**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Modeling of secondary organic aerosol yields from laboratory chamber data" *by* M. N. Chan et al.
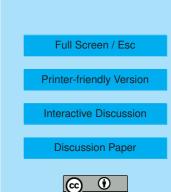
Anonymous Referee #2

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Modeling of secondary organic aerosol yields from laboratory chamber data

Chan et al. take the well studied system of a-pinene ozonolysis (dark, dry, low NOx) and use the established yields of chemical products identified by chemical analysis of previous smog chamber experiments. These yields are considered knowns, and the thermodynamic properties (partitioning coefficient) of each product are estimated. These yields and partitioning coefficients are used to calculate overall aerosol yield (also referred to as aerosol mass fraction) as a function of temperature and organic aerosol loading. In addition to the overall aerosol yield, the detailed product knowledge is used to predict H/C and O/C ratios. These ratios are compared to measured values from aerosol mass spectrometry.

The paper is well organized and addresses an important subject in atmospheric

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aerosols. The modeling of H/C and O/C ratios is novel. Some key results of the work are that O/C ratios are well predicted by the semivolatile partitioning model. H/C ratios are not, and the direction of change in the H/C ratios is different (as organic aerosol loading is increased) than predicted.

Other key results are that when the product yields are known, then the partitioning properties can be estimated from group contribution methods with reasonably good results if the theoretical partitioning coefficients are increased by about 2 orders of magnitude (consistent with other works on this topic). Using a volatility basis set rather than specifying the product identities gives the advantages of (1) better fit to experimental data and (2) avoids highly uncertain multipliers to the partitioning coefficients, but has the disadvantage of giving no predictive model of the elemental ratios or other chemical properties.

Some items that should be addressed prior to final publication in ACP are:

1. The divergence of each model prediction or fit (e.g. the lines in figure 1) from the experimental data, especially at atmospherically relevant aerosol loadings of 0.5-5 ug/m3, should be quantified and discussed. Such a discussion would lead (it seems) to the conclusion that the use of adjustable, fitted parameters (e.g. the volatility basis set approach or another fitted approach) is important to faithful parameterizations at low (atmospherically relevant) organic mass concentrations. These products that dominate aerosol composition at low OM levels are perhaps the ones that are least well characterized by the chemical analyses completed previously.

2. The yields shown in figure 1B stay well above 0.08, even at low aerosol mass loadings (less than 3 μg m-3). This is different than all of the data shown in the multi-author fits of Stanier, Donahue and Pandis 2008 Atmospheric Environment. This paper will be referred to as SDP08 from hereon the interactive comment. See figure 8 of SDP08, which includes data from multiple investigators at using both Carnegie Mellon and Cal Tech chambers. Data other than Schilling et al. (2008) falls below 0.08 at low

aerosol mass fractions. The Schilling et al. (2008) data upon which the fits in Chan et al. rely on at low mass loading are higher than the other datasets.

This is an important item to mention and discuss, because of the potentially large consequences for atmospheric model predictions. Is there new information such that the older (lower yield) data should be ignored? For example, the Schilling et al. data lead to a fitted yield in the 0.01 μg m-3 volatility bin of 0.07, while SDP08 fits the 0.01 and 0.1 volatility bins with yields of 0 (although the uncertainty bounds extend up to yields of 0.05, consistent with nonzero yields in these low volatility bins). The difference is not explained by the different assumed aerosol densities used by Chan et al. and SDP08.

3. Since many temperature dependent model predictions are included, more detail is needed in the text and in table 1 on the equations and/or parameters that drive the temperature-dependent partitioning changes. Methods are included by reference only (line 19, page 9466) but should be explained explicitly.

4. Chan et al. commment on the mismatch between experimental and modeled overall aerosol yields at different temperatures. Perhaps the paper could comment on methods for improving the model representation of the temperature effect. SDP08 includes a method within the volatility basis set framework for fitting an effective dH so that the measured temperature sensitivity is matched by the model. When that is done with the data fitted in that paper, the result is 33 kJ/mol. The resulting changes with temperature are smaller than those calculated by Chan's model, and more in line with the experimental data. Can chemical hypotheses (particle phase reactions or oligomerization) explain this apparent decrease in the effective enthalpy of evaporation?

Minor editorial comments

Line 24, page 9467. Sentence is confusing. I assume this means the terpenylic acid was not reported by anyone until it was reported by Claeys.

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Page 9471, line 26. Possibly rephrase

Typo in figure 2 caption

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 9457, 2009.