

Atmos. Meas. Tech. Discuss., referee comment RC1
<https://doi.org/10.5194/amt-2021-384-RC1>, 2021
© Author(s) 2021. This work is distributed under
the Creative Commons Attribution 4.0 License.

Comment on amt-2021-384

Anonymous Referee #1

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-RC1>, 2021

General comments:

This manuscript describes a combined experimental and theoretical study on the observation of (hydro)peroxides using PTR-based mass spectrometers. The authors argue that due to fragmentation of the peroxides upon addition of the ionizing proton, the (quantifiable) detectability of peroxides is severely hampered, and does not appear to be a viable approach. They clearly document their reasons for this assertion, based on observations of peroxides (or the lack thereof) and an extensive set of theoretical calculations showing facile decomposition pathways for a myriad of protonated peroxides. The paper is well written, reads easily with a clear message founded in high-quality results. I support publication of the manuscript, with only some minor comments below. Note, however, that I am not able to properly assess the experimental part of the paper and focus mostly on the theoretical part.

Specific comments:

p. 12, line 285: "This may change if an oxygenated substituent is present, since very low or no reaction barriers were observed from calculations involving proton transfer to and from these groups."

Do the authors mean to say that migration to adjacent oxygen groups is slow, but transfer to more distant groups is faster? If so, at what distance would the transfer become sufficiently fast to occur under the conditions in this paper ?

The use of molecular dynamics to determine energy transfer parameters is not new, and it might be useful to reference earlier efforts. Examples include
Barker, J. R.: Energy transfer in master equation simulations: A new approach, Int. J. Chem. Kinet., 41, 748–763, <https://doi.org/10.1002/kin.20447>, 2009.
Barker, J. R. and Weston, R. E., Jr.: Collisional Energy Transfer Probability Densities P(E,

J; E', J') for Monatomics Colliding with Large Molecules, J. Phys. Chem. A, 114, 10619–10633, <https://doi.org/10.1021/jp106443d>, Jasper, A. W., Pelzer, K. M., Miller, J. A., Kamarchik, E., Harding, L. B., and Klippenstein, S. J.: Predictive a priori pressure-dependent kinetics, Science, 346, 1212–1215, <https://doi.org/10.1126/science.1260856>, 2014.2010.

SI: "In particular, it is apparent that the models used by MESMER significantly underestimate the collision rate between nitrogen gas and a large gas-phase molecule, and therefore when using the default parameters the rate of thermalization is in turn underestimated." and

"The selected parameter values, in special σ , are much higher than those offered by MESMER as default ($\epsilon/k_B = 50$ K and $\sigma = 5$ Å)"

I don't understand the emphasis on the default collision model parameters in MESMER. It can only have a single default value, but only by chance would these values be appropriate for any study. Default values should not be used as a black box but rather require explicit deliberation, given that it is well known that collision parameters are dependent on the molecule considered, and extensive work exists determining appropriate values for many compounds experimentally and theoretically. The manual of Multiwell, for example, even has a handy table of collision parameters for a variety of molecular sizes. The values obtained by the authors in the current work are by no means surprising for molecules of the size studied here. I propose the authors remove this awkward consideration that default values in MESMER might somehow have been appropriate, and rather look in collisional energy transfer literature for studies that examine the dependence of the parameters on molecular size to state that the values obtained from the MD calculations are not that unexpected (the references in the Multiwell manual would be good start). There are also methods for estimating such molecule-specific parameters that are not based on quantum chemical or MD calculations.

SI: "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 temperatures of the gas and analyte become closer."

I would avoid stating that "the models used by MESMER significantly underestimate the collision rate", as the problem appears to be not so much the models but the inappropriate use of black box defaults. The histograms derived from the MD calculations confirms the collisional models in MESMER, i.e. that the amount of energy transferred is roughly exponential for both up- and down-transitions, and that it is the small asymmetric between these curves that causes thermalization. This has been already described extensively in the literature. Some references to this literature would be appropriate.

The authors do not discuss an E-dependence of ΔE_{down} . Is this because they do not have sufficient data to derive the dependence, or did they find only a negligible dependence ?

SI, p. 12, start of lower paragraph: "Reaction dynamics simulations for MeOOH₂+ revealed that this species decomposes only at thermal rates".

Add : "across the pressure range considered here"

Typographic comments:

Add page numbers to SI

p. 6, line 163: 10^{-5} Hartree : superscript on exponent -5

SI, p. 2, 3th line from bottom: "theory" ; remove spaces

SI: throughout the text "kcal.mol⁻¹". SI notation of units does not use periods (neither for the abbreviation nor for the multiplication)

SI : "Molecular structures carrying the double-dagger symbol ‡ are transition states." This is evident from the schemes and need not be indicated explicitly.