

Interactive comment on “Temperature dependence of secondary organic aerosol yield from the ozonolysis of β -pinene” by C. Stenby et al.

Anonymous Referee #3

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General Comments

As its title appropriately states, this paper focuses on temperature dependence of secondary organic aerosol yields from ozonolysis of beta-pinene. It is new in that the bulk of the previous work focused on this topic has been computational rather than experimental. This previous work is appropriately cited. The topic is appropriate for publication in ACP. It is well written and interesting, and I see no issues with their experimental approach, the amount of detail on experiments contained in the manuscript, or the mathematics/units used. However, there are some issues with the analysis (and accompanying conclusions) that preclude me from recommending publication at this time. These issues are outlined specifically below.

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Specific Comments

Page 10278, lines 21-24. I find it a little inappropriate to state that the system design avoids 'unnecessary high reactant concentrations' when the concentrations that are being used (600 ppb to 11 ppm for beta-pinene and 200 ppb to 2.4 ppm for ozone) are far in excess of what is atmospherically relevant.

Page 10280, last line. Their expression that the amount of beta-pinene lost is proportional to the amount of ozone lost (factor of 1.35) only holds when it is assumed that OH is in steady state. This should be stated explicitly.

Section 3.2. In this section, I would think it very appropriate to discuss the limitations of the two-product model. In fact, I feel that the authors put too much credence in this model. The derived parameters are only fitting parameters and do not really give any indication about the true product distribution. This needs to be stated explicitly in the manuscript.

Page 10282, line 21. What are these test calculations used to get starting values of the two alphas? More detail is needed here. What is the basis of these calculations?

Equation (9). Is the denominator the measured (i.e., data) standard deviation of the yield at a given temperature T for a given experiment i? If so, the letter y should probably appear in the subscript. If it is not this value, it needs to be defined.

Page 10285. A concentration of 250 micrograms per cubic meter of SOA is highly unrealistic when considering the true atmosphere. The authors would be better served doing a comparison at several lower, more representative concentrations.

Page 10286 and conclusions. Here is where I believe the biggest problem with the analysis of the authors lies. The authors alter their partitioning coefficients according to the Clausius Clapeyron equation using constant enthalpies of vaporization from a previous modeling study. They then use these temperature-adjusted partitioning values in a residual minimization technique to derive temperature-dependent alpha values.

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The implicit assumption made is that the products that go into the aerosol phase are the same over the entire range of temperatures. Is this valid? Where is the support for that assumption? Are there any product studies that would verify this claim?

I would actually think that the product distribution would change remarkably as a function of temperature due to more volatile species condensing into the aerosol at lower temperature and because of a change in reaction rate constants of both gas- and particle-phase reactions. Changes in the average partitioning coefficient are due to both product mix (more species) and temperature changes (change in vapor pressure).

I agree that both partitioning coefficients and alphas should be temperature dependent. However, I do not agree with the approach of the authors for estimating the temperature dependence of the alpha values. Instead, I recommend deriving new alphas and new partitioning coefficients for each temperature. These partitioning coefficients could then be compared to those calculated using Clausius Clapeyron as a means to estimate if the product distribution changes with temperature. Of course, it would be best to have speciation data, but that does not appear to be a viable option.

In addition, the authors should stress that this is simply a fitting technique. While their results imply certain facts, they can not be truly proven in this manner. The alpha and partitioning constant values give no indication whatsoever about the true products that constitute secondary organic aerosol.

Technical Corrections

Font in Table 1 is rather small.

Symbols in Figure 3 are also rather small.

Page 10276, line 23. Comma needed before the beta.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 10275, 2006.