**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Distribution of gaseous and particulate organic composition during dark α-pinene ozonolysis" *by* M. Camredon et al.

Anonymous Referee #1

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This paper presents the results of a detailed mechanistic examination of the chemistry leading to the formation of secondary organic aerosol (SOA) from the ozonolysis of alpha-pinene in both the absence and presence of an OH radical scavenger in the EU-PHORE chamber. The evolution of the experiments is characterised using a suite of instrumentation, including measurement of the distribution of organic compounds in the gaseous phase (using CIR-TOF-MS, GC-MS and HPLC) and in the condensed phase (using ESI-MS and LC-MSn). The experiments are simulated using a detailed chemical model, in which the gaseous phase chemistry is based on the Master Chemical Mechanism (MCM), and the absorptive partitioning of monomeric organic products is represented using the Pankow model, with species vapour pressures calculated using the Myrdal and Yalkowsky method. The combination of methods is found to give a very reasonable description of the system, and some discussion is given to the sensitivity of

the simulated mass loading of SOA formed to the method used to calculate the species vapour pressures, and to the omission of condensed phase chemistry in the model. The possible occurrence of a series of accretion reactions is then examined based on the simulated distribution of monomers in the condensed phase. The inferred dimer mass distribution resulting from each reaction type is compared with that observed in the corresponding mass range to draw conclusions about their relative roles.

The paper is clearly written and addresses a topic which is entirely appropriate for publication in ACP. The results of the experimental studies are valuable, and provide a good level of validation for the modelling work, which is performed to a high standard. This paper should proceed to full publication in ACP, subject to consideration of the points outlined below. Most of these points relate to the sensitivity of the simulations to model assumptions. Although the points are relatively minor, the paper would be improved through slightly more discussion of these sensitivities, and possibly a slightly fuller presentation of their potential impacts.

Specific comments:

The combination of the MCM chemistry and the applied vapour pressure estimation method (based on Myrdal and Yalkowsky coupled with Joback boiling temperatures) in the simulations allows the observed SOA mass loadings to be recreated well, although slightly overestimated. On page 27852, it is commented that a factor of 2 increase in the vapour pressures would actually lead to a good agreement. Given the uncertainties in vapour pressure estimation methods, this is apparently an exceptionally good result. At a number of points in the paper, however, the possible impacts of omissions in the model are mentioned or discussed. To my mind, it seems that each of these omissions would increase the simulated SOA mass loading, such that a systematic increase in the vapour pressures by much greater than a factor of 2 would actually be required to get good agreement if all the omissions were treated rigorously.

The first such point is on page 27847, where it is indicated that the theoretical studies of

Peeters and co-workers have identified possible alternative pathways which may have a significant impact. Given the nature of the pathways generally involves isomerisations to give products with a larger number of polar substituents, this would presumably tend to make the product distribution less volatile. Does the model-measurement comparison allow any view to be formed in relation to the importance of these omitted pathways through identification (or not) of the masses corresponding to the postulated products? It would be good to be able to either confirm of refute the pathways (e.g., in section 5.1 or section 5.2).

The second instance is on page 27848, where it is commented that "No chemical reactions were implemented in the condensed phase." The possible impact of this omission is then considered Section 4.1, through parameterised formation of non-volatile products of condensed phase reactions. Presumably, the relatively small effect (about a factor of 1.5) reflects the fact that a relatively large proportion of the oxidised organic material is already present in the condensed phase in the base case simulations. The impact of including the condensed phase chemistry would no doubt be much greater if one of the alternative methods of vapour pressure estimation (yielding systematically higher vapour pressures) had been used in the base case simulations – or at the least if the factor of 2 increase mentioned in section 4.2 was applied. It would therefore seem important to point out that the perceived impact of the condensed phase chemistry is sensitive to the applied vapour pressure estimation method, and probably to demonstrate this. I also note that the mass distribution presented in Figure 6 seems to suggest that the mass contribution of the detected dimers is somewhat greater than that of the detected monomers, such that the importance of the condensed phase chemistry is greater than the sensitivity test in section 4.1 implies.

The consideration of the impacts of the dimer reactions on the mass distribution in section 5.3 is a very nice approach, and the discussion of this is interesting and informative. The results provide some good support for the role of the esterification reactions and possibly hint at a role for one or more of the other reactions to account

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for the highest masses. On page 27865, it is commented that hemiacetals and peroxyhemiacetals might be converted back to monomers during ESI-MS analysis. Can the authors comment further on this, or provide a reference or supporting material? It would seem to be a very important point, not only for quantification of the role of these reactions, but also because the decomposition might lead to different monomers via a concerted rearrangement.

Page 27844, line 23: An upper limit mixing ratio for NO is provided in support of the statement about NOx-free conditions. Owing to the presence of 100 ppb ozone, and absence of light, NOx would be expected to be entirely NO2. A quantification of NO2 should therefore more appropriately be provided.

Technical corrections:

Figure 6, lower panel: the ESI-MS intensity scale appears to have a typo.