

Interactive comment on “Peroxy radical chemistry and OH radical production during the NO₃-initiated oxidation of isoprene” by A. J. Kwan et al.

Anonymous Referee #1

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General comments

This manuscript describes chamber experiments aimed at investigating the role of RO₂ + HO₂ and RO₂ + RO₂ reactions in the NO₃-initiated oxidation of isoprene. The work was inspired by a previous study of SOA yields for this system carried out in the same lab. Due to the use of a selective chemical ionization mass spectrometry approach for the measurement of many of the relevant product species, many new insights are gained into the mechanism of this process. However, due to the complexity of the system, much of the interpretation must be considered tentative. Nonetheless, because the authors do thoroughly discuss the uncertainties in the analysis, I have little doubt that the work will be a quite useful contribution to our understanding of isoprene oxidation chemistry. While the manuscript is generally clearly written, I suggest that the

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authors consider the following points in preparing a revised version of the paper:

- 1) p. 2263, line 13: The experimental conditions are clearly aimed at low NO_x conditions, and the authors make a broad claim here that these are also the relevant atmospheric conditions. However, there are atmospheric situations (urban environments), where higher NO_x levels at night are possible.
- 2) p. 2263, line 24: Is the thermal decomposition of N₂O₅ virtually immediate on the time scale of mixing? This should be quantitatively justified.
- 3) p. 2267, line 21: The discussion of NO₂ levels in the system made me wonder if the authors specifically considered (and apparently discounted) possible RO₂ + NO₂ reactions in their model (I don't see a RO₂ + NO₂ reaction listed in Table 2).
- 4) p. 2268, line 29: I'm not sure I understand how experimental conditions would affect the distribution of isomers. Is this expected to be sensitive to pressure and/or temperature, or some other experimental condition?
- 5) p. 2269, line 3: In the discussion of the carbon yield analysis, it is mentioned that some isoprene reacts immediately and that this complicates the analysis. Why couldn't a blank experiment be conducted (w/o N₂O₅) to determine the actual starting isoprene concentration in the chamber?
- 6) p. 2269, line 19: Since OH production is a major finding of this work, I think it deserves some further elaboration. In particular, it would be helpful to include a figure with the relevant products (and associated m/z carriers) to accompany this discussion.
- 7) p. 2273, line 6: OH production has also been observed from aromatic systems (JPC A, 2011, 115, 5397-5407).
- 8) p. 2277, line 23: Exactly how is the mechanism analogous to the formation of bicyclic peroxy radicals for aromatic compounds?

Editorial comments

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p. 2261, line 10 and many other places: I think the use of the term “dimer” is not appropriate. These compounds should be referred to as organic peroxides to emphasize that they originate from the self-reactions of peroxy radicals.

Table 1: please add a column that computes the percent yield of each of the products.

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