Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

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This paper presents the results of an experimental study to investigate the dependence of secondary organic aerosol (SOA) yields from the ozonolysis of beta-pinene over the temperature range 263-303 K, and interpretation of the results using a classical two partitioning product model. The results demonstrate an "oscillating" dependence of the observed yields on temperature, indicative of the influence of a number of factors over and above partitioning product volatility considerations. The resultant main conclusion of the work is that it is important to consider the effect of temperature on the chemical pathways occurring in the gaseous and condensed phases. The paper is a useful and interesting contribution to the literature in this subject area, and should ultimately proceed to full publication in ACP. However, the authors need to consider a number of points before this can be recommended.

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Page 10280, final paragraph: The discussion of the additional removal of beta-pinene by reaction with OH radicals formed from the ozonolysis reaction is important, as it almost certainly leads to additional loss of the terpene to generate products which have a lower propensity to make SOA. However, the fact that kOH $>>$ kO3 is not justification that all the OH radicals will react with beta-pinene - it is the competition of "OH + beta-pinene" with "OH + other species in the system" which is the key. Whereas the reasoning that D[beta-pinene] = 1.35 (D[ozone]) is probably correct for the experiments with beta-pinene in excess, it may be more of an approximation for experiments with ozone in excess, because OH may react with other species as [beta-pinene] tends to zero. The authors may wish to perform some simulations to reassure themselves on this point.

Although the OH + beta-pinene products are less good at making SOA, the statement that "SOA yield from OH reactions are (is?) negligible" may be a bit extreme. If the OH + beta-pinene products are generated in the presence of a reasonable concentration of pre-existing aerosol (the formation of which has been promoted by the ozonolysis chemistry), then a proportion of them will partition into the condensed phase, even if the OH-initiated chemistry in isolation generates negligible amounts of SOA.

Page 10282. fitting procedure: The procedure used for fitting the data to the two product model seems very convoluted. Is it not possible to fit the data at each temperature separately to obtain the two pairs of alpha and Kom values, rather than relying on previous modelling results? Furthermore, it is stated that the procedure makes use of DvapS and Tb values from Jenkin (2004) and the lumping procedure of Bian and Bowman (2002). The Jenkin study considered 200 partitioning species, for which the above properties were only reported for very few examples. Where do the values used by the authors come from, and which particular species were considered?

Some general comments about the use of the two product model, and its approximations, would also seem warranted. Although the method has proved to be a useful way of interpreting smog chamber data, the derived yield and partitioning parameters do

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not represent reality, being a gross oversimplification of what is actually happening. In some respects, the results of this paper show that this is the case.

Pages 10283-10286, Results and Discussion: The presented results are discussed in relation to the results of previous experimental and modelling studies. Although some attempt is made to outline differences in experimental procedures and assumptions adopted in the various studies, these could perhaps be stated and discussed more clearly, as certain features are not pointed out. The current study considers experiments carried out in the absence of an OH scavenger and seed aerosol, using an SOA density of 1.2 g cm-3. As with most earlier studies, Hoffmann et al. (1997) assumed a density of 1 g cm-3, as discussed on page 10284, but also used ammonium sulphate seed particles. Can this effect the comparison?

As also indicated on page 10284, the study of Griffin et al. (1999) used 2-butanol to scavenge OH radicals. Whereas the use of the similar scavenger, 2-propanol, has been shown to reduce SOA yields (Docherty and Ziemann, 2003), this is in comparison with using cyclohexane as a scavenger, and results from influences of changing the [HO2]/[RO2] ratio. When comparing with using no scavenger at all, the additional fact that beta-pinene is only removed by reactions with ozone in the Griffin et al. (1999) studies also needs to be considered. This will have a compensating increasing effect on the yields. Note that Griffin et al. also assumed an SOA density of 1 g cm-3, and used an ammonium sulphate seed aerosol.

The comparison with the modelling results of Jenkin (2004) should also recognise that the model was optimised on the basis of reported data which assumed an SOA density of 1 g cm-3. If the reference experiments had assumed 1.2 g cm-3, the Jenkin model would predict yields which are a factor of 1.2 greater. However, the temperature-dependence illustration of Jenkin (2004) assumed the presence of cyclohexane as an OH scavenger, such that absence of a scavenger would have a compensating lowering effect, as also demonstrated for 298 K in that paper.

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

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