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Atmospheric Chemistry and Physics
Discussions

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

Anonymous Referee #2

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Oligomer formation in secondary organic aerosol (SOA) has been a topic of interest over the last decade. Smog chamber experiments have indicated that a large fraction of the organic compounds in the condensed phase may exist in the form of oligomers, yet their various possible formation mechanisms and the degree of reversible dimerization and oligomerization have raised a number of questions and apparent contradictions.

Trump and Donahue present an interesting modeling study looking at the potential influence of reversible dimer formation from monomers of the ozone oxidation of α-pinene as a model system. This work is based on a simplified description of dimerization coming from a single volatility bin in a volatility basis set approach of

SOA formation. Several of the chosen simplifications likely make the model somewhat unrealistic, as indicated by the authors. However, these simplifications allow to focus on the potential effects of the introduced dimerization reactions and show that most experimental constraints regarding SOA formation mass yields and dynamical evaporation behavior can be met even with such a simple model.

The paper is well written and explores interesting questions about the role of reversible oligomer formation. I recommend publication in ACP after consideration of my minor comments given below.

General comments

1. 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 temperature dependence of the dimerization reaction) seems to be important for the model to reproduce the evaporation 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.
2. Dynamic considerations. The dynamical model formulation includes the assumption that the condensed phase is uniform and that no diffusion limitations ex-

ist (page 24612). On the other hand, high molecular mass molecules, such as dimers and oligomers, tend to form highly viscous organic phases at room temperature, 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. Isothermal 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 transport and evaporation of semivolatile molecules while isothermoal 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 dilution and heating cases would be of interest in the context of the discussion on page 24623.

Specific comments

- 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).

  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 into monomers.

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

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

Technical corrections

- Page 24621, line 7: “biomolecular” or rather bimolecular?

- Page 24624, line 1: “is it” should be “it is”.

References

- Camredon, M., Hamilton, J. F., Alam, M. S.,Wyche, K. P., Carr, T., White, I. R., Monks, P. S., Rickard, A. R., and Bloss, W. J.: Distribution of gaseous and particulate organic composition during dark α-pinene ozonolysis, Atmos. Chem. Phys., 10, 2893–2917, 2010.

- Shiraiwa, M., Zuend, A., Bertram, A. K., and Seinfeld, J. H.: Gas-particle partitioning of atmospheric aerosols: interplay of physical state, non-ideal mixing and morphology, Phys. Chem. Chem. Phys., 15, 11441-11453, 2013a.
- Shiraiwa, M., Yee, L. D., Schilling, K. A., Loza, C. L., Craven, J. S., Zuend, A., Ziemann, P. J., and Seinfeld, J. H.: Size distribution dynamics reveal particle-phase chemistry in organic aerosol formation, PNAS, 110, 11746-11750, 2013b.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 24605, 2013.