

The authors are presenting experimental results on product formation from the OH + isoprene reaction conducted in a flow-through apparatus with a residence time of about 60 s applying very high OH radical concentrations. OH radicals were produced by means of ozone photolysis in the presence of water vapor. Total peroxides were determined by an iodometric method and MVK and MACR (and other carbonyls) by means of DNPH derivatization. No direct measurements of RO₂ radicals, HO₂ or hydroxy hydroperoxides are provided. Based on modeling results the authors concluded that RO₂ radicals mainly reacted with HO₂ or via RO₂ self- and cross-reactions. Nothing is said regarding the possible contribution of the RO₂ + NO reaction for product formation. The authors obviously neglected the RO₂ + OH reaction, even for the very high OH levels in the experiments. No explanation for that is given.

The authors are stating as a result of their experiments increasing formation yields of MVK and MACR from the HO-C₅H₈O₂ + HO₂ reaction with rising RH, i.e., an increase of C₄ carbonyl production by a factor of 5 increasing RH from “dry” to 80%. This result is very surprising and would change our understanding of product formation from OH + isoprene for low-NO conditions, as also pointed out in the manuscript based on modeling results.

I think there are some weak points in the experiment, especially in the analytical technique:

- Now it's well-known that hydroxy hydroperoxides, which should be the primary product of HO-C₅H₈O₂ + HO₂ due to our current knowledge, are labile substances that tend to decompose at surfaces finally forming the corresponding carbonyls, see f.i. doi.org/10.1002/2014GL061919. This path of heterogeneous MVK/MACR formation was neglected, or checked the authors a contribution from that? Dosing the different HO-C₅H₈OOH isomers should clearly show what happens during sampling and DNPH derivatization. This test is necessarily needed in order to trust the carbonyl yields. Note, the “questionable” RH dependence in MVK/MACR yields in former studies was most likely due to heterogeneous MVK/MACR production.
- Why running the experiments with super high OH levels? There is no need for OH exposures simulating a day. A possible water-mediated HO-C₅H₈O₂ + HO₂ reaction proceeds at a time scale of seconds or less for atmospheric reactant concentrations. So it would be much better to run the reaction for almost atmospheric conditions, pushing back unwanted pathways that can become important due to the high radical levels in the experiments.
- Nothing is said regarding hydrotrioxide formation in this reaction system. And also the hydrotrioxides are labile substances representing possible MVK/MACR precursors.

Although this work is dealing with a very interesting topic, I cannot recommend acceptance even after some modifications. I would like encourage the authors to reinvestigate the possible water-dependence in this reaction system using an improved experimental approach including the test for heterogeneous carbonyl formation.