

## **Supporting Information: Photochemical Aging of Secondary Organic Aerosol Particles Generated from the Oxidation of d-Limonene**

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Figure 1 presents a sample negative ion mode ESI (electrospray ionization) mass spectrum of limonene-derived SOA extracts. The spectrum was obtained by collecting SOA on filters as described in the text, extracting the filter content with dichloromethane, diluting in methanol, and injecting the resulting extract into a commercial ESI-MS instrument without prior chromatographic separation. In the negative ion mode, the largest peaks are expected to come from carboxylic acids appearing at  $m/z = m/z_{\text{parent}} - 1$  and resulting from the following ionization pathway:



Complexes between the primary acid and other acids,  $\text{R}'\text{-C(O)OH} \cdots \text{R-C(O)O}^-$ , are also possible but their occurrence was deliberately minimized by appropriately diluting the sample.

Peaks at 157.1 and 239.0 Da (Dalton = atomic mass unit) are from impurities in the solvent. Starting from about 200 Da, the density of major peaks reaches approximately  $1 \text{ Da}^{-1}$  at the resolving power of 8000. There are clear patterns observed in the mass spectrum: (1) groups of peaks separated by  $\sim 200 \text{ Da}$  probably correspond to various oligomerization products produced in ozonolysis: “monomer”, “dimer”, “trimer”, “tetramer”, etc. (2) Groups of peaks separated by 14-16 amu correspond to molecules differing by  $\text{CH}_2$  group or by one oxygen atom. (3) The spectrum is dominated by odd masses separated by 2 Da; even masses are considerably smaller in intensity. Assuming that the reaction (1) is the dominant ionization mechanism, this shows that the majority of products of ozonolysis of limonene have even masses.

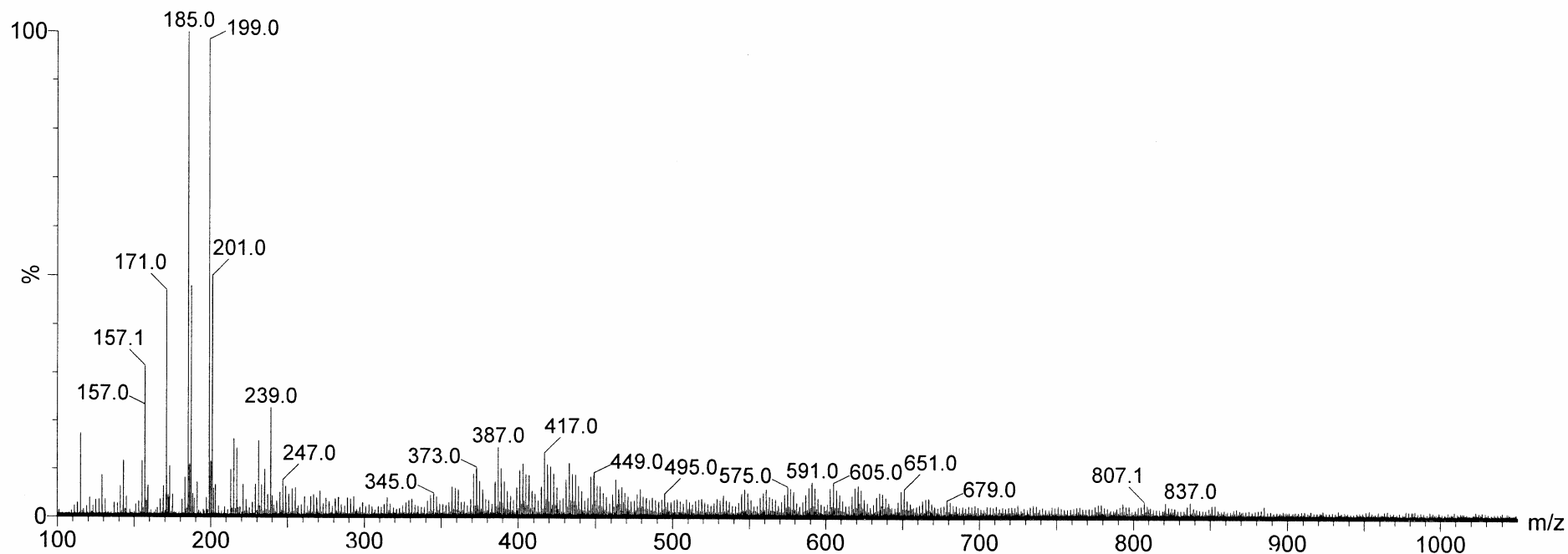
The strongest peaks have been examined at higher mass accuracy (20 ppm) allowing for an unambiguous determination of composition. The exact assignment is still ambiguous as there are many structural isomers amongst products of the gas-phase ozonolysis of limonene. The most likely assignments are given in Figures 2-5. They are consistent with assignments proposed in the literature.\*

The rest of the peaks in the mass spectrum are unassigned. We are currently working on a more complete assignment of this mass-spectrum using MS/MS and high-resolution MS techniques with a particular emphasis of identifying photochemically active peroxidic compounds amongst the ozonolysis products. This analysis will be reported elsewhere.

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\* (1) Warscheid, B.; Hoffmann, T. *Rap. Comm. Mass. Spectr.* **2001**, *15*, 2259. (2) Leungsakul, S.; Jaoui, M.; Kamens, R. M. *Envir. Sci. Technol.* **2005**, *39*, 9583.

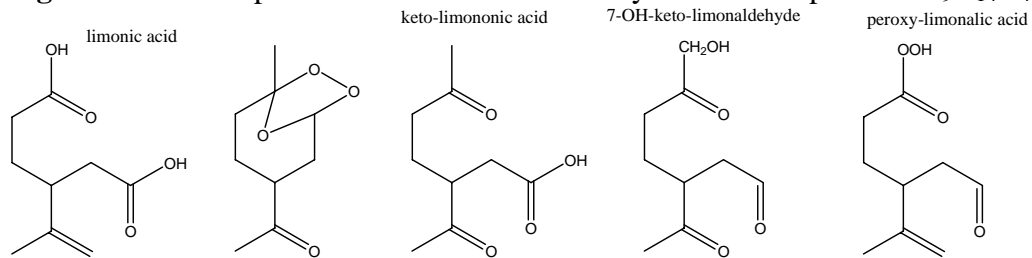
**Figure 1:** Sample negative ion ESI-MS spectrum of Limonene SOA components.



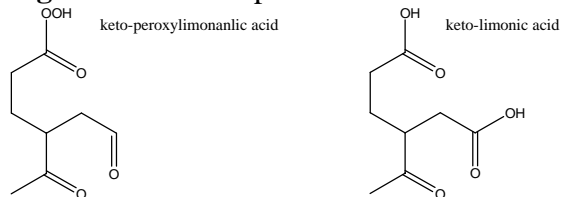
**Table 1:** Masses of the strongest peaks determined by high-resolution mass spectrometry with 20 ppm mass tolerance. The neutral mass is calculated by adding the mass of  $^1\text{H}$  atom (1.007825 Da) to the experimentally determined mass assuming that the molecules ionize via reaction (1). The composition was unique at the 20 ppm mass tolerance; the structures cannot be uniquely identified from ESI-MS only.

Observed m/z (Da)	Composition (mass)	Corresponding neutral mass
185.0816	$\text{C}_9\text{H}_{13}\text{O}_4$ (185.0814)	186.0894
187.0616	$\text{C}_8\text{H}_{11}\text{O}_5$ (187.0606)	188.0694
199.0969	$\text{C}_{10}\text{H}_{15}\text{O}_4$ (199.0970)	200.1047
201.0776	$\text{C}_9\text{H}_{13}\text{O}_5$ (201.0763)	202.0854

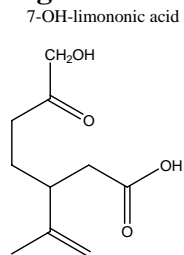
**Figure 2:** Possible products of Limonene ozonolysis with composition  $C_9H_{14}O_4$  (186.1 Da).



**Figure 3:** Possible products of Limonene ozonolysis with composition  $C_8H_{12}O_5$  (188.1 Da).



**Figure 4:** Possible product of Limonene ozonolysis with composition  $C_{10}H_{16}O_4$  (200.1 Da).



**Figure 5:** Possible products of Limonene ozonolysis with composition  $C_9H_{14}O_5$  (202.1 Da). The last two products require  $H_2O$  for their formation.

