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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Particle mass yield in secondary organic aerosol formed by the dark ozonolysis of α-pinene" *by* J. E. Shilling et al.

J. E. Shilling et al.

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Response to Anonymous Referee 2

We thank the reviewer for the helpful comments. We address the specific concerns of the reviewer in the responses below.

Reviewer Comment: In my opinion, Table 4 is unnecessary. The findings are well-summarized in the text, and I find the table somewhat confusing.

Response: We feel that Table 4 is important because it shows the control experiments undertaken and visually organizes the information for the reader. These experiments are very important for ruling out alternative, reasonable, but ultimately unlikely explanations of our observations. Since our yields are higher than some of the literature data, it is very important to emphasize the steps we have taken to ensure that our data was

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free of experimental artifacts.

Reviewer Comment: Table 5 adequately describes the modeling done to confirm that gas-phase mixtures should have been similar across experimental modes. I recommend omitting Figure 6, which is a bit busy and confusing, and is used to make the same point.

Response: Figure 6 is important for emphasizing the differences in ROO chemistry that are possible because of different chamber configurations. A pressing issue for the larger community is the possible important role of peroxides in forming SOA particle mass (Docherty *et al.*, 2005). Figure 6 shows that the peak ROO concentrations and hence any possible chemistry deriving from reactions involving ROO radicals occur on different timescales for different chamber configurations.

Reviewers Specific comments:

Reviewer Comment: Page 17941, line 5: Based on Fig. 5, it looks like one can only really claim equivalence of AMS/SMPS mass loading measurements up to 2 ug/m3. Can you comment on the discrepancy already apparent at 4ug/m3? Is this already the effect of the (unmeasured by SMPS) tail of the size distribution?

Response: For the data shown in Figure 5, there was no evidence of the size distribution tailing out of the SMPSs measurement range, as was evident at higher loadings. As an example, Figure S1, Panel C shows the size distribution for the experiment on 1/24/2007 (organic loading 6.97 μg m^{-3}). The size distribution lies almost entirely below mobility diameters of 500 nm, which was the cutoff of the SMPS system under the study conditions.

Although there are two data points on the graph at loadings greater than 4 μg m^{-3} in which the AMS measures larger loadings than the SMPS, there are not enough replicate measurements at these loadings to assess whether this trend indicates an instrumental bias or whether the trend is random error. Based on the agreement of the AMS and SMPS data at lower loadings, for which more replicate measurements are available, and the lack of any obvious experimental artifacts as observed at higher loadings, we feel the discrepancy is likely due to random error. In the worst case (for data show in Figure 5), the SMPS data are 28% lower than the AMS data. This level of accuracy is similar to what has been reported in the literature for comparison of the AMS to other aerosol measurement techniques (Takegawa *et al.*, 2005).

Reviewer Comment: Page 17941, line 7: Suggest adding a sentence describing why you chose a different OH scavenger.

Response: We initially used 1-butanol because it was readily available in a higher purity ($>$99.7%) than 2-butanol ($>$99%).

Reviewer Comment: Page 17941, line 17: Suggest rewording the first sentence of this paragraph.

Response: We have reworded the sentence at the reviewers suggestion.

Updated Text: A potential concern in comparing yields among experiments is that the gas-phase chemistry of the dark ozonolysis of α-pinene could change among different experimental configurations and conditions, principally because of second-order reactions of peroxy radicals.

Reviewer Comment: Page 17941, line 27: Suggest replacing the results given with a more descriptive phrase: maybe, the relative concentrations of species across different experimental modes

Response: We have made the change the reviewer suggests.

Updated Text: Although the model omits SOA particle growth and gas-phase species scavenging to the walls and although the MCM is incomplete as indicated by the absence of species of sufficiently low volatility to form SOA (Jenkin, 2004), the relative concentrations of species across different experimental modes (Table 5) nevertheless show that the composition of the predicted gas-phase products should be basically similar in the continuous-flow and batch modes for ozone concentrations of 300 ppbv.

Reviewer Comment: Technical Corrections Page 17936, line 27. The cited numbers dont seem to match the data shown in Fig. 1.

Response: Figure 1 shows the approach of the chamber to steady state. The initial transient period (t $<$ 600min) must be ignored as the system has not yet reached equilibrium. The average loading for steady-state data shown in Figure 1 (t$>$ 600 min) do indeed correspond to the stated numbers. In the revised manuscript, we added a phrase clarifying that the cited numbers correspond to the data once steady state is reached.

Updated Text: This example corresponds to the steady-state portion of the time traces of the data shown in Figure 1.

Reviewer Comment: Page 17964, last sentence of Table 2 caption: replace Equations with Model Fits.

Response: We have made the change the reviewer suggests.

Updated Text: Model Fits are plotted in Figure 3.

Reviewer Comment: Page 17959, Table 5 caption: add a bit more description of results,; i.e., Results are shown as concentrations difference relative to and, if removing Fig. 6, remove line referring to it and add any addition description of simulations here.

Response: As the reviewer suggests, we have updated the caption for Table 5 to better describe the results.

Updated Text: Relative concentrations (given as a molar percentage of the total gas-phase product concentration) of the predicted gas-phase product yields using the Master Chemical Mechanism (MCM), V3.1 (Saunders*et al.*, 2003) for the dark ozonolysis of α-pinene. Results are shown for simulations of continuous-flow, short-time batch, short-time batch under high ozone, and long-time batch modes of chamber operation.

The short-time column shows the relative gas-phase concentrations 15 min after the start of the reaction, which is the time point of maximum of [ROO] (cf. Fig. 6). The long-time column corresponds to 2000 min after the start of the reaction. The second column for the batch-mode results shows the ratio of the relative concentrations to the continuous-flow results. Products shown account for 95% of the C_5 and greater products, excluding the remaining α-pinene. Conditions of the simulations are given in the caption of Fig. 6. The short-time batch-mode high-ozone simulation was run at 1500 ppbv ozone. The model predicts gas-phase products and omits SOA production and scavenging of species to the walls. Products are labeled as the SMILES strings of the MCM.

References:

Takegawa, N., Miyazaki, Y., Kondo, Y., Komazaki, Y., Miyakawa, T., Jiminez, J. L., Jayne, J. T., Worsnop, D. R., Allan, J. D. and Weber, R. J.: Characterization of an Aerodyne aerosol mass spectrometer (AMS): Intercomparison with other aerosol instruments, Aerosol Sci. Technol., 39, 760-770, 2005.

Docherty, K. S., Wu, W., Lim, Y. B. and Ziemann, P. J.: Contributions of organic peroxides to secondary aerosol formed from reaction of monoterpenes with O_3, Environ. Sci. Technol., 39, 4049-4059, 2005.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 17927, 2007.

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