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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Oligomerization Reactions of Criegee Intermediates with Hydroxyalkyl Hydroperoxides: Mechanism, Kinetics, and Structure-Reactivity Relationship" *by* Long Chen et al.

Anonymous Referee #2

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Comment on the manuscript "Oligomerization Reactions of Criegee Intermediates with Hydroxyalkyl Hydroperoxides: Mechanism, Kinetics, and Structure-Reactivity Relstionship.

by: Long Chen, Yu Huang, Yonggang Xue, Zhenxing Shen, Junji Cao, and Wenliang Wang

Chen and co-workers report an interesting work regarding the reaction of small carbonyl oxides (H2COO, HCH3COO and (CH3)2COO) with small hydroxy methyl hy-

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droperoxides (HHPs). The issue is interesting for understanding the first steps in the nucleation processes in the aerosol formation. However, in my opinion, there are several points that should be considered before publication.

First of all, I think that the title of this study goes too far. The main focus of this study refers just to the reaction of Carbonyl oxides with HHPs, although a second step, namely the mechanisms for the interaction of the products of these reaction with Carbonyl oxides is taken into account.

Along the text, the authors refer to several reaction products, as for instance, P2c, P2b and so on, but the structure of these compounds is not mentioned, which makes the work difficult to follow.

Some important references misses, as for instance CPL, 2001,337, 199, JPCA, 2001,105,446, JACS, 1997, 119, 330, CPC 2002, 2, 215, JPCA, 2003, 107, 5812, J. Atmos Chem, 2000, 35, 165 and references therein.

Regarding the theoretical approach, the authors state that all stationary points have been computing using the M06-2X functional, and for some selected elementary reactions they have performed single point energy calculations at CCSD(T) level of theory, pointing out that the deviations in the free energy barriers computed with both approaches range between 1.5 – 1.6 kcal/mol. The authors should clarify in which cases they have computed the energy barriers using both approaches, if they have taken into account basis set superposition corrections. They should compare the results of both approaches, for instance with results from the literature involving the reaction with water vapor (section 3.1) with results from the literature, where energy barriers are reported at CCSD(T)/CBS level of theory.

Regarding the kinetics, the authors should clarify if they have considered the prereactive complexes in the kinetic study and if they play a role in the temperature dependence of the rate constants.

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The authors report rate constants for the reactions of the carbonyl oxides considered with HHP's (Table 2), but no mention is done for the reactions of P1x with Carbonyl oxides. Moreover, that authors should clarify if they have considered all different conformers of the stationary points in the kinetic study. In addition, they should estimate the errors in the these calculated rate constants, since they can be between one and two orders of magnitude according to the errors in the computed free energy barriers.

With respect to the atmospheric implications, the authors compare the reaction rates of the reaction investigated with those between carbonyl oxides with formic acid. In my opinion, the reactions rates of carbonyl oxides with water and water dimer, but also the reactions rates of HHPs with water should be also taken into account, because the high concentration of water vapor in the atmosphere. For the last, there are free energy barriers in the literature to compare with.

An hydrogen misses in the structure of P1a in Figure 2. In addition some addition structures of the P2x compounds should be drawn if the different figures and the numbers should have a larger size.

Please also note the supplement to this comment:
https://www.atmos-chem-phys-discuss.net/acp-2018-935/acp-2018-935-RC2-supplement.pdf

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