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Comment on acp-2022-376

Anonymous Referee #1

Referee comment on "Oligomer formation from the gas-phase reactions of Criegee intermediates with hydroperoxide esters: mechanism and kinetics" by Long Chen et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2022-376-RC1, 2022

General comments: The authors use density functional theory (DFT) and transition state theory (TST) to study two categories of Criegee intermediate (CI) reactions for the parent, anti-methyl, syn-methyl, and dimethyl CI. The first category is the reaction of each CI with HCOOH and the second category is the reaction of each CI with the hydroperoxy ester formed in the HCOOH reaction. The novelty is considering the hydroperoxy ester + CI reactions as a possible oligomerization mechanism. The theoretical methods are qualitatively reasonable and there are a few chemical insights. However, the atmospheric relevance of the work is either misrepresented or under-discussed.

Specific comments:

- The authors should explain their variational TST calculations for barrierless reactions (p. 7) in more detail, particularly since they consistently predict higher CI + HCOOH rate constants than experiment (pp. 10-11).
- The trend in exothermicity with substitution pattern (pp. 8-9) should be explained.
- The analysis of possible bimolecular CI reactions (p. 21) should be extended to the three substituted CIs.
- Since the CI is clearly the limiting reactant in the CI + HCOOH reaction, the atmospheric concentration of HPMF (and the other hydroperoxy esters) is much better estimated to be the CI concentration. (This, of course, will greatly lower the predicted pseudo-first-order rate constants for the CI + HPMF reaction.)
- Since a big motivation for the computations is the potential for CI + hydroperoxy ester reactions to lead to SOA, there should be some specific discussion, perhaps buttressed by rough calculations, of how many cycles of CI addition are required before a given adduct is expected to have low volatility. The approach of Chhantyal-Pun et al. (*ACS Earth Space Chem.* 2018, 2, 8, 833–842) is an example of the approach the authors should take.

Technical corrections:

- On p. 6, line 145: "saddle point" should be "minimum"
- On p. 6, line 162: "precision" should be "accuracy"
- On p. 7, line 182: "decomposes" should be "rearranges"
- On p. 14, lines 341-322, use a non-breaking hyphen
- On p. 15, line 372, "intermolecular" should be "intramolecular"
- On p. 17, lines 413-414, use a non-breaking hyphen