

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

Anonymous Referee #2

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This paper presents results from a combined experimental/modeling study of secondary organic aerosol (SOA) formation from α -pinene ozonolysis. Measurements are made in the EUPHORE chamber, and are compared to simulations using the Master Chemical Mechanism (MCM). This study differs from previous chamber-MCM comparisons [e.g., Jenkin, ACP, 4:1741] in that (1) a different vapor pressure estimation technique is used; (2) oligomer formation is included using a kinetic treatment; and (3) comparisons extend beyond just a few quantities (total SOA loading, select gas-phase species) to include a wide range of gas- and condensed-phase products. This last difference is particularly novel, in that chemical ionization (CI) and electrospray ionization (ESI) mass spectra are predicted based on the MCM results and are compared directly to experimental measurements. Extremely good agreement is found between measurements and the simulations of SOA loading, and agreement of gas-

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and condensed-phase composition is also reasonably good. From these results, some mechanistic conclusions (such as the importance of esterification reactions) are made. This is a useful study, and the work is certainly worthy of publication in ACP. It is well-written and clear, and the figures and level of technical detail are appropriate. However, I would recommend that some of the results be discussed in more detail, particularly with regards to potential sources of error in the model. Specific comments are discussed below.

- As the authors point out, the choice of vapor pressure estimation method is a critical determinant of calculated SOA loading. As discussed by other reviewers, the method chosen (and used to obtain the results shown in Fig 3) may substantially underestimate SVOC vapor pressures; this would have the effect of masking other deficiencies in the model. An investigation into possible offsetting factors would seem to be warranted. Examples include the formation of low-volatility species (such as acids) via unidentified mechanisms, or accretion reactions involving the heterogeneous uptake of gas-phase species. In the current study, oligomer formation only occurs by reaction of particulate SVOCs, so relatively volatile species could not be incorporated into the aerosol (which is believed to happen for molecules such as glyoxal). On the other hand, the model does not include the loss of SVOCs to the chamber walls, which might significantly lower predicted loading (Hildebrant, ACP 9:2973). It would be helpful to include these in the model, or at least discuss what effects these processes might have on modeled results.

- the doubling of SOA mass when condensed-phase reactions (forming NVOCs) are assumed to occur rapidly suggests that the average SVOC initially formed from α -pinene ozonolysis is partitioned between the gas and particle phases roughly equally. Is there any experimental evidence for this? Some comparison of the gas-phase (CI) and condensed-phase (ESI) chemical composition measurements would seem to be worthwhile. I do not see any obvious correspondence between the two (Figures 5 and 6). This could be a result of oligomer-forming reactions having gone to completion; but

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in that case, the aerosol would no longer be composed of semivolatile organics.

- there is little discussion of the time dependence of individual species (mass spectrometric peaks) in the gas phase. (Time-dependent measurements cannot be made of the particulate organics, given that only one filter sample is made per experiment.) If different peaks in the CI measurements or simulated CI mass spectra exhibit significant differences in their time evolution, the model-measurement comparisons for these species would provide a powerful test of the MCM description of α -pinene ozonolysis.

- p. 27858, 1st paragraph: It would seem that a third possibility is that these compounds simply are not formed, contrary to the model predictions.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 27837, 2009.

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