

Atmos. Meas. Tech. Discuss., referee comment RC2
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Comment on amt-2021-384

Anonymous Referee #2

Referee comment on "Fragmentation inside proton-transfer-reaction-based mass spectrometers limits the detection of ROOR and ROOH peroxides" by Haiyan Li et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2021-384-RC2>, 2021

This manuscript shows the reason why recently developed PTR-based mass spectrometers are not easily able to detect ROOR and ROOH species via extensive experiments and theoretical calculations. The authors used α -pinene and cyclohexene ozonolysis experiments as well as model peroxide, hydroperoxide molecules for the calculation. Among various factors, they have investigated Pressure of FIMR, DC voltage, model compound, and substitutes were investigated. In the experiment, they showed dimers are hardly detected and confirmed that it was not because of low transmission on that mass per charge range. With increasing pressure, less fragmentation was observed and calculated. That was because of more frequent collisions with gas molecules which release excess internal energy. In addition, higher DC voltage in FIMR had a negligible effect on fragmentation. Varying model molecules showed several different results. For example, MeOOMeH⁺ showed less fragmentation because of their inductive effect and hyperconjugation which stabilize the transition state. Oxygen-based substitutes have a lower level of fragmentation because their initial protonation isomer has a lower barrier for isomerization thus more stable. For hydroperoxides, because of the higher degree of polarizability and smaller proton affinity, they were not easy to be detected by the instrument. This systematic study of model molecules in both experiment and theoretical calculation is well conducted and the manuscript is well written, and the interpretation of the results is reasonable. It is a very informative paper and falls well within the scope of AMT. Therefore, I recommend this paper to publish with some very minor comments and some questions.

1. Do you have any idea why α -pinene dimers were not detected at all but some cyclohexene dimers are detected?
2. I think in the introduction, not much about hydroperoxides is mentioned.

3. Would it be different if the experiment is conducted in higher relative humidity like 50 %?

4. Page 7.

How is the reaction ratio between RO₂+RO₂ / RO₂+HO₂?

Do you also have a similar experiment at higher RO₂ + HO₂? Like in the presence of CO?

5. Page 17, line 383

Can you explain more about why the opposite trend was observed for hydroperoxide?

6. Supplement S2.4 Page 7. Result and discussion, end of it (with the same page with Figure S4 and Table S1)

"The overall temperature equilibration must therefore arise from the relatively small asymmetry in this histogram, which we see from Figure S4 becomes more symmetric as the simulation proceeds and the temperature of the gas and analyte become closer."

--> It is hard to see how asymmetry (I agree it is small) become more symmetric as simulation proceed. No systematic change with increasing time. Can you give us more explanation about this?

7. Supplement S2.4 Page 8(Fitting MESMER parameters)

I still did not get why cyclohexene has a longer time for the molecule temperature to be equilibrium as surrounding gas than EtOOHEt+ besides higher collision frequency and larger energy transfer. Can you explain more about this?

8. This paper can be added as a reference. This provides basic information about the fragmentation patterns from PTR-MS.

Pagonis D, Sekimoto K, de Gouw J. A Library of Proton-Transfer Reactions of H₃O⁺ Ions Used for Trace Gas Detection. J Am Soc Mass Spectrom. 2019 Jul;30(7):1330-1335. DOI: 10.1007/s13361-019-02209-3. Epub 2019 Apr 29. PMID: 31037568.

For correction

- Supplement page 2, line 6
theory remove empty spaces
- Add page numbers in supplement
- Two S2.4 (Result and discussion, Fitting MESMER parameters)
- Remove dot from kcal.mole⁻¹
- Supplement Page 11 8th line from the bottom
"stabilised" --> stabilized (unify UK/US English)