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

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

Reviewer 3

Reviewer: General comment

The manuscript "Acid-catalyzed hydrolysis kinetics of organic hydroperoxides: Computational strategy and structure-activity relationship" presents an updated DFT-calculated proton model probing the structure activity relationships of organic peroxides, varied functional groups and acid-catalyed hydrolysis. The manuscript incorporates empirical data for four initial compounds and once the model fits with observed values, expands the model to include several functional groups. The manuscript is clearly written and describes the work. However, there are several locations where clarification or additional information is needed before the manuscript is ready for publication. I recommend for publication after addressing the following questions and corrections:

Response: Thanks for the comment. We have carefully revised the manuscript to improve its overall quality.

Reviewer: Special Suggestions and Comments

Reviewer: 1). *The abstract (line 13) uses of the word solved and this is a broad assertion, since the model is built using a sparse set of empirically derived data points. Are you asserting that this method replaces the need for all authentic ROOH standards and can be used in lieu of authentic ROOH standards? If not, I recommend changing this word. Additionally, (line 17) define C_α prior to first use and clarify if the 52 ROOHs include the four ROOH stated in the previous sentence because it is unclear where the total 52 compounds originate.*

Response: Thanks for the suggestion. We have revised the manuscript accordingly: (1) The phrase "solved this issue" has been replaced with "addressed this limitation"; (2) C_α is clearly

defined at its first mention as the carbon atom directly bonded to the -OOH group; (3) We have clarified the composition of the selected ROOHs. Following suggestions from Reviewer 1, we added one DMS-derived ROOH, updating the total number from 52 to 53. The final dataset includes 45 model compounds and 8 atmospherically relevant species, excluding 4 ROOHs used for protonated cluster model selection. Please see lines 13, 17 - 19 in the revised manuscript.

Reviewer: 2). *The introduction needs to be expanded to further detail the work this manuscript is building on. Specifics include: (line 31) clarify what is meant by lack of kinetic data in this sentence, there are many types of kinetics data beyond acid-catalyzed hydrolysis. Similar to the abstract, (line 68) please clarify if 45 ROOH model compounds were used or if 52 compounds were used as is stated in the abstract and (line 68) define C_α and C_β prior to first use. The methods section is well written and straight forward, however the empirical values are not referenced explicitly, (line 100-101) please clarify if C_{13} α-AH, C_{12} α-$AH_{(1)}$,C_{12} α-$AH_{(2)}$, and C_{10} α-HH were chosen based on a specific reference, i.e., Hu 2022. Figure 1 in the results and discussion section should be altered to clearly designate the empirically derived values. Currently, the experimental values are currently orange and difficult to see on the graph. Please consider changing to a different contrasting color, such as black, so the empirical data will be distinct from the model data. Section 3.3 Acid-catalyzed hydrolysis of atmospheric ROOHs needs to be expanded. Specifically, (lines 239-241) please clarify if these seven compounds have experimental kinetics data and if they were used in the model.*

Response: Thanks for the comment. We have revised the manuscript accordingly: (1) In the introduction, we clarify that the "lack of kinetic data" refers specifically to aqueous-phase processes, including acid-catalyzed hydrolysis, esterification, oxidation, photosensitization, and oligomerization. Please see lines 33 - 34; (2) We specified the ROOH dataset composition (45 model compounds and 8 atmospheric species) and defined C_α (the carbon atom directly bonded to the -OOH group) and C_β (the carbon attached to C_α) at their first mention. Please see lines 72, 74 - 76; (3) We added the reference to support the selection of C_{13} α-AH, C_{12} α-$AH_{(1)}$,

C_{12} α-$AH_{(2)}$, and C_{10} α-HH in the methods. Please see line 108; (4) Fig. 1 was revised to improve clarity by changing the color of experimental data markers to dark grey. Please see Fig. 1; (5) In Section 3.3, we clarified that the hydrolysis rate constants for the eight atmospheric ROOHs were predicted using the screened $H^+(H_2O)_2$ model via the density functional theory calculations, and to the best of our knowledge, their experimental hydrolysis rates remain unavailable. Please see line 283 in the revised manuscript.

Reviewer: 3). *The supplemental information needs to be more thoroughly explained. Figure S1 needs to have the chemical formulas and molecular weights for the molecules listed (a-d) beneath the molecules. For figures S3-S6, please clarify how the products were determined, i.e., the reactions including H_2O, NO_3^-, $(SO_4)^{2-}$. Those products appear to be uniformly formed regardless of case. In addition, the SI must include a reference for the four compounds with empirical data need to be referenced here.*

Response: Thanks for the comment. We have added the chemical formulas and molecular weights for the molecules in Fig. S1. For Figs. S3-S6, the reaction product of carbocation intermediates with H_2O, NO_3^-, and $(SO_4)^{2-}$ were assessed based on their reaction thermodynamics and kinetics information. A more detailed discussion has been added in the revised manuscript. Additionally, the relevant references have also been cited in the SI. Please see lines 303 - 316 in the revised manuscript, and Fig. S1, references in the SI.