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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The Aarhus Chamber Campaign on Highly Oxidized Multifunctional Organic Molecules and Aerosols (ACCHA): Particle Formation and Detailed Chemical Composition at Different Temperatures" *by* Kasper Kristensen et al.

Anonymous Referee #2

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General comments: This work by Kristensen et al. studied ïĄą-pinene SOA formation and composition at different temperatures (20ïĆřC, 0ïĆřC, and -15ïĆřC) in a chamber facility. This study examined organic acids and dimer esters in the SOA composition through off-line LC-MS analysis. These chemicals were estimated to account for substantial fractions (15 – 30% and 4 – 11%, respectively) of total SOA mass. Dimers with lower O:C ratios (< 0.4) were found to increase at lower temperatures. In temperature ramping experiments, SOA mass and composition were found to be governed mostly

by initial temperatures. Overall, the manuscript is well written and demonstrates new findings regarding temperature effects on ïĄą-pinene SOA composition on the molecular level, especially at very low temperatures. But a few major concerns need to be addressed before this manuscript can be considered publishing.

Specific comments: 1. This manuscript has several companion papers published, as mentioned in the Introduction. If comparisons will be made with these papers, I suggest adding a section in the Results that briefly describes the main findings of these companion studies relevant to this work would be helpful.

2. Line 167 – 169. The influence of injection flow rate was not motivated clearly. Why did the authors think changing injection flow rate could affect the experiments? Without clear motivation, this part should be removed.

3. What is the scientific basis that made the authors to use O:C ratios of 0.4 as the threshold? What if one chooses 0.5? Instead of using an arbitrary value, showing histogram as a function of O:C ratios (by 0.1 increment) might be better.

4. Line 290 – 297. The authors observed different results compared to Kourtchev et al. (2016). The explanation should be explained to some extent. For example, whether the higher SOA mass loading under higher VOC lead to condensation of SVOC, which as a result lower oligomer fraction, as a competing process with the mechanism presented by Kourtchev et al. (2016).

5. As direct comparisons were made for the LCMS measured organic acids and dimer esters between different temperature conditions, one would expect that the quantified concentrations are reproducible and the relative abundance between different conditions are reproducible as well. In the current form of the manuscript, the reproducibility or uncertainty range was not discussed and should be addressed in the revised manuscript (e.g., error bars on Figures 5 and 6 representative of reproducibility).

6. Line 312 – 317. The authors argue that higher O:C dimers are formed through RO2-

RO2 reactions, followed by diacyl peroxide decomposition; while lower O:C dimers could be diacyl peroxides. However, it is not necessary that diacyl peroxides have lower O:C ratios than their decomposition products (loss of CO2). This argument needs to be better justified.

7. Section 3.4. After temperature ramping to 20 ïĆřC or -15ïĆřC, the SOA mass do not merge to the level in constant 20 ïĆřC or -15ïĆřC. The similar temperature effects have been studied in prior studies (Warren et al. 2009; Zhao et al., 2019). Zhao et al. (2019) provided some possible explanations for this behavior. The molecular results here, are likely better quantified and thus are in better position to explore more on the mechanistic explanation. However, it is missing from this section in the current form, except that the authors claimed the initial temperatures play a bigger role in final SOA mass.

8. From the title, it appears linking HOMs with organic acids and dimer esters is a key subject for this study. However, the manuscript discussed very little on this connection (only Section 3.5). The results of the referred companion study using NO3-CIMS should be discussed more extensively. Further, it is true that at lower temperature, HOM formation via RO2 autoxidation is limited, bimolecular RO2 reaction is expected to increase. But this does not necessarily mean that RO2-RO2 dimer formation is going to be enhanced. How about RO2 + HO2 and RO2 + RO2 which lead to monomeric products? These two reactions are both temperature dependent and are likely more important than RO2 autoxidation (5-10%) and RO2+RO2 to ROOR (5 – 10%). Thus, the temperature effects on RO2 + HO2 and RO2 + RO2 could more likely govern the changes in RO2 autoxidation and dimer formation. It is a four-factor relationship, but only the two less dominant pathways are discussed. In addition, as pointed by the authors, RO2 + RO2 might only explain some of the dimer esters.

Technical comments: 1. Line 41. Add “(SOA)” followed by “secondary organic aerosol”. With this change, the “secondary organic aerosol” at Line 45 could be removed.

2. Line 43 – 46. ïĄą-pinene is also dominant OA source at other locations. For example, Zhang et al. 2018, 115, 2038, PNAS and Lee and Thornton et al., 2020, ACS Earth and Space Chem. (in press) show monoterpene SOA are the largest sources of PM in the southeastern US.

3. Line 49. A new study (Zhao et al., 2019, 3, 2549, ACS Earth and Space Chem.) performed similar temperature-ramping experiments with compositional analysis like this work and should be added in this list and perhaps later discussion (Section 3.4).

4. Line 130 – 146. Are the suite of online instrumentation situated in the cold room as well? It should be provided and if not, potential influence caused by temperature variation should be discussed.

5. Line 150 – 154. Two sentences have repeated texts. Please reword.

6. Line 161. This sentence should clarify if the temperature ramping started before or after SOA formation reached plateau.

7. Section 2.1. Slight RH variations between different temperature conditions are shown in Table 1, but should also be mentioned (one sentence) in the description.

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