possibly acid-catalyzed particle-phase reactions between carboxyl and alcohol groups.⁸ As will be discussed below, the results of the functional groups analyses of SOA formed in the environmental chamber experiments can be used to help interpret the SOAS field samples that were also analyzed by the CU and SIO methods.

5.3.3 Analysis of SOAS Field Samples. Four field samples from the SOAS campaign were analyzed by both the FTIR and Deriv-Spec methods. Each field sample contained several filter samples that were collected under similar atmospheric conditions to provide enough mass

to be analyzed by both methods. As described above, the four field samples, two from the Centerville, AL (CTR) site and two from the Look Rock, TN (LRK) site, were grouped as follows: 1) combined daytime and nighttime samples from LRK during low-NO_x conditions 2) combined daytime and nighttime samples from LRK during high-NO_x conditions 3) nighttime samples from CTR during low-NO_x conditions and 4) daytime samples from CTR during high-NO_x conditions. It should be noted that although the field samples have been assigned as high- or low-NO_x, the actual NO_x conditions under which the aerosol was formed are difficult to determine because the history of the SOA in the atmosphere is uncertain, especially for pooled samples like those analyzed here.

The results of these measurements are shown in Figure 5.3, though it is important to note that for the reasons stated above peroxide and nitrate groups were not analyzed with the Deriv-Spec methods, and because FTIR analyses of nitrate groups were below the limit of quantification at both sites (approximately 5% of total organic matter),¹⁶⁴ neither peroxide or nitrate groups are included in the figure. Furthermore, whereas groups 1 (carboxyl + alcohol + peroxide) and 2 (ketone/aldehyde + ester) are the same as those defined for the laboratory studies, groups 3 (amine) and 4 (alkane + alkene + aromatic) have been modified because of the possible contributions of new functional groups to the FTIR analyses. Instead of being nitrate, group 3 is now amine, which can be measured by FTIR but not the Deriv-Spec methods, and for group 4 alkene and aromatic groups have been added to alkane groups since they can be measured by the FTIR (but not the Deriv-Spec) methods. When grouped in this manner the agreement between the methods is quite good, especially considering the complexity of ambient samples, and the large amount of time that lapsed between the FTIR analysis and the Deriv-Spec

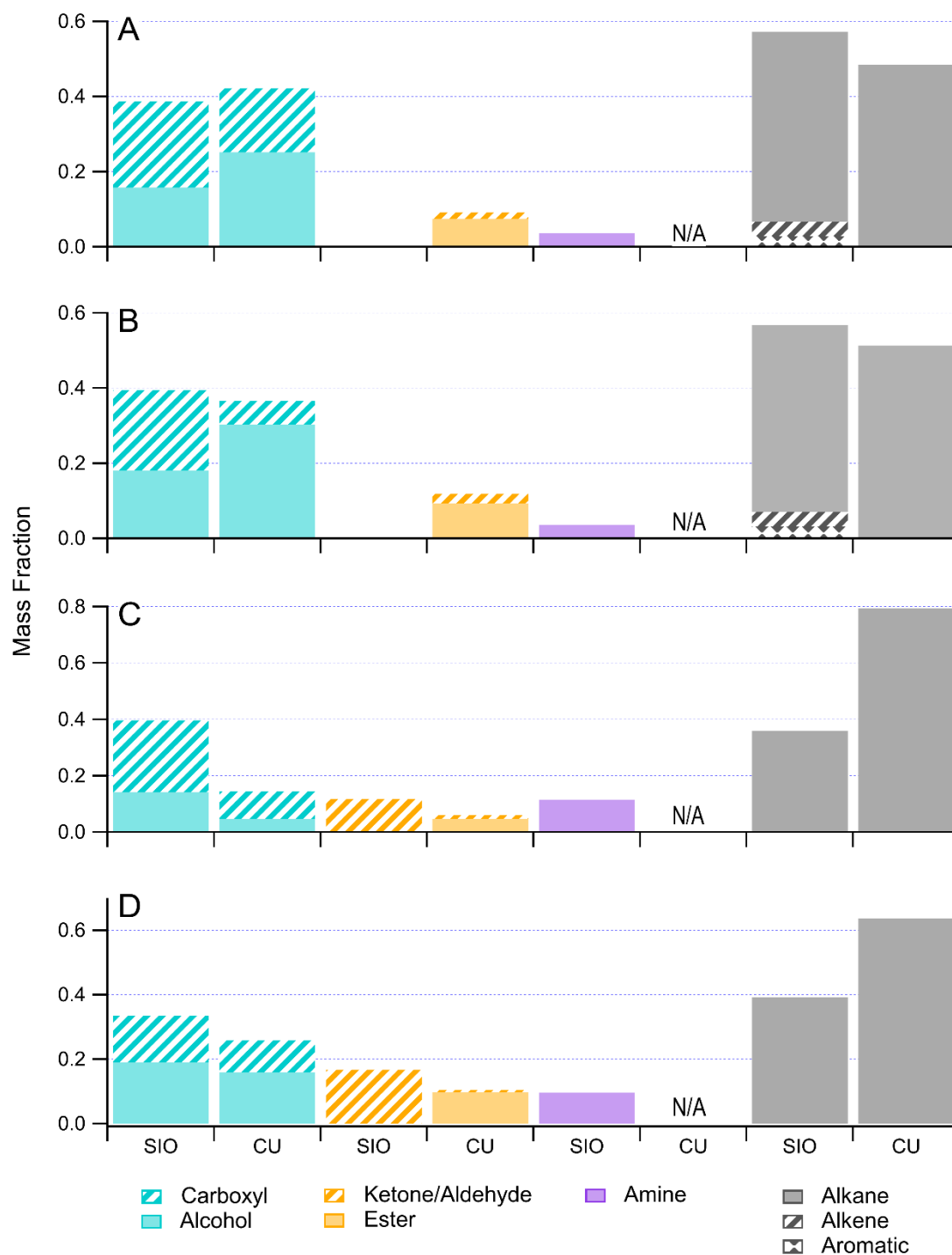


Figure 5.3. Functional group composition of SOAS samples collected at (A,B) Look Rock, TN and (C,D) Centerville, AL measured by derivatization-spectrophotometric (CU) and FTIR methods (SIO). (A) and (B) were combined daytime + nighttime samples collected under (A) low NO_x conditions and (B) high NO_x conditions. (C) nighttime low NO_x and (D) daytime high NO_x conditions.

analysis (> 1 year). It does appear that there are discrepancies between the results obtained from the two methods, however, which will be discussed for the LRK and CTR samples separately.

The results for the LRK samples (Figure 5.3A and 5.3B) show excellent agreement for group 1, with measurements being within 10% of each other. Good agreement is also seen for group 4, where the measurements are within 17% and 11% for the low-NO_x (Figure 5.3A) and high-NO_x (Figure 5.3B) samples. When comparing group 2, however, there is a similar trend in both LRK samples. The Deriv-Spec methods measure significant ester content with small contribution from carbonyl groups for both the LRK low-NO_x (Figure 5.3A) and high-NO_x (Figure 5.3B) samples, whereas the FTIR method did not detect any contribution from this group to the LRK aerosol composition. A possible reason for this discrepancy is that for both LRK samples the FTIR method measures more carboxyl than the Deriv-Spec methods (factors of 1.4 and 3.5 higher for the low- and high-NO_x samples). As discussed above, the FTIR non-acid carbonyl measurement involves subtraction of the acid-carbonyl content from the total carbonyl content. From this comparison it appears that the FTIR method may have attributed too much of the total carbonyl content to the acid-carbonyl and thus potentially underestimated the non-acid carbonyl content of the LRK aerosol.

The results for the CTR low-NO_x nighttime sample (Figure 5.3C) show good agreement for group 2, within a factor of two, but there are discrepancies in the results obtained for groups 1 and 4. For group 1, the FTIR method measured 2.3 and 2.8 times more carboxyl and alcohol content than the Deriv-Spec methods, which could be due to interference from other groups that absorb in the C–OH stretching region of the FTIR spectrum and thus overestimate the amounts of these groups. Owing to the complexity of ambient samples, however, this is only speculation. For group 4, the Deriv-Spec method measured 2.2 times more alkane than the FTIR method. A

possible reason for this could be that the Deriv-Spec alkane fraction is not determined by direct measurement, but by difference assuming a mass balance. Because any aerosol mass that was not measured as carbonyl, carboxyl, ester, or alcohol groups by the Deriv-Spec methods was assumed to be alkane groups, significant contributions from unmeasured groups such as amines, ethers, nitrates, or organosulfates would result in an over estimate of the Deriv-Spec alkane measurement. The results for the CTR high-NO_x daytime sample (Figure 5.3D) shows reasonably good agreement for groups 1 and 2, within a factor of 1.3 and 1.5, respectively, and the 1.6 times higher value for group 4 may again be due to the mass-balance approach employed to measure alkane groups.

5.3.4 Comparison to Chamber Samples. The results of the analyses of SOA formed in the environmental chamber experiments can be used to help interpret the SOA field samples analyzed using the Deriv-Spec and FTIR methods. The following interpretations are based on the more specific Deriv-Spec analyses. As shown in Figure 5.3, all field samples contained significant contributions from carboxyl, ester, and alcohol groups and relatively little ketone and aldehyde groups. Comparing this composition with Figure 5.1 and 5.2 indicates that this SOA was formed with a significant contribution from reactions of isoprene with OH radicals under high-NO_x conditions. This is consistent with other measurements made at SOAS that attribute ~20% of the total organic aerosol to isoprene oxidation products at both the LRK and CTR field sites.^{162,164} The Deriv-Spec results also indicate that the carboxyl groups in the nighttime SOA sample (Figure 5.3C) is from the reaction of monoterpenes with O₃, since NO₃ reactions do not produce these groups. This is consistent with the PMF analysis of AMS data conducted by Massoli et al.¹⁶⁰ for the CTR site, which concluded that the nighttime terpene factor was due mostly to products of monoterpene ozonolysis. The high amount of ester groups measured in all

samples is strong evidence that particle-phase reactions have occurred, either through Baeyer-Villager reactions involving the oxidation of carbonyls by hydroperoxides or peroxyacids (Chapter 4) or through acid-catalyzed reactions of carboxyl and alcohol groups. This observation is consistent with other SOAS studies that associated the presence of acidic sulfate seed aerosol with evidence of heterogeneous chemistry during the campaign.^{161,165}

5.4 Conclusions

In this study, the SIO FTIR and CU Deriv-Spec methods for quantifying the functional group composition of SOA were compared. When used to quantify SOA composition generated from a series of environmental chamber reactions, the methods agreed quite well when the results were grouped into four categories: 1) functional groups that contain an O–H bond, 2) non-acid functional groups containing a C=O moiety, 3) nitrate groups, and 4) alkane groups. While the agreement between the methods was quite good, discrepancies were observed in groups 1 and 2 that appear to stem from interferences in the FTIR spectrum that affect the assignment of acid- and non-acid carbonyl groups using the SIO FTIR algorithm. Overall, the agreement between the two methods signals that either is adequate for measuring the functional group composition of SOA, especially if the discrepancies described above are resolved. While the Deriv-Spec methods offer more specificity, they also require more time and aerosol mass for sample analysis than the FTIR methods. Depending on the type of information desired, one method might be more favorable than the other.

Comparison of the functional group composition of SOA formed from a variety of different VOC + oxidant reactions resulted in a number of observations. 1) SOA formed from reactions of monoterpenes with NO₃ radicals had a large contribution from nitrate groups with negligible amounts of peroxide and alcohol groups. This has implications for understanding the

importance of particle-phase processing, such hydrolysis and oligomerization reactions that form acetals, while also providing insight into the fate of gas-phase $\text{RO}_2^\bullet$ radicals in these experiments. 2) SOA formed from either isoprene or monoterpenes with OH radicals in the presence of NO_x contained similar amounts of nitrate groups as in the NO_3 radical reactions, but also contained significant amounts of carboxyl, carbonyl, and ester groups. This difference in composition might be used to distinguish contributions to SOA from daytime OH/high- NO_x and nighttime NO_3 reactions. 3) SOA generated from reactions of isoprene with OH radicals in the presence of NO_x and from the ozonolysis of monoterpenes contained significant amounts of carboxyl groups. Therefore, the presence of large amounts of carboxyl and nitrate groups in ambient samples containing may indicate the reaction of isoprene with OH/ NO_x as the SOA source, whereas the presence of carboxyl groups with little nitrate may indicate monoterpene ozonolysis as the source. 4) Lastly, the presence of ester groups is a sign of particle-phase processing, either through the Baeyer-Villager oxidation of ketones by peroxides or through acid-catalyzed esterification reactions.

These observations were used to help interpret the results of functional group analyses made on a few SOAS aerosol samples, which resulted in a number of conclusions. 1) There appears to be a significant contribution to samples taken at the LRK and CTR field sites from SOA formed from the reaction of isoprene with OH radicals in the presence of NO_x . This was inferred from the large amounts of carboxyl, ester, and alcohol groups and relatively little carbonyl content. 2) SOA formed from monoterpene ozonolysis was indicated as the source of the nighttime CTR sample based on the large amounts of carboxyl groups, which are not a product of the reaction of monoterpenes with NO_3 radicals. Because the nighttime CTR samples analyzed were collected under low- NO_x conditions, however, it would be interesting to also

measure the composition of samples collected during high-NO_x nighttime conditions. 3) The large amounts of ester groups measured in all the field samples indicates the importance of heterogenous Baeyer-Villager or oligomerization reactions in these ambient samples.

The results of this study demonstrate that measuring the functional group composition of SOA can give information as to the sources and environmental conditions under which the aerosol was formed, especially when paired with laboratory experiments that target potentially important reaction systems. Furthermore, it was shown that by using certain functional group composition signatures it is sometimes possible to determine the type of oxidation (for example, reactions initiated by NO₃ radicals or OH radicals in the presence of NO_x) responsible for the formation of aerosol.

Chapter 6

Thesis Conclusions

The results presented in this thesis provide fundamental insight into the oxidation reactions of monoterpenes and the subsequent SOA formation. The measurements made across the various reaction systems highlight the importance of particle-phase reactions in SOA formation and demonstrate the value of bulk functional group composition measurements for constraining the reaction mechanisms of SOA formation in complex systems, especially when a more detailed molecular analysis is not feasible.

The components of the SOA formed from the reaction of β -pinene with NO_3 radicals were identified and quantified using a variety of analytical methods including, liquid chromatography paired with electron, chemical, and electrospray ionization mass spectrometry for molecular analysis, and derivatization-spectrophotometry and attenuated total reflectance-Fourier transform infrared spectroscopy for bulk functional group analysis. Overall, ~95% of the SOA mass was identified and quantified for this reaction system that is of interest to the atmospheric chemistry research community due to its ability to efficiently form aerosol with high SOA yields. Eight speciated products were identified in the SOA, of which more than 90% by mass consisted of acetal heterodimers and heterotrimers. The molar yield of the major oligomer product (C_{20} dinitrate acetal) was 16.7%, the yields of the other 6 oligomers ranged from 1.1% to 2.9%, and the yield of the only monomer identified in the SOA (tricarboxylnitrate) was 2.0%, for a total yield of 30.7%. Yields of the monomer building blocks could also be determined and were

23.6% and 25.9% for the 2 major monomer building blocks, while the yields of the other 4 ranged from 2.0% to 4.8%, for a total monomer yield of 62.4%. The identification of the SOA products was used to develop gas- and particle-phase reaction mechanisms. From the measurements and developed mechanisms it appears that the accretion reactions were promoted by the structures of the monomers; these compounds usually contained carbonyl groups that were activated by the presence of an adjacent electron-withdrawing nitrate group, and highly reactive tertiary hydroxyl groups. The presence of both groups made these compounds especially susceptible to hemiacetal formation, followed by dehydration reactions to form the acetals in the phase-separated aerosol. The results of this study demonstrate the importance of ring-opening, alkoxy radical decomposition, and oligomerization reactions in the NO_3 radical-initiated oxidation of β -pinene and the subsequent formation of SOA, and should be applicable to other monoterpene reactions, especially those that form radical intermediates and oxidation products with similar structures to those identified here. These results are currently being used with more recent measurements of a few gas-phase products to develop a comprehensive, quantitative kinetic model that includes gas- and particle-phase reactions and gas-wall partitioning, which should be useful for modeling this and similar systems in the laboratory and atmosphere.

The overwhelming presence of oligomers (initially formed through hemiacetal reactions followed by acetal formation) that were identified in the SOA formed from the reaction of β -pinene with NO_3 radicals prompted a follow-up study detailing how these compounds respond to detection with thermal desorption methods. The results showed that when hemiacetal compounds were analyzed by thermal desorption mass spectrometry in real time, by rapid vaporization, they were ionized and detected as the intact oligomer. However, when they were analyzed using slow thermal desorption the hemiacetal decomposed to its precursors before the monomers were

desorbed into the ionization region and detected. The different responses of the hemiacetal to these analyses is due to differences in the desorption timescales of each method, with only the slow thermal desorption method allowing sufficient time for the hemiacetal dimer to decompose prior to desorption and detection. This decomposition is also promoted by the mechanism of hemiacetal formation, which involves the rearrangement of a few atoms with no additional reactants or eliminations, thus allowing for a simple reverse of this process during the slow thermal desorption. From these experiments, it was also clear that thermal decomposition reactions of hemiacetals are highly dependent on the structure of the hemiacetal. When a hemiacetal trimer, formed by two hemiacetal reactions, was subjected to slow thermal desorption it stayed intact throughout the desorption process and was ionized and detected as the intact compound. This effect is likely due to an acetal linkage that is added when the trimer is formed, and which adds stability throughout the heating process, a result that also explains previous observations made for peroxyhemiacetals in our laboratory. Unlike with the hemiacetal dimers, thermal decomposition was not observed when dimers and trimers containing acetal linkages were analyzed by the same methods. This is likely because acetals are formed through dehydration reactions, so the reverse reaction to reform the monomer precursors requires the presence of water that is not available during these analyses due to rapid evaporation at the early stages of heating. From these measurements, it appears that if the aerosol being analyzed by thermal desorption methods contains oligomers bound by a single hemiacetal or peroxyhemiacetal linkage they will decompose to their precursors before detection. But if the oligomers contain more than one of these linkages, or acetal or ester (also formed by dehydration) linkages, they will desorb and be detected as the intact oligomer. Using these insights when interpreting the results of thermal desorption analyses could allow information to

be extracted about the types of linkages binding oligomers in the SOA, and subsequently the types of accretion reactions that caused them to form.

The composition of SOA formed from α -pinene ozonolysis over a range of α -pinene concentrations and humidities, including conditions that promote the formation of highly oxidized multifunctional compounds (HOMs) through autoxidation, was characterized for its functional group composition using derivatization-spectrophotometric methods that quantify the contributions of peroxide, ester, carbonyl, carboxyl, and hydroxyl groups in the aerosol. By normalizing the functional group composition to the carbon number of the parent VOC, the results were used to estimate the number of each functional group per molecule, the total number of functional groups per molecule, the total number of oxygen atoms per molecule, and the atomic O/C and H/C ratios. In this study, we demonstrated that all the information gathered from the functional group composition can be useful for developing and evaluating gas- and particle-phase reactions mechanisms and models of VOC oxidation and SOA formation. The results from the high concentration experiments were similar under dry and humid conditions, making it appear that the gas-phase products that contributed to SOA in both cases were similar, consisting of monomers that contained on average 3–4 peroxide, carbonyl, carbonyl, or hydroxyl groups. While the measured total number of functional groups was similar to that predicted by the Master Chemical Mechanism (MCM) model, the distribution of the functional groups was considerably different. The likely cause of this discrepancy is that particle-phase reactions are not accounted for in the MCM. In the low concentration experiments, where the presence of gas-phase HOMs was verified using a NO_3 -CIMS, the total number of functional groups per molecule ranged from 3–5, and was higher when the SOA was formed under humid conditions. The distribution of functional groups between dry and humid conditions differed significantly as

well. The reasons for these distributions were tied to changes in the gas-phase chemistry, including the addition of autoxidation reactions, gas-phase dimer formation, particle-phase hydrolysis reactions, and gas-to-particle partitioning of small carbonyl compounds. Overall, it appeared that gas-phase monomer and dimer products formed through $\text{RO}_2^\bullet + \text{RO}_2^\bullet$, $\text{RO}_2^\bullet + \text{HO}_2$, $\text{RO}_2^\bullet$ isomerization, and stabilized Criegee intermediate + carboxylic acid or water reactions all contributed to SOA formation, but that upon entering particles the aldehyde and ketone groups in these compounds were often oxidized to carboxyl and ester groups through Baeyer-Villager reactions with hydroperoxides and peroxydicarboxylic acids. The aerosol composition measurements reported provide constraints for models and future experimental work attempting speciated molecular analysis on this widely studied reaction system.

The last section of this thesis compared two methods that have been developed to quantify the functional group composition of SOA: 1) a Fourier Transform Infrared (FTIR) spectroscopy method developed by the Russell group at the Scripps Institute of Oceanography (SIO) and 2) a derivatization-spectrophotometric method developed by the Ziemann group at the University of Colorado, Boulder (CU). The two methods were compared by measuring functional group compositions of SOA generated from a series of environmental chamber reactions and using ambient aerosol samples collected during the Southern Oxidant and Aerosol Study (SOAS) campaign. Using the laboratory generated SOA, the two methods measure functional group compositions that agree well when the results are grouped into four categories: 1) functional groups that contain an O–H bond, 2) non-acid functional groups containing a C=O moiety, 3) nitrate, and 4) alkane functional groups. While some discrepancies were observed with the SIO method, overall the comparisons show that either is acceptable for measuring SOA composition. In addition to using the laboratory generated SOA to compare the two methods, the

SOA compositions measured in those experiments were also used to identify trends in composition in different oxidation systems. 1) SOA formed from reactions of monoterpenes with NO_3 radicals had a large contribution from nitrate groups with negligible amounts of peroxide and alcohol groups. 2) SOA formed from either isoprene or monoterpenes with OH radicals in the presence of NO_x contained similar amounts of nitrate groups to SOA formed from NO_3 radical reactions, but the SOA formed from the OH/high- NO_x reactions also contained significant amounts of carboxyl, carbonyl, and ester groups. 3) SOA generated from the reaction of isoprene with OH radicals in the presence of NO_x and from the ozonolysis of monoterpenes both contained significant amounts of carboxyl groups. 4) The presence of ester groups is a sign of particle-phase processing, either through Baeyer-Villager oxidation of ketones by peroxides or acid-catalyzed esterification reactions. These observations were then used to interpret the composition of ambient samples in an effort to identify aerosol sources, and allowed for a number of conclusions. 1) The oxidation of isoprene by OH radicals in the presence of NO_x appears to significantly contribute to aerosol samples collected at both the Look Rock, TN and Centreville, AL sites. 2) Monoterpene ozonolysis was determined to be the source of the nighttime CTR samples. 3) The large amounts of ester groups measured in all the field samples analyzed in this work indicates the importance of heterogeneous reactions in these ambient samples. The results of this study show that the functional group composition measurements made using the SIO FTIR and CU derivatization-spectrophotometric methods are comparable, with the choice of method depending on the type information desired. Furthermore, it was shown that functional group composition measurements, when paired with targeted laboratory experiments, can give information on the sources and environmental conditions under which SOA was formed.

The results reported in this thesis provide significant advances in the understanding of gas- and particle-phase reaction products and mechanisms involved in the formation of SOA from the oxidation of monoterpenes. As demonstrated by the work presented here, by conducting an extensive series of laboratory studies that employ a variety of online and offline analytical methods to characterize the molecular and functional group composition of SOA it is possible to obtain substantial insights into complex gas- and particle-phase reactions through molecular identification and quantification of reaction products, or through top-down measurements of functional group compositions that provide constraints on molecular analysis.

While the results presented in this thesis advance the understanding of the gas- and particle-phase reactions occurring in these systems, they also draw attention to several fundamental processes that should be studied in the future, including the following: 1) the kinetics of relevant particle-phase reactions in authentic aerosol systems, 2) the effect of molecular structure on the kinetics and equilibria of these particle-phase reactions, 3) the extent of phase separation in aerosols, and the impact of this separation on the role of strong acids in catalytic reactions, and 4) the effect of complex parent VOC structures, like monoterpenes, on $\text{RO}_2^\bullet$ isomerization reaction rates. Progress on all of these research fronts are necessary for constraining these processes and implementing them into models.

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