Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-509-RC2, 2019

Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

Received and published: 20 September 2019

This paper makes a timely and well thought out extension to the 2D-VBS volatility formulation by considering the chemistry of peroxy radicals (RO2) explicitly. The kinetics of autooxidation are specifically included, since these reactions are now thought to lead to small yields of condensible products within a single generation.

The methodology is to run a relatively simple 0-D box model with parameterization of various reaction rates and product yields to obtain the estimated volatility and O:C ratios of the products. The model addresses a range of temperatures and NOx levels. I like the concept of relating the probability of dimer formation to the volatility of the peroxy radical(s) involved in its formation. This is something that should be explored further.

Alpha pinene is used as the test/surrogate molecule in the model. This is appropriate

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Discussion paper

in the sense that the most is known about alpha pinene. Notwithstanding, there is still a lot we don't know about that molecule, and we know even less about others. The authors are obviously aware of this, and discuss it, but it should probably be made more clear that this is something of an exploratory sensitivity test, rather than an attempt to explicitly represent this chemistry in models at the moment. However, it is a very valuable exercise, and could be modified relatively easily as more data become available.

The paper is logically written and well explained, and can by published subject to the relatively minor comments below.

Technical comments 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.

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

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".

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

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.

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 NOx levels.

Supplememtal 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.

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

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.

Minor comments Page 1, line 21. “are” is repeated.

Page 12, line 23. “at” should be “a”.

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 (a-pinene + O3) is reduced)

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

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).

Figure 6, caption. Delete “without”.

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?

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