Author responses and changes to Manuscript: egusphere-2025-165

Dear reviewer:

We are very grateful for the constructive comments from you on our manuscript (ID: **egusphere-2025-165**, original title: **Chloric Acid-Driven Nucleation Enhanced by Dimethylamine and Sulfuric acid in the Arctic: Mechanistic Study**. We have studied these comments carefully and have made corresponding revisions which marked in red in the revised manuscript. The all comments and our replies are listed as follows:

<<Comments from Reviewer #RC1>>

Wang et al. comparatively studied chloric acid (CA)-based nucleation enhanced by dimethylamine (DMA) and sulfuric acid (SA) in the Arctic oceanic atmosphere. The manuscript uses quantum chemistry calculations combined with ACDC simulations to obtain the cluster thermodynamic data, nucleation rate and cluster growth pathway. A main finding is that the nucleation rate of CA-DMA system is higher than that of the CA-SA system and CA-DMA nucleation contributes to new particle formation (NPF) in the Arctic. This is currently a hot research topic relevant to the contribution of chlorine-containing species to marine NPF. The provided descriptions and figures support the results. After the authors address the following comments and questions, I will recommend the manuscript for publication.

(1) Introduction: There is no description about the relevance of chlorine cycle and

chloric acid. The sources of chloric acid should be discussed.

>>**Response:** Thank you for your nice comment. Research by Tham et al. indicates that the CA and PA observed in the Arctic atmosphere are primarily generated through homogeneous reactions involving chlorine, involving photochemical processes involving HO_x and bromine chemistry(Tham et al., 2023). Fang et al.(Fang et al., 2024) employed quantum mechanical/molecular mechanical methods to investigate that chloric acid or perchloric acid may form as the final oxidation step of chlorine oxides.

(2) How did the authors obtain the global minima of (CA)1-4 clusters? Please provide the configurations of (CA)1-4 in the Figure 1.

>>**Response:** Thank you for your nice comment. We have provided the structures of $(CA)_{1\text{-}4}$ in Figure 1.

(3) What is the boundary clusters of CA-SA system?

>>**Response:** Thank you for your nice comment. For $(CA)_m(SA)_n$ (m = 0−4, n = 0−4) clusters, we select $(CA)_5(SA)_4$ cluster as the boundary clusters for chlorine oxoacid system in the 4 × 4 box simulation. We have placed this section of the content in the supplementary materials.

(4) Line 220, What is PA? PA is not above-mentioned. If the authors also investigated the CA-PA nucleation mechanism in this study, please provide the relevant descriptions in the preceding sections.

>>**Response:** Thank you for your nice comment. PA is perchloric acid. We have

provided nucleation information for the CA-PA cluster in the supplementary materials.

(5) As shown in Figures 4 and 5a, J seems to be lower at 258.15 K than that at 278.15 K, which is in contrast with the description “the decrease in temperature further increases the J value of the CA-DMA cluster system to a higher level”. Please check and explain this.

>>**Response:** Thank you for your nice comment. When we previously used a script to calculate the CA-DMA cluster formation rate at 278.15 K, we employed a script for 3×3 cluster. We used a script designed for 4×4 clusters to calculate the CA-DMA cluster rate at 258.15 K. This discrepancy resulted in the observed outcome. By correcting to the 4×4 script for calculating the CA-DMA cluster rate at 278.15 K, the results have been adjusted. We have revised the conclusion. We have concluded that CA-DMA nucleation may not effectively contribute to Arctic NPF.

(6) Line 231 and Figure 5b, in my opinion, the Arctic atmosphere is relatively pristine, therefore, I question whether [DMA] can reach 10 ppt. If the actual [DMA] is very low in the Arctic, CA-DMA nucleation may not effectively contribute to Arctic NPF based on the J values of Figure 5b.

>>**Response:** Thank you for your nice comment. We have revised the conclusion. Widely dispersed DMA has an atmospheric concentration of 0.4 − 10 pptv over the ocean and plays a key role in marine NPF(Van Pinxteren et al., 2019). DMA at concentrations up to 100 ppt is primarily used for prediction. We have concluded that CA-DMA nucleation may not effectively contribute to Arctic NPF.

(7) Figure 6 shows the growth paths of CA-DMA system at 278.15 K, [CA] = 106 cm-3 and [DMA] = 1 ppt. However, the absolute J of CA-DMA is very low (10-13 cm-3 s-1) at this condition. I think the authors should mainly study the growth path at the condition that J is efficient, e.g. at 238.15 K and high precursor concentration.

>>**Response:** Thank you for your nice comment. We have plotted the nucleation pathway of the CA-DMA cluster at 238K in Figure 6(c). Compared to the nucleation pathways observed at 278K in the CA-DMA system, pathways at 238K involve in the formation of $(CA)_2(DMA)_2$ to $(CA)_2(DMA)_4$ clusters, as well as the combination of $(CA)_4(DMA)_4$ clusters with a single $(CA)_1(DMA)_1$ cluster to generate $(CA)_5(DMA)_5$ clusters.

(8) All the figures in the SI should be explained in the manuscript, otherwise readers may find it difficult to understand the necessity of including such materials in the SI.

>>**Response:** Thank you for your nice comment. The CA-PA cluster system has a lower *J* value (Figure. S13-17). This may be due to the weak bond energies of Cl-O...Cl-O halogen bonds in the process of CA-PA nucleation (Figure. S12).

(9) Many minor mistakes are shown in the manuscript, e.g., line 47, formatting error in the reference citation, “O’ dowdg”; lines 110-111, grammatical error, “based on the ω B97X-D/6-31++G(d,p) theory level is performed on the geometry”; line 159, “CA atom” should be “Cl atom”; line 157, “O-O...O-Cl” should be “O-Cl...O-Cl” et al. The authors should totally and carefully recheck the whole

manuscript and correct all the mistakes.

>>**Response:** Thank you for your nice comment. We have made the modifications.

(10) Some sentences are redundant and some expression is unclear and unnecessarily verbose in the manuscript, e.g., lines 117-119, "The free energy of formation (ΔG) of individual clusters is calculated at different temperatures 238, 258, and 278 K." or "The ΔG of individual clusters is calculated at different temperatures." should be deleted; lines 185-188, "The smaller value of $\Sigma\gamma$ means that the stability of CA-DMA clusters is higher and the clusters shrink further." or "The smaller value of $\Sigma\gamma$ implies the higher stability of CA-DMA clusters and further contraction of the clusters." should be deleted; lines123-125 and lines 127-129, Two sentences can be summarized to one sentence; lines 126, "……the experimental results obtained using the birth and death equations" is incorrect since birth-death equations is used to obtain ACDC simulation results rather than experimental results. Please carefully recheck the whole manuscript, delete the redundant sentences and rewrite the inappropriate expression.

>>**Response:** Thank you for your nice comment. We have made the modifications.

Fang, Y.-G., Wei, L., Francisco, J. S., Zhu, C., and Fang, W.-H.: Mechanistic Insights into Chloric Acid Production by Hydrolysis of Chlorine Trioxide at an Air–Water Interface, Journal of the American Chemical Society, 146, 21052-21060, 2024.
Tham, Y. J., Sarnela, N., Iyer, S., Li, Q., Angot, H., Quéléver, L. L., Beck, I., Laurila, T., Beck, L. J., and Boyer, M.: Widespread detection of chlorine oxyacids in the Arctic atmosphere, Nature Communications, 14, 1769, 2023.
van Pinxteren, M., Fomba, K. W., van Pinxteren, D., Triesch, N., Hoffmann, E. H., Cree, C. H., Fitzsimons, M. F., von Tümpling, W., and Herrmann, H.: Aliphatic amines at the Cape Verde Atmospheric Observatory: Abundance, origins and sea-air fluxes, Atmos. Environ., 203, 183-195, 2019.

Sincerely

Prof. Qingzhu Zhang

Environment Research Institute

Shandong University

Qingdao 266237

P. R. China