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Atmospheric Chemistry and Physics Discussions

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 #1

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General Comments:

This manuscript describes laboratory studies of oligomeric compounds formed from the reactions of cyclic alkenes with ozone. The reactions were carried out in a large reaction vessel and the aerosol composition monitored in real time using atmospheric pressure chemical ionization particle mass spectrometry. Particle samples were also collected on filters and the extracts analyzed by HPLC with electrospray ionization mass spectrometry. The particle-phase reaction products were identified by interpretation of the mass spectra and by comparison of the spectra and HPLC retention times

with those of authentic oligomeric ester standards synthesized in the laboratory.

The experiments are well done and the product analyses are convincing. I am very pleased that it was possible to synthesize standards of the oligomeric ester products for definitive identification. I think that one of the major problems with many studies of aerosol oligomers is that the number of possible oligomers is so large that it is very difficult to be certain about identification based solely on mass spectra. As a result, it is difficult to learn much about the types of reactions that form oligomers. I believe this is the first study to use authentic standards and therefore represents one of the most impressive studies to date on oligomer chemistry. This is a topic of much current interest and has the potential to significantly impact the understanding of atmospheric secondary organic aerosol formation. Unfortunately, the mechanism of ester formation still remains speculative and needs further study. It would certainly be interesting if there are gas-phase mechanisms for creating esters. The paper is well written and the figures, tables, and references are fine. I think the paper is appropriate for Atmospheric Chemistry and Physics and recommend that it be published. I have a few additional comments.

Specific Comments:

1. Page 13888, lines 10-12: The authors should be aware of potential artifacts from preparing samples by sonication. I am not sure if results have been published, but the Paulson group at UCLA has shown that sonication of samples containing water generates large concentrations of hydrogen peroxide. Hydrogen peroxide can potentially react with species such as aldehydes to make oligomeric compounds.

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?

3. Page 13895, lines 17-21 and Figure 10; Page 13896, lines 14-20 and Figure 11:

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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. These curves represent signals that have all been normalized using different scaling factors and so do not represent actual concentrations. If one instead multiplied the curves by factors necessary to convert each of the signals into concentrations, it is quite possible that the relative slopes of the curves would change entirely. However, even if this were done, in this case I do not think it would help in the data analysis. I think it is only possible to make statements about the order in which products are formed if there is a clear time lag in the appearance of products, such that one clearly appears much later than another. In these experiments, the onset of product formation appears to occur at essentially the same time for all these curves, and thus such statements would not be valid.

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 13883, 2007.