

Manuscript ID: egusphere-2026-4704

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

The corresponding authors: Prof. Taicheng An

Dear Anonymous Referee #2,

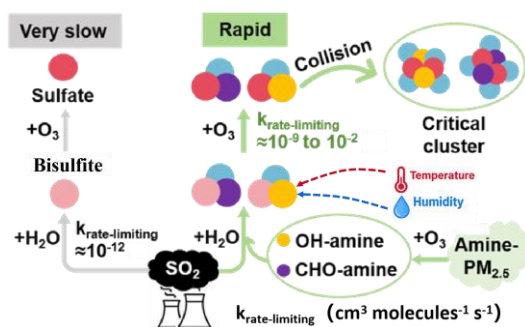
Thank you for the helpful and valuable review and comment. We have made careful revisions on the original manuscript according to your kind and helpful comments. The changed sentences have been marked as red color in the revised manuscript. Below is our point-by-point response to your comments:

General Comments: *This manuscript presents a comprehensive theoretical investigation into the nucleation activity of amine ozonation products, combining quantum chemical calculations with cluster dynamics simulations. The findings are novel and of significant interest to the atmospheric chemistry community, particularly regarding the sustained role of amine derivatives in sulfate-driven new particle formation (NPF) under humid and dark conditions.*

Response: We are truly grateful to the reviewer for the thorough reading of our manuscript and for the highly positive and encouraging evaluation.

Question 1. *The abstract and conclusion state that “humidity strongly activates all systems”, which is correct. However, the temperature effects (3–14 orders of magnitude drop for OH-amines, 1 order for CHO-amines) are equally striking and deserve more prominent emphasis in the graphical abstract.*

Response: We have updated the graphical abstract and incorporated the effects of temperature and humidity into the graphic.



Question 2. The paper demonstrates that the pseudo-first-order hydrolysis rate constants k_p of these amine derivatives are orders-of-magnitude higher than the $\cdot OH$ -initiated SO_2 oxidation rate constant from literature. It should be noted that k_p and real-atmosphere effective rate, considering realistic low ambient concentrations of these OH-/CHO- amines. Readers need to better understand under what real-world concentration ranges this non-radical pathway can outcompete traditional $\cdot OH$ oxidation.

Response: We agree with the reviewer's point. k_p here includes water concentration at variable humidity values. Actually, it is hard to directly calculate the reaction rate values of OH-/CHO-amine promoted reactions because we cannot find related atmospheric concentrations. Therefore, according to your advice, we reconsidered that we should delete direct comparisons with OH-initiated oxidation. Around Line 190, we have revised the discussions into "This suggests that even the less efficient CHO-amine pathway is a potential sulfate formation route besides conventional OH-initiated oxidation channel under favorable humidity conditions." We deleted the description that "... can compete with the OH-initiated oxidation channel". Meanwhile, we deleted "The apparent pseudo-first-order rate constants...under haze conditions." in Conclusions.

Question 3. The conclusion that CHO-amines require $RH > 80\%$ to be effective (Section 3.4) is valuable, yet the manuscript does not quantify how often such high humidity co-occurs with elevated ozone and amine emissions in typical haze episodes. A brief discussion using representative field data would contextualize the practical relevance of this pathway.

Response: Thank you for your careful reading of our manuscript and for raising these critical structural concerns.

We have added in revise manuscript: “These conditions occur in marine environments, where ozone concentrations and amine emissions are both high. Under high humidity, amines dissolve directly in aerosols. (Liu et al., 2018;Yang et al., 2026).” around Line 300.

Question 4. *In the ACDC simulations, the concentrations of OH-/CHO- amines is fixed at 1 ppt. However, the actual atmospheric concentrations of these amine ozonation products may be significantly lower than their parent amines, and would dynamically change with the ozonation process. Although the paper notes that the J values for certain products are comparable to their parent methylamine, this is based on the assumption that the product concentration is identical to the parent amine. If product concentrations were significantly lower (e.g., 10-100 times lower), would the J values still remain comparable? I suggest the authors include additional scenario simulations at different amine concentrations (e.g., 0.1 ppt, 0.01 ppt) to assess the impact of concentration changes on the conclusion of “functional equivalence” and to more realistically reflect the NPF potential under atmospheric conditions.*

Response: We thank the reviewer for this constructive comment. We agree that fixing all amine species at 1 ppt may overestimate the NPF potential of the ozonation products if their steady-state concentrations are substantially lower than those of the parent amines. In the revised manuscript, we have performed additional ACDC simulations at 0.1 and 0.01 ppt for all five OH-/CHO-amines (Figure R1), and compared them with the original 1 ppt baseline.

Accordingly, we added discussions around Lines 270 - 280 “It should be noted that the above comparison assumes equal concentrations for the ozonation products and their parent amines. In reality, the steady-state concentrations of OH-/CHO- amines are determined by the balance between production from parent amine ozonation and loss via further oxidation, deposition, and cluster growth, and may be lower than those of the parent amines. Therefore, their initial concentrations should be lower than their parent amines. Accordingly, we performed additional ACDC simulations at 0.1 and 0.01 ppt of OH-/CHO-amines. As shown in Fig. S21, J decreases with decreasing OH-/CHO-amines concentration, approximately following a power-law dependence. When the concentrations of the five OH-

/CHO-amines are reduced from 1 ppt to 0.1 ppt, their J decrease by about 1 order of magnitude; at 0.01 ppt, their decreases are about 2 orders of magnitude. Moreover, it can be observed that even when the concentration of the amine oxidation products drops to 0.01 ppt, the J value of CH_2NOH 's cluster remains 12.8 orders at 0.01 ppt and 13.8 orders at 0.1 ppt, which are comparable to that of parent MA (14 orders). Likewise, the J of CH_3NHCHO 's cluster is 12.0 orders at 0.01 ppt and 13.0 orders at 0.1 ppt, which is also comparable to that of parent DMA (13.6 orders). Therefore, CH_2NOH and CH_3NHCHO can sustain their ability of promoting NPF like their parent amines.”

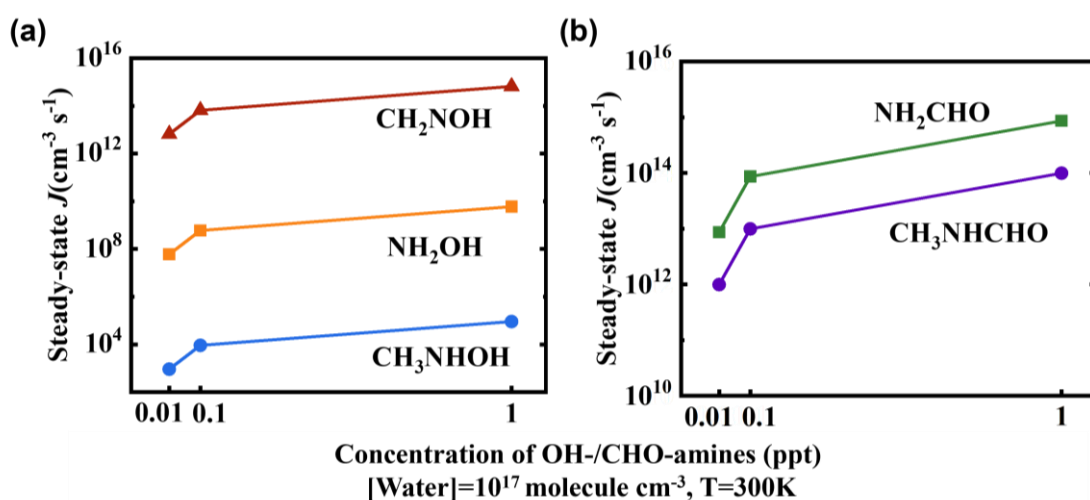


Figure R1 Formation rates (J) of critical clusters from ACDC simulations. (a) J as a function of [OH-amine] at $[\text{H}_2\text{O}] = 10^{17}$ molecules cm^{-3} and 300 K; (b) J as a function of [CHO-amine] at $[\text{H}_2\text{O}] = 10^{17}$ molecules cm^{-3} and 300 K.

Question 5. The protonated form, such as $\text{NH}_3\text{OH}^+ \cdot \text{HSO}_3^-$ in Figure 1b should be properly noted and described in the manuscript text.

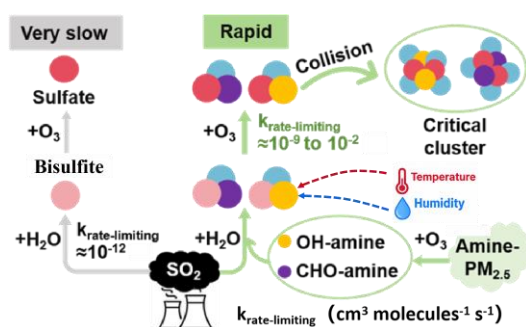
Response: We thank the reviewer for this valuable question. NH_2OH is not protonated during hydrolysis reaction, but CH_3NHOH occurs. For the latter, this occurs because during the promotion of SO_2 hydrolysis, CH_3NHOH accepts a proton from H_2O to form $\text{CH}_3\text{NH}_2\text{OH}^+$. The reaction process and the molecular composition during the reaction are illustrated in Fig. S2 - S4. Therefore, in the subsequent ozonation reaction for sulfate formation, $\text{CH}_3\text{NH}_2\text{OH}^+$ participate in their molecular forms.

Accordingly, we have revised Fig. 1b in the revised manuscript and added the following clarification in Section 3.1 around Line 125: “During the promotion of SO_2 hydrolysis, CH_3NHOH accepts a proton from H_2O to form $\text{CH}_3\text{NH}_2\text{OH}^+$,

which then participates in the subsequent ozonation reaction in its protonated form. Both NH_2OH and CH_2NOH participate in subsequent reactions in their molecular forms."

Question 6. In the graphical abstract, the term "bisulfate" should be corrected to "bisulfite", which means HSO_3^- . Such errors should be carefully checked and corrected throughout the manuscript.

Response: We appreciate this careful correction. We have carried out full-text search and proof-reading to eliminate similar terminology mistakes throughout manuscript, figures and captions. The graphical abstract is as follows.



References

- Liu, F., Bi, X., Zhang, G., Lian, X., Fu, Y., Yang, Y., Lin, Q., Jiang, F., Wang, X., Peng, P. a., and Sheng, G.: Gas-to-particle partitioning of atmospheric amines observed at a mountain site in southern China, *Atmospheric Environment*, 195, 1-11, <https://doi.org/10.1016/j.atmosenv.2018.09.038>, 2018.
- Yang, X. Y., Cao, F., Wu, C. L., Zhang, Y. X., Song, W. H., Lin, Y. C., and Zhang, Y. L.: Secondary formation dominated low molecular weight amines origins in aerosols over the marginal seas of China, *Atmos. Chem. Phys.*, 26, 7031-7046, 10.5194/acp-26-7031-2026, 2026.