

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.

Anonymous Referee #2

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Müller et al. report on the identification of esters in laboratory-generated secondary organic aerosols (SOA) from cyclohexene and cyclohexene + α -pinene ozonolysis. As noted by the authors, unambiguous identification of particle-phase constituents has been difficult; particularly the identification of higher-molecular weight constituents (e.g., oligomers). The lack of information on the structure and formation mechanisms of oligomers has hindered the incorporation of oligomer formation in SOA models. Therefore, the goal of this work was to unambiguously identify oligomers in SOA.

The motivation, methodology and results of this work are presented clearly. Addition-

ally, the use of synthesized esters as reference compounds and the investigation of cross-product (oxidation products of different precursors) dimer formation are unique. It is recommended that this paper be published in Atmospheric Chemistry and Physics upon the authors addressing the specific and technical comments below.

Specific comments:

p. 8, Section 3.4: In the discussion of possible reaction mechanisms, the authors bring up the important point that there are several possible reaction mechanisms for the formation of the observed esters and that more work needs to be done to identify the reaction mechanism(s). However, the authors make several statements that aren't well supported.

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 (<1% RH, section 2.2). 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.

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

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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.

Technical comments:

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

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

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.

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. The discussion of volatility is somewhat confusing. The authors state that the esters identified in the Gao et al., 2004 and Yu et al., 1999 chamber studies "will have a smaller influence on the SOA mass yield." It is assumed that the authors are comparing the esters to the parent carboxylic acids, but it is expected that the authors would be comparing those esters to the esters that they've identified. In addition, the authors don't state anything about the volatility of the esters identified in Surratt et al., 2006. 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 esters being identified in other chamber studies.

Fig. 2: It is suggested that the authors reorder the panels in Fig. 2 to correspond to

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the order in which they are discussed in the text.

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