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Interactive comment on "Oligomer formation within secondary organic aerosol: equilibrium and dynamic considerations" *by* E. R. Trump and N. M. Donahue

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"On page 24608, the authors describe an apparent contradiction posed by the formation of large oligomers that are of extremely low volatility, yet mass yields of α-pinene SOA drop below 0.05 for small total SOA concentrations. It is written: "Specifically, high-precision mass spectrometry suggests that a large fraction of SOA derived from α-pinene may be in the form of oligomers that are sufficiently stable to survive collection and ionization in a mass spectrometer." However, the dimerization description in the simplified model is based on the reversibility of non-covalently bonded carboxylic acid dimers formed in the condensed phase. This reversibility (and the assumed weak

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temperature dependence of the dimer- ization reaction) seems to be important for the model to reproduce the evapora- tion behavior of the SOA system. Do the authors imply that such carboxylic acid dimers would survive the collection and ionization in a mass spectrometer or is this a remaining apparent contradiction? Please comment."

Our model is not solely based on non-covalently bonded dimers, and this assumption is not essential to the model. We discuss non-covalently bonded dimers because there is literature evidence to support their presence in α-pinene SOA. The work of DePalma et al. (2013) was discussed as motivation for choosing the volatility bin of the active monomer species – this assumption is an over simplification that allows us to cleanly describe the dimer system. The short answer to the question is that we do not know if the model resolves the apparent contradiction mentioned in the introduction.

"Dynamic considerations. The dynamical model formulation includes the assumption that the condensed phase is uniform and that no diffusion limitations exist (page 24612). On the other hand, high molecular mass molecules, such as dimers and oligomers, tend to form highly viscous organic phases at room tem- perature, which in effect may limit to some extent both the rapid evaporation of semivolatile monomers upon dilution (see, e.g., Shiraiwa et al. 2013a), as well as the slower dissociation of dimers and evaporation of monomers, affecting the overall timescale and evaporation behavior in experiments. This is ignored in the current model simulations. Isother- mal dilution at temperatures close to room temperature and evaporation behavior upon heating to 75 or 100 C are likely influenced differently by effects of a highly viscous organic phase: heating to high temperatures may dramatically decrease viscosity and allow rapid bulk trans- port and evaporation of semivolatile molecules while isother- moal dilution may be much more affected by a highly viscous particle phase. Also, some dimers of low or extremely low volatility may actually become semivolatile at the higher temperatures, increasing the rate of evaporation in a thermodenuder. A brief discussion on how such effects may resolve (or increase?) the shown discrepancies between model simulations and measured evaporation dynamics for isothermal dilu-

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tion and heating cases would be of interest in the context of the discussion on page 24623."

Shiraiwa et al. (2011) give an equation for the characteristic timescale for mass transport by molecular diffusion. Given that the characteristic timescale of the dimer dissociation process is on the order of one hour, the "limiting diffusion coefficient" is on the order of 10-15 cm2 s-1. As long as the SOA diffusion coefficient exceeds this value, diffusion will not limit the processes described in this paper.

Recent work by Renbaum-Wolff (2013) demonstrates that the diffusion constant of the water-soluble component of α-pinene SOA typically exceeds 10-15 cm2 s-1 for relative humidity > 30%. Recent experimental evidence shows that toluene diffuses into α-pinene SOA particles within minutes, even at low relative humidity (Robinson et al., J. Phys. Chem. A, 2013). The evidence over the full range of conditions is that α-pinene SOA is less viscous (higher diffusion constant) than the limiting diffusion constant used for this work.

"page 24607, line 25: "classical" dimer formation from several products of α- pinene oxidation have also been studied experimentally and with a box model by Camredon et al. (2010), which would be worth mentioning at this point (and on page 24614, line 5)."

We added citations for this work.

"A recent paper by Shiraiwa et al. (2013b) shows a case of peroxyhemiacetal dimer formation from monomers of rather different molecular size and distinct volatility in a SOA system from the oxidation of dodecane. In a more general sense indicating the importance and variety of possibilities when it comes to the formation of low-volatility or (nearly) non-volatile dimers. This may be worth mentioning in the introduction. That paper also presents a case for a SOA system where simple dimers may not be considered non-volatile (further oligomerization would need to take place) and so even when the oligomerization reaction is considered irreversible, certain dimerization products may slowly evaporate upon dilution or heating perturbations without prior dissociation

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into monomers."

We added a citation for this work.

"Page 24618, line 4: What is the basis for the chosen first-order loss frequency value (reference / formula)?"

This was calculated using the α-pinene + ozone rate constant given in Seinfeld and Pandis (2006). The loss frequency value is based on reaction with 700 ppb ozone. We updated the manuscript to state this clearly.

"Fig. 1: An additional panel showing the ratio of Dimer/Total COA, particularly at low COA would be nice to see the predicted dimer contribution in the range of atmospherically relevant OA concentrations."

We decided not to add this panel to avoid redundancy. The ratio could be estimated based on the data shown in panels b & d.

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