Chapter 9

Particle Phase Acidity and Oligomer Formation in Secondary Organic Aerosol[*]

9.1. Abstract

A series of controlled laboratory experiments are carried out in dual teflon chambers to examine the presence of oligomers in secondary organic aerosols (SOA) from hydrocarbon ozonolysis as well as to explore the effect of particle phase acidity on SOA formation. In all seven hydrocarbon systems studied, i.e., α-pinene, cyclohexene, 1-methyl cyclopentene, cycloheptene, 1-methyl cyclohexene, cyclooctene, and terpinolene, oligomers with MW from 250 to 1600 are present in the SOA formed, both in the absence and presence of seed particles and regardless of the seed particle acidity. These oligomers are comparable to, and in some cases, exceed the low-MW species (MW < 250) in ion intensities in the ion trap mass spectra, suggesting they may comprise a substantial fraction of the total aerosol mass. It is possible that oligomers are widely present in atmospheric organic aerosols, formed through acid- or base-catalyzed heterogeneous reactions. In addition, as the seed particle acidity increases, larger oligomers are formed more abundantly in the SOA; consequently, the overall SOA yield also increases. This explicit effect of particle phase acidity on the composition and yield of SOA may have important climatic consequences and need to be considered in relevant models.

9.2. Introduction

Organic compounds are a major component of atmospheric aerosols and are important contributors to the climate forcing and human health effects of airborne particles (*1*). A significant fraction of atmospheric organic aerosols are formed through in-situ oxidation of precursor hydrocarbons in the gas phase followed by partitioning of low-volatility products into the aerosol phase (*2*). These are referred to as secondary organic aerosols (SOA). Recently, higher-molecular-weight species beyond the first-generation oxidation products have been identified in SOA (*3-6*). An increase in the yield of SOA formed on acidic seed

particles has also been reported (*3, 7, 8*). In the previous conceptual model for atmospheric formation of SOA (*2*), once the oxidation products are in the aerosol phase, no further chemical reaction is assumed to occur. However, with aerosol-phase reactions occurring as suggested by recent studies, the overall yield of aerosol from precursor oxidation would increase beyond that resulting from pure equilibrium partitioning. The consequence is that the amount of SOA in the atmosphere may substantially exceed that predicted by current models used in global climate assessments (*9*).

Several fundamental questions arise. What is the increase in SOA yield in the presence of an acidic substrate for precursor hydrocarbons at or near ambient mixing ratios? Is an acidic substrate required for oligomer formation? What is the chemical nature of these oligomers and what reactions produce them? Is oligomer formation the primary cause for the increased yield of SOA formed on more acidic particles? Is there a quantitative relationship among particle phase acidity, oligomer formation and SOA yield? And finally, is oligomer formation in SOA a ubiquitous phenomenon?

Recent work has addressed some of these questions. Kalberer et al. (*5*) focused on the photolysis of 1,3,5-trimethylbenzene in the absence of seed particles while Tolocka et al. (*6*) concentrated on the ozonolysis of α-pinene in the presence of acidic inorganic seed particles. Uncertainties still exist when results from different work are compared, such as whether a pre-existing, acidic substrate is necessary for oligomer formation. To fully assess the roles of oligomers in SOA formation as well as in the broader atmospheric chemistry, a wide variety of SOA-forming systems need to be studied. This work addresses the above questions through an extensive series of dual-chamber laboratory experiments. We consider the ozonolysis of α-pinene (mixing ratio from 12 to 135 ppb), one of the most

common biogenic hydrocarbons, and of six cycloalkenes, i.e., cyclohexene, 1-methyl cyclopentene, cycloheptene, 1-methyl cyclohexene, cyclooctene, and terpinolene (mixing ratio from 25 to 300 ppb), serving as model compounds for many atmospheric hydrocarbons bearing similar molecular skeletons, in the absence or presence of seed particles of controlled acidity. We demonstrate and explain the explicit effect of particle-phase acidity on the amounts and composition of SOA formed. Moreover, we find that oligomers are present in each system studied regardless of the initial particle acidity, and speculate that oligomer formation is a ubiquitous phenomenon in ambient aerosols. These results have important implications for predicting the amounts and composition of SOA in the atmosphere.

9.3. Experimental

All experiments were carried out under dark conditions in Caltech's dual 28 m^3 teflon chambers. In most experiments, seed solutions were first nebulized into the clean chamber to form seed particles (wet seeds for most α-pinene experiments and dry seeds for cycloalkene experiments). To examine the effect of seed particle acidity on SOA formation, we used two "nonacid" seeds, containing either $MgSO_4$ or $(NH_4)_2SO_4$, and two "acid" seeds, containing either $[MgSO_4+H_2SO_4]$ or $[(NH_4)_2SO_4+H_2SO_4]$. The salt-only solutions were 0.03M each, and acidified solutions contained 0.03M salt and 0.05M H_2SO_4. Cyclohexane was then injected to act as a hydroxyl radical scavenger, followed by hydrocarbon and ozone injection. Relative humidity and temperature were controlled (e.g., at 55% and 20 ºC for the α-pinene ozonolysis experiments). Aerosol number concentration, size distribution, hygroscopic growth, and hydrocarbon mixing ratio were continuously measured. Aerosol loss to the chamber wall was accounted for in data analysis.

In each pair of "nonacid" and "acid" experiments, filter samples (47mm teflo membrane filters) were collected at nearly the same elapsed time (5~7 h) from the onset of reaction for nearly the same duration (1~2 h). Each filter was extracted in HPLC-grade methanol by sonication. The extract was then blown dry under a gentle N_2 stream and reconstituted by an acetic acid solution/methanol mixed solvent. A portion of the filter extract was analyzed by a Hewlett-Packard 1100 series Liquid Chromatography – Mass Spectrometry (LC-MS) system to identify and quantify low-molecular-weight species (MW < 250 Da). Another portion of the filter extract was analyzed by an LCQ classic ion trap mass spectrometer (IT-MS) to identify SOA components with molecular weights ranging from 80 to 1600 Da. Both negative and positive (Na^+ added) ion modes of the IT-MS detection were carried out, so that compounds of different acidity and polarity could be detected. In addition, some specific ions were isolated and further fragmented by collision-induced dissociation to produce so-called tandem MS. Most of the MS/MS in this work were produced under the negative ion mode, since the isolated ions had less interference and the backgrounds were cleaner than the positive ion mode.

We carried out each pair of "nonacid" and "acid" experiments in the two chambers in parallel, with all other conditions held identical. Thermodynamic calculations (10) show that the four seed particles, once stabilized in the chamber, had distinct pH values. For example, at the RH = 55% for α-pinene ozonolysis experiments, the pH values for [$MgSO_4$-only] seed and [$MgSO_4+H_2SO_4$] seed were 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 were 4.6 and 2.4, respectively. The acidity increase from the "nonacid" to the "acid" seed in the $MgSO_4$ case exceeded that of the $(NH_4)_2SO_4$ case by 4.6 pH units.

9.4. Results and Discussion

Figure 9.1 shows the relative yield difference (RYD) of SOA between the acid and nonacid cases for seven pairs of α-pinene ozonolysis experiments on $MgSO_4$ particles, two pairs on $(NH_4)_2SO_4$ particles, as well as two pairs of terpinolene ozonolysis experiments on $MgSO_4$ particles. Within the range of α-pinene mixing ratios studied, the SOA yield increases by about 10 ~ 40% on the acidic $MgSO_4$ seed over the $MgSO_4$-only seed. The linear decrease in the RYD with increasing initial α-pinene may be related to the decreasing amount of H_2SO_4 in the particles. Initial SOA growth rates for the acid and nonacid cases at two α-pinene mixing ratios are shown by the two insets in Figure 9.1. By comparison, the SOA yield only increases by about 5% on acidic $(NH_4)_2SO_4$ particles over pure $(NH_4)_2SO_4$ particles. This is likely due to the markedly smaller acidity difference between the nonacid and acid particles of $(NH_4)_2SO_4$, as compared with $MgSO_4$.

The SOA composition difference between nonacid and acid cases is consistent with the overall yield difference. Our LC-MS analyses have identified a number of low-molecular-weight (low-MW) species (MW < 250), containing carbonyl, hydroxyl, and carboxyl groups, in the SOA from the ozonolysis of cycloalkenes and α-pinene, consistent with other studies (*11 – 14*). In the $C_5 – C_8$ cycloalkene-ozone systems, diacids, carbonyl acids, hydroxylated diacids, and diacid alkyl esters are consistently the most abundant low-MW SOA components. In the α-pinene-ozone system, regardless of the seed, cis-pinic acid, norpinic acid and hydroxy pinonic acid, detected with m/z of 185, 171 and 199 (in the negative ion mode), respectively, are the most abundant low-MW SOA components (all may have isomers present; see Supporting Information, Figure 9.S1). These three acidic species are also consistently detected by the ion trap mass spectrometry (IT-MS) in the

negative ion mode (see Supporting Information, Figure 9.S2). However, negative ions with

m/z of 329, 343, 357, 371 and 385 are also detected by the IT-MS (see Supporting

Information, Figure 9.S2). The presence of these high-MW species is confirmed by the

detection of ions with m/z of 353, 367, 381, 395 and 409 in the positive ion mode IT-MS,

as shown in Figure 9.2(a). These ions are pseudomolecular ions $[M+23]^+$, formed by the

addition of a Na^+ to the neutral molecules. A broad range of compounds can be detected as

their Na^+ adducts in the positive ion mode IT-MS, thus better reflecting the overall

composition of SOA. Figure 9.2(a) illustrates that in the SOA formed on the nearly neutral

$MgSO_4$ seed, small oligomers (MW from 250 to 450) are the most abundant species. These

species are separated regularly by mass units such as 14, 16, 18 and 30, which is

characteristic of a co-polymer system (*15*), indicating the difference of CH_2, O, H_2O

groups, or a combination of them, among monomers and oligomers. It is striking that the

low-MW species (MW < 250) comprise only a minor fraction of the total ion signals in the

mass spectrum. In previous studies, high-MW species may have decomposed during

sample preparation or instrumental analyses (such as in a GC oven) (*16*), resulting in a

possible overestimation of low-MW species. The ion trap MS employs an electrospray

ionization source that better preserves molecular integrity by soft ionization (*17*).

When the seed becomes much more acidic ($MgSO_4$-H_2SO_4), as shown in Figure 9.2(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 2 those in the SOA formed on $MgSO_4$-only seed. Some even larger

oligomers (MW from 950 to 1600) are now 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 remains roughly in the same pattern, with a slight decrease in some ion intensities. A similar difference in SOA composition between nonacid and acid $MgSO_4$ seeds is consistently observed in all other six pairs of experiments on the α-pinene system (see Supporting Information, Figure 9.S4, for the MS of another pair) . Our hygroscopicity measurements (*18*) show that these SOA contained approximately 10 – 20 % water at the time of filter collection; thus, the increased types and amounts of oligomers formed on the more acidic seed are the primary cause for the increased SOA yield (see Figure 9.1).

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. As shown in Figures 9.2(c) and 2(d), there is only a modest increase in the types and amounts of small oligomers in the SOA formed on the more acidic seed, and there is essentially no change in the mass distribution of the large oligomers. This is consistent with the very small yield increase observed. The composition and yield differences between the two sets of nonacid vs. acid seeds clearly demonstrate that seed acidity has a direct impact on the composition and amounts of SOA formed.

That the higher-MW species (MW > 250) shown in Figure 9.2 are indeed oligomers is confirmed from the tandem MS of these ions. For example, Figure 9.3 shows the MS/MS (negative ion mode) of 357 and 245 ions in SOA from the ozonolysis of α-pinene and 1-methyl cyclopentene, respectively. The molecular structures shown alongside the MS/MS explain all major and some minor fragments. Their corresponding monomers are norpinonic acid, C_5, C_6 carbonyl acids and C_5 diacid-- all first-generation oxidation products. There are at least three possible structures for the 245 ion, illustrating the complexity of the oligomeric system in the SOA. Similar to the 357 ion, other higher-MW

species in the SOA from α-pinene ozonolysis, such as the 329, 343, 371 and 385 ions, correspond to the possible combination of first-generation ozonolysis products (see Supporting Information, Figure 9.S2, for detail). 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 (*13*), the small oligomers (MW from 250 to 450) are probably dimers, whereas larger oligomers (MW from 450 to 950) are likely trimers, tetramers, and pentamers, consistent with the discussion in Tolocka et al. (*6*). Based on the structures of oligomers and corresponding monomers, we propose three possible reaction pathways in the aerosol phase: aldol reaction between carbonyls, gem-diol reaction between carbonyls with the participation of a water molecule, and acid dehydration with the loss of a water molecule. The first two reactions have been discussed in some recent works (*3, 5, 6, 7, 8*). All three reactions require acid or base catalysis. Detailed reaction mechanisms are well established in organic chemistry literature. 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.

The SOA composition difference between nonacid and acid cases actually reflects the kinetics of these acid-catalyzed reactions. As seed acidity increases, oligomer formation accelerates, 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, as shown in Figures 9.2(a) and 9.2(b), may actually reflect their transformation into larger oligomers, at roughly 5 h from the onset of ozonolysis. In similar experiments on dry $(NH_4)_2SO_4$ seed, abundant small and large oligomers are detected in SOA from α-pinene

ozonolysis, even without H_2SO_4 in the seed, as shown in Figure 9.4. Apparently, the higher acidity of the dry seed, as compared with the wet seed, facilitates faster formation of large oligomers.

Despite the sensitivity of SOA formation to the particle phase acidity, we find that oligomers (MW from 250 up to 1600) are present in SOA in all of the systems studied, regardless of seed pH. As an example of the cycloalkene ozonolysis system, Figure 9.S6 (Supporting Information) shows the presence of oligomers with MW up to 700 (i.e., structurally up to possibly pentamers) in the SOA from cycloheptene ozonolysis. Of particular importance, in the α-pinene ozonolysis system where a variety of seed particles are examined, similar types of oligomers are present in SOA, both in the presence and absence of seed particles (see Figure 9.5 for the latter case). This suggests that organic acids produced from the gas-phase hydrocarbon oxidation itself may actually provide necessary acidity for catalytic reactions. No pre-existing, acidic substrate is required for oligomer formation, consistent with the finding by Kalberer et al. (5). Since ambient aerosols tend to be somewhat acidic, we speculate that oligomers are widely present in atmospheric organic aerosols, and they may comprise a substantial fraction of the total aerosol mass. Since the proposed heterogeneous reactions take place readily under base catalysis as well, the ubiquity of oligomers in ambient aerosols appears all the more likely.

9.5. Acknowledgements

9.6. References

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Figure 9.1. The relative yield difference (RYD) of SOA between the acid and nonacid cases

for seven pairs of α-pinene ozonolysis experiments on $MgSO_4$ seeds, two pairs on

$(NH_4)_2SO_4$ seeds, as well as two pairs of terpinolene ozonolysis experiments on $MgSO_4$

seeds. The absolute SOA yield is defined as the mass of SOA produced relative to the mass

of hydrocarbon consumed. The RYD is defined as the difference in the absolute SOA yield

between the acid and nonacid cases normalized to the nonacid-case yield. Corresponding

to the seven α-pinene mixing ratios shown (i.e., 12ppb, 25ppb, 48ppb, 52ppb, 96ppb,

120ppb and 135ppb), the absolute SOA yields are 0.30, 0.32, 0.35, 0.38, 0.46, 0.52 and

0.53, respectively, for the nonacid cases, and are 0.41, 0.43, 0.44, 0.47, 0.53, 0.57, 0.57,

respectively, for the acid cases.
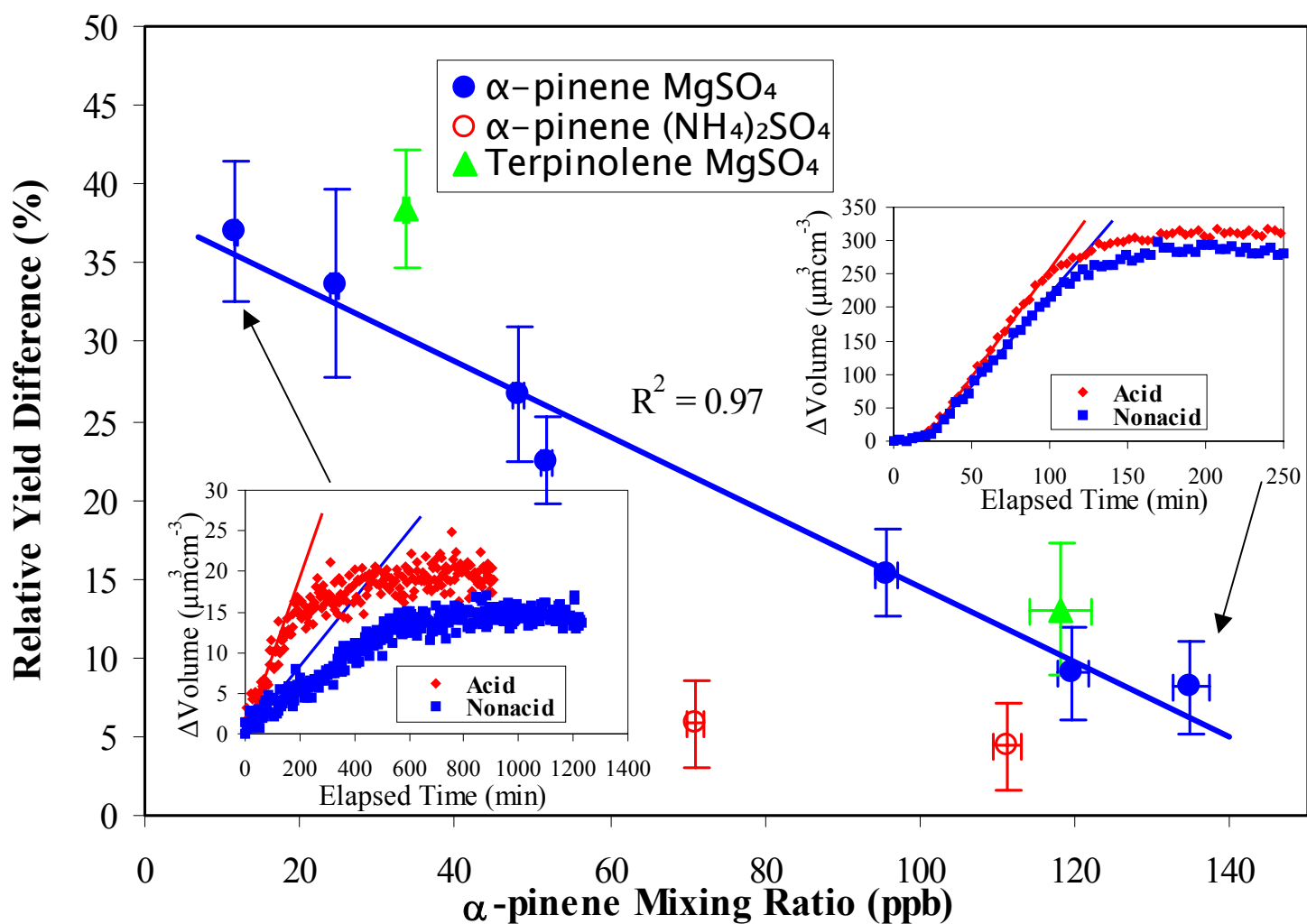
Figure 9.2. Ion trap mass spectrum (+ ion mode) of the extract of SOA from the ozonolysis of (a) 120 ppb α-pinene on MgSO$_4$-only seed (RH = 55%). In the m/z range up to 1600, the average background ion intensity is ~ 400000, which is labeled as the dashed line in this and the following MS, unless noted otherwise. See Supporting Information, Figure 9.S3, for a typical background MS. (b) 120 ppb α-pinene on MgSO$_4$-H$_2$SO$_4$ seed. Other experimental conditions are identical to (a). (c) 72 ppb α-pinene on (NH$_4$)$_2$SO$_4$-only seed. Other experimental conditions are identical to (a). (d) 72 ppb α-pinene on (NH$_4$)$_2$SO$_4$-H$_2$SO$_4$ seed. Other experimental conditions are identical to (a).
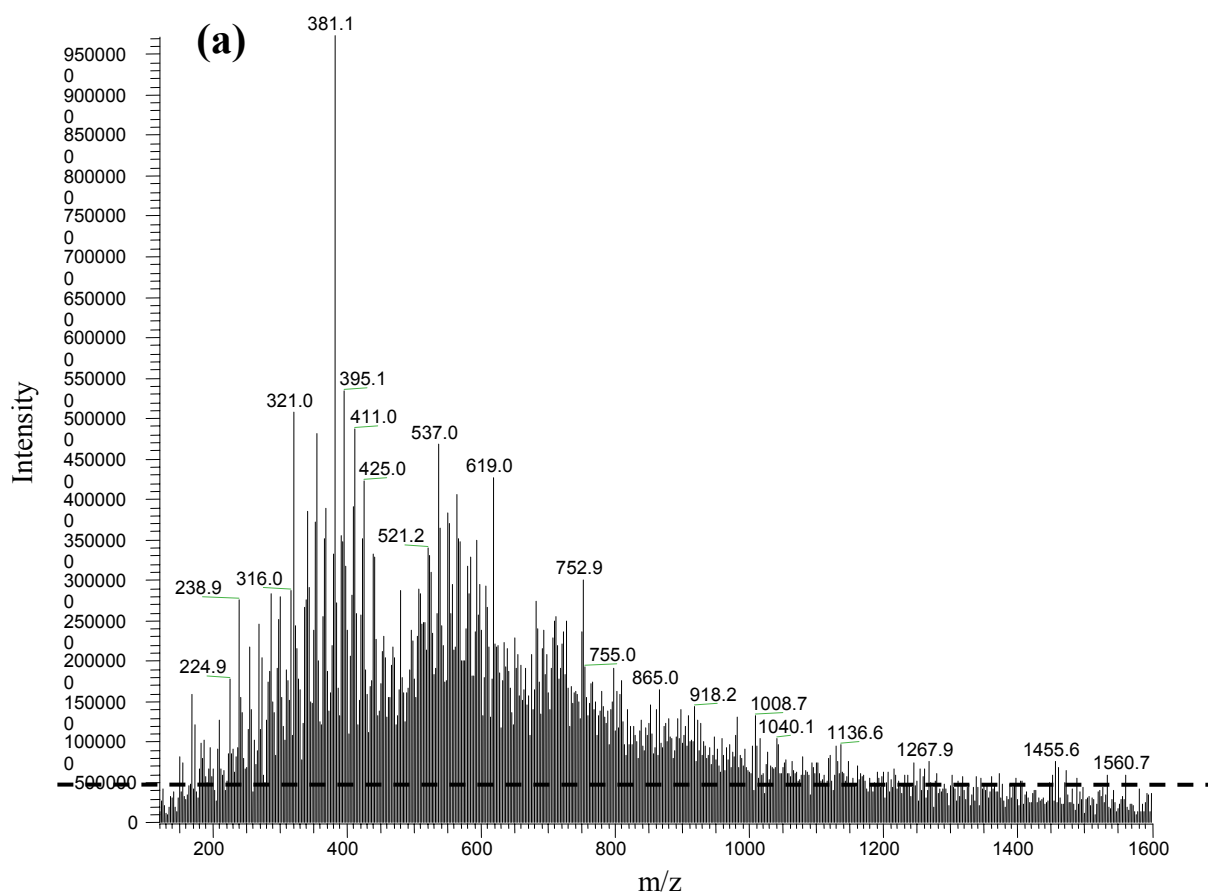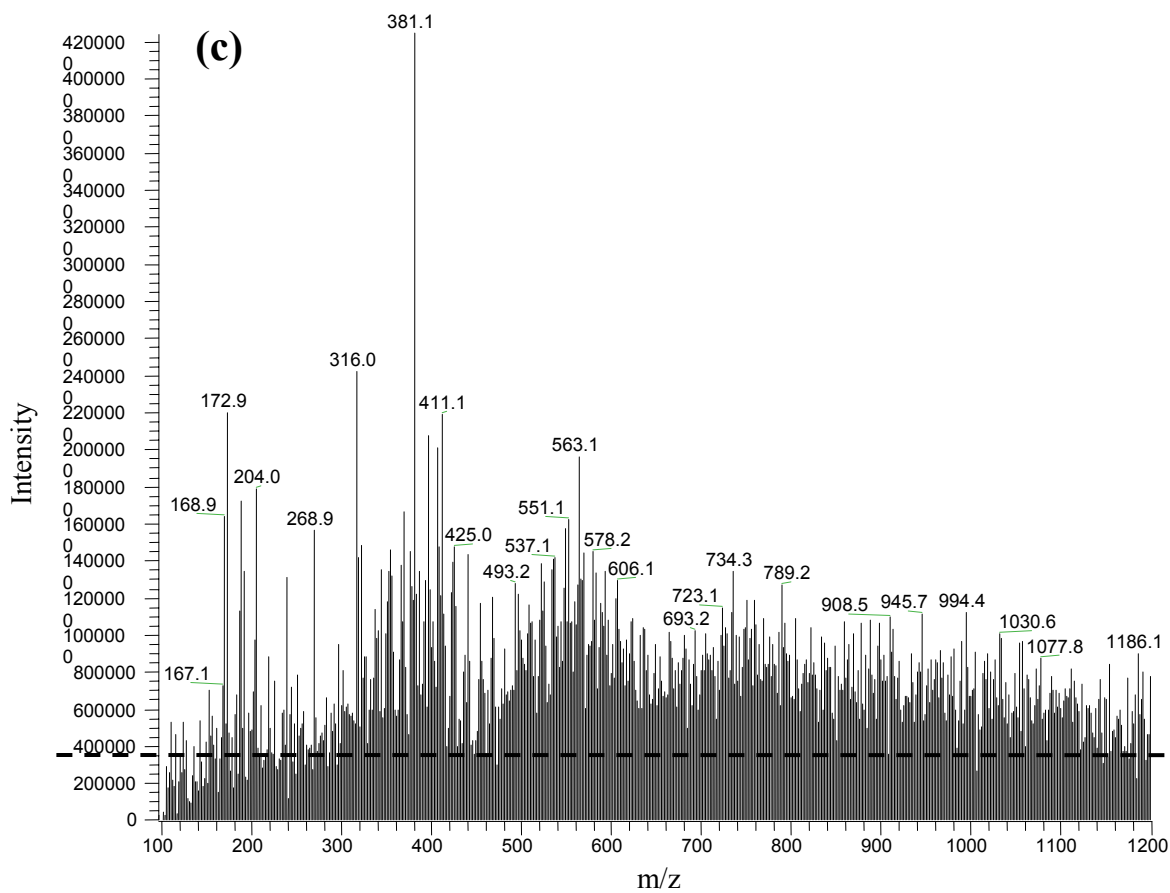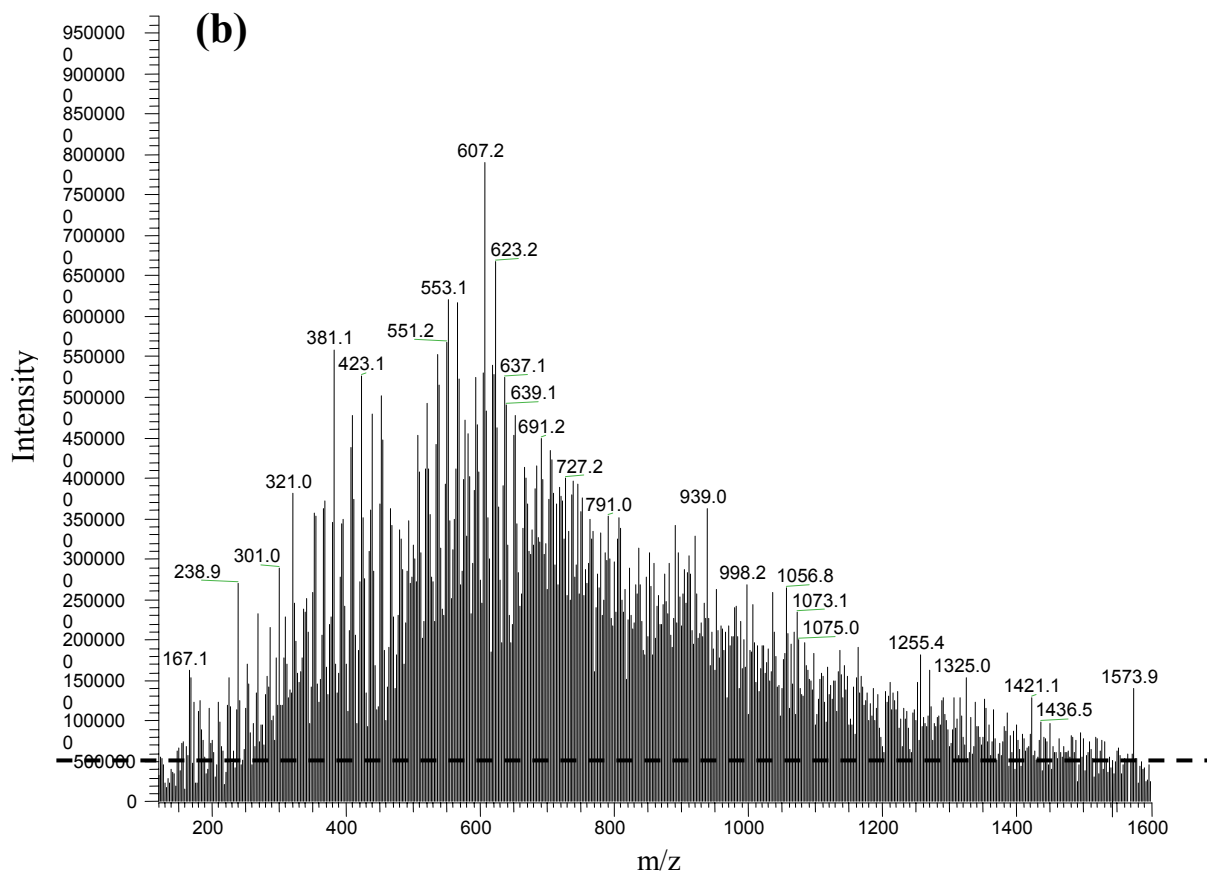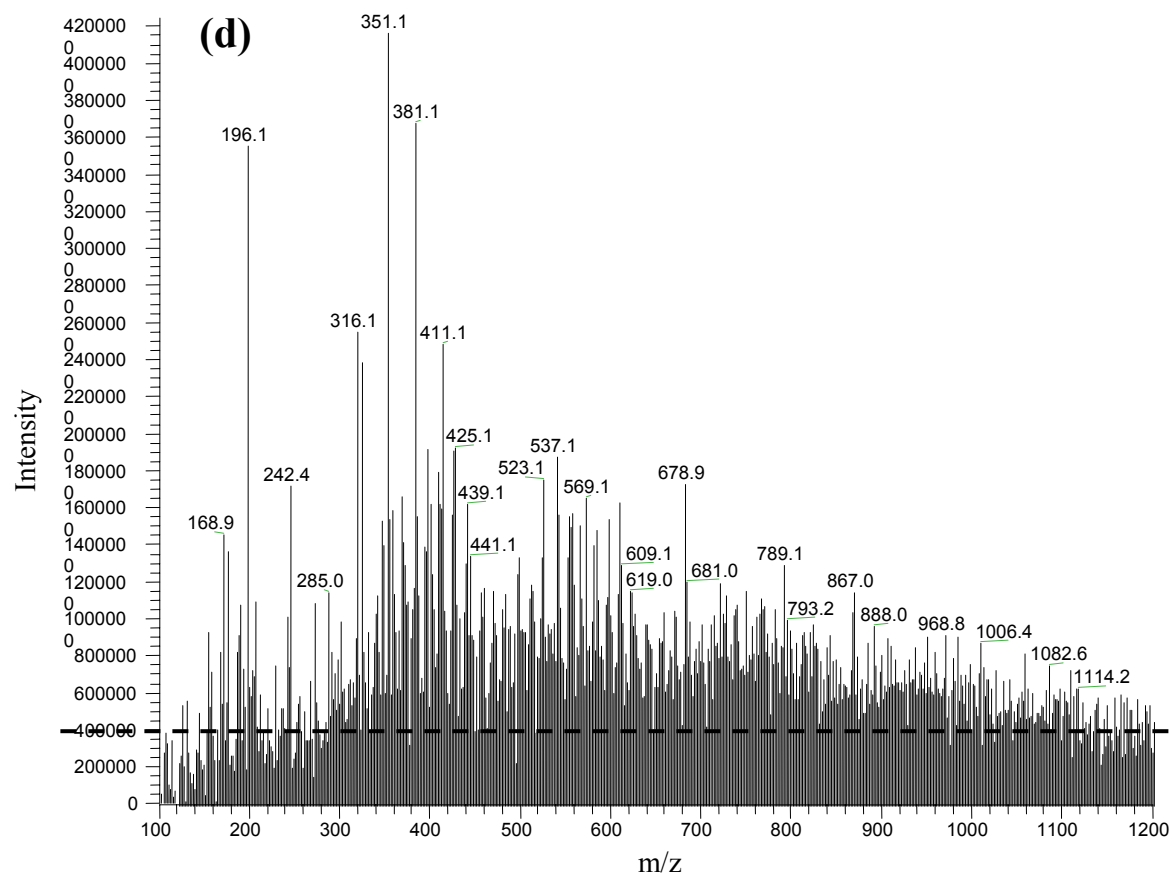
Figure 9.3. MS/MS (- ion mode) of (a) 357 ion in the SOA from the same α-pinene ozonolysis experiment as in Figure 9.2(a), its likely structure and fragmentation (hydrogen rearrangement and dehydrogenation not shown), and the structure of the monomer. See Supporting Information, Figure C.5 for the detailed structures of fragment ions. (b) 245 ion in the SOA from 1-methyl cyclopentene ozonolysis, its likely structures and fragmentation, and the structures of the monomers.
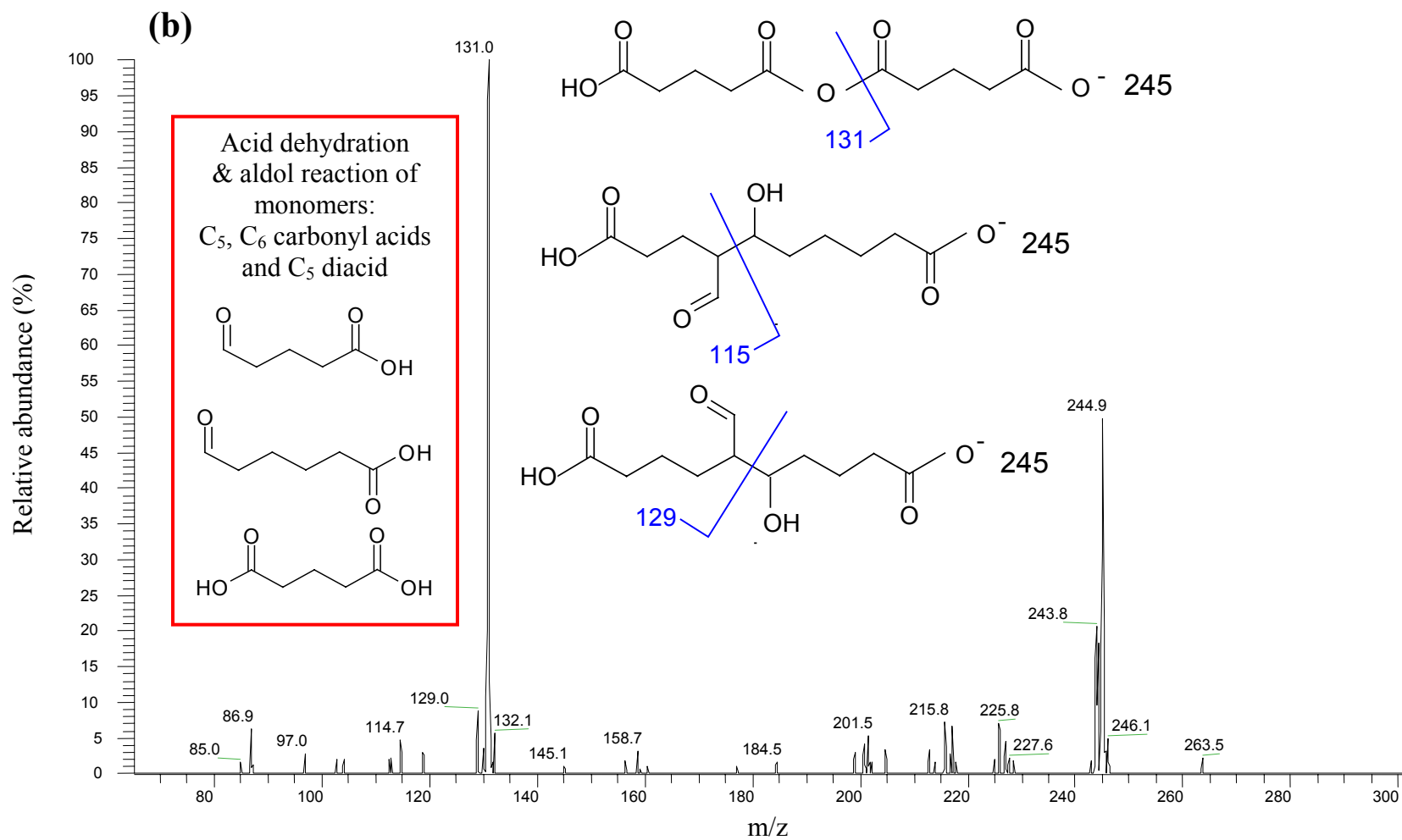
(b)

Acid dehydration & aldol reaction of monomers: C_5, C_6 carbonyl acids and C_5 diacid
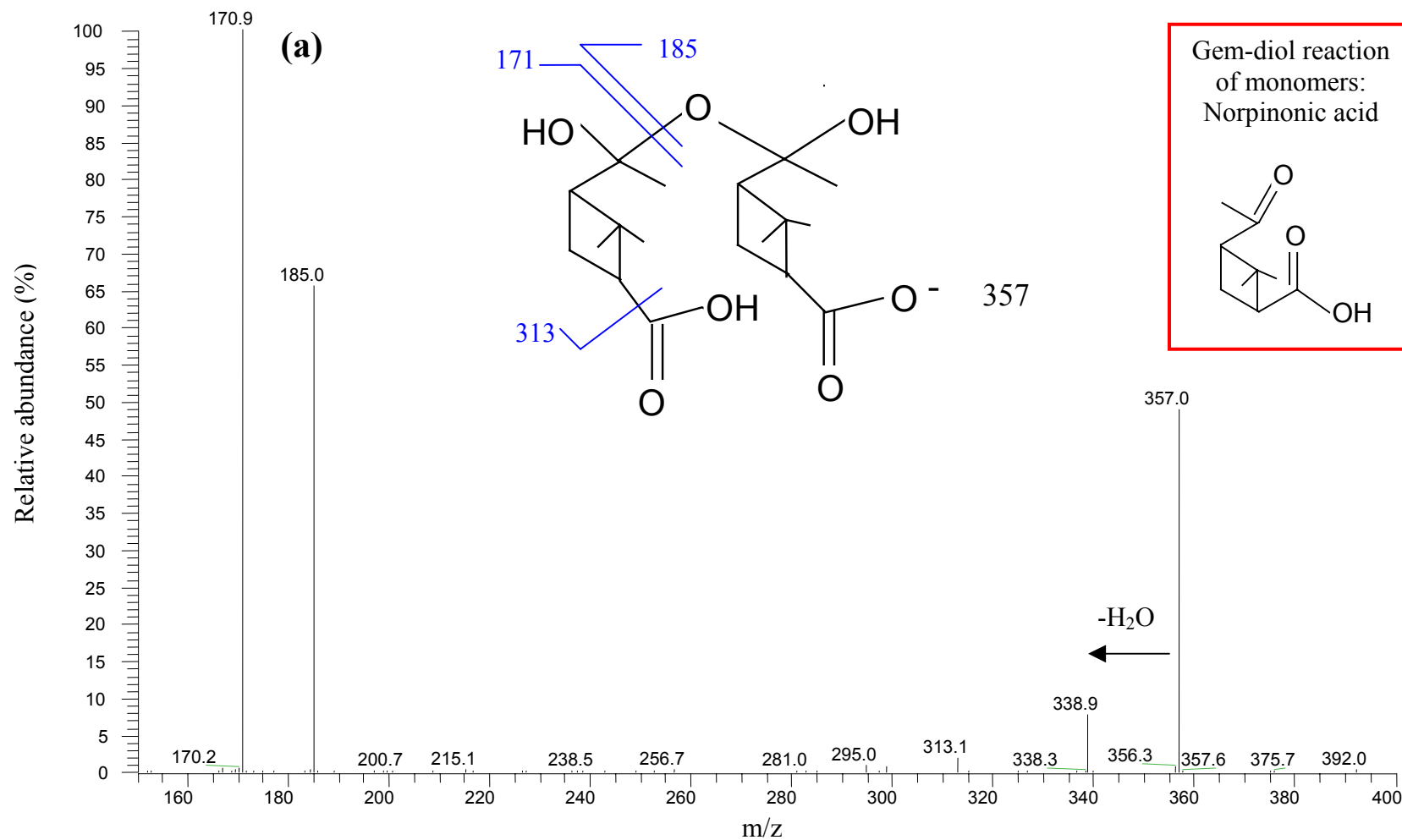
Figure 9.4. Ion trap mass spectrum (+ ion mode) of the extract of SOA from the ozonolysis of 180ppb α-pinene in the presence of dry $(NH_4)_2SO_4$-only seed. Large amounts of both small and large oligomers are present in this SOA.
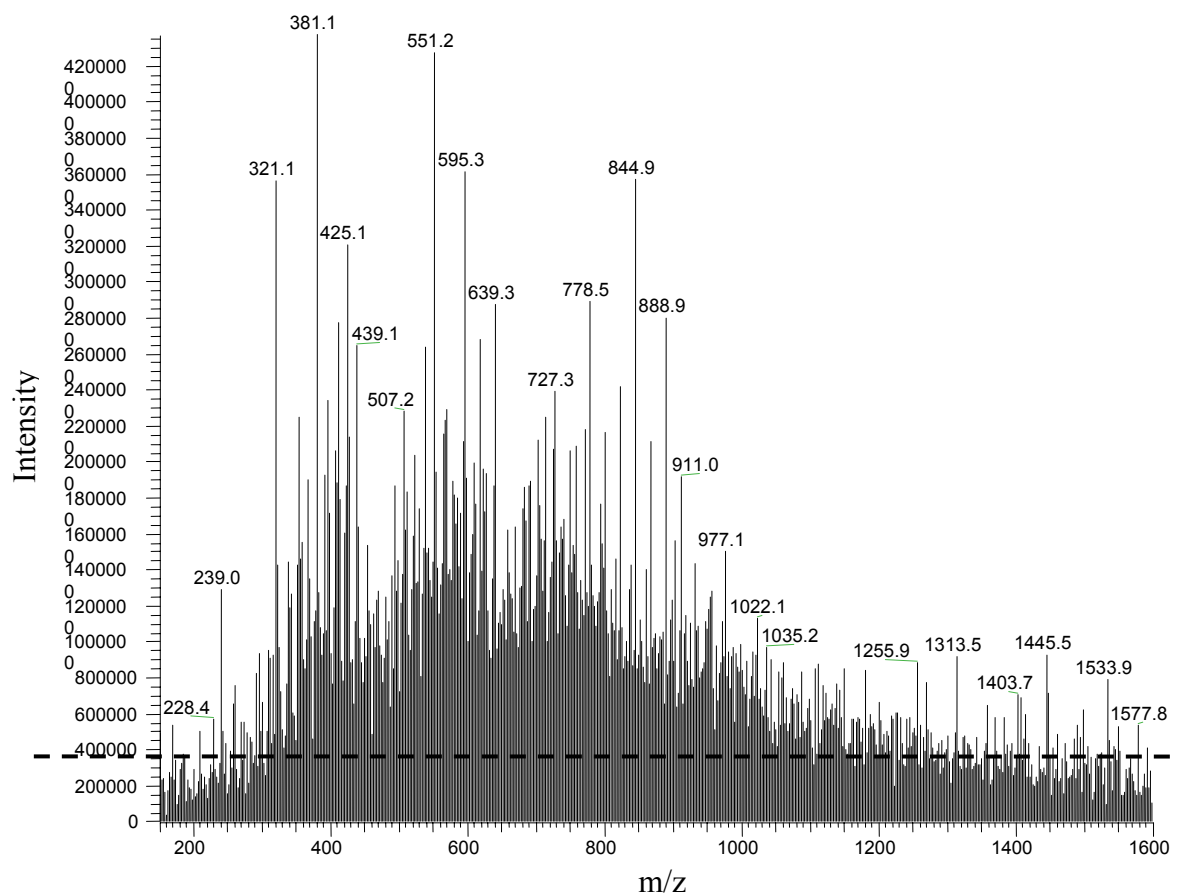
Figure 9.5. Ion trap mass spectrum (+ ion mode) of the extract of SOA from the ozonolysis of 50ppb α-pinene in the absence of seed particles. This IT-MS is similar to that of the SOA from its parallel ozonolysis experiment in the presence of $MgSO_4$ seed particles, and is also similar to that of the SOA from other α-pinene ozonolysis experiments, such as the one shown in Figure 9.2(a). The background ion intensities are lower than 5% of the maximum intensity (m/z = 381.0, designated as 100%).