

***Interactive comment on* “Evolution of organic
aerosol mass spectra upon heating: implications
for
OA phase and partitioning behavior” by
C. D. Cappa and K. R. Wilson**

Anonymous Referee #2

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General Comments

This manuscript describes the results of experiments carried out at the Advanced Light Source in which organic aerosol formed from lubricating oil and from the reaction of alpha-pinene + O₃ were analyzed using a thermal denuder (TD) coupled to a thermal desorption mass spectrometer. The mass spectrometer employed low desorption temperatures and VUV radiation to minimize ion fragmentation and thereby yield mass spectra that were more representative of the molecular distribution. Variations in the mass spectra with TD temperature were used to probe the degree to which aerosol

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evaporated by distillation of components due to a range of volatilities, in accordance with absorptive partitioning theory, or not. The results were analyzed using models for evaporation and condensation and conclude that although lubricating oil particles behave according to absorptive partitioning theory, the alpha-pinene SOA particles do not. The authors then propose that the latter particles are glassy rather than liquid, and present a new model based on this assumption to explain their results. This conclusion is consistent with some recent observations published by others. This is an important paper and the results presented justify the interpretation and conclusions made by the authors. An understanding of particle phase and its effect on aerosol growth and evaporation is critical for modeling atmospheric aerosol-related phenomena. The manuscript is extremely well written. It contains necessary and appropriate references and figures. I think it should be published in ACP, although I have a few comments that should be addressed.

Specific Comments

1. Page 28435, line 4: Is this diesel lubricating oil, and is it the same type used by the CMU group to develop their basis set?
2. Page 28436, line 11: Please provide a reference for the assumed alpha-pinene SOA density.
3. Page 28438, lines 1-4: It might be worthwhile adding a comment and reference regarding the carbon number distribution of diesel lubricating oil and comparing it to the observed mass spectrum. For example, there is a chromatogram in Sakurai et al., *Atmos. Environ.* 37, 1199-1210 (2003) for 15W40 diesel oil, or perhaps the authors know other references.
4. Page 28438, line 27 through Page 28439, line 25: How does the mass spectrum obtained with VUV compare with those obtained by Murray Johnston and co-workers, who have published a number of papers on alpha-pinene + O₃ SOA analyzed by electrospray MS. The comparison is probably worth noting, since both are presumably soft

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ionization methods.

5. Sections 3.1 and 3.5.1: Might some of the differences between the CMU dilution experiments indicating equilibrium partitioning, the Docherty et al. (2005) desorption experiments, and the results observed here be due to the differences in the timescales for evaporation, which are very different?

6. Page 28442, line 25 through Page 28443, line 2: It seems like an alternative model that could explain the observations for alpha-pinene SOA is that the SOA is composed primarily of oligomers and that evaporation does not occur layer-by-layer but monomer-by-monomer as monomers with constant average composition dissociate from essentially non-volatile oligomers. This would not require any assumptions about the particle phase.

7. Page 28444, lines 7-8: More appropriate diffusion coefficients for comparison than water at 150-160 K are probably values in glassy organic polymers, such as $4 \times 10^{-18} \text{ m}^2 \text{ s}^{-1}$ for iodohexane in polystyrene [Hui et al., J. Appl. Phys. 61, 5137-5149 (1987)] or $3 \times 10^{-20} \text{ m}^2 \text{ s}^{-1}$ for a small oligomer (640 g/mol) in polymethylmethacrylate [Bucknall et al. Chem. Eng. Sci. 56, 5473–5483 (2001)].

8. It would be useful to quote, with references, typical values of glass transition temperatures for organic polymers for comparison with the TD temperature range of these experiments. This will add support for the proposal that the alpha-pinene SOA is always in a glassy state in the TD.

Technical Corrections

I did not find any technical errors.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 28431, 2010.

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