Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC2
https://doi.org/10.5194/acp-2021-964-RC2, 2022
© Author(s) 2022. This work is distributed under
the Creative Commons Attribution 4.0 License.

Comment on acp-2021-964

Anonymous Referee #2

Referee comment on "Autoxidation of terpenes, a common pathway in tropospheric and low temperature combustion conditions: the case of limonene and α-pinene" by Roland Benoit et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-964-RC2, 2022

MS No. acp-2021-964

This work is dealing with a comparison of product formation from the oxidation of two monoterpenes carried out at room temperature or at 590 K, standing for low-temperature combustion conditions. The authors conducted the experiments at 590 K in a jet-stirred flow reactor with a residence time of 2 s. Products were trapped in acetonitrile and analyzed by mass spectrometric techniques. The fuel feed was about 1% and the oxidations was initiated by H abstraction via the reaction of O_2 with the terpenes. The authors did not perform any experiments at room-temperature conditions. They used information from the literature for comparison taken from ozonolysis reactions of both terpenes conducted using different approaches. In their data analysis, the authors came to the conclusion that more than 40% of the detected "chemical formulae" are based on autoxidation processes.

While a deeper mechanistic understanding of oxidation processes in cool flames and for atmospheric conditions is a very important topic, especially with respect to autoxidation, I have some doubts regarding significance of this work in this field.

- Comparison of "chemical formulae": I think the authors mean the comparison of product signals appearing with the same exact mass or the same chemical formula.
- Why not performing own experiments on terpene oxidation for lower temperature than 590 K down to 300 K? I know it´s more challenging to run such experiments at reduced temperature without disturbing the unimolecular processes important in autoxidation. But, it would allow a more direct comparison of formed products, and likely of

important reaction paths, depending on temperature using the same analytical technique.

- Products were trapped in a solvent and stored in a freezer. Can we rule out any processing of products before analysis, especially for highly oxidized products?
- No mass spectra are shown. Would give the readership an impression what are the measured data used in the analysis. Nothing is said regarding weighting of measured signals, i.e., stands a bigger signal for higher concentration? Only the identification of a product with a certain formula (and without structural information) does not help to get out any information on the important pathways in a reaction system. So, what does it mean that 40% of the detected "chemical formulae" can be ascribed to autoxidation processes? Do we learn anything about the chemical steps going on?
- I think, an analytical journal could be a better place for this manuscript.