Atmospheric Chemistry and Physics Discussions

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Comment on acp-2021-890

Anonymous Referee #1

Referee comment on "OH-initiated atmospheric degradation of hydroxyalkyl hydroperoxides: mechanism, kinetics, and structure–activity relationship" by Long Chen et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-890-RC1, 2021

This manuscript describes the gas-phase reaction of a number of different hydroxyalkyl hydroperoxides (HHPs) originated from Criegee intermediate reaction with water vapour with hydroxyl radical by using quantum chemical and kinetics modeling methods. The H-abstraction from the -OOH group of distinct HHPs by OH radical is predominate as the main products RO_2 radicals in the OH-initiated oxidation of distinct HHPs. The subsequent reactions involving self-reaction, autoxidation and reaction with HO_2 radical are taken into account in the absence of NO, while the subsequent reactions including addition, decomposition and H-abstraction by O_2 are considered in the presence of NO. The relative importance of different channels varies strongly depending on the conformation, size and complexity of RO_2 radicals, and the concentrations of coreactants. The investigated reactions may play a role in the processes of SOA and/or new particle formation. I recommend this manuscript for publication after addressing the following comments:

- The investigated HHPs are generated from the reactions of CH_2OO, anti-CH_3CHOO and $(CH_3)_2COO$ with water vapor, not considering the HHP from the bimolecular reaction of syn-CH_3CHOO with water. This should be stated.
- Line 226-228, the reaction barriers are reduced in the order of 6.4 (R1) > 5.8 (R3) > 5.1 (R2) > 1.5 (R4) kcal·mol^{-1}, indicating that H-abstraction from the -OOH group is the most favorable. The authors should explain the order of TS1, TS3, TS2, and TS4 in the initial H-abstraction reactions.
- The authors discuss the mechanism of RO_2 reactions with HO_2. But there is no information provided on HO_2. They must describe how HO_2 is formed in the atmosphere, what is its concentration, and where this reaction could be relevant.
- Authors should compare $k_{MC\text{-}TST}$ and the pseudo first-order rates (k'_{HO2} and k'_{NO}) for the bimolecular processes (HO_2 reaction and NO reaction) as a function of concentration. See the recent review of autoxidation by Bianchi et al. (Chem. Rev. 2019, 119, 6, 3472-3509).
- For the alkoxy radical fragmentation, the author should calculate rate constants in the

temperature range studied.

- The prefix ‘anti’ should be italicized throughout the manuscript.
- The italics/non-italics energies in Fig. S1 and S2 in the supplement are not always in the same vertical order.
- There are some grammatical and logical errors in this manuscript. I suggest revising the grammatical errors accordingly.