Re: Manuscript egusphere-2025-1662

Dear Prof. Jason Surratt,

Thanks for handling our manuscript and giving insightful comments. All your comments have been addressed in the revised manuscript. We hope that the following responses are satisfying and that the paper can be accepted for publication.

Thanks for your consideration!

Sincerely yours,

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

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

Editor: **Suggestions and Comments**

Editor: 1) *Page 13, where you added new text on lines 310-324:*

You mention the possibility of forming organic nitrates and organic sulfates, but don't cite any prior papers of these being found in aerosols and possibly formed through aqueous-phase reactions. Please include some references to prior work.

Response: Thanks for the comment. We have added the discussion and relevant references citations in the revised manuscript. Please see lines 316 - 329 in pages 13 and 14.

Editor: 2) *Related to # 1 above, I think it is important to note the possible formation of organic nitrates and organic sulfates from aqueous-phase chemistry of ROOHs is not a mechanism well represented in current models for these important reservoir species of N and S. Furthermore, is it possible to speculate if any prior reported organic sulfates (especially since they seem more favorable based on your work) in* $PM_{2.5}$ *analyzed from field studies (e.g., Surratt et al., 2008, J. Phys. Chem. A) could form from this pathway? I understand if you don't want to, but in some of the original work on organic sulfates (such as the one I cite here), it was unclear at that time what the exact sources of the organic sulfate were (despite knowing isoprene and monoterpene oxidation in the presence of acidic sulfate aerosols could yield these). As the authors know, at least for isoprene oxidation, many of these organic sulfates have been shown to form from aqueous-phase chemistry of epoxides in the presence of* H^+ *and* SO_4^{2-} *(Surratt et al., 2010, PNAS; Lin et al., 2012, ES&T; Cooke et al., 2024, ES&T).*

Response: We appreciate the editor's insightful comment regarding the formation of organic sulfates through the aqueous-phase chemistry of organic hydroperoxides (ROOHs). In this study, we present a plausible carbocation-mediated organic sulfates formation mechanism that occurs during the aqueous-phase transformation of ROOHs in the presence of H^+ and SO_4^{2-}.

However, our structure-activity relationship analysis indicates that, among our studied ROOHs, only those with C_α substituents such as -OH, $-OCH_3$, $-NH_2$, and $-N(CH_3)_2$, can effectively generate the corresponding carbocation intermediates on the lifetime scale of aerosols under the considered pH conditions (pH 3.8 and 0.9). In the atmosphere, such ROOHs primarily derive from the reactions of water, alcohols, or ammonia with Criegee intermediates produced via ozonolysis of unsaturated hydrocarbons or from ·OH oxidation of tertiary amines (Wang et al., 2023; Li et al., 2024; Kjaergaard et al., 2023). Therefore, we speculate that the proposed carbocation-mediated mechanism would be helpful to explain organic sulfates formation in SOA derived from the aforementioned reactions, whereas its applicability to other sources such as $\cdot OH/NO_3\cdot$ oxidation of volatile organic compounds (Surratt et al., 2008) could be limited unless the precursor compounds contain activating substituents that support the formation of the α-substituted ROOHs mentioned above. We have added the corresponding discussion in the revised manuscript, please see lines 316 - 329 in pages 13 and 14.

References

Kjaergaard, E. R., Moller, K. H., Berndt, T., and Kjaergaard, H. G.: Highly efficient autoxidation of triethylamine, J. Phys. Chem. A, 127, 8623-8632, 10.1021/acs.jpca.3c04341, 2023.

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Surratt, J. D., Gómez-González, Y., Chan, A. W. H., Vermeylen, R., Shahgholi, M., Kleindienst, T. E., Edney, E. O., Offenberg, J. H., Lewandowski, M., Jaoui, M., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Organosulfate formation in biogenic secondary organic aerosol, J. Phys. Chem. A, 112, 8345-8378, 10.1021/jp802310p, 2008.

Wang, S., Zhao, Y., Chan, A. W. H., Yao, M., Chen, Z., and Abbatt, J. P. D.: Organic peroxides in aerosol: Key reactive intermediates for multiphase processes in the atmosphere, Chem. Rev., 123, 1635-1679, 10.1021/acs.chemrev.2c00430, 2023.