

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

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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.

C1

The efficiency of dimer formation is in our assessment a rapidly moving target. Other than the empirical observation that very highly oxidized RO₂ appear to make dimers with high efficiency and very small RO₂ (i.e. CH₃O₂) 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 RO₂ 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 C^o(ref) ever defined? Were different values considered (explore!)?

The value of C^o(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^o(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 in the simulation.

Page 9 line 3. Here (and in a few other places) α-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 NO₃ when NO_x is present. Our simulations are thus driven initially by ozonolysis but include all three oxidants.

C2

Page 11, line 5. I don't see the factor of 40-80 in the figure. Looks more like 10 or 20.

The RO₂ in Fig. 4 are the "OxRO₂" including at least one -OOH group as shown also in Fig. 3. As one can see in Fig. 2, the "simple" RO₂ also has a maximum concentration above $2.5 \times 10^8 \text{ cm}^{-3}$ so the sum is well over 2.5×10^8 . We have clarified this in the figures and text.

Page 11, line 6. Is this the first reference to photolysis being "on"? Maybe it should be mentioned in the general description of the set up on Page 10. Until then, I had assumed the ozonolysis would take place in the dark.

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

Figure 4 could maybe be made a little clearer. It took me a while, but I eventually figured out that the labels on the right axis corresponded to the HO₂ and RO₂ for the different NO_x levels.

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".

Supplemental Table, page 2. The branching from AP + O₃ seems to contradict the text. Here, the radical RO₂ is allowed to isomerize, so it actually corresponds to OxoRO₂ in the text. So the yield should be 0.25 not 0.75? The less reactive radical SVOC should then correspond to RO₂ in the text.

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

C3

Do the SVOC/RO₂ radicals participate in subsequent chemistry (reaction with HO₂, cross reactions)?

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

Also, the coefficients in the Table are all 0.75/0.25, while in the text it is stated that alpha(OH) is 0.1 and alpha(NO₃) is 0. Just typos? This all needs to be tidied up.

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

Page 1, line 21. "are" is repeated.

Fixed.

Page 12, line 23. "at" should be "a".

Yep.

Figure 2. Left axis should read "concentration". Caption line 2. Is a little simplistic. Of course the radicals are reacting away all the time. It's just that the source (α-pinene + O₃) is reduced)

The revised caption reads "as α-pinene decays and the RO₂ react away"

Figure 4, caption. "before gradually decaying". Does this refer to their behavior with time, or as a function of NO?

C4

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

Figure 5. This is probably a stylistic thing. I find the lengthy caption inappropriate. Much of this is discussion, which might be better off in the text. I prefer captions to be punchy, with just enough description to be able to understand the figure (which isn't always the case here).

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.

Figure 6, caption. Delete "without".

Done.

Figures in general. A couple of times, the top of a curve is missing (figs 3 and 8, for example). Can these be scaled differently, without introducing an extra decade in the Y-axis?

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.

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