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

Anonymous Referee #2

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This paper presents the results of an experimental study to investigate the temperature dependence of secondary organic aerosol (SOA) yields from the ozonolysis of beta-pinene over the temperature range 263-303 K, under nominal dry and humid conditions, and interpretation of the results using a classical two partitioning product model. The results are rather unusual in that they demonstrate a strongly "oscillating" (but on average negative) dependence of the observed yields on temperature under dry conditions, but a smooth positive temperature dependence under humid conditions. These observations suggest that a number of factors over and above partitioning product volatility considerations influence SOA formation. The resultant main conclusion of the work is that it is important to consider the effect of temperature and humidity on the chemical pathways occurring in the gaseous and condensed phases. The paper is an interesting discussion paper in this subject area. However, the authors need to address and respond to a number of points before a revised version of this paper is suitable for full publication in ACP.

First, it is noted that this is a revised version of a paper previously submitted to ACPD. Although the authors did not respond formally to the referee comments of that paper, it is clear that changes have been made in this version in an attempt to clarify and enlarge some of the issues raised by the referees previously.

In the first paper, the authors referred to "a two-product model based on detailed gas phase chemistry Jenkin (2004)", which I took as referring to the two-product model developed in the authors' own work, informed by the detailed chemistry and results presented by Jenkin (2004). However, it is now clear that the authors are under the erroneous impression that Jenkin (2004) developed and applied a two-product model for SOA formation. In practice the work of Jenkin was using a 200-product model to simulate the yields and detailed composition of the aerosol from alpha- and beta-pinene. The gas phase mechanism included many temperature dependent reactions, and the partitioning of each product was assigned a specific temperature dependence. As a result, the discussion in the present paper consistently misrepresents the work of Jenkin (2004), even stating that products were lumped on the basis of their vapour pressures to develop the two-product model (section 2.7.2). This is simply not true, and suggests that the authors should re-read the paper carefully. This would also help with making the first paragraph of that section clearer, in which several statements are made but not really clarified or explained. Importantly, the illustrative temperature-dependence simulations in Jenkin (2004) (not the main thrust of the paper) specify the presence of cyclohexane as an OH scavenger. Are the results directly comparable with the present experimental results performed without a scavenger?

Section 2.4: 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.

The main conclusion of this work is that complex temperature and humidity dependences of elementary reaction rates and mechanisms account for the unusual observations. At the bottom of page 2108, the important point is made that constant RH with changing temperature results in a strong variation in absolute water vapour concentration. Given that a gas-phase reaction competition would depend on the absolute concentration, it should perhaps be pointed out that the positive temperature dependence under "humid" conditions could actually be a water vapour concentration dependence. I suspect this is what the authors are getting at in this paragraph, but it could be stated more categorically.

It seems somewhat surprising that the present results are not discussed in relation to those of Bonn et al. (2002), performed in the same apparatus. In section 1, it is stated that Bonn et al. found that the presence of water vapour (at 295 K) reduced SOA production from beta-pinene (on a volume concentration basis). However, the present results show that the SOA yield close to that temperature is at least as great under humid conditions. This discrepancy must be discussed and, if possible, explained.

Also mentioned in the introduction is that poor understanding of the temperature dependence of SOA formation may be the key to model-measurement discrepancies in the free troposphere. The present results show a much milder (average) negative temperature dependence than reported by Sheehan and Bowman (2001) under dry conditions, and a positive dependence under humid conditions. Implementation of the present results would therefore make the model-measurement discrepancies worse, indicating that there are still other factors to be taken into account. Perhaps this should be stated in the final paragraph.

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