

Interactive comment on “Unambiguous identification of esters as oligomers in secondary organic aerosol formed from cyclohexene and cyclohexene/ α -pinene ozonolysis” by L. Müller et al.

L. Müller et al.

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The authors thank the referees for their careful evaluation of the work presented. We continue with individual Author Replies (AR) to the comments.

Anonymous Referee 1:

1. Page 13888, lines 10-12: The authors should be aware of potential artifacts from preparing samples by sonication.

AR1: Artifacts due to individual sample preparation steps are generally difficult to be completely excluded. However, the benefit of the combination of on-line APCI-MS/MS

and HPLC-ESI-MS/MS presented in the paper is the possibility to verify off-line detected compounds by on-line MS/MS experiments. As can be seen in Figures 5 and 7, we compared MS/MS spectra of dimers from on- and off-line techniques. Due to isobaric interferences in the on-line MS/MS spectra also other masses can be seen, however, the main product ions match to the LC/MS/MS spectra. Therefore, we are sure that these compounds are not artifacts resulting from sample preparation.

2. Page 13895, lines 8-11: Considering that HTDMA measurements show that SOA typically absorbs very little water except at very high RH, I think it is quite likely that water generated by the condensation reaction would evaporate. What range of RH was investigated here?

AR2: In our experiments we investigated a RH range from 1-50

3. Page 13895, lines 17-21 and Figure 10; Page 13896, lines 14-20 and Figure 11: I do not think it is possible to draw conclusions about which product concentrations are rising faster or slower based on the data in Figures 10 and 11.

AR3: We do agree partly with the referee in this point. One could in fact imagine chemical systems for which also a second generation product formed in a consecutive reaction (such as an ester formation from first generation carboxylic acids) builds up at the same speed as the first generation products (if the rate constant of the consecutive reaction is very high). However, the major conclusion of Figure 10 is still that the very rapid formation of the esters does not support classical esterification reactions - without excluding them. We added a respective statement in the text.

Another possible explanation for this temporal behaviour is the lower vapour pressure of the dimeric compounds. In the beginning of the reactions, at low organic particle mass, products of low volatility are partitioning to a higher fraction into the particle phase due to their larger partitioning coefficient (Odum 1996). As the organic mass grows during the course of the experiment, the gas-particle-partitioning of compounds having higher vapour pressures is shifted more and more to the particle phase. As a

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result the concentration of the higher volatile products increase while the concentration of the lower volatile compounds stay constant or even decreases by this dilution effect.

Technical Comments: 1. Page 13893, line 20, and Figure 7: I believe the adduct is formed with cyclohexane diol, not cyclohexene oxide. I think the latter compound is an epoxide.

AR4: Whether the formation of the ester is via the epoxide or the diol is not clear yet. In the synthesis experiments it could be formed by the diol and epoxide, respectively. The formation by the epoxide might occur after hydrolysis to the diol or directly. Currently, we are performing experimental studies on this topic.

Anonymous Referee 2:

In regard to relative humidity (RH)- The authors state that no influence of RH was observed, though from the manuscript, it appears the experiments were conducted under dry conditions only. It is suggested that the authors include a summary of the experimental conditions and results at different RH values. Additionally, while one effect of lowering RH would be to promote ester formation as the authors suggest, there are other factors to consider. One is the phase in which the ester formation occurs: if reactions occur in the particle phase, the amount of particle phase water (not RH) would be the parameter of interest. Another is the amount of water relative to the amount of reactant(s) and value of the equilibrium constant for the esterification reaction(s). If the amount of reactant(s) and/or the equilibrium constant are large relative to the amount of water, changing RH (or particle liquid water content) may have no effect on ester formation.

AR5: We agree with the referee that for the interpretation of the influence of water a careful consideration of the possible reaction site (gas or condensed phase) has to be done. Especially the discussion whether classical esterification is happening or not these considerations (i.e. particle phase water, equilibrium constants) have to be taken into account. We included a respective statement in the text.

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In regard to the temporal behavior of the signal intensities of monomers and dimers shown in Fig. 10- The authors state that the temporal behavior of "ester educt" and expected ester product concentrations do not suggest a second order reaction between the acid and the alcohol in the particle phase. However, I am not sure that relative signal intensities are a direct measure of concentrations. Additionally, as the authors mention, the volatilities of the monomers and dimers will affect their concentrations in the particle phase, as will the total concentration of monomer or dimer (gas + plus particle phase) and the total particle (aerosol) mass, both of which will have some time dependence.

AR6: see AR3.

Technical comments: p.1, Abstract: "built-up" should be "build-up"

AR7: Has been corrected

p.2, top of page: SOA does not need to be redefined (already defined in Introduction, p.1).

AR8: Has been corrected

p.6, Section 3.1.1: It is suggested that the authors include subsection 3.1.1 as a paragraph in section 3.1, rather than a separate subsection. The authors begin discussion of the mass spectra of the synthesized esters on pp.5-6. It is somewhat confusing then to come to the subsection: mass spectra of reference ester.

AR9: Has been corrected

p.9, Conclusions: As written, it is not clear how the second paragraph of the conclusions section contributes to the discussion of the authors; results or implications of those results, except to indicate that in other investigations of chamber-derived SOA esters have been identified;It is suggested that the authors either expand this paragraph to be a complete discussion of the volatility of esters identified in chamber studies, including their own; or, condense this paragraph to one or two sentences about

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esters being identified in other chamber studies.

AR10: The paragraph has been condensed.

Fig. 2: It is suggested that the authors reorder the panels in Fig. 2 to correspond to the order in which they are discussed in the text.

AR11: Has been corrected

Anonymous Referee 3:

Minor comments: p.13887, line 24: Experiments were performed at alpha-pinene and cyclohexene concentration of 200ppb and 1000ppb, respectively. How were these concentration determined?

AR12: The VOCs were added into the chamber by using temperature-controlled, nitrogen flushed test gas sources, which were based on an open tube diffusion technique. Tubes containing the VOCs were weighted before and after the experiment. Using this mass loss and the total flow through the chamber the concentrations can be calculated.

p. 13888, line 9: The residence time in the reactor is about 19min, however filters were collected for six hours; a much longer time. Since no denuders were used for filter sampling the ozonolysis reactions probably continue on the filter and the overall reaction time is therefore much longer than 19min. A respective remark including potential artifacts should be added.

AR13: See AR1.

p.13896, line 10: However, in the experimental section only dry experiments are mentioned. Please clarify. If water is present in large excess in the SOA particles compared to the amount generated by the ester reaction, it might not influence the equilibrium of the esterification react and therefore I doubt that this is a valid argument against condensed-phase esterification.

AR14: See AR2.

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