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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Secondary Organic Aerosol (SOA) formation from the β-pinene + NO_3 system: effect of humidity and peroxy radical fate" *by* C. M. Boyd et al.

Anonymous Referee #1

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This paper presents a comprehensive set of chamber experiments on an high-yield and yet poorly understood mechanism for SOA formation that has been shown in field studies to be important in the ambient atmosphere. As such, it will certainly be of great interest to the readership of ACP. The paper is well written, well structured, and clear to follow. The data are extensive and offer key new insights into chemical mechanisms of aerosol formation. However there are some points of the analysis that are a bit confusing where I suggest revisions and have questions. Mainly: the comparability of the yields from two peroxy radical fate conditions could be better justified by showing kinetic modeling of VOC oxidation in both cases, since they will be very different given

the differing provision of NO3 radical in each case. There are also apparent discrepancies in delta(VOC) and molecular structures of the proposed mechanism that should be reviewed, and the discussion of Figure 9 should be clarified.

Specific comments/questions:

1. First paragraph of intro: suggest a slight rewording - leading with BVOCs being a major source of SOA does not make the observation of "modern" carbon a discrepancy – it resolves it – maybe instead of "However, . . .", "This resolves the apparent contradiction that ambient organic aerosols . . ."?

2. P. 2686 line 4 & SI material about HCHO required: How well do you know the amount of HCHO present at the beginning of the HO2+RO2 experiments? Are you able to constrain it by any measurement (HCHO, production rate of any products?), or is it determined by the volume of solution injected?

3. P. 2686 line 8-9: I suggest modeling the oxidation of β-pinene in both conditions to both demonstrate clearly this dominance of NO3 in the HO2 conditions, and show the difference in rate and how it affects the timing of aerosol yield calculations. I see you have O3 measurements – you could use these to constrain this model experimentally?

4. p. 2687 line 15-16: Can you put an uncertainty estimate on the initial [HC] based on the volume measurement accuracy?

5. P. 2690 line 21-22: The reference for wall losses refers to measurements made in a different chamber. If such data are already published for this chamber, could refer to that, else perhaps include the size-dependent wall loss rates measured for this chamber in the supplemental?

6. Ibid line 26: suggest "aerosol mass concentration produced (deltaMo)"

7. Ibid line 29: Can you add some text about at what time the SMPS aerosol volume was taken for the mass yields – fixed time after injection? Or peak in volume? If the latter, how different was the lag time between starting reactions & aerosol peak for

each type of experiment? Perhaps label the time of delta(Mo) on Figure 2.

8. P. 2691 line 5: Is it your view that these dry/humid conditions numbers are significantly different from one another?

9. P. 2692 line 5: "which make up about 11% of the total organics signal" – wording is slightly confusing – are NO+ and NO2+ part of the organics signal (sounds like it with this phrasing) or is their magnitude equal to 11% of the organics signal (what I think you mean)

10. Ibid around line 10: General question: why would the NO+:NO2+ ratio be different for different oxidant regimes if the apparent product composition is largely identical? Or are these not really significantly different?

11. Ibid line 19-21: I don't think this generalization really follows from the previous sentence, since these are 2 specific terpenes, and these fragments could be highly structure dependent.

12. P. 2694, line 24-25: the product of reaction 9 in the scheme shown is not a dihydroxynitrate.

13. P. 2695 line 22: "1.5h shift" should read "1,5-H shift"

14. P. 2699 2nd paragraph: general question about yield fitting: How do you interpret that the coefficient at 10 ug/m3 is exactly zero? Did you do any sensitivity tests e.g. with a bigger basis set, or removing a point, to check how robust this fit is?

15. P. 2702 line 18-19, refers to SI figure S9: my reading of figure S9 is not that RO2+RO2 reaction "are not significant" – in fact a substantial fraction appears to go via these cross-reactions

16. P. 2704 line 3: what does "relative reactivity for both reaction channels" mean? In general, this figure (Fig. 9) and its interpretation were confusing. You seem to be asserting that the trend is the same across both oxidant conditions, but if the bars are

correctly labeled (on the righthand panel the dry and humid are switched), the similarity in trend is not apparent.

17. Furthermore, line 6: this molecular assignment is wrong/inconsistent. The formula you have listed would have m/z =245, not 244, and the reaction you refer to (R22) you have elsewhere (bottom of 2695) described as producing a carboxylic acid, not a hydroperoxide. This should be clarified in the figure as well, by making the functional group unambiguous. This UHPLC portion of the evidence is most difficult to understand and I suggest reworking the discussion of this data. If you stick with the reasoning about R22 being an alternate pathway to a different, high-NO3 product, it would be useful to have that competing pathway also indicated on the mechanism scheme.

18. P. 2706 line 10 "carbons, the upper-bound molar organic nitrate"

19. P. 2707 lines 17-19: Could there not be some RO2+NO3 vs RO2+HO2 difference in organic nitrate hydrolysis rate because subsequent reactions render some products more likely to "keep" the nitrate moiety intact where others might jettison the NO2? Did you compare different oxidant fates and see no difference?

20. Ibid line 28: Suggest to replace "nitrate radical chemistry" with "nitrate +β-pinene" – because many terpenes have internal double bonds, this feature of producing few tertiary nitrates is unique to β-pinene and shouldn't overgeneralized

21. Same comment @ p. 2708 lines 16-19: this is only true where terminal double bonds dominate – so, where dominated by β-pinene.

22. P. 2711 line 6: inversely? Does this mean this partitioning coefficient is wall/gas, not gas/wall? Clarify.

23. Ibid, line 10: this phrase is unclear: "causing these compounds to re-partition back to the gas phase to re-establish equilibrium." The oxidized molecules partition to the walls more quickly, only to partition back faster?

24. Table 1: the range of delta(HC) here doesn't seem to match Fig. 7, where the

range of initial b-pinene concentrations is 9-21 ppb, which would be 50-117 ug m-3. Also, I suggest using the same units throughout. If the times after chemistry initiation at which yields were evaluated is vastly different for different conditions, maybe include that time in this table?

25. Fig. 3: Looks to me like the second-lowest point drives the shape of the yield curve – maybe check fit parameters without that point to see if robust. Also, you refer to x axis error bars which are not present in the plot.

26. Fig. 4 same missing x axis error bars. Why not include the unseeded yields on here too (currently in Figure S8)? This would make the comparison easier, rather than eyeballing data vs. the seeded fit line in the supplemental. If this makes the plot too busy, I retract the comment, just thought it would ease comparison.

27. Fig. 7: add into the caption that these data are all for the RO2+NO3 experiments.

28. See comment 16 above about Figure 9 confusion. If you keep this plot, I suggest adding to the caption to state that 235 nm corresponds to ROOR & ROOH and 270 nm to C=O and nitrate functional groups.

29. Figure 10: Was this spectrum selected because agreement was better than RO2+NO3 conditions? Or because more likely to be atmospherically relevant? Would it look any different? I suggest omitting “Fraction of” in the annotation. “Signal x3” is clear.

SI: Suggest modeling the HO2+RO2 experiments as well as RO2+NO3 – since you are producing HO2 simultaneous to NO3+VOC reactions this is slightly more complex – so it would be better to model these conditions using MCM rather than just determining the ratio of HCHO to bpin. I suggest creating an analogous plot to S9 showing dominant fate for both RO2 fate cases.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 2679, 2015.