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Comment on acp-2022-376

Anonymous Referee #3

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-RC3, 2022

General comments:

Chen et al. studied the the oligomerization reaction mechanisms and kinetics of several stabilized Criegee intermediates (SCIs) in the presence of HCOOH using quantum chemical and kinetics modeling methods. The major conclusion is that the oligomerization is mainly initiated by barrierless reactions of SCIs with HCOOH and proceeds through highly exothermic insertion of SCIs into hydroperoxide ester. Meanwhile, the influence of methyl substitution on SCIs were examined. Overall, this paper provides a good amount of data on SCIs chemistry. However, some of the conclusions need to be carefully validated and further discussions are suggested in terms of the mechanism and atmospheric implication.

Specific comments:

For Entry 1 of the initiation reaction, how is it validated that 1,4 O-H insertion is barrierless? Is there a multi-point potential energy surface showing that no barrier is found along the reaction coordinate?

The calculated ktot in this study is greater by a factor of ~3 than several previous studies. Since this is related to one of the major conclusions of the paper, the authors should carefully validate this result. For example, what could be the reason they underestimate the value? Which value can have a better interpretation of the experimental or atmospheric data?

Why are k(TSent2) and k(TSent4) decrease with increasing temperature as they both have positive energy barrier? (Table S2)

The oligomerization reactions are highly dependent on the concentration of the monomers. Here the monomer are highly reactive SCIs and usually has very low concentration in the atmosphere. It seems that the high exothermicity of the oligomerization reaction results from the "stabilization" of SCIs in oligomerization. Also, the calculated free energies represent standard condition. Could the authors correct the Gibbs free energies by incorporating the atmospheric concentrations of SCIs (i.e., $RTln(P/P_{ref})$) to check whether this oligomerization is favored in the atmospheric conditions?

Additionally, it would be helpful if there is some estimation about how much the oligomerization process could contribute to the regional or global SOA.

Technical corrections:

Line 39, "with increasing the number of SCIs" is a bit confusing, it would be better to say "with increasing the number of SCIs added to the oligomer".

Line 491, "netative" should be "negative".

Line 499, "neartly" should be "nearly".