Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2021-703

Anonymous Referee #2

Referee comment on "Secondary organic aerosol and organic nitrogen yields from the nitrate radical (NO_3) oxidation of alpha-pinene from various RO_2 fates" by Kelvin H. Bates et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-703-RC2, 2021

This work comprehensively details how different radical regimes impact the fate of RO2 radicals formed from aPinene + NO_3, which play a large role in determining the SOA yields of formation. When the radical regime is dominated by RO2 + NO3 there are lower yields of formation, but when RO2 + RO2 dominates the radical regime SOA yields are much higher. Additionally, the authors simulated the night-time environment by creating HO2 in the chamber through reactions with H2O2. For monomeric species, the authors were able to model their results and constrain branching ratios of RO2 + HO2 and RO2 + RO2 for specific molecules (PNP and PHN). Additionally, based on yields of formation the authors modeled their results to constrain the reaction rates of RO2 + RO2, RO2 + NO3, and the branching ratio of RO2 + RO2 □ dimers. Overall, the work highlights the importance of RO2 + RO2 □ dimers on the yields of SOA formation, and fills key holes in our understanding regarding the SOA yield of formation from aPinene + NO_3. I have some concerns about the quantification of the RO2 + RO2 □ dimer branching ratio, and suggest that sensitivity analysis is performed to present a range of RO2 + RO2 rates and RO2+RO2 branching ratios. Additionally, addressing quantification of the HRMS is needed since these values are used to constrain the RO2+RO2 branching ratio. I will support publication of this work after my comments are addressed.

Major comments:

In the results section, it is mentioned there are effectively 5 characteristic experiments that were performed: RO2 + NO3 (Fig 1 left), RO2 + RO2 (Figure 1 middle), RO2 + NO (not shown), RO2 + HO2 (not shown) and "simulated night time" (Figure 1 right). The two that are not shown should be included for comparison sake in the supplement.

Line 210: I understand that there must be careful caveats to do this subtraction shown in Figure 2. But if there were control experiments that were performed for each of the experiments listed (see line 122) the information for the control experiments should be added. Also, the SOA yield in Table 2 should indicate if this is the subtracted / corrected yield for NO3 chemistry or the total yield (with O3 contribution included). Where applicable the control experiment SOA yield needs to be included.

Along with these considerations, the authors could consider performing a sensitivity analysis when comparing SOA yields to the fate or RO2 + RO2. On this note, I am surprised it looks like there is no value on Figure 4b that is 0 on the y-axis, all appear to be positive.

Line 322: It should be noted, that regardless of seed concentration, wall loss will still affect SOA yields. See DOI: 10.1021/acs.est.0c03381

Line 339: It appears that there is a disconnect between the lack of nucleation and the assertion that apinene + NO3 produces lower volatility molecules, considering nucleation is connected to the formation of low-volatility or extra low-volatility molecules. Why would apinene + NO3 not nucleate (as discussed in the experiments here), while Toluene SOA from Zhang et al (2014) does? (note the 0 seed surface area is not zero in Zhang et al.) I think more caution is required in the authors statement.

Line 353: It is said that 34% of the peaks are found to come from ozonolysis experiments, how much does this contribute to the overall intensity. It may be good to discuss this in terms of number of peaks and how important is their relative contribution.

Line 374-376: The other option to form trimers would be through the RO2's in Table 2, that combine to form dimers and possess a C=C. This would be nRO2(e and f). These could undergo another reaction with NO_3 to form a C20 RO2, which would react with C10 RO2 radicals to form C30s.

Paragraph (line 398): So the RO2 + RO2 □ dimer branching ratio is based on the dimers measured by the offline measurement. On line 175, the authors state that the HRMS data is qualitative. There is a disconnect between the statement in the methodology and the use of the dimers to constrain the branching ratio of RO2 + RO2. Could the authors talk about error associated with this measurements and how certain they are of the 40-60% reported?

Why are the trimers not included in the contribution for RO2 + RO2? The authors postulate that these molecules could form from C20 dimers.

Also, on line 351, the peaks that are observed in the RO2 + RO2 experiments make up 29% (positive mode) and 39% (negative mode) of the simulated night time experiment. Wouldn't a lower limit of 29% be more appropriate? With the given range, how sensitive is the RO2+RO2 □ dimer branching ratio to the dimer fraction? With the change of the branching to RO2 + RO2, how were the other RO2 + RO2 branching ratios altered? Is the model sensitive to these pathways? (or is it consistent with your findings above)

In the discussion on the synergy of the different reaction pathways of RO2 radicals is suggested in many works including: (Zhao et al., 2018;Heinritzi et al., 2020;Berndt et al., 2018a;Berndt et al., 2018b;McFiggans et al., 2019)

Minor comments:

Line 74: The reference doesn't appear to match the citation of Kurten et al.

Line 80: reinvestigated

Lines 93-94: It could be noteworthy to mention that at elevated humidities, N2O5 uptake into the particle could be an important loss mechanism / source of radicals in the particle phase. Also, at elevated RH there will be some uptake of H2O2, which is useful for your experiments with HO2.

Line 95: RH not defined.

Line 183: minor grammatical comment, do you mean to say something along the lines of: experiment 13 is representative of RO2 + NO3 chemistry? I don't think "easy to isolate" is necessarily the best way to phrase it.

Line 189 minor grammatical comment: a domination? Maybe… achieves a RO_2 + HO_2 that dominates the RO_2 reactivity.

Labelling Figure 2 (a) and (b) could be useful for the discussion.

Figure 4 is mentioned in the text as (a) and (b) However, they are not labeled as such.

Line 284: I believe there is an "alpha" or "beta" missing in front of pinene.

Line 355: Same comment as on Line 352, but just about the usage of RO2 + RO2.

Figure 7 caption. What are the black lines in Figure 7c?

Table 2 and Figure 8: It seems like there is a missing nRO2 from Table 2 that is not included in Figure 8. (nRO2 - f)

Line 352: "Negative mode may overestimate the contributions from dinitrates dimers from nRO2 + nRO2" do you mean RO2 + RO2 chemistry specifically, or generally the experiment where the RO2 + RO2 is the dominant radical pathway?

Line 383: same comment as above about nRO2 + nRO2.

Line 425-426: "This SOA yield corresponds to a 9% particulate nitrate yield for compounds that did not hydrolyze." I don't understand how this was determined, I think there is a citation or two missing. Plus, with the experiments conducted under dry conditions, I don't understand how any molecules here would hydrolyze.