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Atmospheric Chemistry and Physics Discussions

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 #3

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The authors describe experiments where the aqueous phase oxidation of a soluble isoprene oxidation product, MVK, was studied using a number of online solution and aerosol characterization measurements. The main findings are that the oligomers are formed at higher concentrations of the precursor material, which then fragment into smaller acids upon increased oxidation. As well, more SOA is formed as the oxidation reaction progresses reflecting the decreasing volality of the latter reaction products compared to the intial ones. The paper adds to the growing body of information on the aqueous phase oxidation mechanisms that prevail under cloud water conditions. The strength of the paper is the extensive analytical characterization of the products.

However, I do have a number of concerns that need to be addressed prior to publication in ACP:

1. Overall, the writing quality is not strong. As examples: i. An Abstract should be a clear, succinct description of the experiments and results, and so the first paragraph should be removed. ii. The Results section simply lists the results one after the other, without connecting one section to the others, i.e. helping the reader to better understand the work, iii. The Discussion section starts immediately with some highly detailed discussion without codifying the overall results from the study. iv. The Figures have too small labels and axis values. v. References: Please check that all relevant studies related to oligomerization have been included. For example, the work of Aljawhary et al., AMT, 2013 describes the loss, presumably by OH oxidation, of SOA oligomers in solution. The paper should be re-written before re-submission.

2. The authors need to address how the sensitivity of ESI to different classes of compounds affects their results. For example, in Figure 2 how much of the change in shape of the spectrum is due to the formation of polyacids that are detected easily by ESI, when starting with a precursor that does not contain an acid functionality? Are oligomers detected as efficiently as the monomers?

3. For the AMS spectra in Figure 3, has high resolution mass fitting identified the composition of the different ions labelled? For example, m/z 43 may have multiple elemental compositions.

4. When quantitatively comparing data at different times in the reaction (e.g. AMS data in Figure 4), how is it known that the nebulizer output is constant from one time to the other? Nebulizer outputs are affected by the surface tension and volatility of the solution being atomized. Indeed, the numbers of particles being formed is changing dramatically during the experiment as shown by the SMPS scans in Figure 5. Why is that occurring, for a “constant output” TSI atomizer? How does this affect the interpretation of the results? Should the authors normalize all their aerosol results to the

changing number output of the atomizer? Please clarify.

5. As a related question, if the number output of the atomizer is changing I don't understand how a yield can be quantified. For example, if the number of particles being produced by the atomizer is lower at the beginning of the experiment than at the end, then the yield (using equation 2) will be calculated to be lower. This does not reflect changing chemistry, only the changing efficiency of atomization. Unless I am incorrect, this will make the stated yields invalid.

6. Caption to Figure 8. I am not sure what the authors mean by the comparison to the data of Lee et al., 2001?

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