

Interactive
Comment

Interactive comment on “Modeling of secondary organic aerosol yields from laboratory chamber data” by M. N. Chan et al.

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We would like to acknowledge the reviewer’s insightful comments and suggestions. Please see our responses below.

Chan et al. take the well studied system of α -pinene ozonolysis (dark, dry, low NO_x) 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

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from aerosol mass spectrometry. The paper is well organized and addresses an important subject in atmospheric 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.

We calculate the mean absolute fractional error vs. data for the models over the whole range of organic mass loading. We have added the following sentences in the revised ms.

“Overall, the volatility basis set produces the smallest fitting error of SOA yield prediction over the whole range of organic mass loading (mean absolute fractional error, err

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= 0.1572) compared to the $K_p \times 1$ case (err = 0.1688) and the $K_p \times 100$ case (err = 0.1598). ”

2. The yields shown in figure 1B stay well above 0.08, even at low aerosol mass loadings (less than $3 \mu\text{g m}^{-3}$). This is different than all of the data shown in the multiauthor 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 $0.01 \mu\text{g m}^{-3}$ 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.

Shilling et al. (2008) have carefully examined and explained the difference between their results and literature data in their work. They suggested that under the assumption that both their data and the literature data are correct, there are poorly understood factors influencing particle yield in chamber SOA experiments.

In this work, we select the data of ozonolysis of α -pinene under dry, dark conditions in the presence of ammonium sulfate particles at temperature near 293K for optimal fitting. Literature data from some other studies are not included because the experiments were conducted at higher temperatures (301.2K-309.9K), no seed (nucleation experiments), or no OH scavenger (Griffin et al., 1999, Cocker et al., 2001, Presto et al., 2005, Song et al., 2007).

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Stainer et al (2008) observed the largest confidence interval (CI) or uncertainty to occur under 2 conditions: at less than $1 \mu\text{g}/\text{m}^3$ and at temperatures below 20°C . They suggest that the cause of both of these areas of large uncertainty is a relative scarcity of data. The difference in the mass yield of the 0.01 and 0.1 volatility bins is likely attributed to the difference in the number of data available at low organic mass loading for optimal fitting.

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.

We calculate the mean absolute fractional error between the measured and predicted SOA yields at different temperatures. We have added more information about how to calculate the temperature dependence of the K_p of the products. We also calculate the enthalpy of vaporization of major products using the group contribution method developed by Pankow and Asher (2008). By plotting the estimated vapor pressure of the product against the temperature, the ΔH_v of the product can be estimated from the slope of the line following the Clausius-Clapeyron equation. The estimated ΔH_v value of pinonic acid, hydroperoxide, terpenylic acid, pinic acid, and pinonaldehyde are 81.72 kJ/mol, 83.99 kJ/mol, 76.73 kJ/mol, 99.89 kJ/mol, and 69.53 kJ/mol, respectively. This information has been added in the revised ms.

“The temperature-dependent vapor pressure of compounds can be estimated using the group contribution method developed by Pankow and Asher (2008). The temperature dependence of the structural groups ($b(T)$) are assumed to follow $b(T) = B_1/T + B_2 + B_3T + B_4\ln T$. The B coefficients are obtained by optimal fitting to a number of compounds. In the calculation of the K_p , it is assumed that the activity coefficient is unity and the molecular weight of the product is taken as the mean molecular weight of the surrogate mixture. The α_i values determined at 293 K are assumed to be constant over the temperature range studied (273–313 K). The enthalpy of vapor-

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ization, ΔH_v of the products can also be estimated by the group contribution method. By plotting the estimated vapor pressure of the product against the temperature, the ΔH_v of the product can be estimated from the slope of the line following the Clausius-Clapeyron equation (see Appendix A). Estimated values of ΔH_v of major products are listed in Table 1.”

4. Chan et al. comment 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?

As pointed out by the reviewer, a single effective enthalpy of evaporation is fitted. The c^* of volatility bins obeys the Clausius-Clapeyron equation at different temperatures. It is not surprising that the modeled results are well matched with the experimental data. On the other hand, in the product-specific model, the temperature dependence of the vapor pressure of major products is estimated using the group contribution method (Pankow and Asher, 2008). In this approach, a reliable vapor pressure estimation method is required in order to estimate the temperature effect on the K_p of the products. Uncertainties in the vapor pressure estimation using the group contribution method at different temperatures may explain why the predicted SOA yields have a larger deviation from measured ones at lower temperatures.

“In the product-specific model, the temperature dependence of the vapor pressure of major products is estimated directly using the group contribution method (Pankow and Asher, 2008). In this approach, uncertainties in the vapor pressure estimation method will lead to uncertainties in data fitting. Uncertainties in the vapor pressure estimation

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using the group contribution method is likely one factor contributing to a relatively large deviation between measured and predicted values at lower temperatures in the present study.”

As discussed above, using the group contribution method developed by Pankow and Asher (2008), we also calculate the ΔH_v of the ester, which is formed between pinic acid and hydroxy pinonic acid (Müller et al. 2008), as 147.99 kJ/mol, which is larger than that of major products. The estimated ΔH_v of the ester derived from the Pankow and Asher (2008) model is slightly large. Donahue et al. (2006) have reported that measurements and estimates for specific low-volatility compounds (40 – 110 kJ/mol), with higher values corresponding to lower-volatility species. This suggests that particle-phase reactions may not be able to explain the small fitted effective ΔH_v (33 kJ/mol).

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.

The sentence has been changed.

Page 9471, line 26. Possibly rephrase

The sentence in question has been rewritten.

Typo in figure 2 caption

The typo has been fixed.

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

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