

Interactive comment on “Application of chemical derivatization techniques combined with chemical ionization mass spectrometry to detect stabilized Criegee intermediates and peroxy radicals in the gas phase” by Alexander Zaytsev et al.

Anonymous Referee #1

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The authors are describing experimental findings from an online method for the detection of thermalized Criegee intermediates (CI) and RO₂ radicals in different laboratory setups. CIs have been observed via HFA titration or DMPO derivatization and RO₂ radicals via DMPO or TEMPO derivatization. Analysis was carried out by means of a PTR3 mass spectrometer running in the H₃O⁺ or NH₄⁺ mode. CI detection via HFA adducts was successful in the case of the ozonolysis of TME, isoprene, pentene and hexene, but not for the expected CIs arising from the ozonolysis of selected terpenes.

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Also the simplest CI, CH₂OO, was not measurable. Examples for RO₂ measurements are given from the ozonolysis (incl. OH reaction?) of TME and alpha-pinene. The stated detection limit for CIs is about 10(7) molecules/cc and that for RO₂s about 10(8) molecules/cc for 30 s integration time. The topic of this paper is well suited for AMT. Some clarifications are needed before publication can be recommended.

- Line 53: Atmospheric RO₂ radical concentrations in the order of 10(8) molecules/cc are not generally valid. It stands mainly for CH₃O₂, concentration levels of other RO₂ radicals can be much lower.

- Line 104: Please provide a table with the initial reactant concentrations and the calculated amount of reacted olefin for a better understanding what has been done.

- Line 143: Also here, please state the initial reactant conditions. What was the residence time in the respective flow tubes? If I understand it right, in the first flow tube the O₃(OH?) + TME/alpha-pinene reaction was running without OH scavenger and the second flow tube served for product derivatization by DMPO (but TME/alpha-pinene conversion was still running)? Please provide a more precise insight what's going on in the different parts of this flow-through experiment.

- Line 186: The Donahue group, ref: 10.1021/jp108773d, used $k((\text{CH}_3)_2\text{COO} + \text{HFA}) = 2 \times 10^{-13}$ cc/s, about 2 orders of magnitude lower as the rate coefficient used in this work. Is the HFA concentration still high enough for complete conversion of (CH₃)₂COO with HFA?

- Line 197: How good is the agreement model vs. measurement in the case of the ozonolysis of isoprene, pentene and hexene?

- Line 204: What is the detection limit of OH radicals via the TEMPO derivatization as a result of this work? Giorio et al., ref:10.1021/jacs.6b10981, were not able to follow OH production from alpha-pinene ozonolysis using a similar technique. Is it really possible to measure steady-state OH in a reaction system by means of this technique?

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- Line 222: I think these experiments have been done in the double flow-tube setup, right? So, you should see the resulting RO₂ radicals from ozonolysis as well as those from the OH reaction if no OH scavenger is used. That means in the case of TME also the primarily formed HO-C₆H₁₂O₂ radicals should be visible in addition to acetylperoxy radicals from the ozone reaction? And in the case of alpha-pinene, HO-C₁₀H₁₆O₂ radicals (and subsequent autoxidation products) must be there along with the ozonolysis-derived RO₂s. Please comment!

Another point: Hansel et al., ref: 10.1016/j.atmosenv.2018.04.023, are stating a detection limit of 2×10^5 molecules/cc for RO₂ radicals and closed shell products from cyclohexene ozonolysis using a similar(or same) mass spec with NH₄⁺ ionization. That means the authors should be able to monitor the RO₂ radicals directly at the outflow w/o derivatization? That could be helpful for the assessment of the derivatization procedure.

- Line 259 and fig.8: Higher oxidized RO₂ radicals arising from pure autoxidation steps show a mass difference of 32 mass units due to step-by-step insertion of molecular oxygen. A mass difference of 16 mass units points to efficient bimolecular RO₂ steps altering the autoxidation-governed RO₂ distribution. So, as already said, it would be fine to have the complete reaction conditions to get an idea how important RO₂ + RO₂ could be.

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