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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Peroxy radical chemistry and OH radical production during the NO_3-initiated oxidation of isoprene" *by* A. J. Kwan et al.

Anonymous Referee #2

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This paper presents a detailed analysis of a chamber experiment on NO3+isoprene, conducted with excess isoprene to force HO2+RO2 and RO2+RO2 chemistry to dominate over NO3+RO2. This enables the authors to study in greater detail the product channels of HO2+RO2 and RO2+RO2, which were hypothesized in a companion paper (Ng et al., 2008) to be responsible for higher SOA yields. This work addresses important scientific questions in the production of atmospheric nitrates and SOA, within the scope of ACP. The use of CIMS data to constrain RO2/HO2/NO3 reaction productions adds a novel contribution to the literature on NO3 + isoprene. The manuscript is well-written. The product branching ratios and modeling are subject to large uncertainties that must be clearly stated, but the publication of this qualitative picture is likely to be of great value to the research community in identifying important chemistry for follow-up study. I recommend publication after the authors consider the comments & questions

below:

Specific comments: 1) The production of OH seems to be central to discussion of results and implications in this manuscript but is not highlighted in the title or introduction. I suggest adding background on this question of additional oxidant sources upfront.

2) (related to point 1) In the discussion of Figure 4 and in the figure itself: clearly you were tweaking the model to get more OH production. What determined the degree of your tweaks? Can you put any, even approximate, constraint on the likely amount of OH produced based on observed OH-isoprene products? If so it would be great to include the apparent branching ratio of OH production in the manuscript.

3) Table 1 and last paragraph of p. 2266: I'd like to be able to tell if this slow equilibration with surfaces in tubing /instrumentation is a big effect or not – is the peak mixing ratio likely a big underestimate of actual product yield or not? Can you provide any kind of uncertainty estimate due to this effect, e.g. based on other experiments with mass balance? In the heading in Table 1, I suggest labeling as "maximum/peak concentration" to remind/highlight this.

4) Please indicate if the yields are determined on a molar or mass basis.

5) Last paragraph on p. 2268: why would the possibility of radical interconversion make the distribution of isomers more sensitive to initial conditions?

6) Last paragraph of section 3.1, p. 2269: here you say nitrate yields should be considered upper limits, while in the abstract you list yield as "$>\sim$80%", should this be "$<\sim$80%"?

7) Section 3.2: box model is introduced early – do you really need it to demonstrate than HO2+NO cannot possibly be important? Seems you can say this without the model, but it really is needed for the later RO2+HO2 branching – I would move its discussion down there.

8) last paragraph on p. 2272: RO2 /HO2 reactions from isomerized nitrooxy RO2 are

ignored, but earlier you pointed out that this isomerization was facile – how to reconcile this?

9) Last sentence above section 3.2.1 p. 2273: Elaborate please – why do you expect resonance stabilization of the radical reactant to preference the radical propagation product channel?

10) last paragraph, p. 2275: “There remain many uncertainties regarding the mechanism of RO2 +RO2 reactions (Dibble, 2008), so it is difficult to assess whether reported ROOR formation (or lack thereof) is a result of the particular radicals studied or the analytical techniques employed to study their reaction.” Sounds like you’re pointing out discrepancies in previous measurements of RO2/RO2 to yours for isoprene? I don’t see a huge discrepancy as you’ve set it up – perhaps you can start this paragraph in a way that highlights the difference you’re trying to point out? Is it the difference between 38% and 50%?

11) Top of 2277: Why would O2 abstraction be faster for these radicals? Is there a structural explanation?

12) At end of section 3.5: add a wrap-up statement to make clear what you’re saying: you’re proposing that RO2 + isoprene might be an important reaction pathway here

13) Top paragraph on p. 2280: RO2-RO2 reactions are sped up by NO3 electron-withdrawing group: what about your resonance-stabilized radical

14) Since you emphasize a few times the sensitivity to initial conditions, maybe a comment is warranted on how much greater than ambient conditions this experiment is. Do you expect the sensitivity to be primarily in the RATIO of NO3 to isoprene?

Technical corrections: a) Caption to Fig. 1 : suggest “are detected by the CIMS instrument as CF3O- adducts at the indicated. . .” b) Caption to Table 2: suggest “for box model assessment”

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 2259, 2012.