Responses to Reviewers' Comments on Manuscript egusphere-2025-1662

(Acid-catalyzed hydrolysis kinetics of organic hydroperoxides: Computational strategy and structure-activity relationship)

Reviewer 1

Reviewer: General comment

The authors present a computational study investigating the acid-catalyzed hydrolysis rate constants of various hydroperoxides. In a first step, a proton model is screened and tested against experimentally derived hydrolysis rate constants and in a second step, the hydrolysis of a variety of hydroperoxides are investigated and discussed for typical atmospheric conditions. The study aims to overcome limitations of limited availability of authentic standards by using computational methods, which delivers an important contribution to the understanding of the fate of hydroperoxides in the atmosphere. As the reaction also leads to hydrogen peroxide formation, the findings of this study have large implications for the oxidant budget in the atmosphere. The study is well written with a clear flow and logic. I have, however, some concerns about the wide application of a system that was tested for quite narrow conditions. I recommend publication once a few issues have been addressed.

Response: Thanks for the comments. We have revised the manuscript to enhance the quality.

Reviewer: Special Suggestions and Comments

Reviewer: 1) *The authors test their proton model on four compounds that are structurally very similar and all derived from the aqueous-phase ozonolysis of α-pinene with different alcohols as reaction partners of the corresponding Criegee-intermediates. The compounds tested however, span a much wider variety including functional groups such as -NH_2, -PH_2, -SH and -$CH{=}CH_2$ and compounds from much different precursors, such as isoprene and DMS. This might lead to significant uncertainties that should be discussed in more detail. Furthermore, hydroperoxides formed in the gas phase might be structurally quite different, as isomerization*

reactions are expected to be more pronounced.

Response: Thanks for the comment. We acknowledge that the four selected ROOHs (C_{13} α-AH, C_{12} α-$AH_{(1)}$, C_{12} α-$AH_{(2)}$, and C_{10} α-HH) are structurally similar. This was primarily due to the current lack of experimental data for ROOHs containing substituents such as -NH_2, -PH_2, -SH, and -CH=CH_2. Nonetheless, our results show that nearly all studied ROOHs share identical reaction sites (i.e., the -OOH group and its adjacent C_α atom) and follow analogous reaction pathways to C_{13} α-AH, C_{12} α-$AH_{(1)}$, C_{12} α-$AH_{(2)}$, and C_{10} α-HH. This mechanistic consistency suggests that, despite differences in their carbon skeletons and substituents, including those of gas-phase formed ROOHs, the key protonation and subsequent reactions remain localized at the C_α-OOH site, which is a common structural feature among ROOHs. Thus, we believe the screened protonated water cluster model can be reasonably extended to investigate the acid-catalyzed hydrolysis of diverse ROOHs with acceptable uncertainty. We have added the corresponding discussion in the revised manuscript (see lines 168 – 174).

Reviewer: 2) *More to this point, there are some hydroperoxides also commercially available and synthetic procedures have been published for others. Although I recognize that determining the hydrolysis rate constants for these compounds might not be within the scope of this study, the limitations of this procedure should be discussed.*

Response: Thanks for the comment. Although some hydroperoxides are commercially available or synthetically accessible, standard compounds remain limited, especially for ROOHs with heteroatom substituents (e.g., -NH_2, -PH_2, -SH). This limits experimental validation of our computational results. Nevertheless, we emphasize the importance of the synthesis and characterization of a broader range of ROOHs to support future validation. Please see lines 329 - 331 in the revised manuscript.

Reviewer: 3) *The authors apply the model to atmospheric ROOHs described in the literature. The cited study corresponding to DMS oxidation shows in fact, that instead of CH_3SCH_2OOH discussed in this study, a pronounced isomerization step mainly leads to the formation of*

$CHOSCH_2OOH$, again a more functionalized compound. I suggest including this compound in the list of tested compounds.

Response: We appreciate the reviewer's helpful suggestion. $CHOSCH_2OOH$ has now been included in our analysis and discussed in the revised manuscript. Please see Fig. 5, section 3.3 in the revised manuscript, and Fig. S24 in the SI.

Reviewer: 4) *In Line 193 ff., the authors discuss the effect of functional groups in their findings and trace it back to a stabilization of the intermediate step. Although I can support the analysis, I want to point out, that the reaction pathway and the nature of the intermediate step is determined by the method the authors applied. This trend is caused by the input parameters for this analysis, which I think should be reflected by the discussion*.

Response: Thanks for the comment. To assess the robustness of our results, we evaluated the influence of different computational methods on the reaction free-energy barriers using $C(CH_3)_2(X)OOH$ (X = NH_2, OH, OCH_3, $CH{=}CH_2$, SH, and PH_2) as representative compounds. As illustrated in Fig. R1, although the absolute values of the free-energy barriers and reaction free energies vary between the ωB97X-D/6-311++G(3df,2pd)//ωB97X-D/6-31+G(d,p) method and the M06-2X/6-311++G(3df,2pd)//M06-2X/6-31+G(d,p) method, the overall trend across ROOHs with different substituents remains consistent. This confirms that our conclusions are not strongly dependent on the specific method applied. The corresponding discussion has been added in the revised manuscript, please see lines 226-227 in the revised manuscript, and Fig. S13 in the SI.

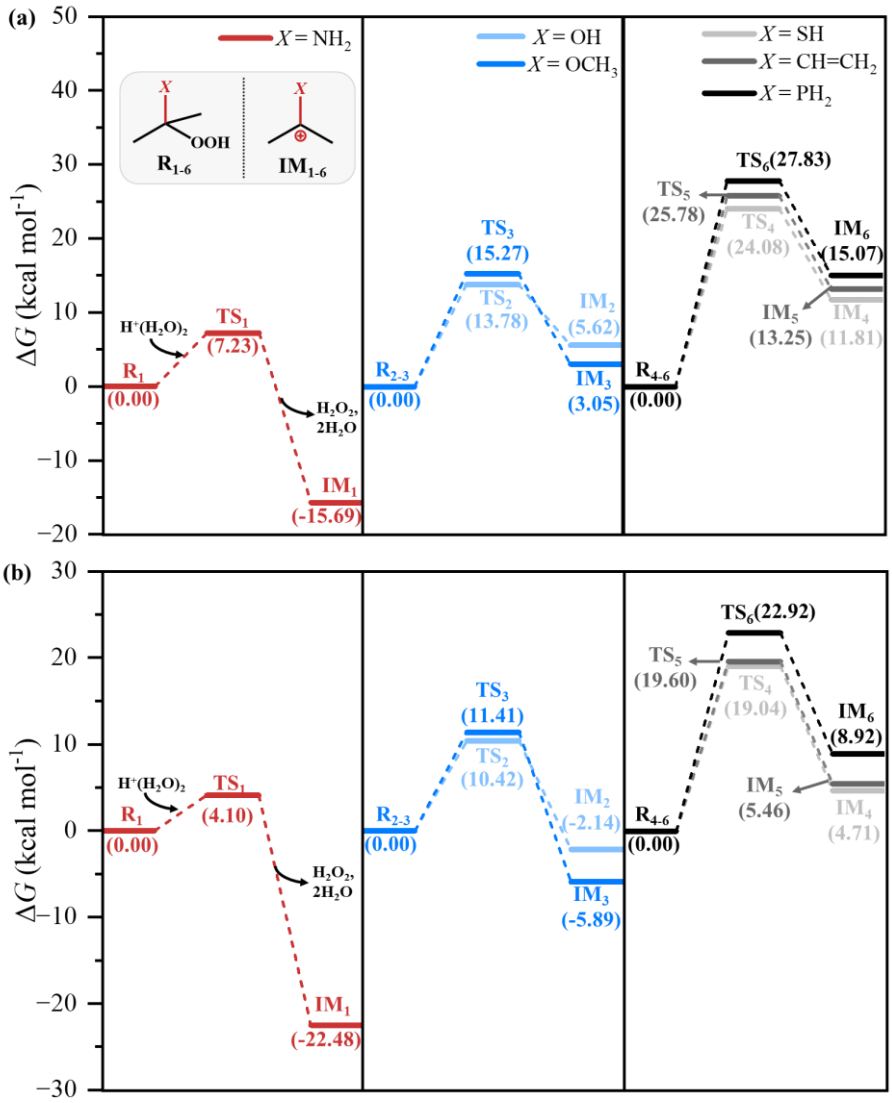

Figure R1. Calculated free-energy surfaces for carbocation formation during the acid-catalyzed hydrolysis of $C(CH_3)_2(X)OOH$, where X = NH_2, OH, OCH_3, $CH=CH_2$, SH, or PH_2. Free energies are computed at (a) M06-2X/6-311++G(3df,2pd)//M06-2X/6-31+G(d,p) and (b) ωB97X-D/6-311++G(3df,2pd)//ωB97X-D/6-31+G(d,p) levels with the SMD solvation model. R, TS, and IM denote the reactant, transition state, and intermediate, respectively.

Reviewer: 5) *Similarly, in lines 254, the authors claim, that the results prove that the SAR can be applied to atmospheric ROOHs, but as far as I understand there is no proof that the hydrolysis constants derived are valid for atmospheric conditions. I suggest to rephrase that section to better reflect that point.*

Response: Thanks for the comment. We fully agree with the reviewer and have revised the relevant description "…can be effectively extended to atmospheric ROOHs" to "… can be effectively extended to predict the k_A values of structurally diverse ROOHs" accordingly. Please

see line 299 in the revised manuscript.

Reviewer: 6) *In the conclusion, the authors introduce the reaction with sulfate of the intermediate carbocation that was previously not mentioned. This might have large implications in the atmosphere and I would suggest including this reaction pathway as well as potentially the reaction with nitrate in the discussion section.*

Response: We appreciate the reviewer's insightful suggestion. In response, we have expanded the discussion to include the potential reactions of the carbocation intermediate with H_2O, NO_3^-, and SO_4^{2-}. Please see lines 303 - 316 in the revised manuscript.