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Comment

Interactive comment on “High molecular weight SOA formation during limonene ozonolysis: insights from ultrahigh-resolution FT-ICR mass spectrometry characterization” by S. Kundu et al.

S. Kundu et al.

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General comments: This is a good application of FT-MS and demonstrates the use of the technique to atmospheric chemistry. The paper does not delve into much new chemical insight or into the optimization of the FT-ICR-MS method used; it comes off as much more concerned with massaging the data, but does not get into the specifics of the method, either. All in all, it is good work, but the focus prevents it from illuminating the implications of the compounds observed.

Response: We thank the reviewer for carefully reviewing the manuscript. As suggested additional details regarding the method and the observed chemical insights have been

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added throughout the manuscript.

Specific comments (numbered below):

1) You do not mention what temperatures at which you store and transport your samples, or the time between collection and analysis. You do mention that it is “freezing” and “cold”, but that is unspecific, and does not address biological activity or the opportunity for volatilization of compounds. You do not seal your filters in a gas-tight manner, either, which provides the opportunity for gases ambient to your freezer to condense on the filter, including water.

Response: The laboratory generated secondary organic aerosol samples were stored at -20 oC in a freezer. Blue ice was used to keep the samples cold during the overnight transport between laboratories (the temperature during transport was not recorded). Biological degradation of the samples is not expected, because they are chamber experimental samples generated from the ozonolysis of limonene. Consistent with previous studies, the samples were stored in petri dishes sealed with aluminium foil. These points have been mentioned in the revised manuscript.

2) You do not address method artifacts from the exposure of your samples to water during storage and especially in preparation (hydrolysis or hydration of species, for example). Also, do you include an acidic spike to aid in ESI? You do not discuss any methods to assess the extent to which your preparation affects your measured sample composition; what were your findings if you did this?

Response: In this study, we did not evaluate how water affects the degree of the functionalization of analyte molecules. We added a comment about this. Also, please note the mass spectra were collected for negative ions without any pH adjustment. We agree more work could be done to more fully assess the ESI parameters and their effect on the chemical composition of SOA, however this is beyond the scope of the current manuscript.

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3) About your filters: what are the dimensions of the filter? Do you do any cleaning prior to using the filter (i.e. baking)? Do you extract the entire filter or a portion of it?

Response: We collected aerosol samples on pre-fired quartz fiber filters (600°C for >8 hours; diameter: 47 mm). Half of the filter was used in the extraction procedure. These points are mentioned in the revised manuscript.

4) What was the mass loading of aerosol on each filter? You extract them in 5 mL – do you reduce the volume at all to concentrate your samples for analysis?

Response: Accurate mass loading data cannot be obtained from quartz filters, thus mass measurements were not recorded, however, we did record the particle number concentrations. The particle number concentration reached 19360 particles/cm³ at 55 min after the mixture was allowed to react. This information has been provided in the revised manuscript.

5) What grade solvent did you use and what was the source? Did you assess recovery of different classes of compounds from the filter by your extraction method?

Response: Thank you; we added the solvent details. We did not assess the recovery of different classes of compounds with respect to solvent type. It is possible, however, that a minor fraction of SOA material was not extracted with our procedure. This has been mentioned in the revised manuscript.

6) You mention repeatedly results involving the detection of hydroperoxides, gem-diols and hemiacetals. Are you certain that these are reasonable products to be detecting in their native form (i.e. not further reacted to a more stable structure)? How are you certain?

Response: We drew conclusions about the high MW compound formation processes based on the expected trends of elemental ratios (O:C and H:C) and DBE in our chemical formulas and expected fragments of high MW compounds. It confirms that our detected compounds are what we are expected. The trends of elemental ratios and

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DBE values depend upon the reaction channels. The elemental ratios decrease in the condensation (aldol and esterification) reactions and remain unchanged in the non-condensation (Criegee, hydroperoxide and hemi-acetal reactions). The DBE changes by 2 when high MW compounds are formed by the non-condensation processes and DBE changes by 3 when high MW compounds are formed by condensation reactions. Finally, we predict building units of high MW compounds via the reaction matrix and then checked the predicted building units using fragmentation analysis of selected peaks. All these parameters together provide evidence for the importance of non-condensation reactions over the condensation reactions.

7) Space charge effects and future work you may do, you may wish to read Gorshkov et al., J. Am. Soc. Mass Spectrom. 2010, 21, 1846.

Response: We thank the reviewer for the reference. Gorshkov et al. discussed the space charge effect and proposed an m/z calibration rule for achieving zero space charge in the Orbitrap FTMS instruments. We followed the method optimization (including AGC settings) of Soule et al., 2010 which was performed on the instrument we used for this study. This point was clarified; please see the revised manuscript.

8) Technical corrections: In section 2.2: You discuss putting the ESI probe in position “B”. This piece of information is not helpful, as you do not explain the significance of position “B”.

Response: The ESI probe position is adjusted manually. The noted position may be helpful to the users of the Thermo instruments. We clarified this point.

9) You mention the normalized collision energy level being “100%” – this is not a helpful quantity. Provide the real values or at least a range of values.

Response: The infrared multi-photon dissociation technique (IRMPD) of the LTQ FT Ultra uses IR laser radiation from a 20 W CO₂ laser to excite and fragment ions. So, 100% means full laser power, i.e. 20W. We clarified this point in the revised manuscript.

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10) You use the phrase “MS/MS mass spectra” – refer to them as “tandem mass spectra”.

Response: To clarify the sentence we revised it to state, “The MS/MS spectra were measured with a resolving power of 200 000 and 50 transients. . .”

11) Do check your spelling and grammar; there were several problems found.

Response: We carefully rechecked the revised manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 2167, 2012.

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