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Comment

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

C. Stenby et al.

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We thank the referees for the very useful comments and suggestions, and we apologize for the delay in publishing a response. As explained in an earlier interactive comment (Atmos. Chem. Phys. Discuss., 6, S7376-S7377, 2007), we have re-written and enlarged the manuscript for publication as a new, more comprehensive discussion paper in ACPD: Atmos. Chem. Phys. Discuss., 7, 2091-2132, 2007 www.atmos-chem-phys-discuss.net/7/2091/2007/

In the new discussion paper, all referee comments on the old version have been taken into account. Point-by-point responses to the individual comments are given below:

Referee #1 Page 10280, final paragraph. We agree that the assumption, that all OH radicals react with beta-pinene, should be differently justified. For all experiments, also

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those with ozone in excess, not more than 3.9% of the beta-pinene has reacted in the flow reactor. This leads to the conclusion that beta-pinene is always in excess compared to the ozonolysis products. To be an effective OH scavenger a product should have a reaction constant at least 25 times higher than the reaction constant of beta-pinene. We assume a small fraction of the reacted beta-pinene produces products with such high reaction constants. Therefore the amount of OH radicals that react with other species in the system is negligible. The argument that kOH$\gg$kO3 justifies that kO3 is the limiting rate constant. This will be corrected in the revised manuscript.

To our knowledge the amount of SOA produced from OH reactions when SOA particles from ozonolysis are already present has not been assessed. A possible method would be the use of self-seeding suggested by Huff Hartz et al. [2005]. The idea is to produce SOA particles from ozonolysis of beta-pinene with a known particle size distribution. When the ozonolysis has come to an end, an addition of OH-radicals could then reveal how much SOA mass is produced from OH oxidation beta-pinene with SOA particles already present.

Page 10282, fitting procedure. We have performed the suggested calculations fitting the temperatures individually. The results are presented in the new discussion paper: Atmos. Chem. Phys. Discuss., 7, 2091-2132, 2007 www.atmos-chem-phys-discuss.net/7/2091/2007/ From Jenkin [2004] we have adopted the ΔvapS and Tb values for the relevant species reported: nopinone, pinalic-3-acid and pinic acid. We have estimated that acetone and formaldehyde have the same values as nopinone. Unfortunately a mistake in the calculations have resulted in B1 being too high, re-calculation has showed that it should be 4976 K. This was clarified and corrected in the revised manuscript.

The limitations of the two-product model have been clarified in the revised manuscript.

Pages 10283-10286, Results and Discussion. The differences in experimental procedure and assumptions between the previous studies and our study have been clarified

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in the revised manuscript. In the case of beta-pinene ozonolysis the use seed aerosol should only affect the yield when very low amount of particulate mass (Mo) is produced. The lowest total number of particles we have measured is 3.4*105 cm-3 for Mo = 10.1 μg m-3 (see Table 1 in the manuscript). We assume that this particle number should be no restriction to the condensation of oxidation products. This has been added to the revised manuscript.

Page 10284. We agree that the reduction of SOA yield by the use of propanol as a scavenger [Docherty and Ziemann, 2003] is in comparison with cyclohexane as a scavenger. It will be more correct to cite Keywood et al. [2004] who conclude that they expect the SOA yield from beta-pinene ozonolysis in the study by Griffin et al. [1999] to be underestimated. This has been changed in the revised manuscript. The experimental procedure and assumptions used by Griffin et al. [1999] has been clarified in the revised manuscript.

The intention with the comparison with the modelling study by Jenkin [2004] is mainly to show that the model predicts a linear dependence of SOA yield on temperature. To clarify the different assumptions applied in our study and in the study by Jenkin [2004] the comment by the referee has been incorporated in the revised manuscript.

Referee #2 1. In the atmosphere and in chamber studies aerosol particles have been shown to be subject to aging. Two processes have been identified: the oxidation of the aerosol particles leading to higher density and more CCN activity (more polar compounds) and polymerisation leading to displacement of the partitioning equilibrium towards the particulate phase. It is important to notice that these two aging processes take place in the particle phase, thereby only affecting the species that have already partitioned. In the manuscript we show (Figure 3) that the yield from a chamber study reported by Hoffmann et al. (1997) is up to 40% higher than the yield we see in the flow reactor. We state that this discrepancy could be due to aging. It has in the revised manuscript been clarified how aging increases yield. The humidity have been found to increase yield for other monoterpenes [Jonsson et al., 2006] and decrease yield

for beta-pinene [Bonn et al., 2002], when an OH scavenger is applied. In the revised manuscript we have published results on the humidity dependence of the SOA yield for beta-pinene: Atmos. Chem. Phys. Discuss., 7, 2091-2132, 2007 www.atmos-chem-phys-discuss.net/7/2091/2007/ 2. If the temperature-dependence of SOA yield were determined by partitioning effects only, we would expect a linear dependence on $1/T$ according to Clausius-Clapeyron. Thus every significant deviation from linearity indicates that different temperature dependencies of different reaction pathways in the gas phase or in the condensed phase play a role. Reliable discrimination and description of gas phase and condensed phase effects will require advanced experiments and kinetic formalisms that enable a separation and characterization of reactions in the gas phase, at the surface, and in the condensed phase. 3. To our knowledge Takekawa et al. suggested that multiple reaction steps and pathways in the gas phase play a role in determining the different SOA yields from different VOC. This is consistent with (and thus in support of) but not directly related to our suggestion, that different temperature dependencies of multiple reaction pathways influence the temperature dependence of SOA formation from a single VOC.

Page 10279, line 9. The flow rate of the sheath air is decreased to be able to measure larger particles (up to 300 nm). We made a few experiments with different sheath air flow rates to test if this influenced the results. This was not the case.

Page 10284 and 10280. See answer to comment by referee #1.

Page 10279, line 16-18. The assumption is that the particles trapped in the particle filter in the sheath air loop will evaporate if the sheath air is not in equilibrium with the particle phase.

Page 10280. We calculate the amount of reacted beta-pinene as 1.35 times the amount of reacted ozone (line 22).

Page 10286, 3rd paragraph and Table 3. We agree that particle phase reactions do not change the stoichiometric coefficients. The parameters reported in Table 3 are

only fitting values to use for modellers who are already using the two product model. One of our key messages is that the two-product model is insufficient for predicting the temperature dependence of SOA yield. This has been clarified in the paper.

Page 10283, line 11-12. The particle number is believed to decrease with decreasing temperature because less of the nucleating species is produced in the ozonolysis. Another explanation could be that the particles did not grow large enough to be detected by the DMA, but this seems to be unlikely because the modal diameter simultaneously is increased. This has been included in the revised manuscript.

Page 10285, line 9-23. The difference in humidity between the compared experiments has been emphasized in the revised manuscript.

We have stated that heterogeneous reactions are expected to accelerate with increasing temperature. When the gas phase partitioning is decreased with increasing temperature the polymerisation reactions are simultaneously accelerated. In this way the SOA yield can be increased as by the change from 283 K to 293 K. In the manuscript we have stated that the heterogeneous reactions are expected to accelerate with increasing temperature. To investigate how the temperature affects the production of polymers, we need to know how the production of monomers (in the gas phase) is affected. This is not the scope of this study.

All technical corrections have been taken care of.

Referee #3 Page 10278, line 21-24. We agree that the statement that the setup avoids "unnecessary high reactant concentrations" gives a wrong impression. What we actually meant was that the reaction time was maximized within the constraints imposed by the set-up. This means that the concentrations were as low as possible. This has been clarified upon revision.

Page 10280, last line. The assumption that OH is in steady state has been added to the revised manuscript.

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Section 3.2. The limited applicability of the two-product model was actually intended to be a key message of the manuscript. This has been clarified accordingly.

Page 10282, line 21. The starting values for the two alphas were found by manually fitting the two-product model to the data-points. As illustrated by a lack of correlation with the numerically determined best-fit values, and confirmed by test calculations, the selection of starting values had apparently no influence on the fitting results. This has been clarified in the revised manuscript.

Equation (9). The letter y has been added to the subscript of the denominator.

Page 10285. We do agree that 250 μg m-3 is not atmospheric relevant. Nevertheless, we have chosen this value because it is under all conditions well in the saturation range where concentration differences play a minor role, thereby enabling robust comparisons, and providing mechanistic information (as is usually the case for extreme conditions). We have mentioned this in the revised manuscript.

Page 10286 and conclusions. We see and agree with the referee's point. We have performed the suggested calculations fitting the temperatures individually. The results are presented in the new discussion paper: Atmos. Chem. Phys. Discuss., 7, 2091-2132, 2007 www.atmos-chem-phys-discuss.net/7/2091/2007/ Compared to Table 3 in the manuscript there are indeed substantial changes of the Kom values, as expected by the referee.

We fully agree the the two-product model fit parameters are no more than fit parameters, and that temperature-related changes of reaction channel branching ratios may change the composition of the lumped species and therefore also the average Kom values. We have explicitly clarified this in the revised manuscript, and thank the referee again for this as well as all other suggestions.

All technical corrections have been taken care of.

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