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Atmospheric
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Discussions

Interactive comment on “Multi-generation gas-phase oxidation, equilibrium partitioning, and the formation and evolution of secondary organic aerosol” *by* C. D. Cappa and K. R. Wilson

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Comments made by S. H. Jathar and A. L. Robinson.

1. SOA O:C in addition to being a function of the carbon number of the precursor, is also dependent on the molecular structure of the precursor. For instance, aromatics have a much higher O:C (Chhabra et al., ACP, 2010) than similar carbon-number n-alkanes (Presto et al., ES&T, 2010). This would imply that different structures (alkanes, alkenes, aromatics) could have very different oxygen addition kernels which could result in very different product O:Cs.

2. Although n-pentadecane is a low-volatility organic, it is not clear how good a surrogate it is for the vast majority of SVOCs and IVOCs, which are very hard to speciate (Schauer et al., ES&T, 1999-2002). In fact, one thing we do know is the vast majority of SVOCs and IVOCs are not normal alkanes. SVOCs and IVOCs are likely a complex mixture of branched, cyclic and lightly oxygenated compounds (O:C between 0.1 and 0.2) that likely behave differently than a normal alkane. Lightly oxygenated SVOCs and IVOCs are smaller carbon-number compounds with volatility similar to hydrocarbons like n-pentadecane and therefore stand a much larger chance of forming SOA with higher O:C.

3. The SOM is fit to SOA data for alpha-pinene and n-pentadecane photo-oxidation. Since the model fits 6 free parameters (too many in my opinion), I suspect that the fit is not very unique, i.e. there are multiple parameter-sets that are able to fit the data. Have the authors checked how different these fits are by predicting the evolution for these fits beyond the smog chamber data?

4. The authors state on page 3333: "IVOCs and SVOCs do not contribute substantially to the SOA burden. If these compounds comprised a significant fraction of the total OA mass, it would be very difficult to obtain mean O:C values as high as have been observed in the atmosphere (Aiken et al., 2008; Ng et al., 2011)." This conclusion is much too strong; this statement is reserved to highly oxygenated SOA. The authors seem to have equated SOA with highly oxygenated OA (LV-OOA factor which is only one component of ambient OA). This is not correct. Ambient OA (and SOA) has a range of O:C. Although in certain environments (esp. rural), very high O:C (LV-OOA) material can dominate the OA budget, in other environments (urban areas where concentrations and human exposures are generally highest) lower O:C OA (SV-OOA and HOA) can be very important. For example, Dougherty et al. (ES&T, 2008) suggest that the mean O:C of the OA in Riverside during SOAR-1 was 0.35 - it does not seem implausible that SVOC and IVOC SOA could contribute significantly to that OA. Figure 4 in Ng et al. (Atmos. Chem. Phys., 2011) presents SV-OOA (also thought to be SOA) as material that has an O:C from 0.1 to 0.6. Given that range, the author’s model does indicate that

first or second generation of products from SVOCs/IVOCs likely contributes to ambient SOA (SV-OOA factor). In fact, it seems entirely plausible that ambient SV-OOA that rapidly forms in urban areas such as Riverside could be a mixture of somewhat lower O:C SOA from SVOC/IVOC and somewhat higher O:C SOA from single ring aromatics (one must also factor in the more oxygenated SOA from regional transport). Other interesting pieces of evidence to consider are that from Miracolo et al. (ES&T, 2010) who show that SOA from SVOC can look like HOA (which is often thought to be exclusively primary emissions). How much of the HOA could actually be SOA? Finally, simple mass balance arguments based on emissions data presented in Donahue et al. (AE, 2009) and elsewhere suggest that SVOC/IVOC emissions are large enough that they will contribute to ambient SOA. Obviously other components and processes contribute to SOA as well, but the paper needs a more balanced discussion of the potential role of SVOC and IVOC in the context of the overall OA/SOA budget. The paper makes a better case that, based on our current understanding of gas phase chemistry, it seems unlikely that SVOC and IVOC rapidly contribute to LV-OOA. However, this seems like a much narrower conclusion than what is stated in the implications section and abstract. I would argue that even that conclusion is not definitive given the significant uncertainty that exists in the oxidation chemistry of more functionalized compounds. The paper would be improved with a more balanced discussion of these issues.

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