Chapter 8

Low-Molecular-Weight and Oligomeric Components in Secondary Organic Aerosol from the Ozonolysis of Cycloalkenes and α-pinene*

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8.1. Abstract

The composition of secondary organic aerosol (SOA) from the ozonolysis of C_5 – C_8 cycloalkenes and α-pinene, as well as the effects of hydrocarbon precursor structure and particle phase acidity on SOA formation, have been investigated by a series of controlled laboratory chamber experiments. A liquid chromatography – mass spectrometer and an ion trap mass spectrometer are used concurrently to identify and quantify SOA components with molecular weights up to 1600 Da. Diacids, carbonyl-containing acids, diacid alkyl esters, and hydroxy diacids are the four major classes of low-molecular-weight (MW < 250 Da) components in the SOA; together, they comprise 42% - 83% of the total SOA mass, assuming an aerosol density of 1.4 g/cm^3. In addition, oligomers (MW > 250 Da) are found present in all SOA. Using surrogate standards, it is estimated that the mass fraction of oligomers in the total SOA is at least 10% for the cycloalkene systems (with 6 or more carbons) and well over 50% for the α-pinene system. Higher seed particle acidity is found to lead to more rapid oligomer formation and ultimately, to higher SOA yields. Because oligomers are observed to form even in the absence of seed particles, organic acids produced from hydrocarbon oxidation itself may readily promote acid catalysis and oligomer formation. The distinct effects of carbon numbers, substituent groups, and isomeric structures of the precursor hydrocarbons on the composition and yield of SOA formed are also discussed.

8.2. Introduction

Secondary organic aerosol (SOA) is formed when atmospheric oxidation of organic species leads to compounds of increased polarity and decreased vapor pressure that condense into the particulate phase.[1] Predicting the amount of SOA that results from atmospheric oxidation of particular organic molecules has proven challenging because:

(1) oxidation pathways for the relatively larger parent organics that lead to SOA are not well established; and (2) current analytical techniques, especially when a single method is used, commonly fail to identify many SOA components. Traditional techniques such as gas chromatography – mass spectrometry (GC – MS) can typically resolve only about 10% (by mass) of total atmospheric aerosol organics.[2-4]

Recent work has made substantial progress in achieving a better mass closure of SOA, such as by using GC-MS with a double derivatization technique.[5,6] However, the tedious derivatization procedures risk sample contamination and/or loss, and they are compound-specific only. Intrinsically, a substantial fraction of SOA components, such as the least volatile and very polar, may readily evade detection by GC-MS, either never eluting off the column or decomposing during the analysis.[7] Therefore, an analytical method that can preserve molecular integrity and capture the main feature of SOA composition-- especially the very polar and less volatile species-- is desirable.

Another major issue is to understand the relationship between the structures of the parent molecule and the amount and composition of SOA subsequently formed. While previous studies have identified a number of SOA components with various functional groups, polarities, and volatilities, it is generally unclear how factors such as carbon number, presence or absence of double bonds, and presence or absence of alkyl substituent groups affect both resultant SOA amount and composition. Of course, answers to these questions lie in understanding the mechanisms of gas-phase oxidation of the parent hydrocarbons. As we noted above, these oxidation mechanisms tend to be complex. One approach is to use measured SOA yields and compositions as a means to infer the mechanisms that lead to SOA formation. By selecting precursor hydrocarbons that vary structurally in a determined manner, it is possible to infer how structural differences in parent hydrocarbons translate into differences in the SOA formation pathways. It is this approach that we follow in the present work.

The traditional view of SOA formation is that gas-phase oxidation of the parent hydrocarbons leads to multifunctional, low-volatility products that partition themselves between the gas and aerosol phases.[1] The partitioning is strongly affected by temperature and, to a somewhat lesser extent, by the phase state of the aerosol. Because of lacking in direct information to the contrary, it had been assumed that, once in the aerosol phase, the oxidation products did not react further, and that the amount of SOA formed depended entirely on the gas-particle partitioning.

Recent discoveries show that once the gas-phase polar oxidation products condense into the aerosol phase, particle-phase reactions may take place. First, it was demonstrated that acid-catalyzed heterogeneous reactions can occur[8,9]. Second, the presence of oligomers in the aerosol phase was shown.[10-13] A consequence of heterogeneous chemistry and oligomer formation is that species that partition between the gas and aerosol phases are converted to larger compounds of extremely low volatility, thereby locking these compounds into the aerosol phase and increasing the SOA yield over that in the absence of heterogeneous chemistry.

Consequently, fundamental questions arise: Are acids required for heterogeneous reactions and the associated increased SOA yields, and if so, what types of acids? Are heterogeneous reactions directly responsible for the formation of oligomers? Are oligomers ubiquitous in atmospheric organic aerosols?

The major classes of parent hydrocarbons responsible for SOA formation are alkenes and aromatics. While atmospheric aromatics are almost entirely anthropogenic in origin, alkenes arise from both anthropogenic and biogenic sources. On a global basis, it is estimated that the predominance of SOA results from biogenic terpenes.[14] The oxidation of alkenes (including terpenes) includes reactions with O_3, OH, and NO_3. For a number of these alkenes, reaction with O_3 is a dominant path. From a mechanistic point of view, gas-phase O_3 oxidation should be less complex to unravel than photooxidation in the presence of NO_x. With the goal of understanding the effects of hydrocarbon structure and particle-phase acidity on SOA formation, we report here on a series of controlled experiments carried out in Caltech's dual laboratory chambers. We focus on the cycloalkenes of carbon number 5 and greater; these compounds are known to form SOA and, through choice of compounds, key structural factors such as the locations of double bonds and of alkyl substituent groups can be varied in order to discuss the effects of these factors on SOA formation.

Seven cycloalkenes with five to eight carbon numbers-- serving as model compounds for many atmospheric hydrocarbons bearing similar molecular skeletons-- were reacted with ozone under dark conditions. We employ liquid chromatography – mass spectrometry (LC-MS) in tandem with ion trap mass spectrometry (ITMS) to analyze the molecular composition of SOA formed, and to explore the relationship between the SOA composition and hydrocarbon precursor structure. The overall yields of SOA formed in these systems and their relationships with precursor structures are discussed elsewhere.[15] In addition, α-pinene, one of the most common biogenic hydrocarbons, was reacted with ozone under a set of controlled conditions to study the explicit effect of aerosol acidity on the amounts and composition of SOA formed, and to explore the possible ubiquity of oligomers in atmospheric aerosols.

8.3. Experimental

All experiments were carried out under dark conditions in Caltech's dual 28 m^3 teflon chambers. Salt solutions were first nebulized into the pre-cleaned chamber to form seed aerosols. For cycloalkene ozonolysis, dry $(NH_4)_2SO_4$ seed particles were generated from a 0.03M salt solution. For α-pinene ozonolysis, wet $MgSO_4$ and $(NH_4)_2SO_4$ seed particles, and the corresponding particles from acidified solutions, were generated in most cases. A few dry seed particle experiments were also carried out for comparison purposes, as well as a few experiments in the absence of any seed particles. The $MgSO_4$ and $(NH_4)_2SO_4$ solutions were 0.03M each, with their acidified counterparts containing 0.03M salt and 0.05M H_2SO_4. Cyclohexane was then injected into the chamber to act as a hydroxyl radical scavenger, followed by hydrocarbon and ozone injections. Relative humidity was maintained at about 5% (dry chamber) for the cycloalkene experiments and 55% (humid chamber) for the α-pinene experiments. The temperature was always maintained at about 20ºC. Aerosol number concentration, size distribution, hygroscopic growth, and hydrocarbon mixing ratio were continuously measured. Particle loss to the chamber wall was accounted for in analysis of the SOA yield data. More details on these individual measurements and chamber characteristics can be found in Keywood et al.[15]

A series of cycloalkene ozonolysis experiments were carried out with the cycloalkene mixing ratio ranging from about 50 ppb to 300 ppb and the ozone mixing ratio three times that of cycloalkene to ensure adequate oxidation. Detailed experimental conditions are given in Keywood et al.[15]. In each experiment, teflo membrane filter samples (PALL Life Sciences, 47 mm diameter, 1.0 µm pore size) were collected at similar elapsed time (~ 4 - 5 h) from the onset of ozone injection, and for a duration about 2 - 4 h, depending on the amount of SOA generated. During filter sampling, the parent hydrocarbons had already been completely consumed and the aerosol volume had reached its maximum value. In the case of α-pinene ozonolysis, we carried out seven pairs of "nonacid" and "acid" experiments, differing only by the absence or presence of externally added H_2SO_4 in the seed particles, in the two chambers in parallel, with all other conditions held identical. In each pair, filter samples were collected at nearly the same elapsed times (~ 5 - 7 h) from the onset of ozone injection and for nearly the same duration (~ 1 - 2 h). The α-pinene mixing ratios ranged from 12 ppb to 135 ppb (Figure 8.9), whereas the ozone mixing ratio was two times that of α-pinene. In all experiments, the number concentration of the initial seed particles was about 20000 cm^{-3} and the size distribution had a mean diameter of 80 – 100 nm.

Each filter was extracted in 5 ml HPLC-grade methanol by sonication. The extract solution was then blown dry under a gentle stream of N_2, and reconstituted by 1 ml 0.1% acetic acid in water solution with 50% methanol. A portion of this filter extract was analyzed by a Hewlett-Packard 1100 series LC-MS system mainly to identify and quantify low-molecular-weight species (roughly, MW < 250). The electrospray ionization (ESI) mode of the quadruple MS was optimized so that carboxyl-containing species had the highest sensitivities. A Nova-Pak C_{18} column (300 × 3.9 mm, Waters) was used. The eluents were 0.1% acetic acid in water solution (A) and methanol (B), with B programmed from 25% to 60% in 15 min. Another portion of the filter extract was analyzed by a Finnigan LCQ ion trap mass spectrometer (ITMS) to identify species with molecular weights up to 1600 Da and capture the overall feature of SOA composition, including high-molecular-weight species. Both negative and positive (Na^+ added) ion modes of the ITMS were carried out, so that compounds of different acidity and polarity could be detected. In addition, specific ions of interest were isolated from the rest of the sample matrix in the ITMS, and were further fragmented to produce tandem MS, aiding structure elucidation.

8.4. Results and Discussion

8.4.1. Low-Molecular-Weight (Low-MW) Components of SOA from Cycloalkene Ozonolysis

Seven cycloalkenes (Table 8.1)-- cyclopentene, cyclohexene, cycloheptene, cyclooctene, 1-methyl cyclopentene, 1-methyl cyclohexene, 3-methyl cyclohexene-- were reacted with ozone in the laboratory chambers described above at initial mixing ratios from 25 to 300 ppb. Since the low-MW species (MW < 250) in SOA from α-pinene ozonolysis have previously received rather extensive attention in the literature,[16-18] discussion of those species in this system is not reiterated. In addition, because of the similarity of the SOA products of cyclooctene to those of the non-methylated C_5, C_6, and C_7 cycloalkenes, we will not discuss the cyclooctene system in detail here.

Figure 8.1 shows the total ion chromatograms (TIC) of SOA filter extracts from cyclopentene, cyclohexene, cycloheptene, and cyclooctene. After blank correction, each chromatographic peak represents at least one SOA species. Due to the large number of SOA components, however, some peaks are convoluted in the TIC to various extents. To deconvolute these peaks (and thus, identify components) and to accurately quantify each species, extracted ion chromatograms (EIC) can be generated from the TIC for individual ions based on their mass-to-charge ratios (m/z), as can be seen in Figure 8.2, where the TIC and EIC of the extract of SOA from cycloheptene ozonolysis are shown. For illustration, only the ions with m/z of 145, 185, and 243 are shown here, although 20 species in total are identified in this system. Positive identification is based on the matching of (1) retention time and (2) m/z of standard compounds with chromatographic peaks. Under optimal electrospray ionization conditions, all 30 standard compounds are detected in the form of their molecular ions $[M-1]^-$, and display no or minimal fragmentation**.** Table 8.1S (Supporting Information) lists the standard compounds calibrated, the m/z of each molecular ion, and the average and standard deviation of the corresponding retention time from at least three sets of calibrations on different days. The reproducibility of retention times is mostly within 0.05 min and never exceeds 0.1 min. Most species therefore can be chromatographically separated cleanly, and in the cases where there is an overlap of retention times, the m/z often allows definitive identification, such as malonic acid, 2-oxo glutaric acid, and 2-keto gulonic acid. The standard compounds represent a wide range of polarity and carbon numbers, from which a set of rules-of-thumb are deduced with regard to their retention times. For example, for homologous compounds, retention time becomes longer as the carbon number increases. For the same carbon number, the elution sequence from earliest to latest is carbonyl diacid, hydroxy diacid, carbonyl monoacid, and diacid. C_6 and C_7 diacids commonly elute about 1 min earlier than their methyl ester isomers, which, in turn, elute about 1 min earlier than their ethyl ester isomers, whereas for C_5 diacid, this interval decreases to 0.8 min. Based on these rules and some extrapolation, we are able to assign identities to many species with no standards matching their retention times. Some isomers can be separated by their different retention times, such as 2-oxo adipic acid and pimelic acid. However, some isomers elute at nearly the same retention time; in some cases, one of the isomers does not have the standard available. In such cases, we rely on known reaction mechanisms, albeit speculative, to assign an isomeric structure to represent these isomeric components. For example, in the SOA from cyclohexene ozonolysis, a peak eluting closely (~ 0.5 min) after 5-oxo hexanoic acid (for which the standard is available) and having the same MW is identified as 6-oxo hexanoic acid (for which a standard is not available). For non-methylated cycloalkenes, reaction mechanisms point to the formation of ozonolysis products with carbonyl and carboxyl groups at the end, rather than in the middle, of the carbon chain.[6,16] Although it is crucial to know exact structures of isomeric species to deduce reaction pathways, these isomers, with major functional groups being the same, are expected to play more or less identical roles in aerosol and cloud-related processes.

The mass concentration of each identified low-MW component in SOA was quantified with the corresponding standard's calibration curve. If a standard is not available, a surrogate standard is chosen that has both similar MW and major functional groups. The identified and quantified low-MW species in a typical SOA in the six HC systems are listed in Tables 8.2 – 8.7. The mass yield of a SOA component is defined as its mass quantified relative to the mass of the consumed HC. Based on major functional groups in the molecules, these species are grouped into four classes of compounds, i.e., diacid, diacid alkyl ester, hydroxy diacid, and carbonyl-containing acid. The molecular structures and molecular weights of all these species are listed in Table 8.2S (Supporting Information), also grouped into these four classes of compounds. Kalberer et al.[6] also studied the composition of SOA from cyclohexene ozonolysis under somewhat similar conditions, using a well-developed GC-MS speciation technique. Among the most abundant SOA components, seven species were identified and quantified in both Kalberer et al.[6] and this work. The molar yields (%) for adipic acid, glutaric acid, succinic acid, hydroxy adipic acid, hydroxy glutaric acid, 6-oxo hexanoic acid, and 5-oxo pentanoic acid were 0.74%, 0.69%, 0.14%, 0.97%, 1.99%, 0.39%, and 0.39%, respectively, in Kalberer et al.[6], and were 0.89%, 0.64%, 0.05%, 0.04%, 0.16%, 0.12%, and 0.32%, respectively, in this work. Except for the two hydroxyl diacids, which have large uncertainties (to be discussed later), the two sets of measurements agree reasonably well.

In the cyclopentene, cyclohexene, 1-methyl cyclopentene, and 3-methyl cyclohexene systems, a small amount of C_{n+1} diacid was identified in the SOA from the ozonolysis of C_n (n being the total carbon number) hydrocarbon precursor. In addition, C_{n+2} diacid was identified in cyclopentene, cyclohexene, and 1-methyl cyclopentene systems, at lower abundance than the C_{n+1} diacid. And a minimal amount of C_{n+3} diacid was identified in SOA from 1-methyl cyclopentene ozonolysis. Previous studies [19, 20] have shown various carbonyls are gas-phase products from alkene and cycloalkene ozonolysis. For example, from cyclopentene ozonolysis, glyoxal (C_2), propanal, and butanal were produced with yields of 0.15, 0.04, and 0.12, respectively. From cyclohexene ozonolysis, pentanal, butanal, and formaldehyde were produced with yields of 0.16, 0.03, and 0.02 respectively. In addition, formaldehyde, acetaldehyde, and propanal were produced from ozonolysis of C_5 to C_7 linear alkenes with yields from 0.02 to 0.05.[19, 20] From C_n cycloalkene, ozonolysis would initially lead to an excited Criegee intermediate (C_n). With the presence of small carbonyls in the reaction system, both the excited and stabilized Criegee intermediate can react with these carbonyls to form secondary ozonides, which may further rearrange or decompose to form the C_{n+1}, C_{n+2}, and C_{n+3} diacids observed.

Diacid methyl and ethyl esters were also identified in SOA from the ozonolysis of all six cycloalkenes. Standard runs have confirmed that these compounds do not result from the methanol extraction procedures. There are at least two possible reaction pathways involved. One is similar to the formation of C_{n+1}, C_{n+2}, C_{n+3} diacids, where Criegee intermediates can react with small carbonyls to form secondary ozonides. However, rearrangement or decomposition of ozonides may lead to the formation of esters, rather than diacids. Another possibility arises from the recent discovery[21] that a C_5 peracid (RC(O)OOH) is a gas-phase product from cyclohexene ozonolysis. The well-known Baeyer-Villiger reaction between a peracid and a carbonyl[22] would lead to the formation of an ester:

$$\mathrm{RC(O)OOH + R'C(O)R'' \rightarrow RC(O)OH + R'C(O)OR''}$$

Following this reaction, the C_1 and C_2 carbonyls discussed earlier may lead to the formation of methyl and ethyl esters. However, whether and in what phase this reaction takes place requires further study.

We next discuss the relative abundance of identified SOA components in the six cycloalkene ozonolysis systems. Table 8.8 shows the mass percentage of each class of compounds in the total identified low-MW SOA species for the six systems. Rather constant percentages are observed from system to system: on average, diacids comprise 69 (± 7)%, hydroxy diacids comprise 8 (± 4)%, carbonyl-containing acids comprise 15 (± 3)%, and diacid alkyl esters comprise 11 (± 7)% of the total identified low-MW species. C_n or C_{n-1} diacid is consistently the most abundant species, followed by either other diacids, or hydroxy C_n diacids, or C_n esters. Together, C_n, C_{n-1}, and C_{n+1} diacids comprise 62 (± 9)% of the total identified low-MW species. This implies there are stable, dominant reaction pathways of cycloalkene ozonolysis leading to the formation of these diacids, as speculated by earlier work.[6,23]

By comparison, the mass percentage of each class of compounds in the total SOA derived from the aerosol size distribution measurements, assuming an aerosol density of 1.4 g/cm^3, varies greater from one cycloalkene system to another, as can be seen from the first four rows of Table 8.9. This variation is probably in part a result of the very different fractions of total identified low-MW species in the total SOA mass from system to system, as seen in the 5th row of Table 8.9. The use of 1.4 g/cm^3 (estimated for SOA from cyclohexene ozonolysis by Kalberer et al.[6]) as the density for the SOA in all six systems may be an important reason for this variation. Densities of some identified low-MW species are unknown, making it difficult to compute the overall aerosol density. Indeed, the exact density of SOA remains unknown and, as we discuss later, could very well be larger than that assumed. However, with regard to a more accurate SOA mass closure, one correction we can do is to recover the mass of oxalic acid in all SOA. Oxalic acid was identified at substantial amount in the cyclohexene system;[6] mechanistically, it is a degradation or final oxidation product of all cycloalkene ozonolyses. However, oxalic acid eluted off the LC column too quickly to be detected. Since oxalic acid was found by Kalberer et al.[6] to have roughly the same abundance as adipic acid or glutaric acid in the SOA from cyclohexene ozonolysis, we use the amount of the most abundant diacid identified (C_n or C_{n-1}) to estimate the amount of oxalic acid in all SOAs. With this correction, the fractions of total identified low-MW SOA species range from 42% to 83%, as shown in the 6th row of Table 8.9.

One primary reason that Kalberer et al.[6] achieved a mass closure of SOA products from cyclohexene ozonolysis close to 100% is that they identified substantial amounts of hydroxy diacids, even more abundant than diacids. By contrast, in all six SOA systems we studied, hydroxy diacids are far less abundant than diacids. CO was used as the OH scavenger in Kalberer et al.[6], whereas cyclohexane was used in this study. As discussed by Keywood et al.,[24] different OH scavengers can affect the SOA formation due to different amounts of HO_2 vs. RO_2 in the reaction system. In addition, sampling artifacts, such as the use of different filters, presence or absence of denuders and interference during sample preparation, may also have played a role in causing this discrepancy.

At least three categories of compounds are likely to account for the SOA species not identified. Due to their relatively high volatility, less oxidized species such as carbonyls, which could not be identified by the LC-MS method, are expected to comprise only a small fraction of SOA mass in the systems studied here. Indeed, dialdehydes were found to comprise about 5% of the total mass of SOA from cyclohexene ozonolysis by Kalberer et al.[6] On the other hand, highly-oxidized species, such as multi-hydroxy diacids or multi-oxo acids, may also evade LC-MS detection, since they would elute off the column with little or no retention. The mass fractions of such species in the SOA remain unknown at this time. In addition, species eluting late from the LC column were found in all SOAs, all with relatively high molecular weights. Figure 8.3 shows the detection of species with m/z of 243, 259, and 291 (i.e., the corresponding negative ions) in the SOA from the ozonolysis of cycloheptene, 1-methyl cyclohexene and 1-methyl cyclopentene, respectively. Judged from peak areas, they may comprise a substantial portion of the total SOA mass, yet their identities cannot be revealed by LC-MS alone. We next discuss the use of ion trap MS to analyze higher-MW species in SOA.

8.4.2. Oligomeric components of SOA

8.4.2.1. Identification and structure elucidation of oligomers in SOA

The ESI source in the ion trap MS (ITMS) preserves the molecular integrity of analytes by soft ionization. Some acidic species, readily surrendering a proton, are detected in the form of their molecular ions $[M-1]^-$ in the negative ion mode. For example, Figure 8.4 shows the ion trap mass spectrum of a SOA sample from cycloheptene ozonolysis. The 131, 145, and 159 ions correspond to glutaric acid, adipic acid, and pimelic acid, respectively, which were also identified by the LC-MS. However, higher-MW species with m/z such as 259, 329, 373, 417, 461, and 505 are also present in this sample, at intensities comparable to or even higher than the low-MW species. Figure 8.5 shows the ion trap mass spectrum of a SOA sample from 1-methyl cyclopentene ozonolysis. Higher-MW species with m/z such as 245, 261, 299, 381, and 403 are present at intensities comparable to low-MW species. Figure 8.6 (a) shows the ion trap mass spectrum of a SOA sample from α-pinene ozonolysis with pre-existing $MgSO_4$ seed particles. The low-MW species with m/z 171, 185, and 199 correspond to norpinic acid, cis-pinic acid, and OH-pinonic acid, which have previously been identified as major SOA components[16,18] and are also identified by the LC-MS method in this work. Again, higher-MW species with m/z such as 329, 343, 357, 371, and 385 are also present in this SOA. Their presence is confirmed by the corresponding detection of ions with m/z of 353, 367, 381, 395, and 409 (Na^+ adducts of neutral molecules) in the positive ion mode of the ITMS, as shown in Figure 8.6(b). Since a broad range of compounds can be detected as their Na^+ adducts in this mode, the overall composition of SOA can be better captured by the positive ion mode mass spectrum. Figure 8.6(b) illustrates that in the SOA formed on the nearly neutral $MgSO_4$ seed, species with MW from 250 to 450 are the most abundant species, followed by some even larger species (MW > 450). These species are separated regularly by mass units such as 14, 16, 18, and 30, which is characteristic of a copolymer system,[25] indicating the difference of CH_2, O, H_2O groups, or a combination of them, among monomers and oligomers. Strikingly, low-MW species (MW < 250) comprise only a very minor fraction of the total SOA mass, assuming they have similar response factors to oligomers on the MS detector.

That the higher-MW species (MW > 250) shown in Figures 8.4 –8.6 are indeed oligomers is confirmed from the tandem MS of these ions. In the ITMS, specific ions can be isolated and stored and further fragmented by collision-induced dissociation to produce so-called tandem MS. For example, Figure 8.7 shows the MS/MS (negative ion mode) of the 373 ion in SOA from the ozonolysis of cycloheptene. The molecular structure shown alongside the MS/MS explains the major fragment. The corresponding monomers are 1,4-butanedial and 4-oxo butanoic acid, both first-generation oxidation products. Overall, our MS/MS results confirm that oligomers originate from low-MW SOA species in all the systems studied. For the α-pinene ozonolysis system, with the monomers having MW centered about 180 Da,[18] the small oligomers (MW from 250 to 450) are probably dimers, whereas larger oligomers (MW from 450 to 950) likely trimers, tetramers, and pentamers. Based on the structures of oligomers and corresponding monomers, we propose three possible oligomerization reactions in the aerosol phase: aldol reaction, gem-diol reaction, and acid dehydration. All three reactions require acid or base catalysis.[22] We note that since many of the low-MW SOA species have functional groups in branched positions, the oligomers eventually formed may contain both straight-chain and cross-linked sections.

To test whether oligomers may have formed during the electrospray process, individual monomers and cocktails of monomers were analyzed by the ITMS with the same procedures as SOA samples. These monomers include C_6 – C_8 carbonyl acids, pinonic acid and pinic acid. Only minimal amounts of ions with m/z from 250 to 450 were detected under the negative ion mode. Single ion isolation and MS/MS fragmentation indicated they were unstable “adduct” ions, possibly formed during electrospray. Under the positive ion mode, some dimers were present but an overall polymeric signature (up to pentamers) was lacking in these standard mixtures. In addition, the detection of some high-MW species by the LC-MS (e.g., Figure 8.3), such as the 243 and 259 ions in the cycloheptene ozonolysis system (Figure 8.4) and the 357 ion in the α-pinene ozonolysis system (Figure 8.6[a]), also verifies the presence of oligomers in the SOA. Finally, to test whether oligomers may have formed from the oxidation of background hydrocarbons, seed particles were injected into the clean chamber both in the absence and presence of ozone. No oligomers were present in aerosol samples collected.

In summary, oligomers with MW from 250 to 1600 are present in all SOA samples from α-pinene ozonolysis, regardless of initial seed acidity or water content. Oligomers with MW from 200 to 700 are present in all SOA samples from the ozonolysis of cyclohexene, 1-me cyclopentene, cycloheptene, 1-me cyclohexene, and cyclooctene. Oligomers are present in SOA from cyclopentene ozonolysis in only minimal amounts, judged from the ion trap mass spectra. Taken with the fact that 83% of the total mass of this SOA is low-MW species (Table 8.9), it is likely that oligomer formation is not favored with HCs with fewer than 6 carbon atmos. This is not unreasonable since, even after dimerization, most species have relatively small MW (below 250), probably rendering them still too volatile to stay in the aerosol phase.

8.4.2.2. Effect of Particle Phase Acidity on Oligomer Formation in SOA

Even though oligomers are universally present in the SOA studied, an important question arises: how does seed particle acidity affect oligomer formation in SOA? The ozonolysis of α-pinene (mixing ratio from 12 to 135 ppb) was chosen to address this question. We use two “nonacid” seeds, containing either $MgSO_4$ or $(NH_4)_2SO_4$, and two “acid” seeds, containing either $[MgSO_4+H_2SO_4]$ or $[(NH_4)_2SO_4+H_2SO_4]$.

Thermodynamic calculations show that the four seed aerosols, once stabilized at the ambient RH in the chamber, span a spectrum of pH values. For example, at RH = 55% , the pH values for [$MgSO_4$-only] seed and [$MgSO_4$+H_2SO_4] seed are about 6.5 and -0.3, respectively. The pH values for [$(NH_4)_2SO_4$-only] seed and [$(NH_4)_2SO_4$+H_2SO_4] seed are about 4.6 and 2.4, respectively. The acidity increase from the "nonacid" to the "acid" seed for $MgSO_4$ exceeds that in the $(NH_4)_2SO_4$ case by about 4.6 pH units.

Figure 8.8(a) shows the ion trap mass spectrum (positive ion mode) of the SOA from the ozonolysis of 120 ppb α-pinene in the presence of $MgSO_4$-only seed. When the seed becomes much more acidic ($MgSO_4$-H_2SO_4), as shown in Figure 8.8(b), the resultant SOA comprises many more large oligomers (MW from 450 to 950), most of which have higher ion intensities; thus, mass concentrations of these species exceed, by at least a factor of two, those in the SOA formed on $MgSO_4$-only seed. Some even larger oligomers (MW from 950 to 1600) are detected (with signal-to-noise ratios larger than 3) in the SOA formed on the acidic seed. On the other hand, the mass distribution of small oligomers (MW from 250 to 450) remains roughly in the same pattern, with ion intensities changing only modestly. Similar difference in SOA composition between nonacid and acid $MgSO_4$ seeds is observed in all other six pairs of experiments on the α-pinene system, with large oligomers increasing in abundance by two to four times in the acid cases. By comparison, the composition difference between SOA formed on $(NH_4)_2SO_4$-only seed and $(NH_4)_2SO_4$-H_2SO_4 seed is less pronounced than on the corresponding $MgSO_4$ seeds. There is only a moderate increase of types and amounts of small oligomers in the SOA formed on the more acidic seed, and essentially no change in the mass distribution of the large oligomers.

Kinetically, as the acidity of the seed particles increases, acid-catalyzed reactions and oligomer formation accelerate, and larger oligomers form within the same experimental time frame than form on less acidic seed. The slight decrease in the ion intensities of some small oligomers in the more acidic case (e.g., see 381 and 395 ions in Figures 8.8[a] and 8.8[b]) actually may reflect their transformation into larger oligomers.

Oligomerization can be expected to shift the gas-to-particle equilibrium of some condensing low-MW species to the particle phase, eventually increasing the SOA yield over that in the absence of heterogeneous reactions. Indeed, this is confirmed by the overall SOA yield difference between systems containing nonacid and acid seeds. The absolute SOA yield is defined as the mass of SOA produced relative to the mass of hydrocarbon consumed. Figure 8.9 shows the absolute SOA yield versus the α-pinene mixing ratio, for seven pairs of experiments in the presence of acid vs. nonacid seed particles as well as for two experiments in the absence of seed particles. Consistently, the SOA formed on the more acidic $MgSO_4$-H_2SO_4 seed has a higher yield than that formed on the $MgSO_4$-only seed. Overall, within the range of α-pinene mixing ratios studied, the SOA yield increases by 10 – 40% on the acidic seed over the nearly neutral seed. Concurrent hygroscopicity measurements show that these SOA, at the time of filter collection, have approximately 10 – 20 % water content; thus, the increased types and amounts of oligomers formed on the more acidic seed appear to be the primary cause for the increased SOA yield. By comparison, the SOA yield increases by only about 5% on the $(NH_4)_2SO_4$–H_2SO_4 seed over the $(NH_4)_2SO_4$-only seed, at similar α-pinene mixing ratios. This smaller yield increase, consistent with the smaller composition change, is likely a result of the smaller acidity difference between the nonacid and acid seeds of $(NH_4)_2SO_4$, as compared with $MgSO_4$. In all, the above differences in the composition and amounts of SOA formed between these two sets of seed particles clearly demonstrate the direct impact of seed particle acidity.

Importantly, in the α-pinene ozonolysis system, similar types of oligomers are present in SOA both in the presence and absence of pre-existing particles. This suggests that organic acids produced from the gas-phase hydrocarbon oxidation itself may actually provide necessary acidity for catalytic reactions. Interestingly, the yields of SOA in the absence of seed particles appear to be lower than those in the presence of acid seeds but higher than those in the presence of nonacid seeds (see Figure 8.9). While the former is probably due to the higher acidity of the acid seeds and the subsequent SOA as compared with that of the nucleated SOA, the cause for the latter is less clear. One possible explanation is that the organic acids produced from α-pinene ozonolysis are "diluted" by the pre-existing, neutral particles as compared with the freshly nucleated ones, resulting in slower catalytic reactions and ultimately lower SOA yields. On the basis of these observations, we speculate that oligomers are widely present in atmospheric secondary organic aerosols.

8.4.2.3. Assessing Relative Abundance of Oligomers in SOA

It is difficult to quantify individual oligomeric species identified by the ion trap MS, since no standard is available at present and the exact structures of these high-MW species are not known. However, as illustrated by Figure 8.3, some oligomeric species are also identified by the LC-MS, equipped with ESI. Since the retention times of these oligomers are known from the LC-MS data, a surrogate compound with a similar retention time as well as presumed functional groups can be chosen to roughly quantify a detected oligomeric species. For example, a C_{m+n} diacid is chosen as the surrogate for a dimer formed via acid dehydration of C_m and C_n diacids, and a C_{m+n} carbonyl acid is chosen as the surrogate for a dimer formed via aldol reaction of a C_m dialdehyde and a C_n carbonyl acid. All the major high-MW species detected by LC-MS are then quantified using their surrogates' calibration factors, assuming their response factors on the MS are the same. Quantified oligomers are then added with the identified low-MW species, and the mass fractions of the total identified SOA species are listed in the 7th row in Table 8.9. Oligomers quantified this way account for another 3 – 11% of the total SOA mass, bringing the mass closure of analytical speciation to 45 – 90%, or 71% averaged for all six cycloalkene ozonolysis systems. Since only a fraction of oligomers are quantified by the LC-MS, oligomers in total are estimated to comprise at least 10% of the total mass of SOA from cycloalkene (carbon number > 5) ozonolysis in general. In the case of α-pinene ozonolysis, the ITMS data suggest that the majority of SOA mass is composed of oligomeric species.

Indeed, in light of the substantial presence of oligomers in SOA, the common approach to calculating SOA mass closure is thrown into question. Since oligomers may have somewhat higher densities than low-MW species, the overall aerosol density may actually exceed the commonly assumed 1.4 g/cm^3. A higher density would lead to lower mass closures achieved in this work and most previous work. In addition, since oligomers may decompose in the GC injector or column, reverting back to initial monomers, common GC-MS based speciation may overestimate the mass of low-MW species while underestimate the mass of oligomeric species.

8.4.3. Relationship Between HC Precursor Structure and SOA Composition and Yield

Investigating the relationship between parent cycloalkene structure and its SOA composition is a complex issue: (1) The gas-phase chemistry of cycloalkene ozonolysis is not yet fully understood; (2) The heterogeneous reactions involved are even less well understood, and oligomers that form via these reactions appear to comprise a substantial fraction of the final SOA mass; and (3) Even though major gas-phase reactions are probably completed within the first three hours from the onset of ozonolysis, as indicated by the observed disappearance of the cycloalkenes, oligomerization may take place well beyond the time when the parent hydrocarbon has been consumed. For this reason, bulk filter measurements at a certain time during SOA evolution may not be entirely comparable among systems from different parent hydrocarbons. Keeping this kinetic factor in mind, it is still possible to glean important trends from the bulk, average composition measurements, which were taken at similar elapsed times for similar durations.

8.4.3.1. Carbon Number in Homologous Cycloalkenes

Cyclopentene, cyclohexene, and cycloheptene are homologous compounds. As discussed earlier, within the total identified SOA low-MW species, diacids comprise rather constant mass fractions from system to system, as do hydroxy diacids (Table 8.8). These two categories of species are likely the low-MW species with the lowest volatility. While these constant fractions are of interest themselves, this also indicates that low-MW species alone cannot explain the increasing overall SOA yield from C_5 to C_7.[15] On the other hand, the 6th row in Table 8.9 shows that the total identified low-MW species comprises 83% of the total SOA mass in the C_5 system, whereas this fraction decreases dramatically to 42% and 44% for C_6 and C_7 systems, respectively. Incomplete speciation or experimental uncertainties can not explain such a large difference. Since the four classes of compounds identified should represent the major low-MW species, the fraction of oligomers-- which we assume are the main unidentified species by LC-MS-- is therefore probably considerably higher in the SOA from the C_6 and C_7 than the C_5 cycloalkene. Indeed, as noted earlier, the ion trap MS data show minimal amounts of oligomers in the cyclopentene system. The oligomers quantified by LC-MS comprise about 6%, 3%, and 9% of the total SOA mass for C_5, C_6, and C_7 systems, respectively. While an increasing fraction of oligomers in the SOA with increasing carbon number is suggested by the data (considering the quantification was not complete for especially the larger systems), theoretical considerations strongly support this trend simply because increasingly larger monomers would form in these systems from C_5 to C_7, further leading to increasingly less volatile and eventually more abundant oligomers in the SOA. Consequently, it is likely that the density of SOA also increases as the carbon number increases, further increasing the overall yield of SOA, as observed.

8.4.3.2. Methyl-Substitution Effect

1-me cyclopentene and cyclohexene (n = 6) have the same MW, as do 1-me cyclohexene and cycloheptene (n =7). The total identified low-MW species in the SOA is 15% more for 1-me cyclopentene than cyclohexene, and 24% more for 1-me cyclohexene than cycloheptene, as shown in Table 8.9. While this may indicate there are relatively more low-MW species than oligomers in the methyl-substituted systems, the overall SOA yield does not depend solely on the relative amounts of low-MW species and oligomers; instead, it depends on the absolute amount of all species eventually present in the SOA. Known gas-phase reactions[23] suggest that the initial steps of oxidation of 1-me cyclohexene would mainly lead to 6-oxo heptanoic acid (a C_7 carbonyl acid), and no C_7 diacid at all. However, from cycloheptene, initial steps can lead to both C_7 carbonyl acid and C_7 diacid. Consequently, the more abundant 6-oxo heptanoic acid in the 1-me cyclohexene system can lead to the formation of C_{14} and even larger oligomers via aldol reaction or gem diol reaction. By comparison, lesser amounts of C_7 carbonyl acids are available in the cycloheptene system to form C_{14} oligomers, which should have the lowest volatility of all possible dimers (C_{14}, C_{13}, C_{12}, etc.). By shifting gas-to-particle equilibrium, this can eventually transfer more volatile carbonyl species into the aerosol phase in the 1-me cyclohexene system and eventually increase the overall SOA yield, as observed by Keywood et al.[15] Similar explanations should apply to other isomeric pairs of cycloalkene precursors with even higher carbon numbers.

8.4.3.3. Isomeric Effect

3-me cyclohexene differs from 1-me cyclohexene in the position of the methyl substituent group on the ring. Together with cycloheptene, these three compounds comprise a set of isomers that display fascinating patterns of SOA composition and yield. Within the low-MW SOA species, carbonyl acids have the highest mass fraction in the 1-me cyclohexene system (19%) and lowest in the cycloheptene system (12%), consistent with the discussion in Section 8.3.2. Interestingly, almost the same compounds with fewer than six carbon numbers are identified in all three systems, implying that only the initial oxidation pathways differ substantially. After some steps of oxidation, the differences due to the 1-me and 3-me substitution vs. non-substitution diminish, probably because these carbons have been effectively oxidized "off" the main carbon chain, as suggested by known mechanisms.[23] This is also supported by the somewhat different extracted ion chromatograms (EIC) of the 143 (C_7 carbonyl acid) and 129 (C_6 carbonyl acid) ions, but the very similar EICs of the 115 (C_5 carbonyl acid) ion in SOA of these three systems. On the other hand, strikingly, the overall SOA yield is highest for 1-me cyclohexene and lowest for 3-me cyclohexene, differing to a substantial extent.[15]

A look at selected high-MW species detected by the LC-MS reveals contrasting composition patterns. For example, as shown in Figure 8.10, the species detected by m/z of 289 show different extracted ion chromatograms with the three C_7 isomeric cycloalkene systems. At least six major peaks are detected in the SOA from 1-me cyclohexene, corresponding most likely to oligomeric SOA components. By comparison, the SOA from cycloheptene ozonolysis exhibits only three major peaks, all of which are detected in the 1-me cyclohexene case with very similar retention times (differing by less than 0.1 min), indicating they are the same or isomeric species. In sharp contrast, the SOA from 3-me cyclohexene ozonolysis exhibits only two major peaks, with different retention times from the other two isomeric systems. Assuming a similar response factor for all these species, the abundance of 289 decreases from 1-me cyclohexene to cycloheptene to 3-me cyclohexene substantially, indicating decreasing amounts of oligomers are formed in this sequence. Some other high-MW species exhibit similar patterns. Mechanistic considerations provide a consistent explanation for these observed differences. The m/z of 289 corresponds to a dimer of a C_7 carbonyl acid (MW = 144) and a C_7 dicarbonyl (MW = 128) formed via aldol reaction, which requires the enolization of a carbonyl (involving its neighboring α-C and α-H). As depicted in Table 8.10, the mechanistic possibilities of enolization in these three systems differ substantially. Consider the carbonyl group depicted on the right side in the C_7 dicarbonyl and C_7 carbonyl acid, both initial oxidation products. This carbonyl has either a methyl group attached to it as from 1-me cyclohexene ozonolysis, or a methyl group attached to its α-carbon as from 3-me cyclohexene ozonolysis, or has no methyl substitution as from cycloheptene ozonolysis. As explained earlier, larger amounts of C_7 dicarbonyl and carbonyl acid are expected to form in the system of 1-me cyclohexene than cycloheptene and 3-me cyclohexene. In addition, with both the dicarbonyl and carbonyl acid, there are 2 α-carbons and 5 α-hydrogens available for enolization in the 1-me cyclohexene system. By comparison, available α-C and α-H numbers decrease to 1 and 2, respectively, in the cycloheptene system, and 1 and 1, respectively, in the 3-me cyclohexene system. As a result, enolization becomes increasingly difficult moving from 1-me cyclohexene to cycloheptene to 3-me cyclohexene, as does the subsequent dimerization. Either slower reactions or fewer dimerization possibilities ultimately lead to increasingly smaller amounts of oligomers formed in the SOA and therefore smaller overall SOA yield.

8.5. Conclusions

The composition of SOA from cycloalkene ($C_5 – C_8$) and α-pinene ozonolysis is investigated by the concurrent use of a LC-MS and an ion trap MS, both equipped with ESI. A large variety of polar, low-volatility species are identified and quantified. Four classes of compounds, diacids, carbonyl-containing acids, diacid alkyl esters, and hydroxy diacids, comprise relatively constant mass fractions of the total identified low-MW species (MW < 250) in SOA in all six cycloalkene systems; on average, these fractions are 69%, 15%, 11%, and 8%, respectively. In particular, C_n, C_{n-1}, and C_{n+1} diacids comprise on average 62% of the total identified low-MW species. With an estimate for oxalic acid and assuming an SOA density of 1.4 g/cm^3, identified low-MW species comprise 42% to 83% of the total SOA mass in the six cycloalkene systems quantified.

Oligomeric species (MW > 250) are ubiquitous in the SOA from all parent cycloalkenes (although those from cyclopentene are at minimal amounts). Using surrogate standards, it is estimated that oligomers comprise at least 10% of the total mass of SOA from cycloalkene ozonolysis. The mass fraction of oligomers may well exceed

50% in the SOA from α-pinene ozonolysis. Two issues need to be understood more fully before SOA mass closure can be more accurately assessed: how to quantify the mass of oligomers and what is the actual density of the SOA. Mass closures may have been overestimated due to the density values used (e.g., 1.4 g/cm^3 or less calculated on the basis of low-MW components alone).

The acidity of the seed particles upon which SOA components condense has an explicit effect on oligomer formation. Higher acidity appears to lead to more rapid formation of oligomers, ultimately resulting in higher SOA yields than in systems with more neutral seed particles. While acidity is required to facilitate the three heterogeneous reactions proposed, organic acids produced from gas-phase oxidations may readily promote oligomer formation, as suggested by the formation of similar oligomers in SOA both in the presence and absence of seed particles.

Systematic relationships between hydrocarbon precursor structure and the composition and yield of resultant SOA are discussed. Carbon numbers, substituent groups, and isomeric structures all have distinct effects on the SOA formed, either by different gas-phase reaction pathways or by different oligomer formation processes or both. Work remains to quantitatively describe these complex and coupled effects.

8.6. Acknowledgements

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Table 8.1. Molecular structures of precursor hydrocarbons investigated in this study

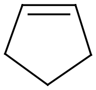
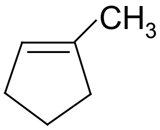
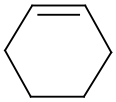
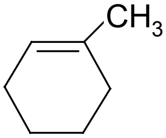
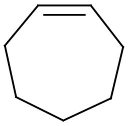
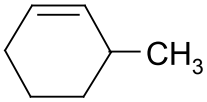
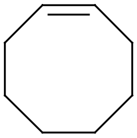
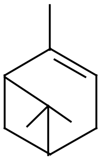
Precursor Hydrocarbon	**Molecular Structure**	**Precursor Hydrocarbon**	**Molecular Structure**
Cyclopentene		1-methyl cyclopentene	
Cyclohexene		1-methyl cyclohexene	
Cycloheptene		3-methyl cyclohexene	
Cyclooctene		α-pinene	

Table 8.2. Low-MW components in SOA from cyclopentene ozonolysis[a]

Class of SOA components	**Identified low-MW species in SOA**	**Surrogate standard for quantification**[b]	**Mass yield (%)**[c]
Diacid	pimelic acid		0.19
	adipic acid		0.27
	glutaric acid		0.40
	succinic acid		2.72
Diacid alkyl ester	adipic acid monomethyl ester		0.01
	glutaric acid monomethyl ester		0.02
	succinic acid monomethyl ester		0.09
	malonic acid monoethyl ester	succinic acid monomethyl ester	0.22
Hydroxy diacid	2-hydroxy glutaric acid	2-OH-2-me succinic acid	0.57
	2-hydroxy succinic acid	succinic acid	0.10
Carbonyl-containing acid	4,5-dioxo pentanoic acid	2-oxo glutaric acid	0.04
	5-oxo pentanoic acid	4-oxo pentanoic acid	0.01
	Sum of identified low-MW species[d]		4.64
	Total SOA mass derived from DMA[e]		6.04

[a] 224 ppb cyclopentene was consumed in this experiment. The filter was collected ~ 5 h from the onset of ozonolysis for a duration of ~ 4 h.

[b] A blank cell indicates a standard was available for quantification. This also applies to Tables 8.3 – 8.7.

[c] To examine the variation of these yields, SOA samples from three cyclopentene ozonolysis experiments are analyzed, and the variation of these yields is on average within ± 25%, caused by analysis uncertainties and slightly different sampling times and duration. For the mass yields of other cycloalkene systems, we estimate the variation to be roughly ± 25% as well.

[d] The sum of identified low-MW species accounts for 77% of the total SOA mass derived from the DMA measurements.

[e] A differential mobility analyzer (DMA) was used to measure the aerosol size distribution. The mass yield of the total SOA reported here, derived from the DMA measurement with the assumption of an aerosol

density of 1.4 g/cm^3, has not corrected for particle loss to the chamber wall, therefore is somewhat lower than the actual total SOA mass yield. This also applies to Tables 8.3 – 8.7. Both the “Sum of identified low-MW species” and the “Total SOA mass derived from DMA” here refer to their yields (in percentage; relative to the mass of the consumed HC) as defined in text similarly for individual SOA components. This applies to Tables 8.3 – 8.7 as well.

Table 8.3. Low-MW components in SOA from cyclohexene ozonolysis[a]

Class of SOA components	Identified low-MW species in SOA	Surrogate standard for quantification	Mass yield (%)
Diacid	suberic acid		0.03
	pimelic acid		0.90
	adipic acid		1.59
	glutaric acid		1.03
	succinic acid		0.08
Diacid alkyl ester	glutaric acid monomethyl ester		0.05
	2-hydroxy succinic acid monoethyl ester	succinic acid monoethyl ester	0.03
Hydroxy diacid	2-hydroxy pimelic acid	pimelic acid	0.01
	2-hydroxy adipic acid	3-OH-3-me glutaric acid	0.08
	2,5-dihydroxy adipic acid	3-OH-3-me glutaric acid	0.02
	2-hydroxy glutaric acid	2-OH-2-me succinic acid	0.28
	2-hydroxy succinic acid	succinic acid	0.03
Carbonyl-containing acid	2-oxo adipic acid		0.02
	5-oxo hexanoic acid		0.02
	6-oxo hexanoic acid	5-oxo hexanoic acid	0.16
	4.5-dioxo pentanoic acid	5-oxo hexanoic acid	0.02
	4-oxo pentanoic acid		0.09
	5-oxo pentanoic acid	4-oxo pentanoic acid	0.37
	Sum of identified low-MW species[b]		4.80
	Total SOA mass derived from DMA		15.37

[a] 313 ppb cyclohexene was consumed in this experiment. The filter was collected ~ 4.5 h from the onset of ozonolysis for a duration of ~ 2 h.

[b] The sum of identified low-MW species accounts for 31% of the total SOA mass derived from the DMA measurements.

Table 8.4. Low-MW components in SOA from cycloheptene ozonolysis[a]

Class of SOA components	**Identified low-MW species in SOA**	**Surrogate standard for quantification**	**Mass yield (%)**
Diacid	pimelic acid		1.66
	adipic acid		1.85
	glutaric acid		0.48
	succinic acid		0.02
	malonic acid		0.02
Diacid alkyl ester	pimelic acid monomethyl ester	suberic acid	0.20
	adipic acid monomethyl ester		0.28
	glutaric acid monoethyl ester	adipic acid monomethyl ester	0.01
	glutaric acid monomethyl ester		0.04
	succinic acid monoethyl ester		0.06
	malonic acid monoethyl ester	succinic acid monomethyl ester	0.10
Hydroxy diacid	2-hydroxy pimelic acid	2-OH-2-isopropyl succinic acid	0.51
	2-hydroxy adipic acid	3-OH-3-me glutaric acid	0.04
	2-hydroxy glutaric acid	2-OH-2-me succinic acid	0.08
	2,6-dihydroxy pimelic acid	2-OH-2-isopropyl succinic acid	0.03
Carbonyl-contaning acid	5,6-dioxo hexanoic acid	5-oxo hexanoic acid	0.02
	8-oxo octanoic acid[b]	7-oxo octanoic acid	0.06
	7-oxo heptanoic acid[b]	6-oxo heptanoic acid	0.26
	6-oxo hexanoic acid[b]	5-oxo hexanoic acid	0.36
	5-oxo pentanoic acid	4-oxo pentanoic acid	0.02
	Sum of identified low-MW species[c]		6.11
	Total SOA mass derived from DMA		18.21

[a] 184 ppb cycloheptene was consumed in this experiment. The filter was collected ~ 5 h from the onset of ozonolysis for a duration of ~ 2 h.

[b] Isomers are present in this SOA based on extracted ion chromatograms, and are quantified together here by the corresponding surrogate standard.

[c] The sum of identified low-MW species accounts for 34% of the total SOA mass derived from the DMA measurements.

Table 8.5. Low-MW components in SOA from 1-methyl cyclopentene ozonolysis[a]

Class of SOA component	Identified low-MW species in SOA	Surrogate standard for quantification	Mass yield (%)
Diacid	azelaic acid		0.01
	suberic acid		0.16
	pimelic acid		0.55
	adipic acid		0.31
	glutaric acid		1.05
	succinic acid		0.25
	malonic acid		0.05
Diacid alkyl ester	pimelic acid monomethyl ester	adipic acid monomethyl ester	0.02
	adipic acid monomethyl ester		0.01
	glutaric acid monomethyl ester		0.19
	succinic acid monoethyl ester		0.06
	malonic acid monoethyl ester	succinic acid monomethyl ester	0.53
	2-hydroxy succinic acid monoethyl ester	succinic acid monoethyl ester	0.05
Hydroxy diacid	2-hydroxy pimelic acid	2-OH-2-isopropyl succinic acid	0.08
	2-hydroxy adipic acid	3-OH-3-me glutaric acid	0.01
	3-hydroxy adipic acid	3-OH-3-me glutaric acid	0.01
	2-hydroxy glutaric acid	2-OH-2-me succinic acid	0.05
	2-hydroxy succinic acid	succinic acid	0.08
Carbonyl-containing acid	5,6-dioxo hexanoic acid	5-oxo hexanoic acid	0.04
	5-oxo hexanoic acid		0.09
	4-oxo pentanoic acid		0.19
	5-oxo-6-hydroxy hexanoic acid	3-OH-3-me glutaric acid	0.17
	5-oxo-4,6-dihydroxy hexanoic acid	2-keto gulonic acid	0.03
	Sum of identified low-MW species[b]		3.96
	Total SOA mass derived from DMA		8.85

[a] 193 ppb 1-methyl cyclopentene was consumed in this experiment. The filter was collected ~ 4.5 h from the onset of ozonolysis for a duration of ~ 3 h.

[b] The sum of identified low-MW species accounts for 45% of the total SOA mass derived from the DMA measurements.

Table 8.6. Low-MW components in SOA from 1-methyl cyclohexene ozonolysis[a]

Class of SOA components	**Identified low-MW species in SOA**	**Surrogate standard for quantification**	**Mass yield (%)**
Diacid	pimelic acid		0.35
	adipic acid		3.38
	glutaric acid		0.36
	succinic acid		0.04
	malonic acid		0.04
Diacid alkyl ester	pimelic acid monomethyl ester	suberic acid	0.03
	adipic acid monomethyl ester		0.47
	glutaric acid monomethyl ester		0.08
	malonic acid monoethyl ester	succinic acid monomethyl ester	0.16
Hydroxy diacid	2-hydroxy pimelic acid	2-OH-2-isopropyl succinic acid	0.03
	2-hydroxy adipic acid	3-OH-3-me glutaric acid	0.02
	2-hydroxy glutaric acid	2-OH-2-me succinic acid	0.03
	2,3,4,5,6-pentahydroxy pimelic acid[b]	2-keto gulonic acid	0.07
Carbonyl-containing acid	6,7-dioxo heptanoic acid[c]	4-oxo pimelic acid	0.42
	6-oxo heptanoic acid		0.10
	5-oxo hexanoic acid		0.15
	4-oxo pentanoic acid		0.04
	6-oxo-7-OH heptanoic acid	4-oxo pimelic acid	0.46
	Sum of identified low-MW species[d]		6.22
	Total SOA mass derived from DMA		14.15

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[a] 157 ppb 1-methyl cyclohexene was consumed in this experiment. The filter was collected ~ 6 h from the onset of ozonolysis for a duration of ~ 3.5 h.

[b] This structure is tentatively identified based on the chromatographic retention time and molecular weight. Other isomeric structures may also be present in this SOA.

[c] Isomers are present in this SOA based on the extracted ion chromatograms, and are quantified together here by the corresponding surrogate standard.

[d] The sum of identified low-MW species accounts for 44% of the total SOA mass derived from the DMA measurements.

Table 8.7. Low-MW components in SOA from 3-methyl cyclohexene ozonolysis[a]

Class of SOA components	Identified low-MW species in SOA	Surrogate standard for quantification	Mass yield (%)
Diacid	suberic acid[b]		0.05
	pimelic acid		0.36
	2-methyl adipic acid	pimelic acid	1.82
	adipic acid		0.35
	2-methyl glutaric acid	adipic acid	0.80
	glutaric acid		0.45
	succinic acid		0.07
Diacid alkyl ester	pimelic acid monomethyl ester	suberic acid	0.11
	adipic acid monomethyl ester		0.08
	glutaric acid monomethyl ester		0.03
	succinic acid monoethyl ester		0.05
	succinic acid monomethyl ester		0.08
	malonic acid monoethyl ester	succinic acid monomethyl ester	0.24
Hydroxy diacid	2-hydroxy pimelic acid	2-OH-2-isopropyl succinic acid	0.19
	2-hydroxy-2-methyl adipic acid	2-OH-2-isopropyl succinic acid	0.12
	2-hydroxy-2-methyl glutaric acid[c]	3-OH-3-me glutaric acid	0.06
	2-hydroxy glutaric acid[d]	2-OH-2-me succinic acid	0.02
	2,6-dihydroxy pimelic acid	2-OH-2-isopropyl succinic acid	0.02
Carbonyl-containing acid	4,5-dioxo-2-methyl pentanoic acid	5-oxo hexanoic acid	0.02
	6-oxo-2-methyl hexanoic acid[e]	6-oxo heptanoic acid	0.40
	5-oxo hexanoic acid		0.26
	6-oxo hexanoic acid[e]	5-oxo hexanoic acid	0.22
	4-oxo pentanoic acid		0.05
	Sum of identified low-MW species[f]		5.84
	Total SOA mass derived from DMA		8.67

[a] 307 ppb 3-methyl cyclohexene was consumed in this experiment. The filter was collected ~ 4.5 h from the onset of ozonolysis for a duration of ~ 2 h.

[b] A likely isomer, also present in this SOA, is 2-methyl pimelic acid.

[c] A likely isomer, also present in this SOA, is 2-hydroxy adipic acid.

[d] A likely isomer, also present in this SOA, is 2-hydroxy-2-methyl succinic acid.

[e] Isomers are present in this SOA based on the extracted ion chromatograms, and are quantified together here by the corresponding surrogate standard.

[f] The sum of identified low-MW species accounts for 67% of the total SOA mass derived from the DMA measurements.

Table 8.8. Mass percentage of each class of compounds in the total identified low-MW SOA species in six ozonolysis systems

Class of compounds	**Cyclopentene**	**Cyclohexene**	**1-methyl cyclopentene**	**1-methyl cyclohexene**	**3-methyl cyclohexene**	**cycloheptene**	**average**	**Standard deviation**
Diacid	77%	75%	60%	67%	67%	66%	69%	7%
Hydroxy diacid	14%	9%	5%	2%	7%	11%	8%	4%
Carbonyl-containing acid	1%	14%	13%	19%	16%	12%	15%	3%
Diacid alkyl ester	7%	2%	22%	12%	10%	11%	11%	7%
Sum							**102%**	

Table 8.9: Fraction of each class of compounds in the total SOA mass derived from the DMA measurements (first four rows). Fractions of identified low-MW species (no oxalic acid) in the total SOA mass (5th row). Fractions of the identified low-MW species (including the estimated oxalic acid) in the total SOA mass (6th row). Fractions of the total identified species, both low-MW and oligomeric, in the total SOA mass (7th row).

Class of compounds	**Cyclopentene**	**cyclohexene**	**1-me cyclopentene**	**1-me cyclohexene**	**3-me cyclohexene**	**cycloheptene**	**average**	**Standard deviation**
Diacid	59%	24%	27%	29%	45%	22%	34%	15%
Hydroxy diacid	11%	3%	2%	1%	5%	4%	4%	4%
Carbonyl-containing acid	1%	4%	6%	8%	11%	4%	6%	4%
Diacid alkyl ester	6%	1%	10%	5%	7%	4%	5%	3%
% of identified low-MW species in the total SOA (no oxalic acid)	77%	31%	45%	44%	67%	34%		
% of identified low-MW species in the total SOA (including oxalic acid)	83%	42%	57%	68%	81%	44%		
% of total identified low-MW and oligomeric species in the total SOA	89%	45%	67%	79%	90%	53%		

Table 8.10: Structures illustrating the numbers of available α-C and α-H for aldol reactions in some initial oxidation products in 1-methyl cyclohexene, cycloheptene, and 3-methyl cyclohexene ozonolysis systems

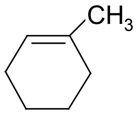
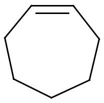
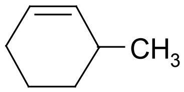
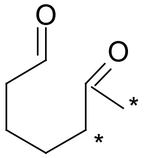
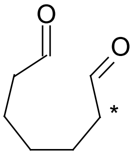
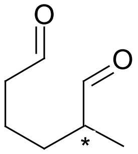
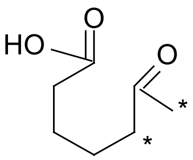
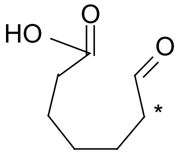
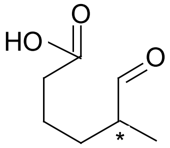
Hydrocarbon precursor			
C_7 dicarbonyl			
Available α-C(*) number	2	1	1
Available α-H number	5	2	1
C_7 carbonyl acid			
Available α-C(*) number	2	1	1
Available α-H number	5	2	1

Figure 8.1. Typical total ion chromatograms of SOA from the ozonolysis of cycloalkenes

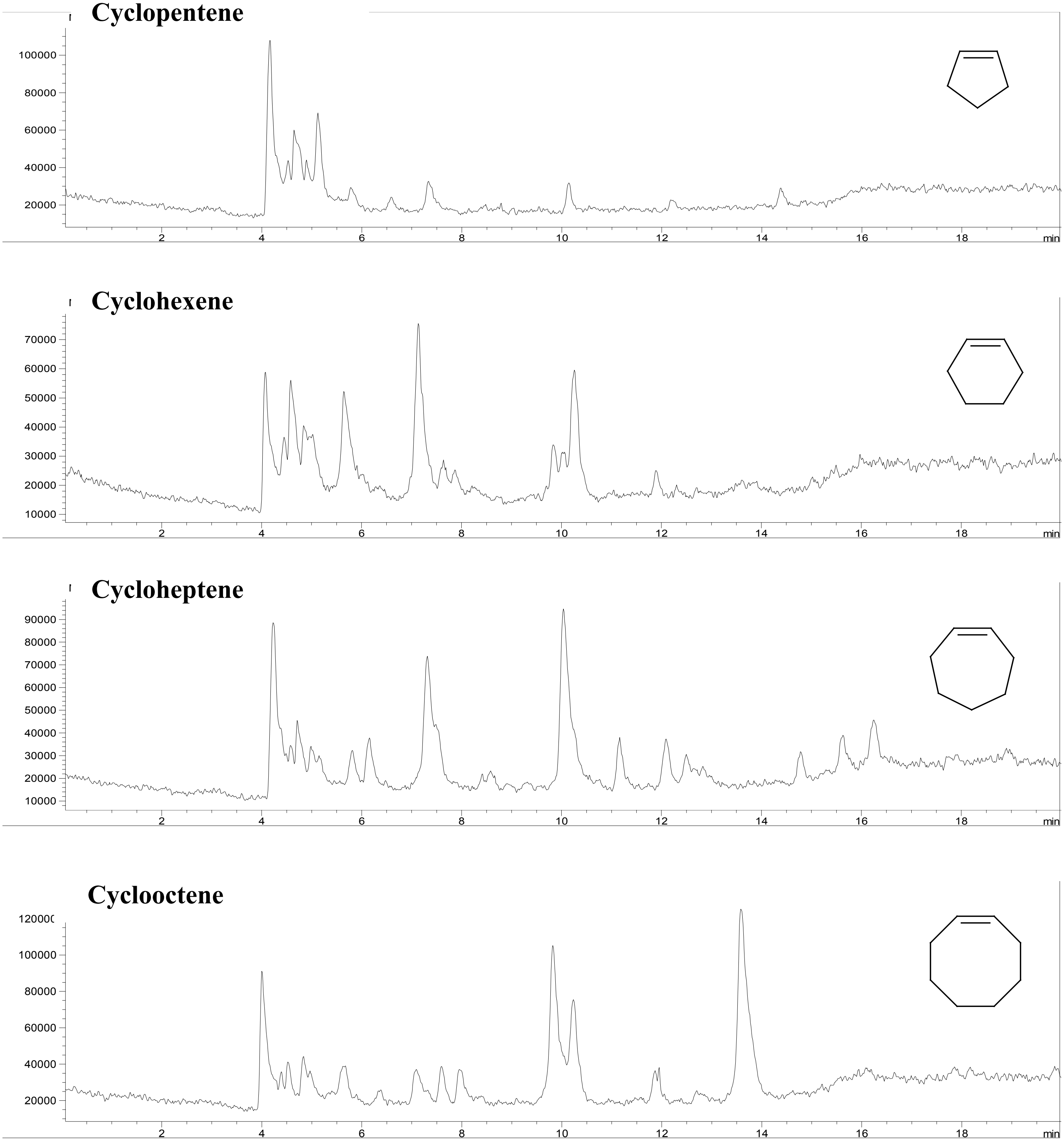


Figure 8.2. Total ion chromatograms (TIC) and extracted ion chromatograms (EIC) of 145, 185, and 243 ions of SOA from cycloheptene ozonolysis

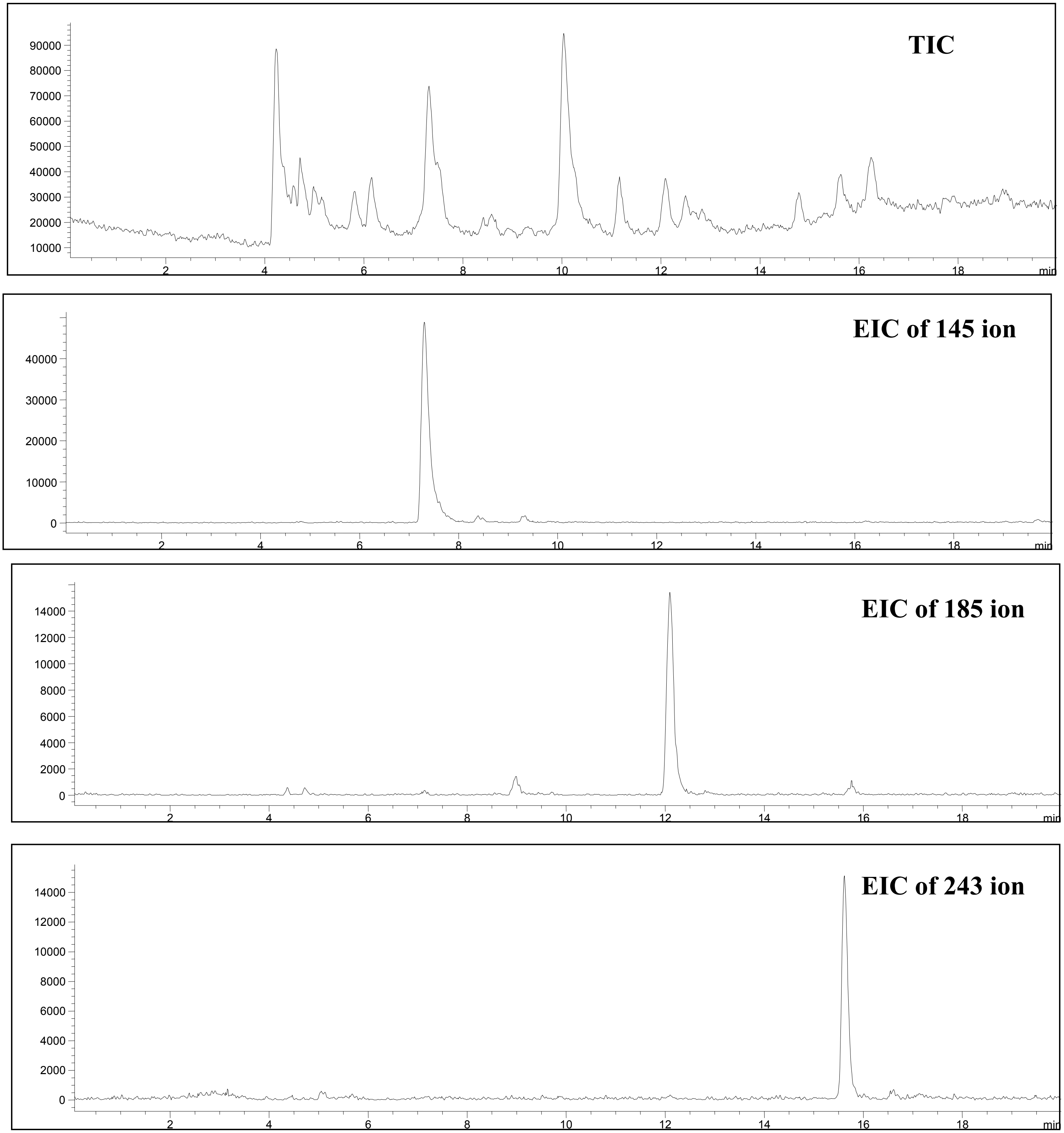


Figure 8.3. Late-eluting chromatographic peaks in SOA from cycloalkene ozonolysis

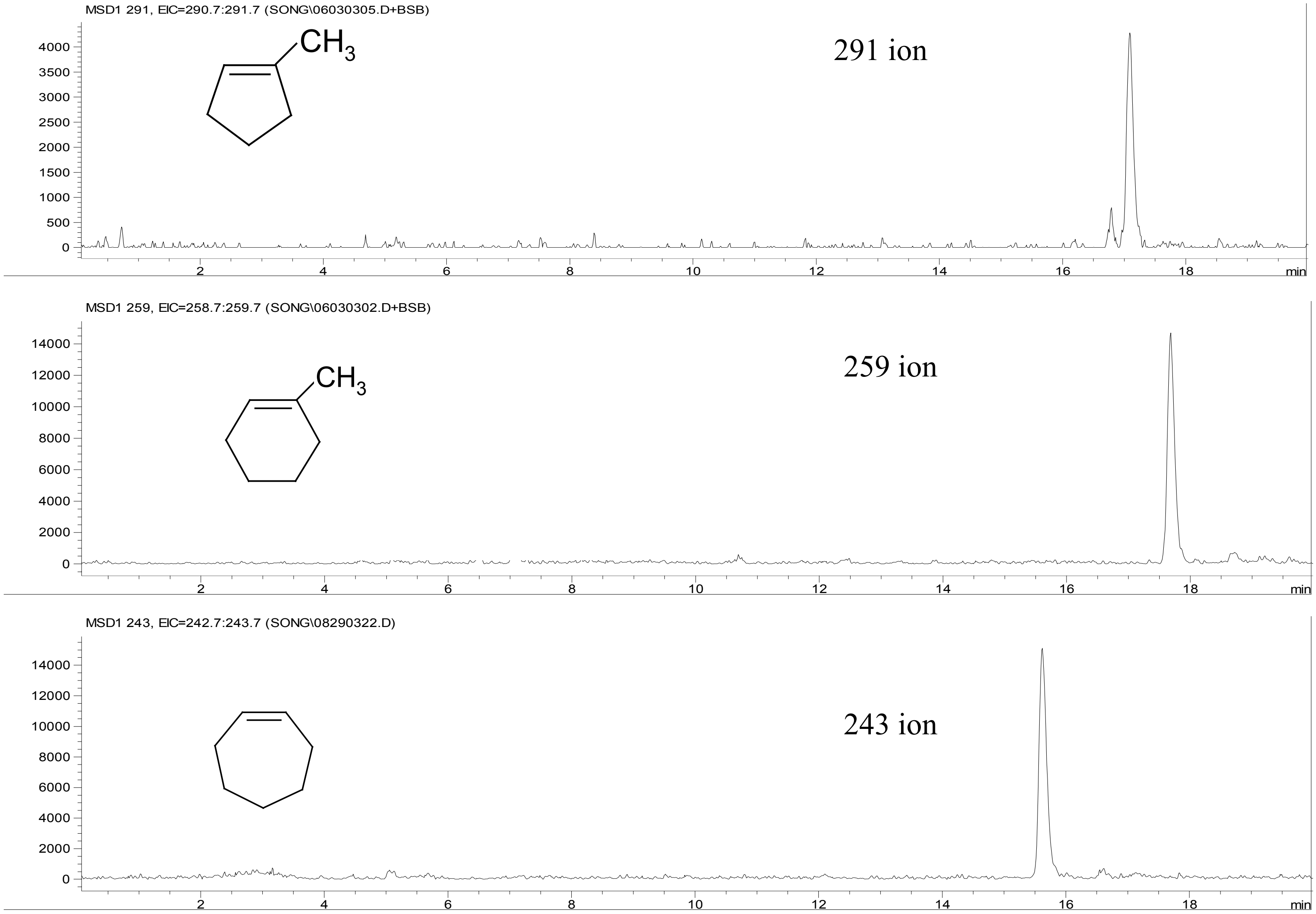


Figure 8.4. Ion trap mass spectrum (- ion mode) of SOA from cycloheptene ozonolysis. The background ion intensities are almost always lower than 5% of the maximum ion intensity (m/z = 373.2 as 100% intensity).

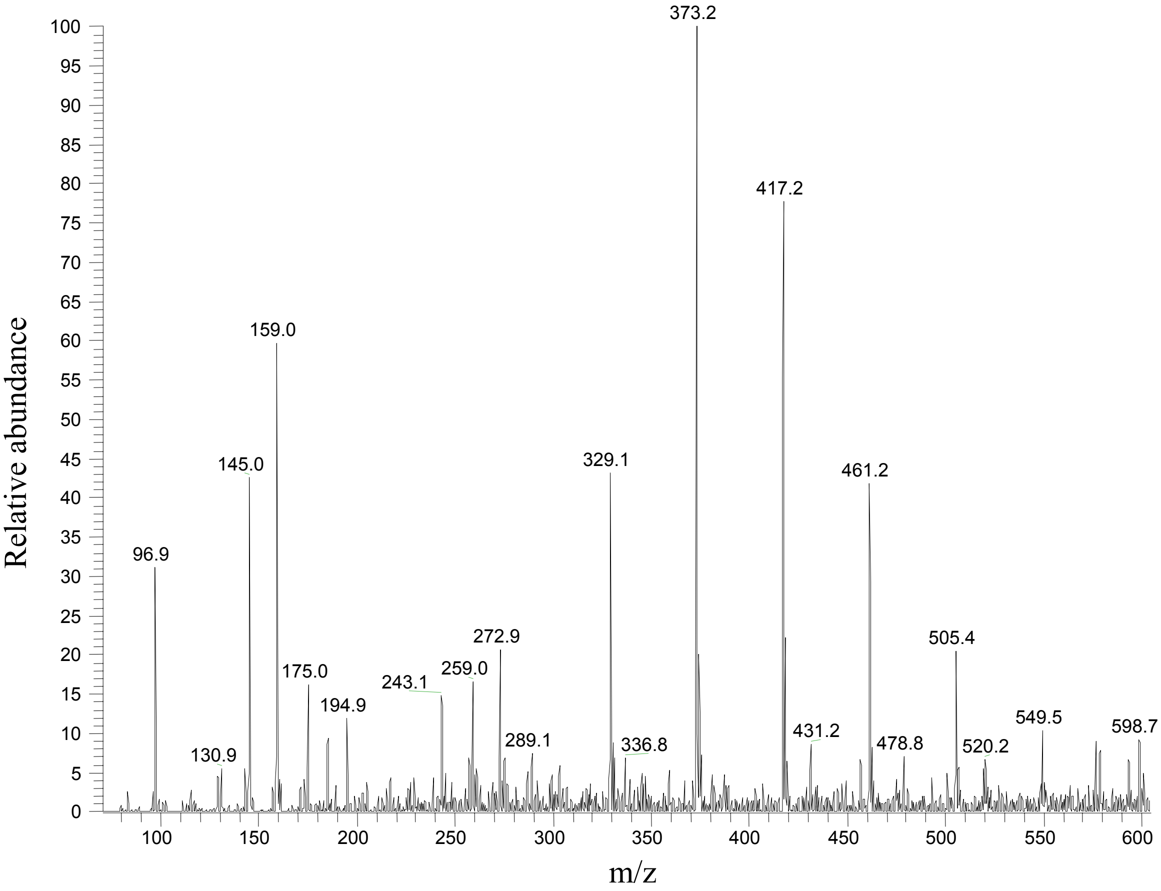


Figure 8.5. Ion trap mass spectrum (- ion mode) of SOA from 1-methyl cyclopentene ozonolysis. The background ion intensities are almost always lower than 9% of the maximum ion intensity (m/z = 131.0 as 100% intensity).

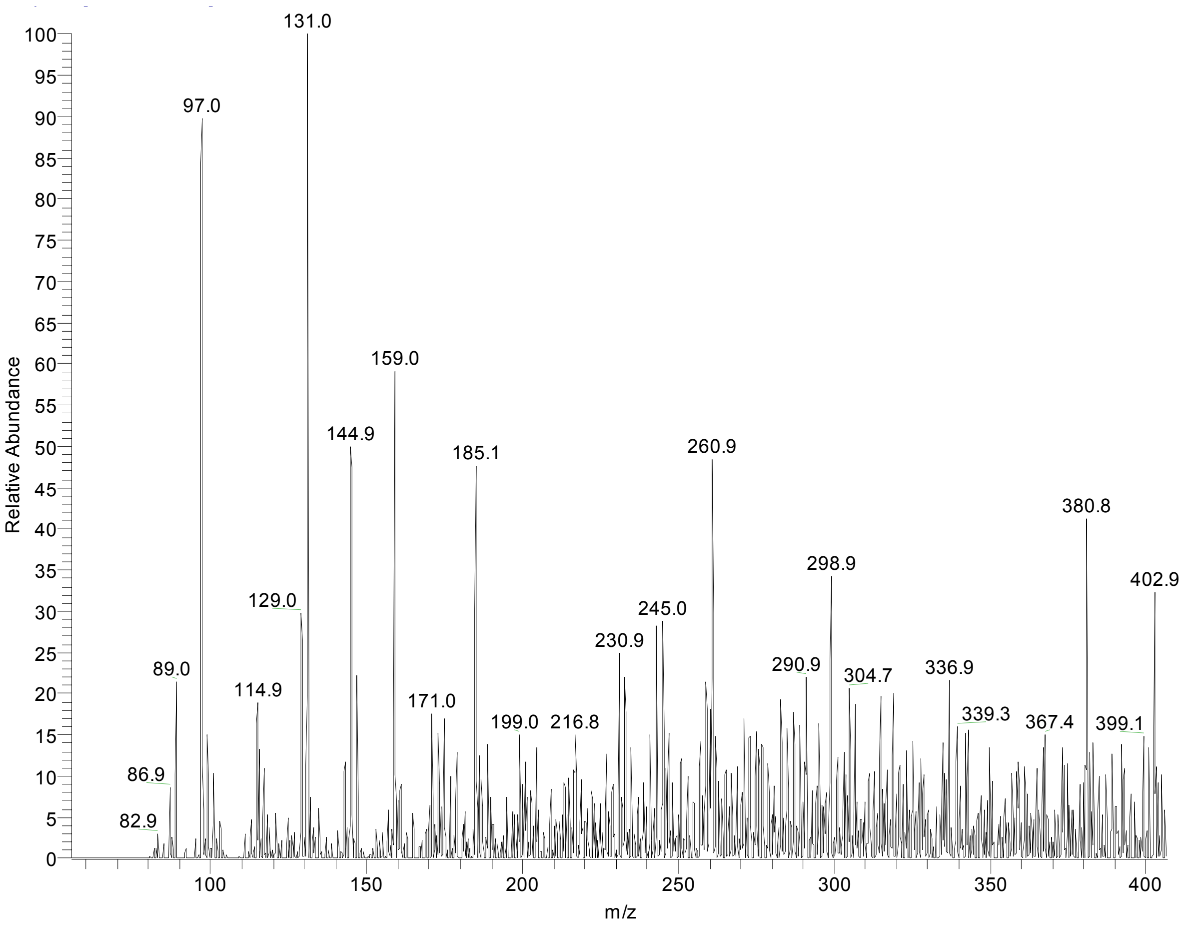
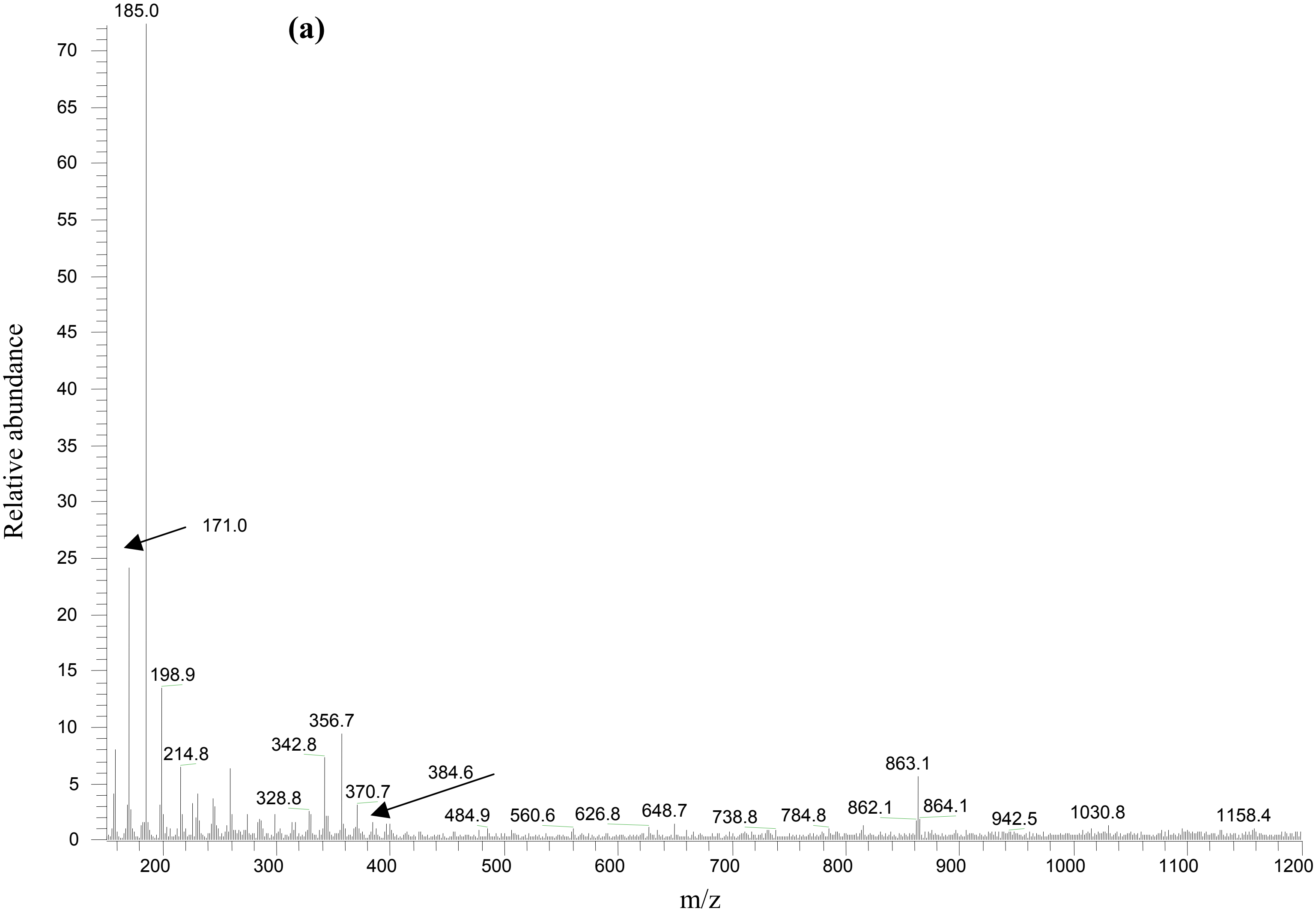


Figure 8.6. (a). Ion trap mass spectrum (- ion mode) of SOA from α-pinene ozonolysis with pre-existing $MgSO_4$ seed particles. The background ion intensities are almost always lower than 1% of the maximum ion intensity (m/z = 185.0 as 100% intensity). The 863.1 ion is from the instrument background (b). Ion trap mass spectrum (+ ion mode) of the same SOA as in (a). The background ion intensities are almost always lower than 6% of the maximum ion intensity (m/z = 381.1 as 100% intensity).



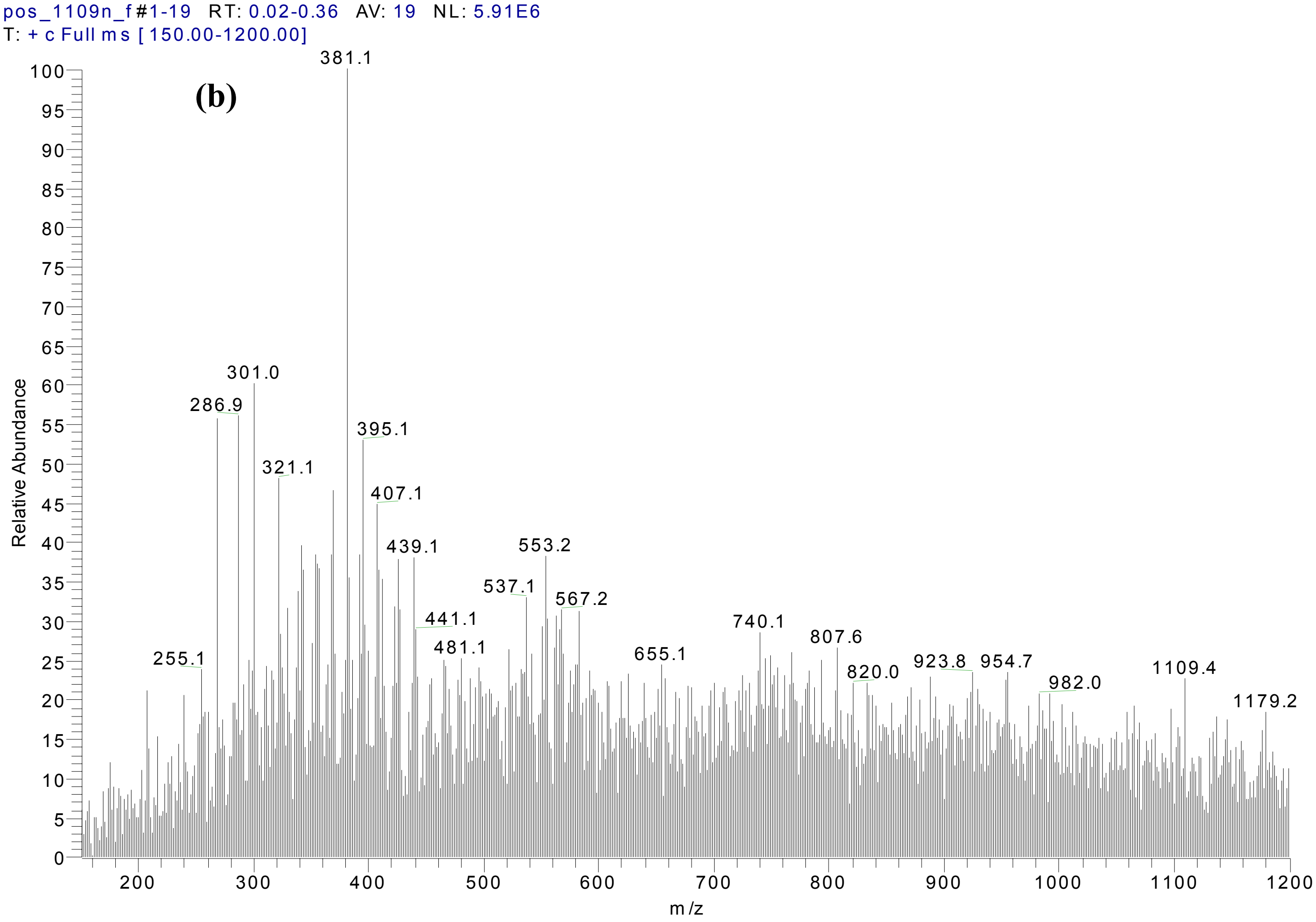

pos_1109n_f #1-19 RT: 0.02-0.36 AV: 19 NL: 5.91E6
T: + c Full ms [150.00-1200.00]
(b)
381.1
301.0
286.9
395.1
321.1
407.1
439.1
553.2
537.1
567.2
441.1
481.1
255.1
740.1
807.6
655.1
820.0
923.8
954.7
982.0
1109.4
1179.2
Relative Abundance
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
200
300
400
500
600
700
800
900
1000
1100
1200
m/z

Figure 8.7. MS/MS (- ion mode) of 373 ion in the SOA from cycloheptene ozonolysis, as shown in Figure 8.4. It is likely formed through gem-diol reaction and acid dehydration of monomers including 1,4-butanedial and 4-oxo butanoic acid.

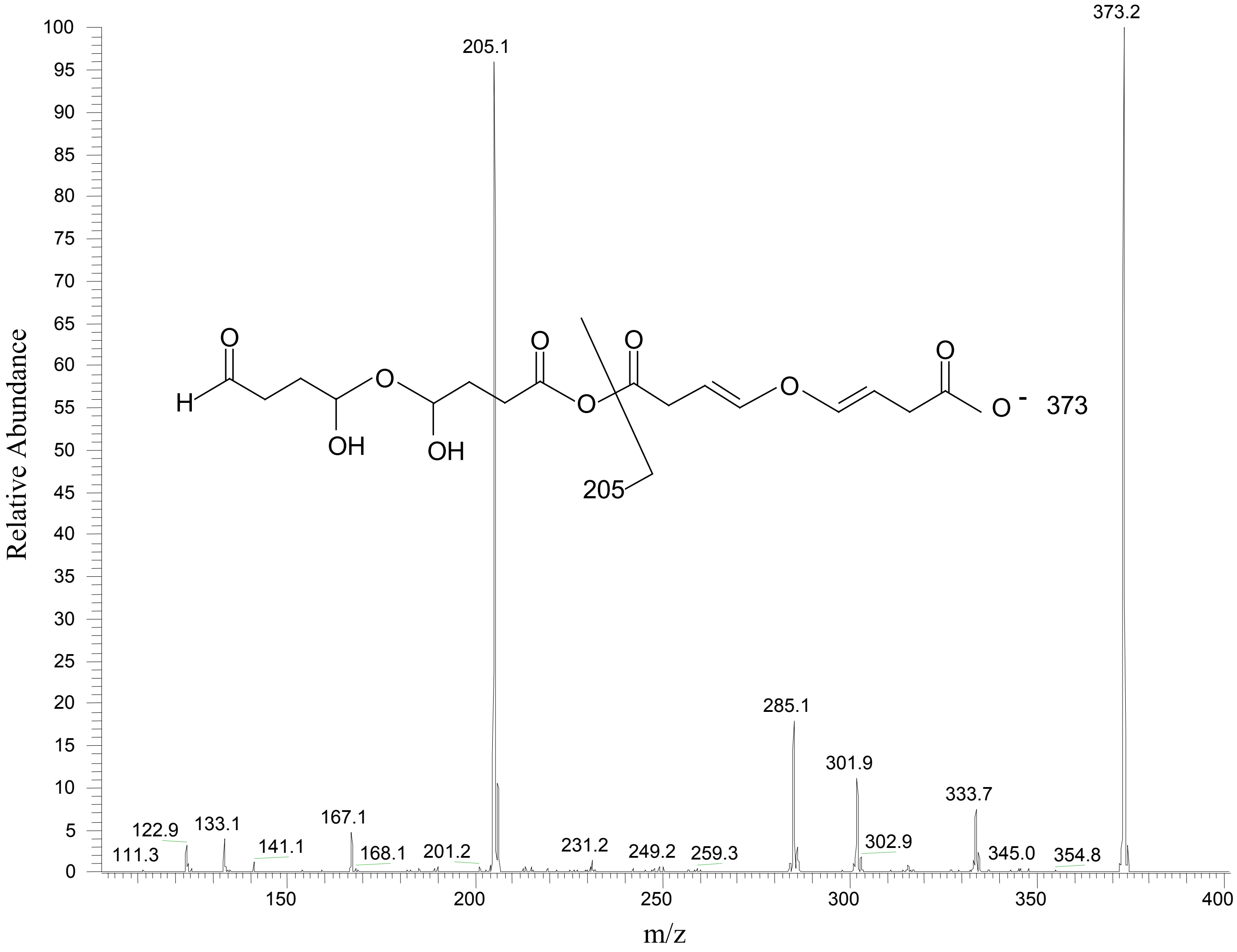
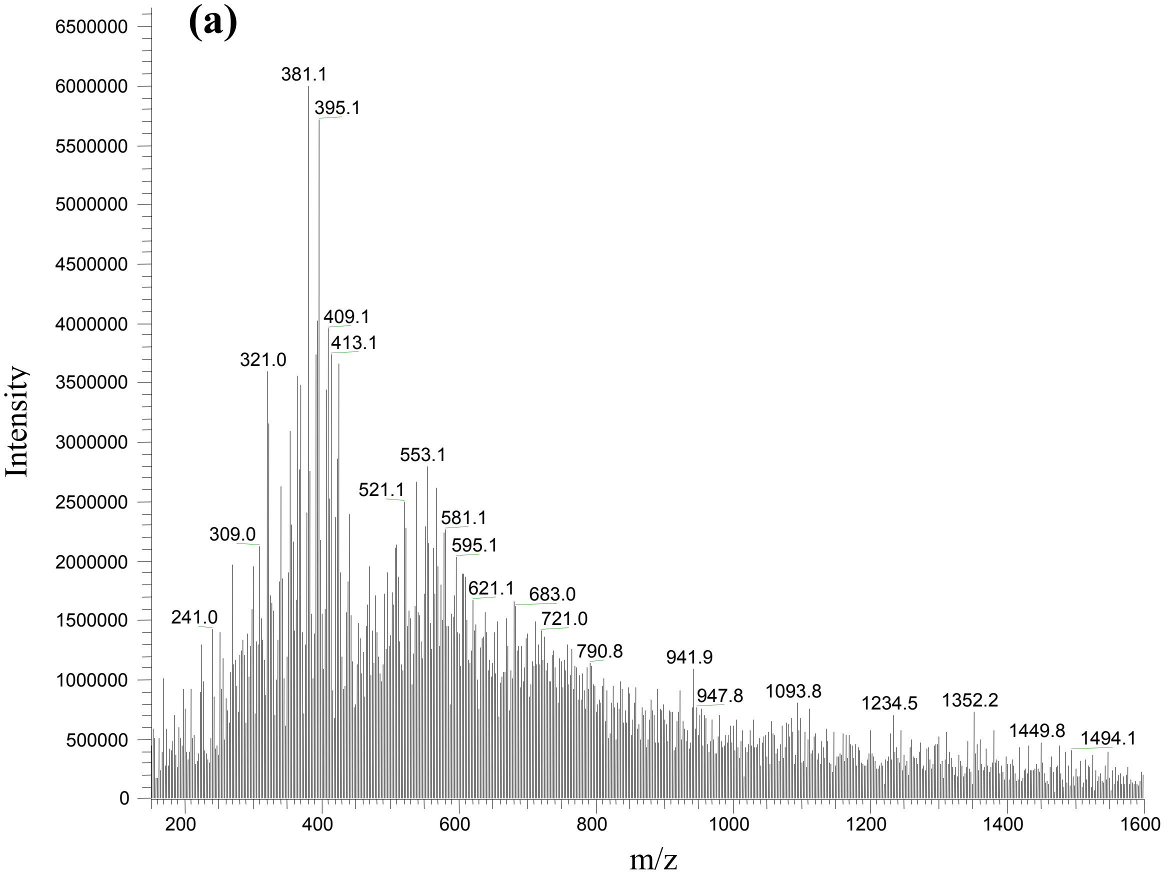


Figure 8.8. (a) Ion trap mass spectrum (+ ion mode) of the SOA from the ozonolysis of 120 ppb α-pinene on $MgSO_4$-only seed; (b) Ion trap mass spectrum (+ ion mode) of the SOA from the ozonolysis of 120 ppb α-pinene on $MgSO_4$-H_2SO_4 seed. The background ion intensities are almost always lower than 400000 in both (a) and (b).



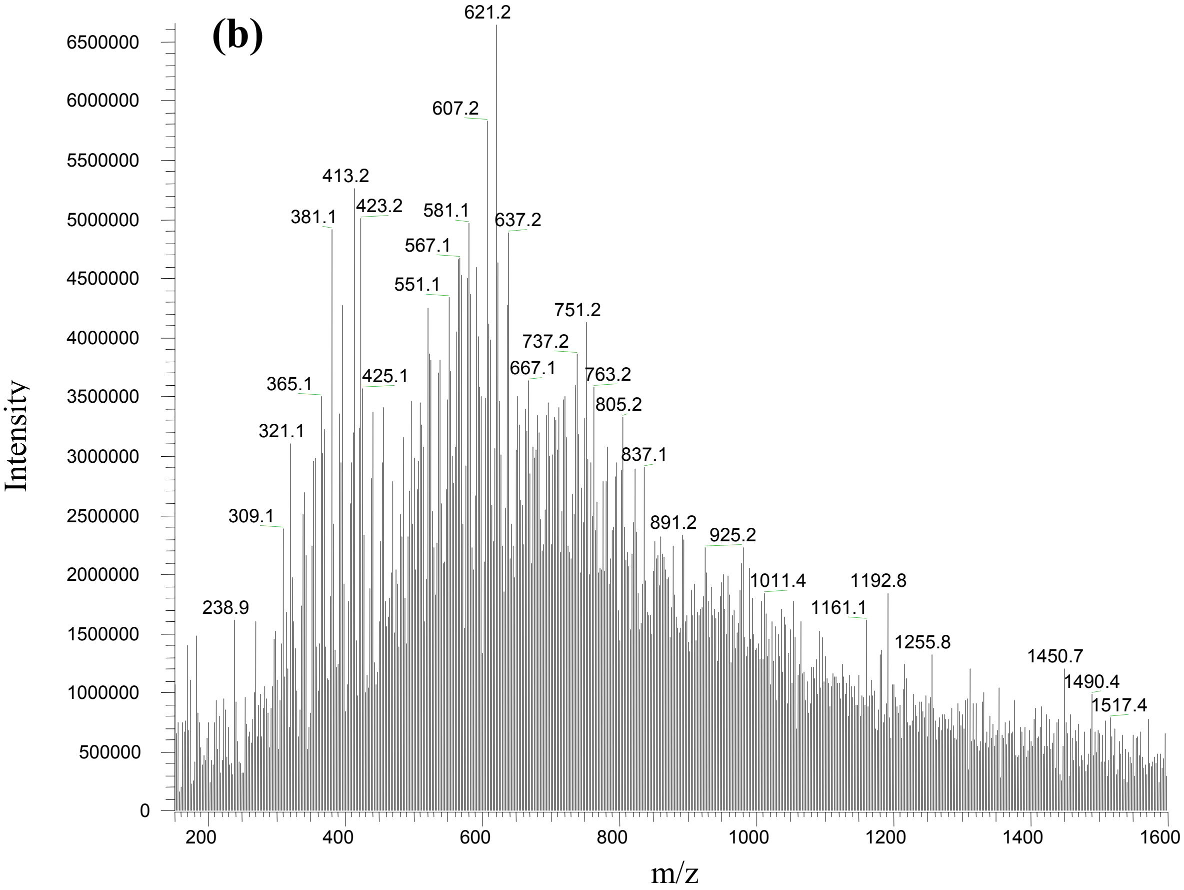

(b)
621.2
607.2
413.2
423.2
381.1
581.1
637.2
567.1
551.1
751.2
737.2
365.1
425.1
667.1
763.2
805.2
321.1
837.1
309.1
891.2
925.2
1011.4
1192.8
238.9
1161.1
1255.8
1450.7
1490.4
1517.4
Intensity
0
500000
1000000
1500000
2000000
2500000
3000000
3500000
4000000
4500000
5000000
5500000
6000000
6500000
200
400
600
800
1000
1200
1400
1600
m/z

Figure 8.9. The absolute yields of SOA formed on nonacid (dotted bars) and acid (lined bars) $MgSO_4$ seed particles at seven initial α-pinene mixing ratios. The relative yield difference (after normalization to the SOA yield in the nonacid case) increases linearly with decreasing mixing ratio of initial α-pinene, possibly due to the relatively increasing amount of H_2SO_4 in the particles. This implies in the atmosphere where α-pinene and other hydrocarbons are usually present at mixing ratios no higher than the lower-end values in this Figure, the effect of particle acidity on SOA yield can be quite substantial. In addition, at 52 ppb and 96 ppb, the absolute yields of SOA in the absence of any seed particles are 0.43 and 0.51, respectively, as roughly shown by the two dashed, horizontal lines. The error bars of the two no-seed SOA yields are similar to those of the with-seed SOA yields at corresponding mixing ratios.

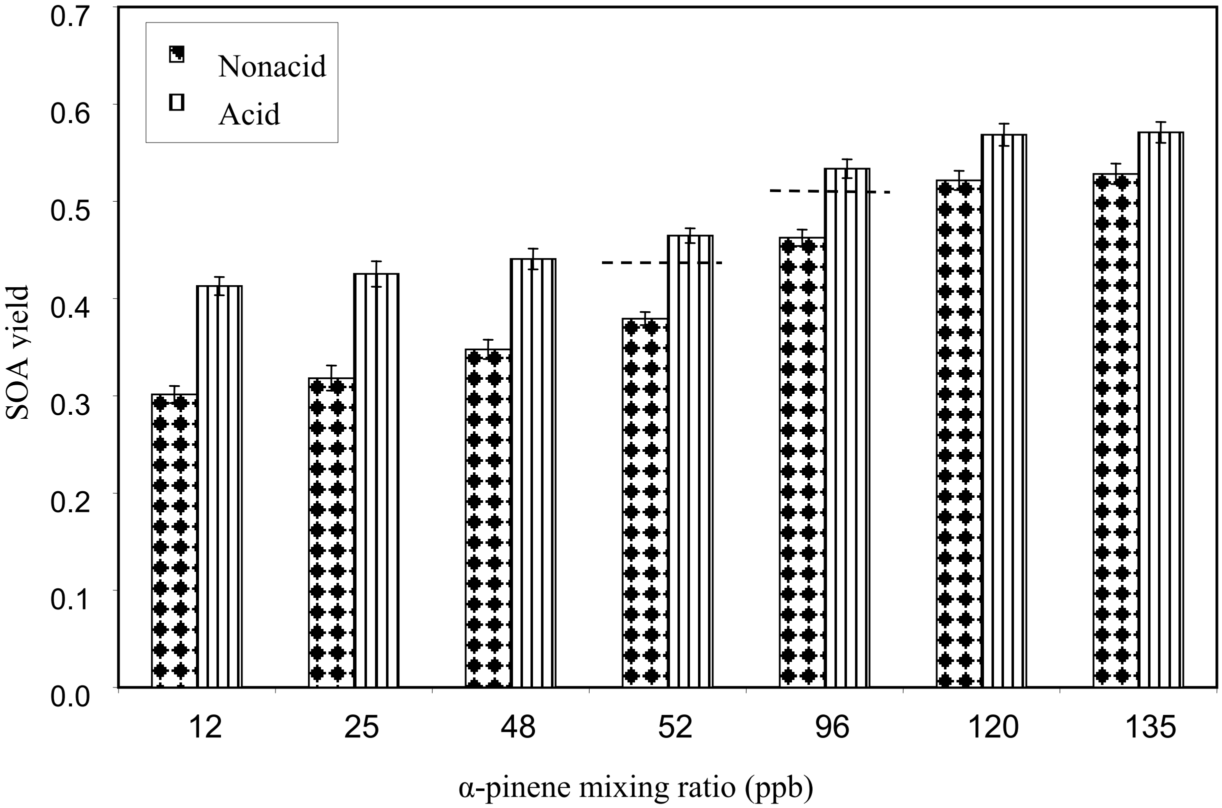

0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
SOA yield
Nonacid
Acid
12
25
48
52
96
120
135
α-pinene mixing ratio (ppb)

Figure 8.10. The extracted ion chromatograms of 289 ion in SOA from the ozonolysis of 1-methyl cyclohexene, cycloheptene, and 3-methyl cyclohexene