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Title: Amine Ozonation Products Promote Sulfate Formation and Accelerate New Particle Growth

The corresponding authors: Prof. Taicheng An

Dear Anonymous Referee #1,

Thank you for the helpful and valuable review and comment. We have made careful revisions on the original manuscript according to your kind and helpful comments. The changed sentences have been marked as red color in the revised manuscript. Below is our point-by-point response to your comments:

General Comments: *This manuscript presents a computational investigation of how amine ozonation products may promote SO₂ hydrolysis and subsequent sulfate-containing cluster growth. The topic is relevant to atmospheric chemistry and new particle formation, and the combination of quantum chemical calculations with ACDC simulations is potentially useful. Overall, the manuscript is interesting and the main conclusions appear to be broadly supported by the calculations, although several methodological details and definitions should be clarified to improve the transparency, reproducibility, and interpretation of the results. I therefore recommend minor revision before publication.*

Response: We sincerely thank you for your critical and constructive comments regarding the experimental transparency of our manuscript.

Question 1. *The manuscript should more clearly distinguish the different energetic and thermodynamic quantities used in the calculations. In Section 2.1, the reaction barriers and reaction energies are defined from single-point electronic energies, whereas Section 2.2 subsequently uses these quantities to derive equilibrium and rate constants. Please clarify whether zero-point energy and entropy corrections are included in the quantities used for K_{eq} , reaction rates, and cluster evaporation rates. If electronic energies and Gibbs free energies are used for different purposes, this distinction should be stated explicitly.*

Response: We thank the reviewer for this important clarification. We apologize for the unclear description in the original manuscript. We have now explicitly clarified the definition of all energy quantities used in this work.

In our calculations, all reported energy barriers, reaction energies, and binding energies are defined as

$$\Delta E = \Delta G + \Delta \text{CCSD(T)}$$

where $\Delta \text{CCSD(T)}$ is the high-level electronic energy difference obtained from single-point calculations at the M06-2X/6-311++G(3df,3pd) level, and ΔG is the thermal Gibbs free energy correction (including zero-point energy, enthalpy, and entropy) obtained from frequency calculations at the M06-2X/6-311G(d,p) level. Therefore, all ΔE values reported in this work correspond to Gibbs free energy changes, not purely electronic energies.

Consequently, the equilibrium constant K_{eq} , the rate constants, and the apparent pseudo-first-order rate constant k_{p} were all derived from these Gibbs free energy quantities. Similarly, the cluster evaporation rates in the ACDC simulations were calculated from the same Gibbs free binding energies. No purely electronic energies were used in the kinetic or ACDC calculations. **We have revised around lines 65-70 to state this explicitly.**

Question 2. *Please define the Core units explicitly at their first occurrence and reconcile their compositions with the cluster notation used in Section 2.4. Consistent notation should be used throughout the text, Table 1, and Fig. 4.*

Response: We thank the reviewer for this important comment.

At the first occurrence around Line 200, we previously stated that “To further evaluate the nucleation potential of the amines investigated above, we simulated the hygroscopic growth of clusters containing an OH-/CHO-amine-sulfate complex as the core...”

According to your suggestion, Consistent notation of “OH-/CHO-amine-sulfate complex is set as one Core” is added in Table 1, and Fig. 4 in the revised manuscript.

Question 3. *The nomenclature and units of the kinetic quantities should also be checked carefully. For example, Tables S1–S3 refer to “unimolecular rate constants” while reporting units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.*

Response: We thank the reviewer for catching this error. We have carefully checked the nomenclature and units of all kinetic quantities. In Tables S1 - S3, the quantities with units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ are bimolecular rate constants, not unimolecular rate constants. We have already made the necessary revisions in this regard. We have also checked all other kinetic quantities in the manuscript and Supplementary Information to ensure that the terms “unimolecular”, “bimolecular”, and “pseudo-first-order” are used consistently with their units.

Question 4. *Section 2.3 states that 500 initial configurations were generated for each cluster composition and that the lowest-energy structure was selected for further optimization. For reproducibility, please provide the Cartesian coordinates and corresponding energies of the optimized structures used in the subsequent cluster analyses, preferably in the Supplementary Information. Please also clarify whether the electronic and/or Gibbs energies used as inputs to the growth-pathway and ACDC calculations.*

Response: We thank the reviewer for this helpful suggestion. For reproducibility, we have included the optimized structures of each cluster in the file of “*the lowest-energy structure*”, and have provided the corresponding ΔG and $\Delta \text{CCSD(T)}$ values for each cluster in Table S4 - S5. Additionally, the cluster energies used in the ACDC calculations were derived from the ΔE values listed in Table 1.

Question 5. *Please provide a clearer description of the ACDC boundary conditions, including the concentrations of all fixed species.*

Response: We thank the reviewer for this request.

The boundary is described around Line 105 “The simulated system comprises clusters of the form $(\text{Core})_m \cdot (\text{H}_2\text{O})_n$, where Core denotes a strongly bound complex of an OH-/CHO-amine with H_2SO_4 and two H_2O molecules, with m ranging from 0 to 3 and n from 0 to 4.”

About concentrations, you can find them in the following sentences “In these simulations, the concentration of Core is fixed at 1 ppt, while the water concentration ($[H_2O]$) is varied from 10^{15} to 10^{17} molecules cm^{-3} to assess its influence on nucleation. The primary simulations are run at 300 K, with additional sets at 280 K and 320 K to evaluate temperature effects.”

Question 6. *Please describe how the collision and evaporation coefficients are calculated in the ACDC simulations, or provide appropriate references for these calculations.*

Response: We thank the reviewer for this request.

In the revised Section 2.4, we added descriptions around Line 115: “The collision coefficients are calculated from hard-sphere collision theory using cluster masses, densities, and effective diameters, while the evaporation coefficients are derived from the Gibbs free binding energies via detailed balance. The detailed methodology is described in McGrath et al. (2012) and Liu et al. (2022)” to calculate the collision and evaporation coefficients.

The detailed information of the two references is as follows:

McGrath, M. J., Olenius, T., Ortega, I. K., Loukonen, V., Paasonen, P., Kurtén, T., Kulmala, M., and Vehkamäki, H.: Atmospheric Cluster Dynamics Code: a flexible method for solution of the birth-death equations, *Atmos. Chem. Phys.*, 12, 2345-2355, 10.5194/acp-12-2345-2012, 2012.

Liu, Y., Xie, H. B., Ma, F., Chen, J., and Elm, J.: Amine-Enhanced Methanesulfonic Acid-Driven Nucleation: Predictive Model and Cluster Formation Mechanism, *Environ Sci Technol*, 56, 7751-7760, 10.1021/acs.est.2c01639, 2022.

Question 7. *Abstract: “Both type amines are found to dominantly reduce SO₂ hydrolysis barrier ...” should be corrected to “Both types of amines are found to substantially reduce the SO₂ hydrolysis barrier ...”. “... and rate-limiting step is changes to ozonation step” should be corrected to “... and the rate-limiting step shifts to the ozonation step”.*

Response: We thank the reviewer for these careful corrections. We have corrected all sentences in the revised manuscript. The change has been highlighted for your easy reference.

Question 8. *Introduction: “... initiating the followed ozonation step” should be corrected to “... initiating the subsequent ozonation step”.*

Response: We thank the reviewer for catching this grammatical error. In the revised manuscript Line 36, we have corrected the sentence in the section of Introduction. The change has been highlighted for your easy reference.