

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 #1

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General comments

This paper presents very interesting results on the evolution of molecular weights of two distinct organic aerosol types as they are passed through a thermodenuder at different temperatures. While the chemical composition of the lubricating oil aerosol evolved to higher molecular weight (MW) components as the temperature of the denuder was increased, the MW spectra of the alpha-pinene + ozone reaction products particles (alphaP) remained almost unchanged when the thermodenuder temperature was increased. These amazing results are explained by the formation of glassy aerosol

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particles in the case of the alphaP particles. These experiments are very interesting and deserve publication in ACP. Yet, I have some major concerns regarding data evaluation and interpretation which might put into question some of the conclusions of the manuscript. These issues have to be addressed by the authors before publication.

Data evaluation

The calculation of the volume loss from the SMPS data takes into account the volume loss of the aerosol as a result of the shrinkage of the individual particles, while the possible full evaporation of a part of the particles is not considered. Especially in the case of the alphaP aerosol with a median particle diameter of only 92 nm, it is probable that the smaller particles fully evaporate due to the Kelvin effect. Moreover, as a consequence of the heating/cooling in the thermodenuder recondensation of a part of the volatilized material can occur and alter the size distribution of the particles. Therefore, an alternative evaluation should be attempted that takes into account the partial loss of particles because of full evaporation or, at least, evidence should be presented showing that this process can be neglected.

Data interpretation

One puzzling finding of this study is that the evolution of the VUV photoionization mass spectrum of the alphaP aerosol showed no distinct changes with temperature as would be expected from absorptive partitioning theory. The authors postulate that this behavior arises from the alphaP particles existing as in a glassy state. They present a conceptual model wherein the secondary OA is formed and then rapidly converted from an absorbing to a non-absorbing form. One difficulty of this model is that the thus formed particles should be “composed of sequential layers that have differing composition, with a greater fractional amount of higher volatility material in the outer layers than in the inner layers” as the authors state themselves. If this is the case, the evolution of the VUV mass spectrum should be temperature dependent because the outer higher volatility material should evaporate first. Another major difficulty of the presented ex-

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planation is that the glassy state should persist up to temperatures as high as 130C. However, the glass transition temperature (T_g) depends among other factors on MW. Hydrophilic substances with MW < 200 have typically T_g close to room temperature or below (e.g. glucose: MW = 180.16, T_g = 303 K ; citric acid: MW = 192.13, T_g = 283 K; tartaric acid: MW = 150.09, T_g = 289 K, glycerol: MW = 92.1, T_g = 180 K; all values from Craig et al., *Int. J. Pharm.*, 179, 179–207, 1999). The alphaP aerosol with virtually all observed MW < 200 should therefore be present as a liquid even at RT. Nevertheless, the viscosity of these particles might be high rendering diffusion slow although the particles are not in a glassy state. Such a discussion of T_g should be added to the manuscript. Recondensation and redistribution of material between aerosol particles is expected to be very fast for semivolatile species that partition strongly to the gas phase. Marcolli et al. (*Atmos. Chem. Phys.*, 4, 2593–2599, 2004) estimated that equilibration times for hydrophobic species with MW up to ca. 250 and highly hydrophilic species with MW up to ca. 100 show equilibration times of less than 1 s. This is fast enough for considerable recondensation already at the end of the heating zone even before the diffusion denuder is reached. The alphaP aerosol contains a large fraction of components in this low molecular weight range (the volatility basis set shows the largest stoichiometric yields (alpha) for C^* = 1000 and 10000 microgram/m³). Therefore, the effect of recondensation of the aerosol within the thermodenuder has to be considered. The effect of such recondensation might be that the low MW fraction would show low net evaporation. Fast recondensation affecting the composition and size distribution of the particles could offer an alternative explanation why the alphaP aerosol mass spectrum is essentially unchanged as a function of evaporation temperature and why such high temperatures are needed to evaporate the alphaP aerosol.

Specific comments

Fig. S-1 in the supplement gives an interesting comparison between EI-AMS and VUV-AMS. It should be included in the main text.

Section 2.2.1: The preparation of the lubricating oil aerosol should be explained in C11411

more detail, especially, the “filter-based diluter”.

Section 3: The volume fraction remaining is evaluated solely based on the changes in the particle size. This evaluation assumes that the whole mass or volume loss of the aerosol is due to the decrease of particle diameter. However, there is also the possibility of mass loss due to decreasing number of particles. This effect should be evaluated by comparing the number concentration of aerosols that passed through the TD at RT and at elevated temperature. Such an evaluation should be feasible because the dependence of particle number loss on temperature in the thermodenuder is rather small (Huffmann et al., 2008). The authors might also show a figure with SMPS spectra of LO and alphaP aerosols that passed the thermodenuder at RT and at elevated temperature.

Fig. 3: Some of the peak thermograms in Fig. 3 show “fraction remaining” values above 1. Is this a consequence of the applied normalization procedure? Can it be explained by recondensation of some of the lubricating oil on the particles in the thermodenuder, either from the same experimental cycle or by contamination from former experimental cycles? Have any tests been performed to exclude contaminations due to re-evaporation of material that has condensed in the thermodenuder during former experiments?

Page 28441: taking the C^*/MW relationship, the alpha and the observed MW do not match. Have you tried to fit the data with alpha that correspond better to the observed mass distribution?

Page 28444: Considering the MW of the alphaP aerosol it is highly unlikely that it persists as a glass up to 130C (see general comment).

Page 28468, Fig. 5b: Hoffmann (1997) and Pathak (2006) are missing from the reference list. The y-axis title is confusing. It should be changed to “SOA mass fraction” as in Pathak (2007a).

Technical comments:

Page 28441, line 12: Lide, 2005 is missing from the reference list.

Page 28441, line 12: state in words what D_g stands for.

Page 28441, line 16: state in words what γ stands for.

Page 28441, line 23: state in words what MFR stands for.

Page 28442, line 2: it should be "Pathak et al. (2007a)" instead of "(2007b)".

Page 28447, Eq. 6: the exponent of "-1" is missing in the formula.

Page 28447, line 22: "Hoffmann" instead of "Hoffman".

Page 28468, Fig. 5c: "Shilling (2009)" instead of "(2008)".

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