Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2019-424-RC1, 2019

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Aerosol Mass yields of selected Biogenic Volatile Organic Compounds – a theoretical study with near explicit gas-phase chemistry" *by* Carlton Xavier et al.

Anonymous Referee #1

Received and published: 23 July 2019

This paper presents a study of the SOA-forming potential of autoxidation mechanisms for several important BVOCs, as expressed in the PRAM chemical mechanism. A suite of box model simulations is performed for both chamber and OFR conditions using the MCM alone and in combination with PRAM. SOA yields simulated using MCM+PRAM show significantly better agreement with experimental data than do the MCM-only simulations, indicating the importance of the autoxidation reactions included in PRAM to SOA production. Sensitivity studies are also presented showing of the influence of temperature and NO variations on the contribution of the autoxidation mechanism to the overall SOA yield. This appears to be a careful and comprehensive study, and is a valuable contribution to the literature. I recommend publication after the following

Printer-friendly version

Discussion paper

points have been addressed.

General comments:

1. As noted by the Editor, it would be extremely helpful to be able to view the Roldin manuscript describing PRAM. I must leave it to the editor's discretion whether publication of the present manuscript should be contingent on publication of Roldin et al (2019). References to Roldin (2018) should be corrected to Roldin (2019) throughout.

2. The discussion is pertinent and interesting but is also convoluted in places and difficult to read. It would benefit from a careful re-writing for language clarity and brevity. For example, lines 243-245 read: "Similarly, the current lack of peroxy radical autoxidation product mechanism for b-caryophyllene and isoprene result in Delta-Y=0 values for PRAM." How about saying something simpler, like: "Peroxy radical autoxidation reactions of b-caryophyllene and isoprene OH products are currently not included in PRAM, so the mechanisms are not compared in these cases (Fig 2b)."?

3. Comparisons with many published experimental results are cited in the text but are not included in the Tables (especially results where no PRAM is yet available). This reviewer suggests that it would be extremely helpful to move these simulation/data comparisons to the yield tables and figures (whether as points or as ranges). Then the agreement (or otherwise) could be summarized in the text without having to list all the specific numbers. This would make the text and its arguments easier to follow.

4. Perhaps I am missing something, but if the peroxy autoxidation reactions are not available for certain species/oxidant combinations, wouldn't it be more correct and less confusing to call the mechanism for those species/oxidant combinations MCM (or MCM-only) instead of MCM+PRAM or PRAM? (Throughout the manuscript, including Figure captions).

5. Please explain whether some of the SOA formed in MCM is converted to different species in PRAM? Put another way, is the SOA formed in PRAM completely additional

to that formed in MCM, or is there some conversion as a result of the autoxidation? If the latter, please discuss the level of "double-counting" of products in the MCM/PRAM side-by-side mass spectra figures.

6. The range of sensitivity conditions seems rather wide: the temperature extremes are beyond usual ambient temperatures. Please discuss whether the results from the extreme cases are likely to be environmentally or observationally relevant.

7. Given that SOA yields in an OFR are sensitive to particle surface area, several points arise. i) The Abstract states that MCM+PRAM overestimates OFR yields and gives increased particle surface area as the reason. The casual ("abstract-plus-figures") reader is left wondering why the simulations didn't use the same particle loadings as the literature. Is it possible to provide a little context in the abstract, to explain? ii) Does the over-prediction of modeled OFR SOA suggest that the literature experiments in the comparisons used too little seed to obtain stable yields? iii) The MCM+PRAM OFR overestimation is not readily apparent from Tables 2 and 3. It would be helpful to include lines that compare the results with measurements under the same loadings if possible, so the disagreement is more apparent to the reader.

8. The earlier termination of the autoxidation mechanism in the OFR cases is attributed to "The higher absolute RO2 concentrations in the OFR simulations .... ie the high RO2 concentrations in the OFR cause termination of the peroxy radical autoxidation chain before the RO2 become highly oxygenated. ..." (line 229 ff.) This disagrees with the conclusions of Peng et al 2019 (https://doi.org/10.5194/acp-19-813-2019, 2019) who found that "for most types of RO2, their bimolecular fates in OFRs are mainly RO2+HO2 and RO2+NO, similar to chambers and atmospheric studies." At low NO, the high concentration of HO2 in the OFR leads to more rapid RO2 loss; at high NO, RO2+NO makes RO2 lifetime very short in the OFR. Please discuss whether the current modeling analysis is consistent with that work.

Specific line-by-line comments:

Printer-friendly version

Discussion paper

Line 29: The scale of SOA contribution... is "still" subjected to high uncertainties. Is there a more recent reference than 2011?

Line 41: Does this mean Ehn (2014)? Ehn (2012) is not listed in the references.

Line 57: Are there any measured O/C ratios in relevant systems that could be compared with?

Line 94: The timing seems confused: MCM+PRAM (Damian et al 2002) vs PRAM (Roldin et al 2018). Please clarify. (Did Damian et al really refer to MCM+PRAM?)

Line 98: What sort of fraction of the peroxy radicals is considered in PRAM?

Line 115-118: Please explain whether there is likely to be any bias from using two different systems to estimate p0 for different species subsets?

Line 188: I think the phrase "contribution to SOA mass" is misleading. It suggests proportion of the SOA made up by species "i", whereas the figure actually shows "SOA mass yield".

Lines 217 & 221, and in general: When referring to "our model" It would be helpful to distinguish at that point which version is being used in each case (MCM+PRAM or MCM), so that the reader is reminded whether or not PRAM is being used. The distinction is made a few sentences later: a little reorganization would help this discussion.

Line 220: The values quoted in the text for OFR-simulation SOA yield from a-pinene ozonolysis do not match the values quoted in Table 2. Why the discrepancy?

Line 240: This section needs an easier-to read introductory sentence.

Line 243 and following: Please list in Table 3 the experimental results of Kristensen 2017 and others cited in Section 3.2.

Line 244: It's not really true that Y=0 in these cases, since Y is the result of a comparison, and here there is nothing to compare (since there really isn't a "PRAM" for these

species-oxidant combinations).

Line 250: It's usual to say that the model results are in good agreement with previous measurements, not the other way around.

Line 274: Please briefly remind the reader why the simulations used more surface area than the experiments? It seems to be an important factor in the disagreement.

Line 297: Section number is missing (3.3). Subsequent section numbers should be updated accordingly.

Line 302: This sentence is difficult to make sense of. Is this what is meant? "Varying NOx concentrations changes the fates of RO2 radicals formed during organic oxidation, thereby impacting . . ."

Line 330: Please be specific that the PRAM contribution increases with increasing NO for NO < 1ppb. (It's not quite clear the way it's currently written.)

Line 382: I suspect this means that the compounds shown in Fig 8 contribute >95% to the SOA mass loading when summed in decreasing order of contribution. Please clarify the text. (It's said better in the caption and in Line 385.)

Line 423: I think this means to say something like "We do not simulate appreciable mass yields from the oxidation of BVOCS with NO3". The current text claims to describe the behavior of the actual compounds, but I think it really intends to describe their behavior in the model. It's an important distinction.

Comments on the Figures:

1. Why are the points in the Figures arranged in clumps/streaks? Please explain early on.

2. The caption to Fig 1 says ". . . from simulations with MCM+PRAM and PRAM." Shouldn't it really say "MCM+PRAM and MCM"?

3. Figs 1 & 2: Please denote the two panels ‘a’ and b’ and refer to them that way in the caption and text. This would help the reader and might help clarify the flow of the discussion.

4. Figs 1 & 2: Please add notes to the figure captions to clarify which species are omitted from the comparison in each case (i.e. which species use MCM-only)

5. Figs 1 & 2, 2nd panels: It is sometimes hard to figure out whether MCM makes any contribution at all. Please make this clearer by either a) plotting the ratio YMCM / Y(MCM+PRAM) instead of (or in addition to) the difference between the two, or at least b) using the same gridline interval in both panels.

6. Please mention Figure 3 somewhere in the text, or remove it.

Comments on the Tables:

1. Table 2: what are the figures in parentheses in the Experimental Yields column? Why are they not always present? Please explain.

2. Table 2: Please include the b-pinene and b-caryophyllene MCM-to-literature comparisons mentioned in the text (lines 203-212).

3. Table S1a: To make this information easier to digest, I suggest listing the compounds in descending order of contribution to SOA mass. Also: Is this just the a-pinene ozonolysis case? Please clarify. If it’s for various precursors, please indicate which precursor is relevant for each product.

Minor Language Editing Suggestions:

Line 29: “. . . is still subject to . . .” (Not “subjected”)

Line 134: “by contrast” might be a better phrase than “on the contrary”

Line 183 (suggestion): Move header for Section 3.1 to after “flow-tube experiments” (in line 187)

Line 240: Replace “resulting” with “result”.

Line 243: the word “Similarly” seems strange here. (It would usually be understood to refer to the previous sentence). Perhaps this means: “As in the ozonolysis case”?

Line 283: “Due to limited experimental constraints, PRAM presently does not consider autoxidation of RO2 formed from NO3 oxidation of VOCS”. I suggest that moving this information to the top of the paragraph would help the reader more quickly make sense of the comparisons presented.

Line 311 almost duplicates Line 302. It would be good to combine these two sentences, for brevity.

Line 335: “. . . the formation OF more volatile . . .” (add word “of”)

Line 348: “. . . and decrease (no ‘s’) to 0.27 at 293.15K AND to 0.1 at 313.15K” (add word “and”)

Line 351-2: Maybe this is “a weak dependence . . . . WHICH becomes more pronounced. . .”? (“which”, not “but”)

Line 385 duplicates some of lines 381-383. Please condense.

Line 428: (suggestion) “substantially lower than that of MCM”

Line 430: MCM *produces* more SVOCs, it doesn’t just “contain” them.

Line 441: delete word “respectively”

Line 473” “has paved THE way” (add word “the”). Or substitute something simpler like “helps us”.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2019-424, 2019.