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Interactive comment on "Peroxy Radical Chemistry and the Volatility Basis Set" *by* Meredith Schervish and Neil M. Donahue

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Received and published: 31 October 2019

Reviewer 2 Responses

We would like to thank the reviewer for the constructive comments and for bringing to our attention some clarity issues that we have attempted to address. In the following the reviewer comments are shown in blue, and our responses in black.

Page 8, line 17. "here we shall explore the possibility that. . ." I was expecting more exploration, for example with different scenarios. Instead it seems like just one situation was considered.

The efficiency of dimer formation is in our assessment a rapidly moving target. Other than the empirical observation that very highly oxidized RO_2 appear to make dimers with high efficiency and very small RO_2 (i.e. CH_3O_2) appear to make little or no dimer, the territory in the middle is uncertain. The efficiency of the avoid curve crossing may well scale with some combination of the oxygenated functional groups near the ROO moieties as well as cluster stabilization allowing for a longer interaction time (functionally the same phenomenon we are exploring here). For this reason we kept a single mechanism for dimer formation in this work; however, it is important to note that this causes the dimer production in our model to extend to ever less functionalized, less oxidized RO_2 as temperature decreases. Temperature dependent measurements of dimer yields with instruments sensitive to the full range of dimers would provide an excellent constraint here.

Page 8 line 26. Is the value of Co(ref) ever defined? Were different values considered (explore!)?

The value of C°(ref) used in this work is 10^{-2} at 298 K and moves 1 order of magnitude lower in volatility per 10 K reduction in temperature. We explored different values of C°(ref) during model development; however, we chose to hold it constant at each temperature for the results presented here to limit the number of tunable parameters is the simulation.

Page 9 line 3. Here (and in a few other places) a-pinene "oxidation" is referred to. Maybe be a little more clear by specifying "ozonolysis".

We use the word "oxidation" to add generality as α-pinene may be oxidized by ozone, OH, or NO_3 when NO_x is present. Our simulations are thus driven initially by ozonolysis but include all three oxidants.

The RO_2 in Fig. 4 are the "OxRO_2" including at least one -OOH group as shown also in Fig. 3. As one can see in Fig. 2, the "simple" RO_2 also has a maximum concentration above 2.5×10^8 cm^{-3} so the sum is well over 2.5×10^8. We have clarified this in the figures and text.

In the revised manuscript we make it clear at the onset that photochemistry is involved.

The top legend incorrectly labeled the blue curves as "NO$_x$"; they are "NO" and we have corrected this. We have also added to the caption to emphasize that the labels along the right-hand y-axis refer to the NO$_x$ concentration for each simulation by inserting "The numbers along the right-hand y-axis refer to the NO$_x$ concentration for each simulation, which is also indicated by the shading of each curve, going from light at low NO$_x$ to dark at high NO$_x$".

Kudos and thank you for close reading! This was a typo in the supplemental material, which we corrected. The main text is correct.

C3

Yes, the peroxy radicals that we do not allow to isomerize may still participate in any of the termination chemistry.

Once again, thank you. These were typos in the supplemental table; the main text is correct and we corrected the typos.

Fixed.

Yep.

The revised caption reads "as α-pinene decays and the RO_2 react away"

C4

We added "As a function of time" to the end of the caption to make this clear.

We simplified the caption and moved some discussion to the main text while retaining enough substance so that a casual reader can understand the figure while scanning over just the "storyboard" of figures, which is our objective. We also reworked the caption so that the sense is temperature increasing; this allows the reader to more easily scan the figures in the natural direction from left to right.

Done.

We are focusing on the oxidized RO_2 (Ox_nRO_2) but the text and captions were not clear. We have revised them to make this clearer.