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Analysis of Secondary Organic Aerosol Compounds from the Photooxidation of *d*-Limonene in the Presence of NO_x and their Detection in Ambient PM_{2.5}

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Chemical analysis of secondary organic aerosol (SOA) from the photooxidation of a *d*-limonene/NO_x/air mixture was carried out. SOA, generated in a smog chamber, was collected on Zefluor filters. To determine the structural characteristics of the compounds, the filter samples were solvent extracted and derivatized using analytical techniques that characterize functional groups contained in the compound: BF₃-methanol derivatization was used for carboxylic groups, BSTFA for acidic and nonacidic hydroxyl groups, and PFBHA for ketone and aldehyde groups. The resulting derivative compounds were analyzed by GC–MS in the methane CI and EI modes. GC–MS analysis showed the occurrence of 103 oxygenated organic compounds in the filter extracts, 28 of which were identified. The major components include five tracer compounds previously identified from the photooxidation of α -pinene/NO_x or β -pinene/NO_x systems, C₄–C₆ linear dicarboxylic acids, ketolimononaldehyde, limonic acid, and ketolimononic acid. Time profiles, yields, and proposed reaction schemes are provided for selected compounds. The laboratory SOA yield was 0.51 at a SOA concentration of 1470 $\mu\text{g m}^{-3}$. To determine the contributions of SOA products from *d*-limonene to ambient PM_{2.5}, an analysis was performed for eight ambient PM_{2.5} samples collected in the southeastern United States in summer 2003. GC–MS analysis showed the occurrence of 21 *d*-limonene SOA compounds, indicating the impact of *d*-limonene on the regional aerosol burden. Based on our analysis, two compounds (nos. 55 and 69), not observed from the photooxidation of α -pinene or β -pinene, are candidate tracers for *d*-limonene in atmospheric particulate matter.

Introduction

Biogenic compounds constitute a significant fraction of hydrocarbons emitted into the atmosphere (1). The primary

mechanism of removal of these hydrocarbons from the atmosphere is through gas-phase reaction with the hydroxyl and nitrate radicals and ozone to produce nonvolatile and semivolatile compounds that can condense onto particulate matter (PM) and contribute to ambient secondary organic aerosol (SOA) and tropospheric ozone production. A number of studies have shown the relationship between exposure to PM_{2.5} (PM with diameter <2.5 μm) and adverse health effects (2). As the understanding of the toxicology associated with these particles develops, more accurate compositional data may be required.

A wide range of organic compounds from primary and secondary sources, including polar oxygenated compounds (POCs) bearing one or more functional groups (e.g., hydroxyl (–OH), carboxylic (–COOH), ketone (>CO), and aldehyde (–HCO)), have been identified in PM_{2.5}, although less than 25% of organic mass has been accounted for. Monoterpenes, particularly α - β -pinene, and *d*-limonene, are emitted in relatively large quantities into ambient atmosphere. While SOA formation from α - and β -pinene has been investigated in many laboratories, few studies have reported *d*-limonene SOA, one of the most frequently emitted monoterpenes from vegetation (3, 4), notwithstanding its high SOA yield (5–13).

Recently, an analytical technique was developed in our laboratory for the characterization of POCs bearing one or more of the following groups: –OH, –COOH, >CO, and –HCO (14). This method is based on derivatizing –COOH groups using BF₃-methanol as the derivatizing reagent, –COOH/–OH groups using BSTFA as the silylation reagent, and >CO/–HCO groups using PFBHA. GC–MS analysis in electron impact (EI) ionization or positive chemical ionization (CI) mode was used for identification and/or quantification of POCs. In the present study, the chemical composition of SOA from the photooxidation of a *d*-limonene/NO_x/air system was determined using the new method (14). In addition, a similar chemical analysis of eight PM_{2.5} field samples (FS) was carried out to determine the occurrence of *d*-limonene tracer compounds. To account for some observed SOA reaction products, a chemical mechanism is proposed in this study.

Materials and Methods

All chemicals, including derivatization reagents (BF₃-methanol, BSTFA 1% trimethylchlorosilane, and PFBHA), were purchased from Aldrich Chemical Co. (Milwaukee, WI) at the highest purity available and were used without further purification. All solvents (GC² quality) were from Burdick and Jackson (Muskegon, MI).

The experiments were carried out in a 14.5-m³ parallel-lepipiped, Teflon-coated stainless steel chamber. Details of the chamber, its operation, and the experimental methods are described elsewhere (15). The derivatization procedures used in this study were reported in our previous paper (14), which included a discussion of the optimization and possible artifacts associated with each procedure. Two sets of experiments were conducted (Table 1). A dynamic experiment (DE) was conducted with a 6-h residence time, chosen to ensure that a highly oxidized aerosol would be produced. SOA was collected for 24 h and multiple derivatization techniques were used to identify compounds. In addition, a static experiment (SE) was carried out for *d*-limonene, in which five 90-min samples were collected, and product time profiles were examined using BSTFA derivatization. No seed aerosol was used in these experiments and *d*-limonene SOA is assumed to be new particle growth.

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TABLE 1. Initial Conditions for the Smog Chamber Experiments

| experiment | NO (ppb) | NO _x (ppb) | <i>d</i> -limonene (ppmC) | RH (%) | SOA ^a (μg m ⁻³) |
|------------|-------------|--------------------------|------------------------------|-----------|---|
| DE | 222 | 226 | 2.88 | 30 | 274 |
| SE | 470 | 497 | 5.33 | 29 | 1592 |

^a Maximum value observed corrected for dilution and wall loss.

Ozone was measured with a Bendix ozone monitor (model 8002, Lewisburg, WV). NO and NO_x were monitored with a TECO oxides of nitrogen analyzer (model 42C, Franklin, MA). Temperature and relative humidity were determined with an Omega digital thermohygrometer (model RH411, Omega Engineering, Inc., Stamford, CT). *d*-Limonene was collected from the chamber using a cryogenic trap and analyzed by GC–FID (model 5890, Hewlett-Packard, Palo Alto, CA). Light intensity was continuously monitored with an integrating radiometer (Eppley Laboratory, Inc., Newport, RI). The NO₂ photolysis rate was approximately 0.17 min⁻¹. SOA was collected at 16.7 L min⁻¹ with a 60-cm XAD4-coated annular denuder (URG, Inc., Chapel Hill, NC) to remove gas-phase products followed by a 47-mm Zefluor filter (Pall Gelman Laboratory, Ann Arbor, MI). SOA concentration was based on gravimetric measurements of the Zefluor filters. The Zefluor filters were Soxhlet extracted for 24 h using methylene chloride before using them. Eight PM_{2.5} samples were collected during summer 2003 in Research Triangle Park, NC. Descriptions of the field site and sampling procedures have been reported previously (16).

Filters collected from the chamber irradiation were Soxhlet extracted for 6 h in dichloromethane, and FS filters were extracted for 24 h in dichloromethane/acetonitrile mixture (1:1 v/v). For this work, field and dynamic samples were used to aid in identification of compounds or for confirmation purposes. Therefore, the four derivatization techniques reported above were used for these samples. Prior to extraction, 20 μg each of *trans*-p-menth-6-ene-2,8-diol (PMD), bornyl acetate (BA), *cis*-ketopinic acid (KPA), and d₅₀-tetracosane (TCS) were added as internal/recovery standards. FS and DE filter extracts were dried with ultrapure dry nitrogen and then were reconstituted with 2 mL of the original solvent. Extracts were split into four equal parts, and each part was placed in a 15-mL tube, evaporated to dryness, and then derivatized as follows. The first extract was derivatized only with BSTFA. The second extract was derivatized with BF₃-methanol, followed by PFBHA, then BSTFA. The third extract was derivatized with PFBHA followed by BSTFA. The fourth extract was derivatized with BF₃-methanol followed by BSTFA. After each derivatization step, 2 μL was analyzed by GC–MS. Up to seven chromatograms were obtained for each sample. For the SE samples, only BSTFA derivatization was used for quantitative analysis. The BSTFA derivatization efficiency was previously found to be greater than 95% (14).

GC–MS analysis was conducted on a ThermoQuest GC coupled with an ion trap mass spectrometer (Austin, TX). The injector, heated to 270 °C, was operated in splitless mode. Compounds were separated on a 60-m-long, 0.25-mm-i.d. RTX-5MS column (Restek, Inc., Bellefonte, PA) with a 0.25-μm film thickness. The GC oven temperature program for the analysis started isothermally at 84 °C for 1 min followed by a temperature ramp of 8 °C min⁻¹ to 200 °C, followed by a 2-min hold, then 10 °C min⁻¹ to 300 °C and a 15-min hold. The ion source, ion trap, and interface temperatures were 200, 200, and 300 °C, respectively.

Results and Discussion

Many compounds identified in *d*-limonene SOA do not have authentic standards and their identifications were based on

the interpretation of the mass spectra of the derivatized compound. For compounds that have standards, comparisons were made between mass spectra of the derivatized sample and the authentic spectra in CI and/or EI mode as well as retention times. For compounds that do not have standards, the general approach for identification was as follows: Initial identification was made based on fragment/adduct peaks in the CI mode that permit an initial determination of the number and identity of functional groups and the molecular weight (MW) of the derivative (Md). Additional confirmatory analyses were made using multiple derivatizations of DE samples to clarify the identity of potentially ambiguous functional groups (e.g., distinguishing –OH groups from alcohol and acid groups).

The analysis of CI mass spectra of POC derivatives involves recognition of characteristic ions associated with a particular derivatization scheme (14–17). PFBHA reacts with each nonacidic >C=O group to form an oxime derivative. In CI mode, the base peak for most oximes is M⁺ + 1 or 181, while other fragments/adducts include *m/z* M⁺ + 29, M⁺ + 41, M⁺ – 181, and M⁺ – 197. BSTFA reacts with –COOH and –OH groups to form BSTFA derivatives. Characteristic ions are *m/z* 73, 75, 117, 147, and 149. Adduct ions from the derivatives include *m/z* M⁺ + 73, M⁺ + 41, M⁺ + 29, and M⁺ + 1; fragment ions include *m/z* M⁺ – 15, M⁺ – 73, M⁺ – 89, M⁺ – 117, M⁺ – 133, and M⁺ – 207. The reaction of BF₃-methanol with carboxylic acids forms methyl esters. Characteristic ions are 59, M⁺ – 59, M⁺ – 31, and M⁺ + 1; weak adducts are M⁺ + 15, M⁺ + 29, and M⁺ + 41. Multiple derivatizations result in adducts and fragments that include characteristic ions from each derivatization. Typically, three to seven adduct/fragment ions are found for each derivatized POC. Finally, in many cases, these samples were run in EI to produce greater fragmentation and additional structural information.

In the present study, mass spectra for 103 compounds have been recorded, and representative examples are shown. The approach used for their detection is as follows: Peaks detected in blank and background samples were eliminated first. An identification number was associated with each remaining peak only if its corresponding mass spectrum was consistent with the fragmentation pattern of the derivatization reagent used as noted above. A typical total ion chromatogram (TIC) of BSTFA derivatives is shown in Figure 1. Table 2 contains proposed structures for products identified, MWs of the underivatized compounds (Mc), and their identification numbers. Table S1 in the Supporting Information shows five intense fragments/adducts for compounds detected in the BSTFA derivatives (Figure 1) and, when possible, tentative Mc and BSTFA Md.

SOA generated from *d*-limonene photooxidation is dominated by oxygenated ring-opening products. However, a few ring-retaining products were observed including 4-isopropenyl-1-methyl-1-hydroxy-2-oxocyclohexane (37), 4-isopropenyl-1-methyl-1,5-dihydroxy-2-oxocyclohexane (76), and limonaketone (101). These compounds have been identified previously as reaction products from the ozonolysis and/or photooxidation of *d*-limonene in the presence of NO_x (6, 8, 13).

Among the ring-opening compounds identified in the present study are 2-isopropyl-1,2-dihydroxy butanol (36), ketonorlimonic acid (38), 3-isopropylpentanedioic acid (47), and ketolimonic acid (53), which were tentatively identified previously in SOA from some monoterpene photooxidation (17). Compounds identified using authentic standards were levulinic acid (6), butanedioic acid (16), maleic acid (21), pentanedioic acid (23), and hexanedioic acid (29).

Other ring-opening compounds in which the endo-*d*-limonene double bond was oxidized were identified in the present study. Limonic acid (42), a dicarboxylic acid retaining

ER153-ZF3-BSTFA-ci

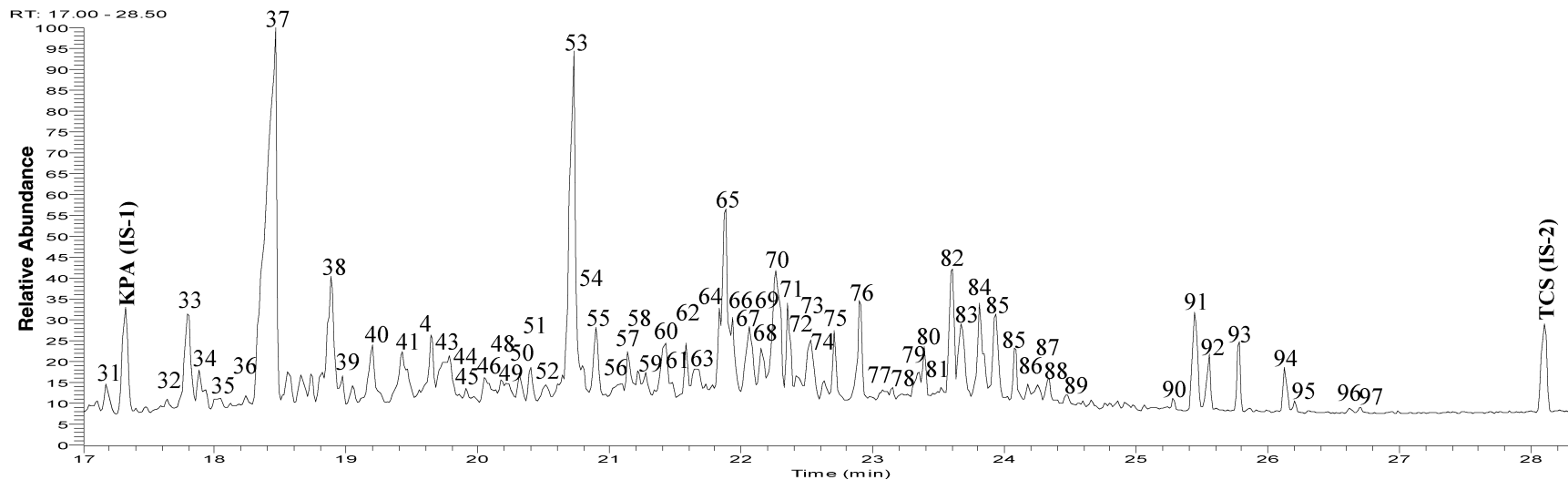
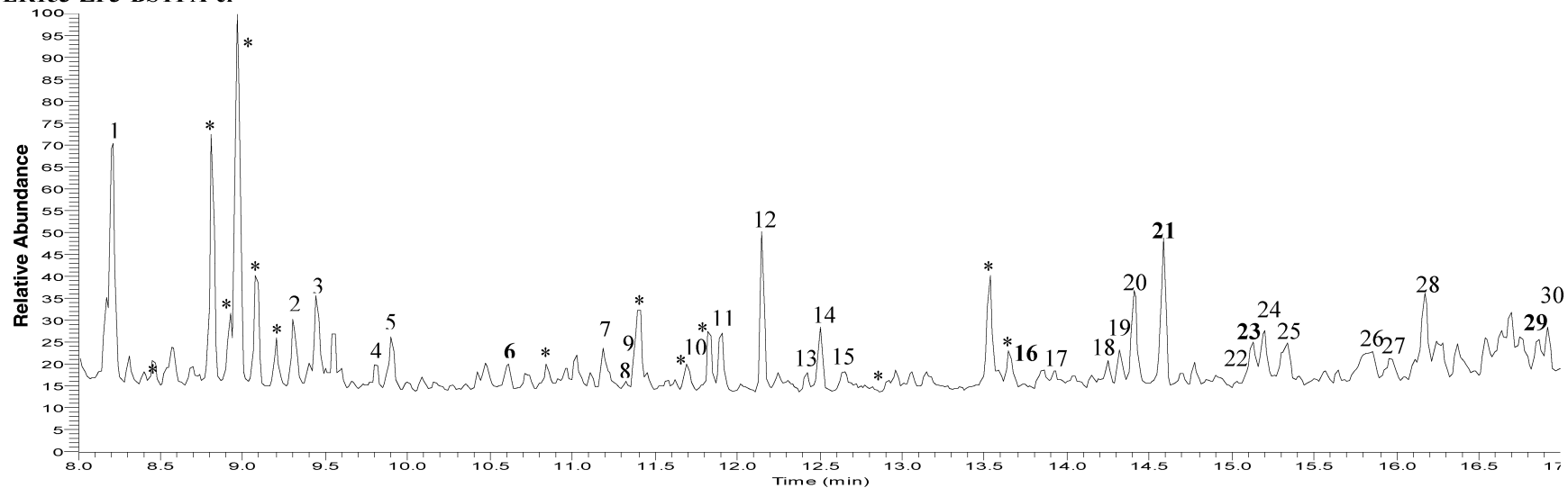


FIGURE 1. Typical total ion chromatogram in CI mode of BSTFA derivatives of *d*-limonene SOA. Peaks detected in blank/background samples are denoted with *, and those in bold were identified using standards.

TABLE 2. *d*-Limonene SOA Compounds Identified in the Present Study

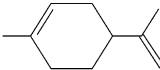
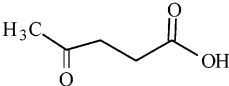
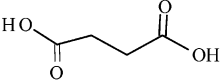
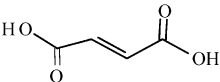
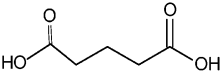
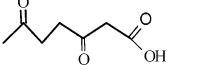
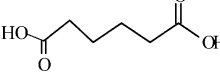
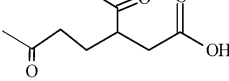
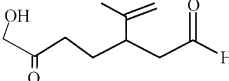
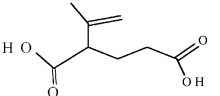
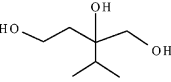
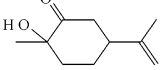
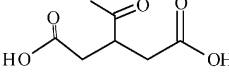
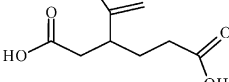
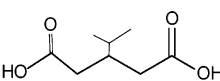
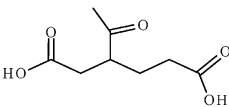
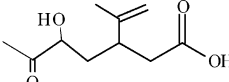
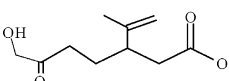
| ID | Nomenclature | Structure | MW (g mol ⁻¹) | Yield (%) |
|-----------------|---|--|------------------------------|-------------------|
| | <i>d</i> -Limonene |  | 136 | |
| 6 | Levulinic acid |  | 116 | 0.14 |
| 16 | Butanedioic acid |  | 118 | 0.04 |
| 21 | Maleic acid |  | 116 | 2.85 |
| 23 | Pentanedioic acid |  | 132 | 0.01 |
| 26 | 3,6-Oxoheptanoic acid |  | 158 | |
| 29 | Hexanedioic acid |  | 146 | 0.01 |
| 30 | Ketolimononic acid |  | 186 | 0.03 ^b |
| 31 | 7-Hydroxylimononaldehyde |  | 184 | 0.07 ^c |
| 32 | Norlimonic acid |  | 172 | |
| 36 ^a | 2-Isopropyl-1,2-dihydroxy butanol |  | 148 | 0.04 ^d |
| 37 ^a | 4-Isopropenyl-1-methyl-1-hydroxy-2-oxocyclohexane |  | 168 | 2.27 ^b |
| 38 | Ketonorlimonic acid |  | 174 | 0.49 ^d |
| 42 | Limonic acid |  | 186 | 0.14 ^e |
| 47 ^a | 3-Isopropylpentanedioic acid |  | 174 | 0.08 ^d |
| 53 | Ketolimonic acid |  | 188 | 0.91 ^b |
| 57 | 5-Hydroxylimononic acid |  | 200 | 0.03 ^f |
| 65 | 7-Hydroxylimononic acid |  | 200 | 0.18 ^g |

TABLE 2 (Continued)

| ID | Nomenclature | Structure | MW (g mol ⁻¹) | Yield (%) |
|-----------------|---|-----------|------------------------------|-------------------|
| 69 | 3-Carboxyheptanedioic acid | | 204 | 0.24 ^b |
| 72 | Limononic acid | | 184 | |
| 76 ^a | 4-Isopropenyl-1-methyl-1,5-dihydroxy-2-oxocyclohexane | | 184 | 0.18 ^b |
| 81 | 5-Hydroxyketolimononic acid | | 202 | 0.32 ^g |
| 85 | 7-Hydroxyketolimononic acid | | 202 | |
| 98 | Limonic acid | | 170 | |
| 99 | Norlimononic acid | | 172 | |
| 100 | 3-Oxobutanal | | 86 | |
| 101 | Limonaketone | | 138 | |
| 102 | Limononaldehyde | | 168 | |
| 103 | Ketolimononaldehyde | | 170 | |

^a Systematic nomenclature is provided for compounds for which terpene nomenclature is not applicable. Surrogates used for the semi-quantification are as follows: ^b Azelaic acid. ^c Pinonic acid. ^d Heptanedioic acid. ^e Pinic acid. ^f Trans-acotinic acid. ^g Undecanedioic acid.

the *exo-d*-limonene double bond, was tentatively identified. Figure 2 shows mass spectra of the **42** BSTFA derivative in CI and EI modes. The **42** CI spectrum shows strong characteristic fragment ions at m/z 315 ($M^+ - 15$), 241 ($M^+ - 89$), and 223 ($M^+ - 107$), and adducts at $M^+ + 1$, $M^+ + 29$, and $M^+ + 41$ that are consistent with the presence of two ($-OH$) groups, indicating a BSTFA Md of 330 amu (all masses Mc and Md are amu and hereafter are not shown). The BF_3 -methanol chromatogram shows peaks with fragments at m/z 183, 151, and 123, and weak adducts at m/z 215, 243, and 255. These fragmentation patterns are consistent with the presence of two carboxylic groups, giving a Md of 214 and 186 for the Mc. The CI spectra of BSTFA derivatives of **42** and pinic acid are very similar except for a few fragments below 150.

Other identified ring-opening compounds containing double bonds are limononaldehyde (**102**), limononic acid (**72**), norlimononic acid (**99**), limonic acid (**98**), 5-hydroxylimononic acid (**57**), and 7-hydroxylimononic acid (**65**). The peak areas of these double-bond compounds are among the

lowest peak areas observed in the TIC, which is consistent with further oxidation that leads to the formation of a variety of compounds including ketolimononic acid (**30**), **38**, **53**, and ketolimononaldehyde (**103**). A number of compounds observed here, including **42**, **72**, **98**, and **99**, were previously identified from the ozonolysis of *d*-limonene (**6**).

Multiple derivatizations were used for the identification, as shown in Figure 3 for compound **26**. Figure 3 displays CI mass spectra for PFBHA + BSTFA and BF_3 -methanol + PFBHA derivatives of this compound. In the PFBHA + BSTFA derivative, an intense ion peak at m/z 621 is present in addition to fragment/adduct ions at m/z 605, 531, 423, 649, and 661. The PFBHA + BSTFA fragmentation pattern of **26** is consistent with a Md of 620. The BF_3 -methanol + PFBHA mass spectrum shown in Figure 3 is consistent with a Md of 562. Based on the analysis of these mass spectra and from kinetic evidence (see mechanism of product formation section), compound **26** was tentatively identified as 3,6-oxoheptanoic acid with a Mc of 158.

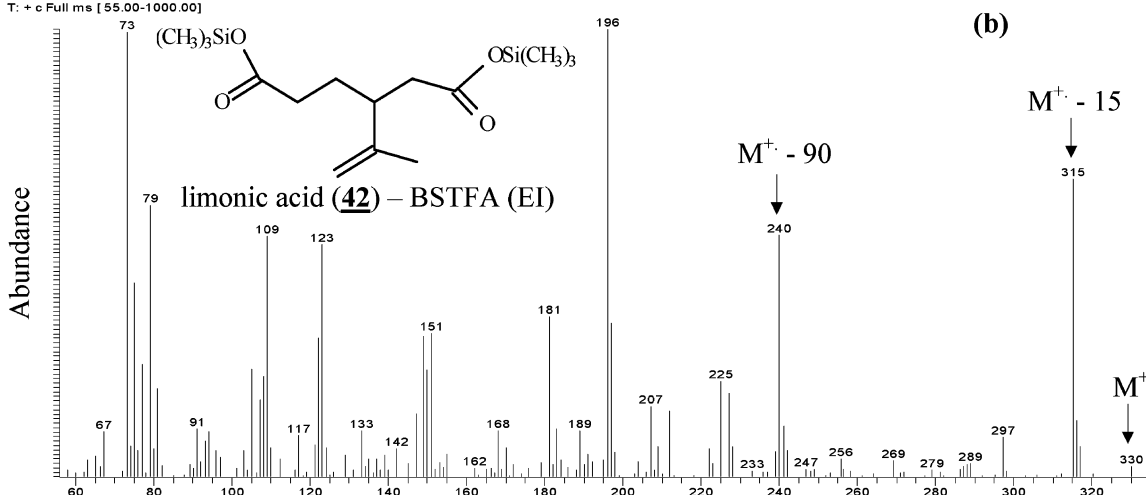
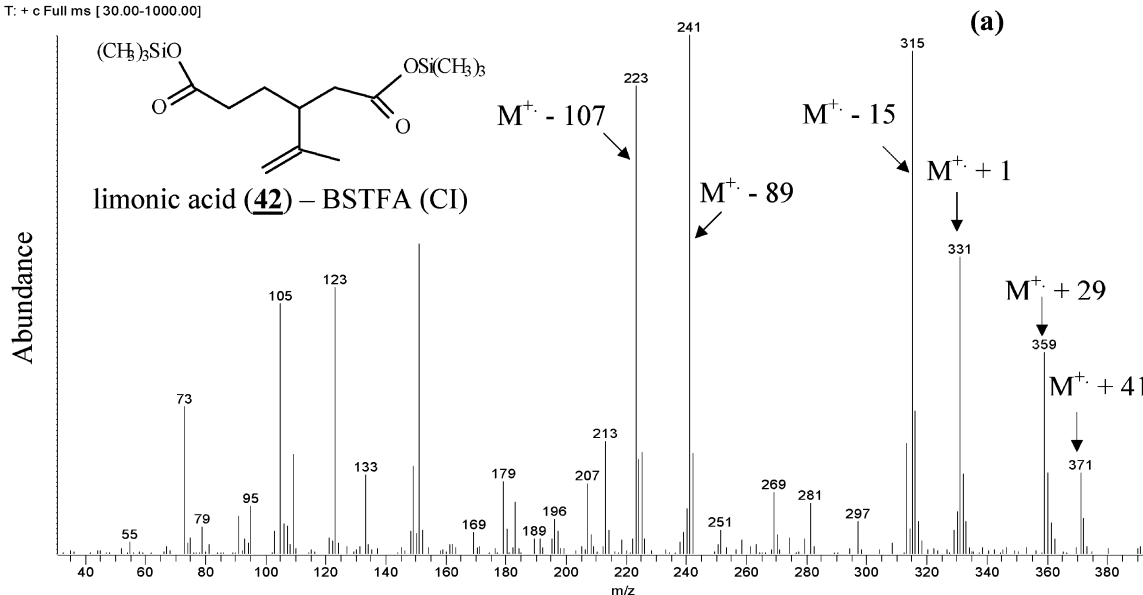


FIGURE 2. Mass spectra of BSTFA derivative of **42** in CI and EI.

Time Profile of SOA Compounds. Figure 4(a) shows the concentrations of *d*-limonene, O₃, NO, NO_x, NO_x – NO, and SOA as a function of irradiation time for the SE experiment. The wall loss rate constant was 0.064 h⁻¹ for SOA. A small amount of SOA was observed prior to ozone buildup in the chamber (<5% of the total SOA). This may be due to *d*-limonene reacting with OH radical formed during its photooxidation. A time series of SOA components was performed in the SE experiment using BSTFA derivatization. A description of their quantification is provided in the Supporting Information. Using our best estimate of the calibration factors, concentrations for the main compounds were determined and are provided in Figure 4b–e as a function of irradiation time. As can be seen in Figure 4b–e, SOA compounds start building up only when ozone starts building up in the chamber. This may be reflecting the importance of ozone chemistry in this system. The concentration of some compounds (e.g., **31** and **65**; Figure 4d) increased at the beginning of the reaction and then decreased suggesting that secondary reactions may be occurring. Among the major abundant compounds are **21**, **38**, **53**, **37**, and 5-hydroxyketolimononic acid (**81**), with concentrations up to 30.7 μg m⁻³. Other compounds were in the 0.5–9 μg m⁻³ range.

The aerosol yield is defined as the ratio of the amount of secondary organic aerosol formed from the photooxidation of *d*-limonene to the amount of *d*-limonene that reacted: $y = (\Delta M_0 / \Delta H C)$, where ΔM_0 (μg m⁻³) is the organic aerosol mass formed after the consumption of $\Delta H C$ (μg m⁻³) of *d*-limonene. ΔM_0 was obtained from gravimetric measurement of the filter. The aerosol yield after all *d*-limonene was consumed was 0.51 for an SOA concentration of 1470 μg m⁻³. This yield is 25% higher than 0.405 measured by Hoffmann et al. (12), whose experimental conditions were different than those used in this study (e.g., presence of a co-reactant propylene, HC-to-NO_x ratio, temperature). The last column in Table 2 shows yields for some reaction products identified in the particle phase along with the surrogate compounds used for their quantification. Products with high molar yields were **21** (~0.029), **37** (0.023), **53** (0.009), and **38** (0.005). The total mass identified from the *d*-limonene photooxidation accounted for approximately 21.2% of the total SOA collected on the filter. The remaining organic mass unaccounted for is probably organic carbon made up of oligomeric forms, and/or humic-like substances as recently observed in ambient and chamber aerosol (18–20). These compounds are difficult to detect using the GC–MS tech-

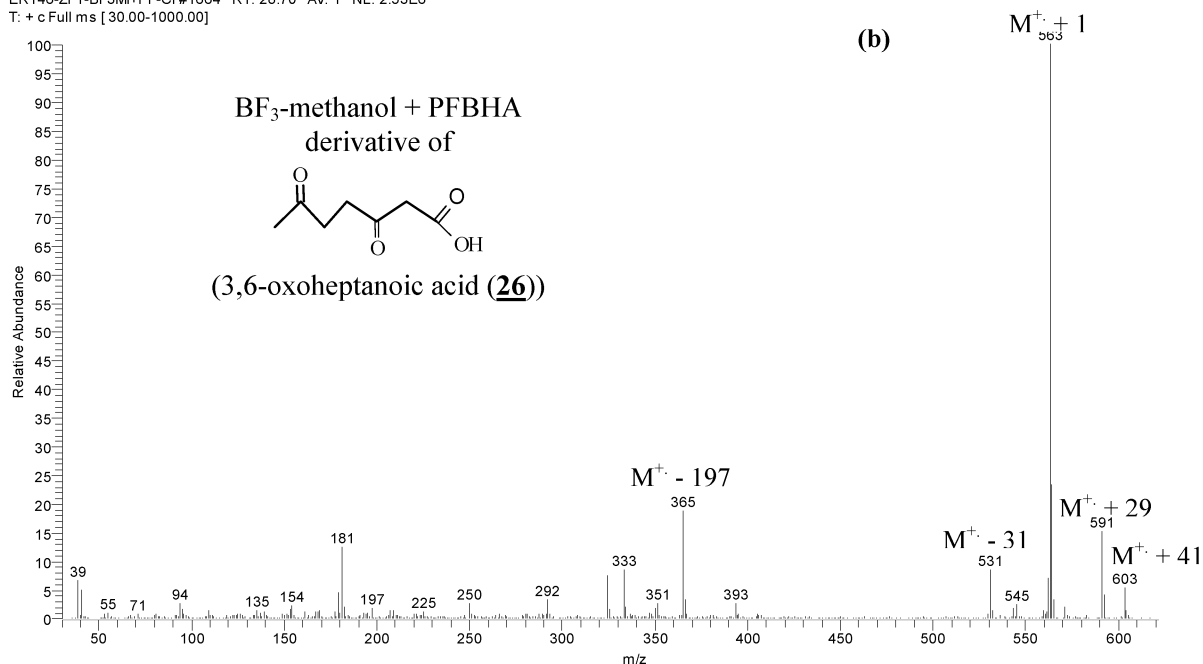
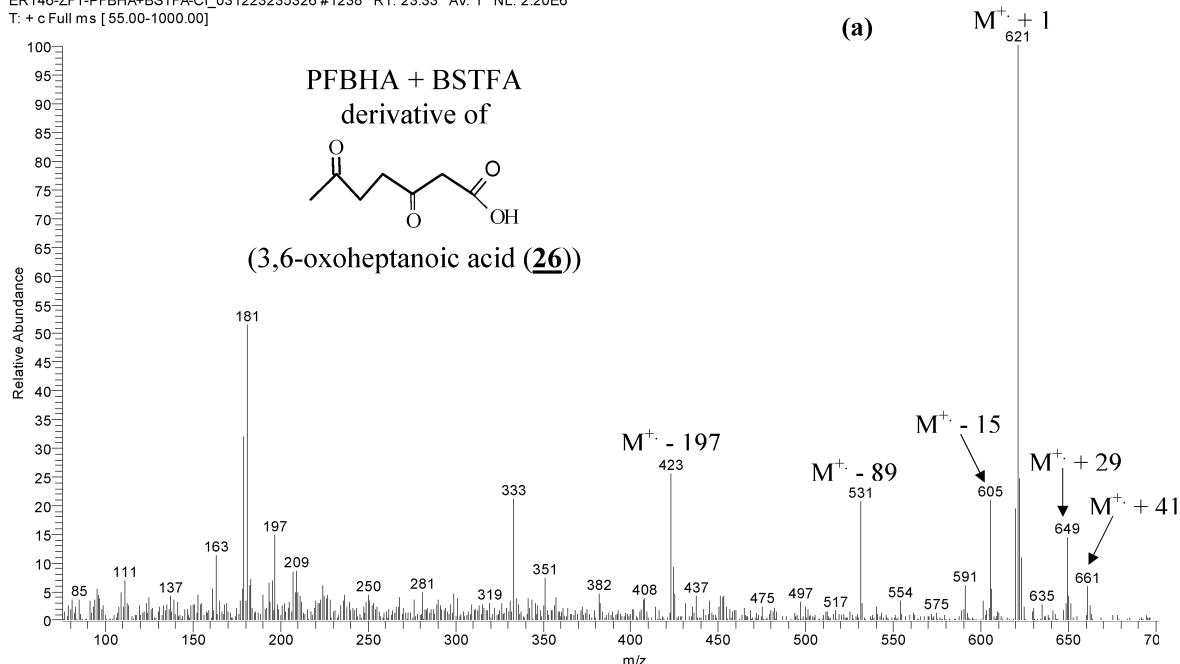


FIGURE 3. Mass spectra of **26**: (a) PFBHA + BSTFA (Cl), and (b) BF₃-methanol + PFBHA (Cl).

nique in this study.

Mechanism of Product Formation. The presence of two double bonds in *d*-limonene yields a variety of products in the particle phase, mainly ring-opening compounds (Figure 1 and Table 2). The time profile from the SE experiment shows an increase in the concentration of SOA compounds as ozone concentration increases. This indicates that ozone reaction is likely involved in the formation of SOA compounds. In the following discussion, mechanistic pathways leading to some major products observed in the particle phase are proposed, based on either OH or ozone reactions.

Mechanistic pathways leading to limononaldehyde (**102**), limonic acid (**72**), and limonaketone (**101**) have been reported in the literature through either ozone or OH reactions with *d*-limonene (8, 13). The reaction of ozone with the limononaldehyde (**102**) double bond leads to the forma-

tion of ketolimononaldehyde (**103**) (Scheme 1). Ketolimononic acid (**30**) is proposed to be formed through H-atom abstraction by OH radicals from the aldehyde group of ketolimononaldehyde (**103**) (Scheme 2) and reaction of limononic acid (**72**) with ozone (Scheme 3). The reaction of ozone with limonaketone (**101**) leads to the formation of ketolimononaldehyde (**103**) (Scheme 4).

Ketolimononic acid (**53**) was present in the particle phase at a high level as soon as SOA started building up in the chamber. Ketolimononic acid (**53**) is proposed to rise from the reaction of ozone with limonic acid (**42**) through similar pathways, shown in Schemes 1 and 3. Limonic acid (**42**) is proposed to be formed by analogy to pinic acid formation from α - and β -pinene (21). Its formation starts with the reaction of ozone with *d*-limonene, which leads to an energy-rich Criegee intermediate, which decomposes to yield OH

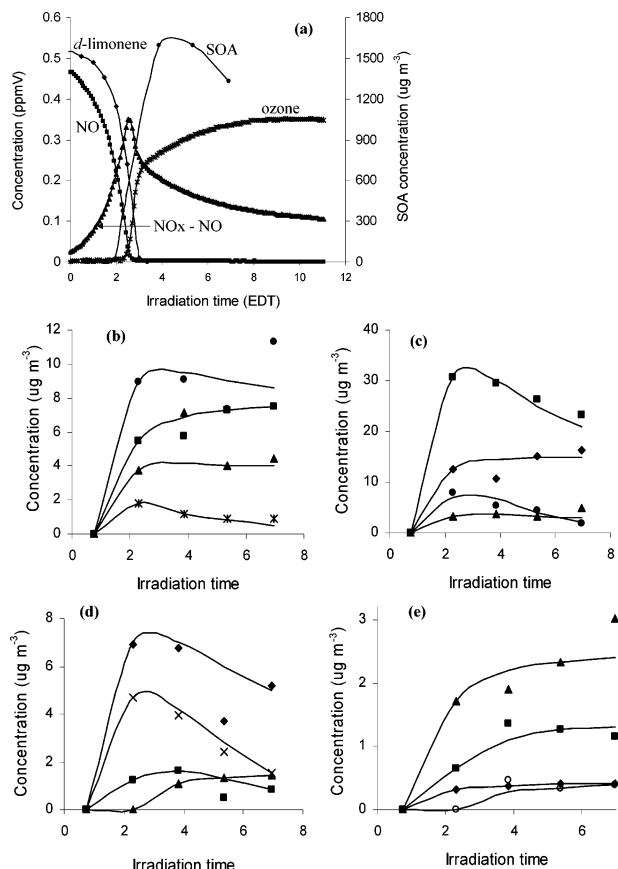
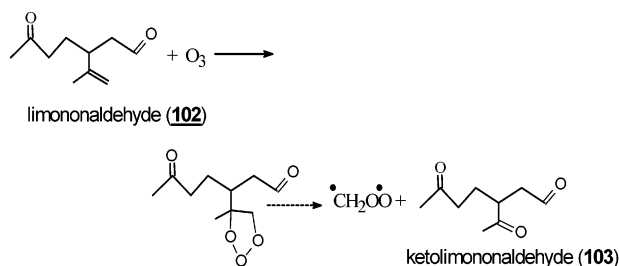
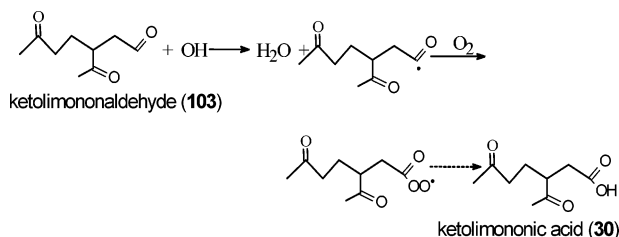


FIGURE 4. Time profile of compounds in SE experiment: (a) NO (■), NO_x - NO (▲), O₃ (x), *d*-limonene (◆), and SOA (●); (b) ●: 81, ▲: 76, ■: 69, *: 57; (c) ◆: 38, ▲: 6, ●: 42, ■: 53; (d) x: 31, ■: 30, ◆: 65, ▲: 36; (e) ▲: 47, ■: 30, ◆: 23, o: 29. Data were corrected for dilution and wall losses. The wall loss rate constant was 6.4%/hour for SOA.

SCHEME 1

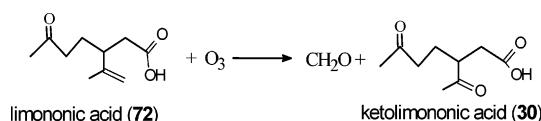


SCHEME 2

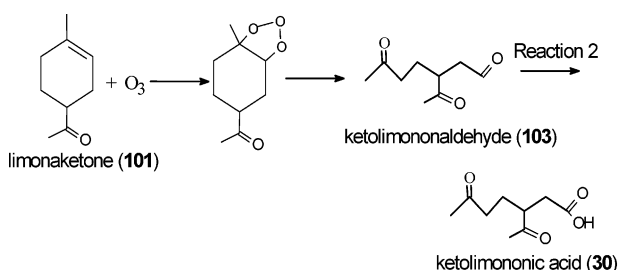


radicals and a peroxy radical in the presence of O₂. The peroxy radical itself decomposes to an alkoxy radical in the presence of RO₂ and through further decomposition followed by isomerization to form limonic acid (42) as shown in Scheme 5. Prior to the formation of limonic acid, an alternative pathway to the alkoxy radical in Scheme 5 is elimination of CO₂ to yield an alkyl radical. This later undergoes transformation into a C8-carboxy-aldehyde, which in turn can be

SCHEME 3



SCHEME 4



transformed to ketonorlimonic acid (38). Compound 38 was observed at high concentration in the present study.

The formation of 3,6-oxoheptanoic acid (26) is consistent with the following pathways proposed in Scheme 6 involving ketolimononic acid (30) as the starting material. It starts with H-atom abstraction by OH radical from ketolimononic acid (30) tertiary carbon, and in the presence of O₂, NO, and/or RO₂ leads to alkoxy radical formation, which then decomposes to yield 3,6-oxoheptanoic acid (26). Scheme 6 also shows 3-oxobutanol (100) formation through the alkoxy radical decomposition.

The formation of linear dicarboxylic acids from *d*-limonene photooxidation is difficult to explain. However, since these and other POCs were found only in the particle phase, it is possible that they are due to particle-phase reactions or gas-surface reactions. Therefore, additional experimental and theoretical studies are needed to explain the origin of these compounds.

Field Measurements. Twenty-one compounds were observed in both laboratory and field samples. These compounds are shown in the extracted ion chromatogram in Figure 5 of a PM_{2.5} sample collected in September 2003. Nine compounds, 16, 23, 29, 36, 38, 47, 53, 55, and 69, were structurally identified (Table 2). The concentrations of these nine compounds were determined in eight ambient samples using the same method used for the SE experiment and are shown in Figure 6. The total PM_{2.5} mass in the atmosphere during this sampling period ranged from 6 to 34 μg m⁻³. The concentrations for individual compounds ranged between 0.3 and 18.1 ng m⁻³. These values are typical of the range of values often seen for individual POCs detected in ambient samples.

Compounds 36, 38, 47, 53, and an isomeric form of 69 were previously observed in SOA originating from the photooxidation of α- or β-pinene (16, 17). Two peaks with identical mass spectra were observed in all field samples that had M⁺ of 420 for their BSTFA derivatives. The first peak was tentatively identified by Kubátová et al. (22), Edney et al. (16), and Jaoui et al. (17) as 3-carboxyheptanedioic acid either in field or laboratory samples, while the second peak corresponding to compound 69 was not reported previously. Compound 55, with Md 406 (BSTFA derivative), was observed in significant amounts in both *d*-limonene SOA and ambient PM_{2.5} analyzed in this study. Compounds 55 and 69 are proposed as tracers for *d*-limonene.

The dicarboxylic acids 16, 23, and 29 were also observed in ambient suburban samples (Centerville, AL, and Oak Grove, MS) by Zheng et al. (23) at similar concentrations. In addition to their primary source (23), the biogenic source

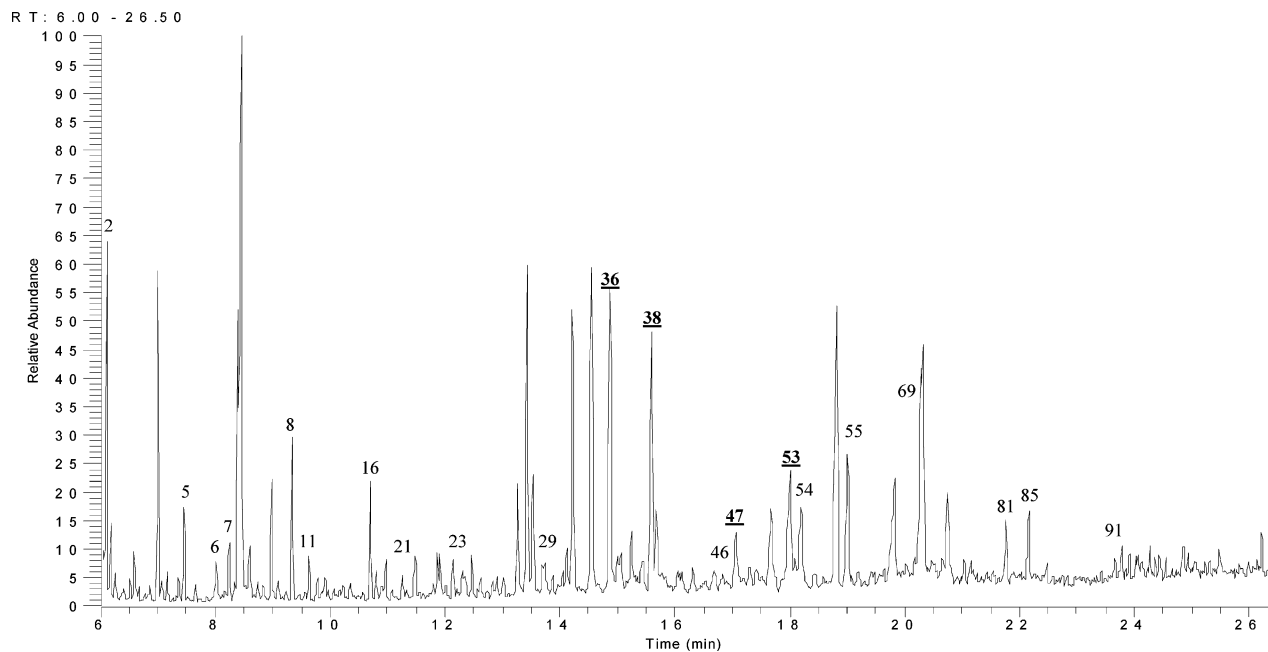
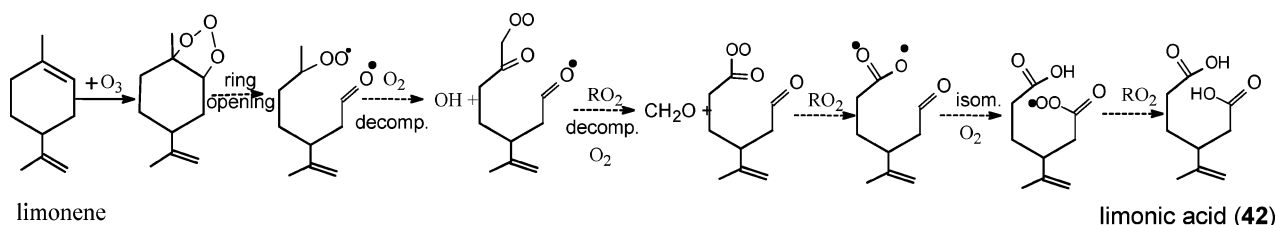
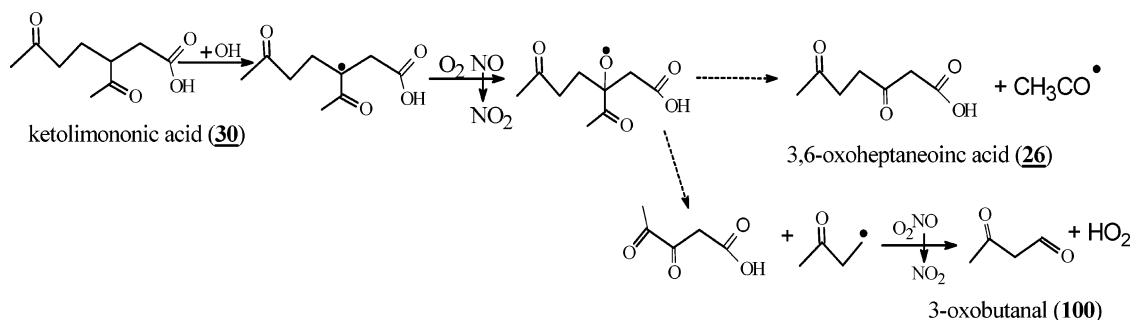


FIGURE 5. Extracted ion chromatogram in CI mode from the BSTFA derivatives of a $\text{PM}_{2.5}$ sample collected in September 2003 showing *d*-limonene SOA compounds. Extracted ions are 99, 125, 174, 187, 201, 217, 229, 231, 233, 243, 245, 247, 249, 257, 285, 346, 349, 377, 391, 405, and 409. Underline bold numbers were present in α - or β -pinene SOA (17).

SCHEME 5



SCHEME 6



from *d*-limonene reaction in the atmosphere is demonstrated in this paper.

The results of this study potentially have atmospheric implications for areas impacted by *d*-limonene oxidation products and contribute to understanding terpene oxidation and SOA formation. Several compounds were detected and identified in both field and smog chamber experiments. For instance, the high molar yields for compounds **21**, **37**, **38**, and **53** in SOA suggest that they might be responsible for the formation and/or the growth of the aerosol. The unexplained presence of linear dicarboxylic acids (**6**, **16**, **23**, and **29**) and their potential formation by heterogeneous and multiphase processes is also very interesting. Compounds **55** and **69** detected in both field and chamber are of particular importance because they are specific to *d*-limonene. Therefore, they could serve as indicators for emitted *d*-limonene into atmospheric particulate matter. However, in the absence of authentic standards, it is difficult to accurately quantify

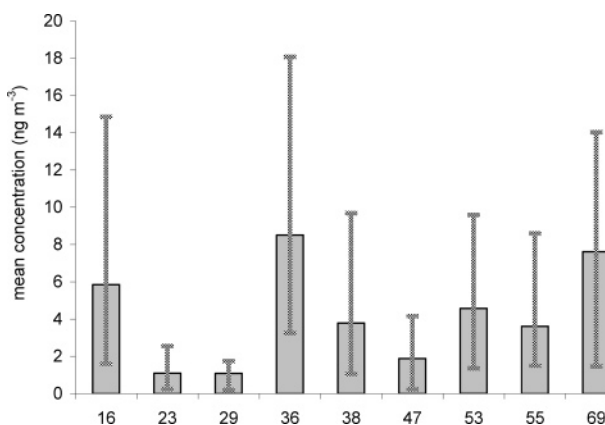


FIGURE 6. Mean and variability composition of some major SOA compounds observed in both ambient $\text{PM}_{2.5}$ and *d*-limonene SOA in terms of ng m^{-3} .

the contribution of SOA originating from *d*-limonene to ambient PM_{2.5}.

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Supporting Information Available

A table showing five intense fragments/adducts for compounds detected in the BSTFA derivatives and a time profile of SOA compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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