

Interactive comment on “Aqueous phase oligomerization of methyl vinyl ketone through photooxidation – Part 1: Aging processes of oligomers” by P. Renard et al.

Anonymous Referee #2

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Renard et al. report an interesting study concerning the concentration dependent aqueous photochemistry of MVK. They make good use of the paired capabilities of LC/MS to examine aqueous phase organic speciation and an HR-AMS + SMPS to study the bulk properties of SOA released upon atomizing and drying the reaction solution. This combination of approaches offers a level of information and insight not often available in lab studies of aqSOA formation. The studies are well designed and the results, for the most part, clearly explained. I have a few suggestions to improve the manuscript before publication.

1. The language in the manuscript is sometimes awkward and there are numerous er-

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rors in English language grammar and syntax. These include singular/plural disagreements between nouns and verbs, improper choice of prepositions, missing subjects, etc.... The manuscript should be edited for language before acceptance for publication.

2. p. 15287, line 12: change "ionic" to "ion"

3. p. 15288, line 13: define "UPLC"

4. p. 15288, line 4: The authors state that the experimental conditions in Table 1 were chosen to be representative of cloud droplets or wet aerosol conditions. While the lowest MVK concentration (200 μM) might represent total WSOC concentrations in some clouds or fogs, it is unlikely to find such high concentrations of a single ketone. The minimum concentration of H_2O_2 (4000 μM) is also much higher than seen in ambient clouds or fogs, where reported observations are generally at least 10x lower. Based on these discrepancies, I would conclude that the lowest MVK and H_2O_2 concentrations are perhaps an order of magnitude or so higher than in ambient clouds and fogs. This should be clarified for the reader.

5. p. 12588, line 14: How were OH concentrations estimated? Were they measured in solution, e.g., by adding a "clock" species with a known OH-rxn rate?

6. p. 15288, line 23: change "its resolution mode" to "its high resolution mode"

7. p. 15289: What mass accuracy was achieved for the instrument?

8. p. 15290, lines 1-3: Given that the 211 nm absorption is proportional to the sum of the H_2O_2 and MVK concentrations, it is unclear to me how measuring at this wavelength defines the MVK oxidation rate. Please clarify. Presumably you need the combination of the K and R bands to separate changes in MVK and H_2O_2 concentrations.

9. p. 15290, line 24: Please give the manufacturer for the TOC/TN instrument.

10. p. 15291: Please clarify use of the NPOC measurement mode for TOC. Using

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this mode on acidified samples should eliminate small molecules, including low MW carboxylic acids. That seems useful if you want to quantify the OC that will be released as OA upon drop evaporation. Is that the intent?

11. Accurate quantification of the CO₂⁺ fragment in the AMS requires good information about the CO₂ concentration in the sample air stream. How was this quantified? Indoor CO₂ concentrations can be much higher than outdoor concentrations.

12. p. 15293, lines 14-15: Why were these fragments "thought to be" C₂H₃O⁺ and CO₂⁺? Aren't you using the high res AMS data where these ions are distinguished from other ions with the same unit mass?

13. p. 15293, line 28: the second ion listed here should be m/z 44.

14. p. 15294, line 10: The AMS collection efficiencies stated (0.07 to 0.21) seem very small for organic aerosols. Please comment on these values relative to those typically reported for OA in other AMS studies.

15. p. 15294, line 22: please change "increasing mode" to "increasing mode size"

16. p. 15296 and elsewhere: The authors need to comment on the possible role of OA concentration in altering the fraction of organic matter that partitions to the aerosol phase. The lower concentration experiments could have lower SOA yields, in part, because at lower OA concentrations a bigger fraction of the organic matter resides in the gas phase. This partitioning effect could also alter the relative oxygenation of the OA produced since only the lowest vapor pressure products will enter the particle phase when OA concentrations are low.

17. pp. 15297-15298: The authors do a nice job talking about the changes in chemistry and SOA yield as a function of oxidation time. This discussion, however, would benefit from tying it back to the ambient atmosphere. Please discuss what yield/time is most relevant for typical atmospheric conditions.

18. p. 15298, line 2: I think the percentage here should be 70 +/- 50%

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19. Fig. 8: The time evolution of the experiments needs to be better displayed in this figure.

20. p. 15302, line 1: change "ones" to "compounds"

21. p. 15302, lines 2-3: This sentence is missing a subject. Latter is an adjective. Latter what...?

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 15283, 2014.

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