



Perchloric acid (HClO_4) drives atmospheric new particle formation enhanced by dimethylamine, ammonia and sulfuric acid: mechanisms and implications

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Abstract. Recent studies have revealed observations of atmospheric perchloric acid (HClO_4 , PA) in the Arctic. There are few studies of PA forming aerosol particles in coastal marine regions. We use quantum chemical calculations and Atmospheric Clusters Dynamic Code (ACDC) to compare the enhancement potential of dimethylamine (DMA), ammonia (NH_3), and sulfuric acid (SA) for PA-based new particle formation (NPF). The results show that DMA and NH_3 can strongly interact with PA through hydrogen bonding and proton transfer. Compared with the nucleation of SA, PA nucleates more easily with DMA. Even if the concentration of NH_3 exceeds that of DMA by 10–100 orders of magnitude, the cluster formation rate of PA-DMA cluster formation is much higher than that of the PA- NH_3 cluster system. Clusters with the same number of PA molecules as DMA molecules play a key role in the growth of PA-DMA clusters. The present results reveal the potential for new particle formation of PA in the Arctic boundary layer.

1 Introduction

At least 50 % of the overall concentration of aerosol particles in the atmosphere is believed to be attributed to new particle formation (NPF) (Gordon et al., 2017; Takegawa et al., 2020; Williamson et al., 2019; Zhang et al., 2012; Zhao et al., 2024). Because they reflect and absorb solar radiation, reduce visibility, and have an indirect and direct impact on the climate, these aerosols have a deleterious impact on human health (Zhang, 2010). The production mechanism and subsequent expansion of aerosol particles are poorly understood, making them one of the biggest uncertainties in global climate models (Masson-Delmotte et al., 2021). Theoretical studies, laboratory experiments, and field measurements of air aerosols and nucleation events are available (Lee et al.,

2019; Chu et al., 2019; Kalivitis et al., 2019). The nucleation of amines and ammonia in the atmosphere using sulfuric acid (SA) is a crucial process in the contaminated boundary layer (Chen et al., 2012; Erupe et al., 2011; Jen et al., 2014; Loukonen et al., 2010; Zhao et al., 2010; Zollner et al., 2012). Nevertheless, SA concentrations in the atmosphere are typically too low to support cluster growth to CCN size. The particle production and subsequent growth stages are significantly influenced by other nucleating agent candidates in the atmosphere.

Abundant atmospheric bases, such as ammonia (NH_3) and alkylamines (methylamine (MA), dimethylamine (DMA), trimethylamine (TMA), and ethylenediamine (EDA) are recognized as important stabilizers for H_2SO_4 -driven nucleation (Almeida et al., 2013; Elm, 2017). A recent theoretical study

found that mixed iodic acid-iodous acid (IA-HIO₂) clusters account for the rapid nucleation rate under neutral conditions due to the basicity of iodous acid (HIO₂) and the production of strong halogen bonds (Zhang et al., 2022b). By discovering significant perchlorate (ClO₄[−]), recent investigations have conjectured the possible formation of perchloric acid (HClO₄, PA) in the lower atmosphere (Dasgupta et al., 2005; Rajagopalan et al., 2009; Furdui and Tomassini, 2010; Barrie et al., 1988). Atmospheric PA, the sinking process of chlorine, was initially identified as a significant component in the polar stratosphere (Sander et al., 1989; Webster et al., 1993; Jaeglé et al., 1996). Tham et al. have shown the presence of chlorine oxyacids including chloric acid and PA in the Arctic region, an atmospheric sink for reactive chlorine that has not been previously considered (Tham et al., 2023). The observed concentration ranges of PA is 3×10^4 – 1×10^6 cm^{−3} in the Arctic atmosphere (Tham et al., 2023). Previous studies have found that chloric acid makes a relatively small contribution to new particle formation (Wang et al., 2025). Engsvang et al. (2024) found PA has a high nucleation potential (Engsvang et al., 2024), but the specific nucleation mechanism remain unclear. Perchloric acid is a major component of chlorine oxyacids, and its contribution to new particle formation requires further investigation (Engsvang et al., 2024). The most prevalent and powerful organic base in the environment is dimethylamine (DMA), which significantly accelerates ion-induced and neutral SA-water nucleation (Ge et al., 2011; Jen et al., 2014). During the Arctic summer, alkylamines have been detected at ppt levels (Ferrero et al., 2019). The concentration of dimethylamine (DMA) is estimated to be between 0.1 and 10 ppt.

In this paper, the nucleation mechanism of (PA)_{1–4}(DMA)_{1–4}, (PA)_{1–4}(NH₃)_{1–4}, and (PA)_{1–4}(SA)_{1–4} systems are investigated using quantum chemical calculations and the Atmospheric Clusters Dynamic Code (ACDC) methods. Furthermore, the relationships between various components and the thermodynamic characteristics of PA-related clusters were examined. Lastly, ACDC used dynamic simulations to examine the evaporation rates, formation paths, dimer concentrations, and particle formation rates of PA-related clusters using thermodynamic data from three PA-DMA, PA-NH₃, and PA-SA systems.

2 Computational methods

To find the global minimum of the (PA)_{1–4}(DMA)_{1–4}, (PA)_{1–4}(NH₃)_{1–4} and (PA)_{1–4}(SA)_{1–4} clusters, we used a multi-step global minimum sampling approach. The AB-Cluster software was employed to randomly construct the initial structures of 1000–10 000 (PA)_{1–4}(DMA)_{1–4}, (PA)_{1–4}(NH₃)_{1–4} and (PA)_{1–4}(SA)_{1–4} clusters (Zhang and Dolg, 2015). In addition, the Universal force field (UFF) (Rappé et al., 1992) was used to describe every molecule in the AB-Cluster software (Zhang and Dolg, 2015). Ini-

tially, from structures (> 2000) produced by the artificial bee colony algorithm (Karaboga et al., 2012) for cluster (AB-Cluster), 1000 structures with comparatively low energy were selected. In the multistep sampling scheme, the geometry optimization is carried out at the PM7, ω B97X-D/6-31+G(d,p) and ω B97X-D/6-31++G(d,p) levels of theory, and the single-point energy calculations are executed at the DLPNO-CCSD(T)/aug-cc-pVTZ level of theory based on the ω B97X-D/6-31++G(d,p) theory level. The PM7 and ω B97X-D computations were carried out utilizing the GAUSSIAN 16 program package (Frisch et al., 2016). ORCA 4.0.0 was implemented to perform DLPNO-CCSD(T) computations (Neese, 2012). Many previous studies have adopted these methods and applied them to a wide range of acid-base cluster systems (Ning et al., 2026; Zhang et al., 2022a; Liu et al., 2023). The initial structures will be modified and re-optimized until the optimization is successful in order to address convergence issues and failures, such as terminating with a false frequency in the optimization of the (PA)_{1–4}(DMA)_{1–4}, (PA)_{1–4}(NH₃)_{1–4} and (PA)_{1–4}(SA)_{1–4} cluster geometries. In addition, these computational methods were also applied to CA-PA cluster systems (Figs. S13–18). PA-DMA clusters' free energy of formation (ΔG) is computed at various temperatures (238, 258, and 278 K). Previous study (Liu et al., 2023) show detailed atmospheric conditions are 253 K at April 2015 in Greenland, 268 K at May 2013 in Ny-Ålesund and 290 K at August 2019 in Helsinki. The temperatures of 238, 258, and 278 K encompass both mid-latitude coastal regions (e.g., Mace Head) and high-latitude regions (e.g., Greenland). The structures of (SA)_{1–4}, (NH₃)_{1–4} and (DMA)_{1–4} clusters were obtained from previous studies and are recalculated here (Xie et al., 2017; Ge et al., 2011; Jen et al., 2014; Almeida et al., 2013).

Atmospheric Cluster Dynamics Code (ACDC) Simulation

ACDC was applied to compute the growth pathway, steady-state concentrations, and time-evolving cluster formation rates for the (PA)_{1–4}(DMA)_{1–4}, (PA)_{1–4}(NH₃)_{1–4} and (PA)_{1–4}(SA)_{1–4} clusters (McGrath et al., 2012). The results of the experiments employing the birth and death equations and the conclusions of the ACDC simulations correspond well (McGrath et al., 2012). In this study, ACDC simulations were performed to model the formation process of PA-DMA, PA-NH₃ and PA-SA neutral clusters without considering the effects of charge and water (McGrath et al., 2012). For the studied PA-DMA clusters, the $\beta_{\text{DMA}}C_{\text{DMA}}/\Sigma\gamma$ of (PA)₅(DMA)₅ cluster is greater than 1. The resulting PA-DMA systems (PA)₅(DMA)₅ and (PA)₅(DMA)₄ clusters are set as boundary clusters. The concentration ranges of [PA], [SA], [DMA] and [NH₃] were defined at 10^6 – 10^8 cm^{−3}, 10^6 – 10^8 cm^{−3}, 0.1–100 and 1–100 ppt, respectively (Xie et al., 2017; Ge et al., 2011; Jen et al., 2014; Almeida et al., 2013).

3 Results and discussion

3.1 Cluster structures and cluster formation free energy

Figure 1 displays the (PA)_{1–4}(DMA)_{1–4} clusters identified minimum free energy configurations at the DLPNO-CCSD(T)/aug-cc-pVTZ// ω B97X-D/6-31++G(d,p) level of theory. Proton transfer and hydrogen bonding stabilize the majority of PA-DMA clusters. The formation of halogen bond is not found in PA-DMA clusters. All PA-DMA heteromolecular clusters have been discovered to undergo proton transfer, in which the hydrogen atom of hydroxyl group in the PA molecule moves to the nitrogen atom of the NH₂⁺ group in the DMA to produce N–H...O–Cl hydrogen bond. Each PA molecule donates a proton to a DMA molecule when the quantity of PA molecules and DMA molecules is equal.

When the number of PA molecules is not equal to the number of DMA molecules, the number of proton transfers between PA and DMA depends on the smaller value of the number of PA or DMA molecules. In the PA-NH₃ cluster system (Fig. S1), NH₃ accepts hydrogen atoms from the hydroxyl group in PA to generate NH₄⁺ and ClO₄[−]. It should be noted that when the number of PA molecules is greater than or equal to the number of NH₃ molecules, all NH₃ will be fully protonated. Similar to the PA-DMA cluster system, halogen bonds do not appear in the PA-NH₃ cluster system. The nitrogen atom of NH₃ and the hydrogen atom of the hydroxyl group in PA combine to form the N–H...O–Cl hydrogen bond. However, proton transfer does not take place in any of the PA-SA heteromolecular clusters (Fig. S10). Thus, hydrogen bonds (P–O...H–O and O–H...O–S) and electrostatic interactions sustain the PA-SA cluster system.

The ΔG values of (PA)_{1–4}(DMA)_{1–4}, (PA)_{1–4}(NH₃)_{1–4} and (PA)_{1–4}(SA)_{1–4} clusters at the DLPNO-CCSD(T)/aug-cc-pVTZ// ω B97X-D/6-31++G(d,p) level of 278 K, are shown in Fig. 2. The ΔG values of (PA)₂, (PA)₃ and (PA)₄ clusters are −0.06, −0.99 and 2.90 kcal mol^{−1}, respectively, indicating that pure PA molecules are thermodynamically susceptible to forming clusters. The PA-DMA cluster growth is more thermodynamically advantageous than the PA-NH₃ cluster growth, as indicated by the fact that all ΔG values of the PA-DMA cluster system are lower than those of the PA-NH₃ cluster system. The (PA)_{1–4}(DMA)₁ clusters are 15.15–38.79 kcal mol^{−1} lower than those of the corresponding (PA)_{1–4} clusters. The (PA)₁(DMA)₁, (PA)₁(NH₃)₁, and (PA)₁(SA)₁ initial clusters are quite significant in the corresponding cluster systems, with ΔG values of −15.15, −9.73, and −4.08 kcal mol^{−1}, respectively. The (PA)₄(DMA)₄ cluster has the lowest ΔG value, as low as −127.04 kcal mol^{−1}. The PA-SA cluster system exhibits the greatest ΔG values among the PA-DMA, PA-NH₃, and PA-SA cluster systems, suggesting that it is a thermodynamically least stable system. In conclusion, DMA has greater potential for PA-driven nucleation than NH₃ and SA based on the thermodynamic data.

3.2 Evaporation Rates and Cluster Stability

The stability of the PA-DMA, PA-NH₃, and PA-SA cluster systems is further assessed by calculating the evaporation rates at 278 K based on the determined ΔG values. The evaporation rate of DMA-rich clusters is higher than that of PA-rich clusters, as illustrated in Fig. 3, suggesting that clusters with more PA molecules are more stable. (PA)₁(DMA)₁, (PA)₂(DMA)₂, (PA)₃(DMA)₃, and (PA)₄(DMA)₄ clusters are all highly stable, with evaporation rates of 8×10^{-2} , 4×10^{-10} , 2×10^{-5} , and 4×10^{-5} s^{−1}, respectively. All pure PA and DMA clusters are unstable, with evaporation rates exceeding 10⁹ s^{−1}. The PA-rich heteromolecular clusters are more stable, probably because PA-rich clusters tend to contain more hydrogen bonds and various intermolecular interactions.

With the exception of the (PA)₄(DMA)₂, (PA)₄(DMA)₃, and (PA)₄(DMA)₄ clusters, the evaporation rates of the majority of PA-DMA cluster systems are lower than those of the comparable clusters of PA-NH₃ cluster systems. Similarly, (PA)₁(NH₃)₁, (PA)₂(NH₃)₂, (PA)₃(NH₃)₃, and (PA)₄(NH₃)₄ clusters are the stable clusters of the PA-NH₃ cluster system, which have evaporation rates of 3×10^{-2} , 2×10^{-1} , 3×10^0 , and 2×10^{-8} s^{−1}, respectively. (PA)₁(SA)₁ cluster is the most stable cluster with an evaporation rate as high as 6×10^6 s^{−1}, suggesting the instability of PA-SA clusters.

The actual Gibbs free energies of the PA-DMA systems affected by temperature and vapor concentration were calculated, as shown in Fig. 4. At 278 K, for the PA-DMA cluster system, (PA)₁(DMA)₁, (PA)₂(DMA)₂, (PA)₃(DMA)₃, and (PA)₄(DMA)₄ clusters are the primary pathways and the growth process is unimpeded. The fact that the clusters on diagonal has the lowest actual free energy has also been seen in other acid-base systems (Olenius et al., 2013; Elm, 2017). The decreasing trend of the actual Gibbs free energy during the formation of the PA-DMA system is more pronounced with decreasing temperature, implying the thermodynamic stability of the PA-DMA system.

3.3 Steady-State Cluster Concentrations and Nucleation Rate

To further assess the enhancement potential of DMA and NH₃ for PA-driven nucleation, the simulated steady-state PA dimer concentration ($\sum[(PA)_2]$ (cm^{−3})) (a) and the simulated cluster formation rate of the system, J (cm^{−3} s^{−1}) (b), at 278 K as the function of [PA] are shown in Fig. 5. It can be seen that the values of $\sum[(PA)_2]$ and J of the PA-DMA system gradually increase with the increase of [PA] and [DMA] under simulated conditions. However, the effects of [PA] and [DMA] on $\sum[(PA)_2]$ and J values gradually diminish with the increase of [PA] and [DMA]. In the PA-DMA system, neither $\sum[(PA)_2]$ nor J values were saturated with respect to [DMA] at [DMA] = 0.1–10 ppt and [PA] = 10⁶–10⁸ cm^{−3}. J values for the SA-DMA cluster system were about 10^{−5}–

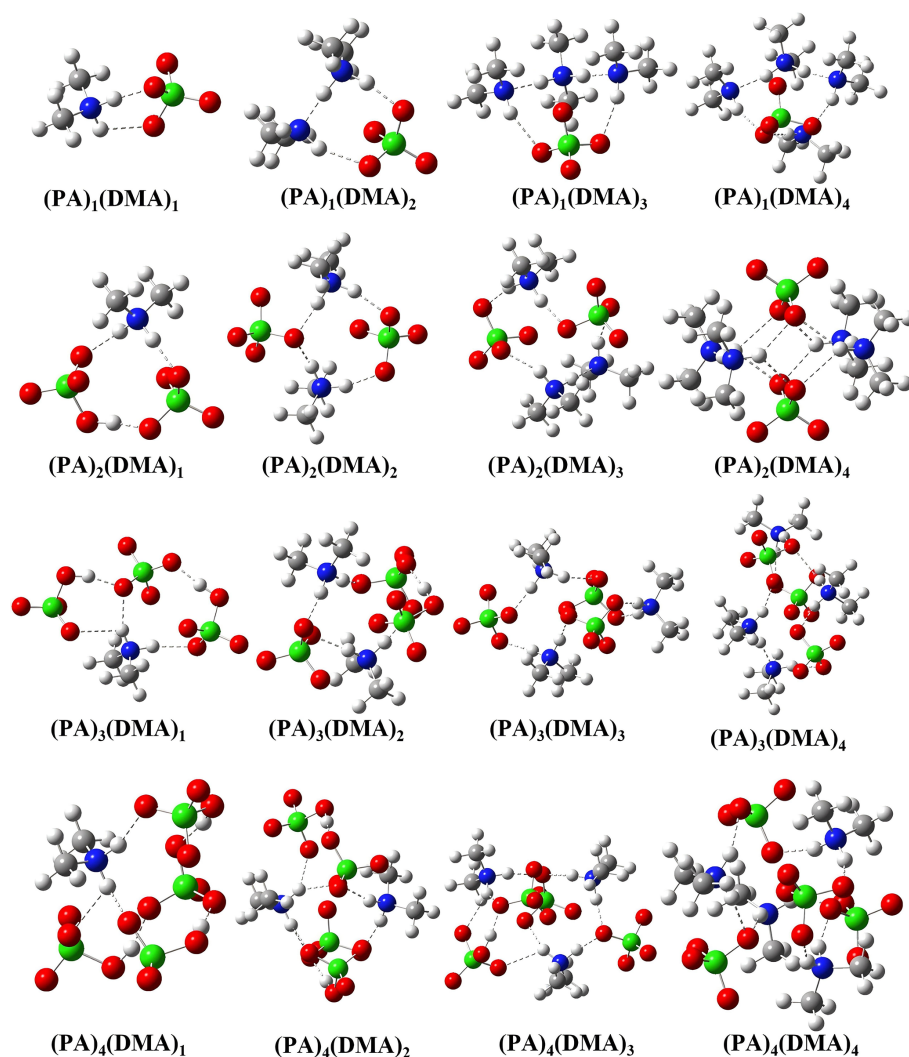


Figure 1. Identified minimum free energy configurations of the (PA)_{1–4}(DMA)_{1–4} clusters at the DLPNO-CCSD(T)/aug-cc-pVTZ// ω B97X-D/6-31++G(d,p) level of theory. The atoms of oxygen, nitrogen, chlorine, carbon, and hydrogen are represented by the red, blue, green, gray, and white balls, respectively. Hydrogen bonds are indicated by the dashed white lines.

$10^0 \text{ cm}^{-3} \text{ s}^{-1}$ at 278 K, $[\text{DMA}] = 1 \text{ ppt}$ and $[\text{SA}] = 10^6\text{--}10^7 \text{ cm}^{-3}$ (Xie et al., 2017). J values for the PA-DMA system were about $10^{-1}\text{--}10^3 \text{ cm}^{-3} \text{ s}^{-1}$ at 278 K, $[\text{DMA}] = 1 \text{ ppt}$ and $[\text{PA}] = 10^6\text{--}10^7 \text{ cm}^{-3}$. Therefore, the cluster formation rate in the PA-DMA cluster system is 3 to 4 times higher than that in the SA-DMA cluster system. Comparison of the cluster formation rates, J ($\text{cm}^{-3} \text{ s}^{-1}$), of PA-DMA and PA-NH₃ systems at 278 K; $[\text{PA}] = 10^6\text{--}10^8 \text{ cm}^{-3}$; $[\text{DMA}] = 1 \text{ ppt}$; $[\text{NH}_3] = 100 \text{ ppt}$; $\text{CS} = 2 \times 10^{-3} \text{ s}^{-1}$, as shown in Fig. 5c. Even the concentrations of NH₃ are 2 orders of magnitude higher than those of the DMA concentration, the J values of the PA-DMA cluster system are 8–10 orders of magnitude higher than those of the PA-NH₃ cluster system for NH₃ concentrations that are 2 orders of magnitude higher than those of the DMA concentration. This is not an isolated finding. For example, Ning et al. also found that the

cluster formation rate of HIO₃-DMA is higher than that of the HIO₃-NH₃ cluster system (Ning et al., 2022). In addition, the trends of J for the PA-DMA cluster system at temperature of 238, 258 and 298 K; $[\text{PA}]$ ($10^6\text{--}10^8 \text{ cm}^{-3}$) and $[\text{DMA}]$ (0.1, 1 and 10 ppt) are shown in Fig. 6. As the temperature decreases (from 298 to 258 K), the J value of the PA-DMA cluster system increases. As also discussed above, this is a direct consequence of lower T leading to a lower free energy and in turn leading to a lower evaporation rate. When the temperature range is 238–258 K, the J value of PA-DMA cluster system tends to be saturated and does not change significantly with temperature. The J value of the PA-DMA system is $1.65 \text{ cm}^{-3} \text{ s}^{-1}$ at 258 K, $[\text{DMA}] = 1 \text{ ppt}$ and $[\text{PA}] = 10^6 \text{ cm}^{-3}$.

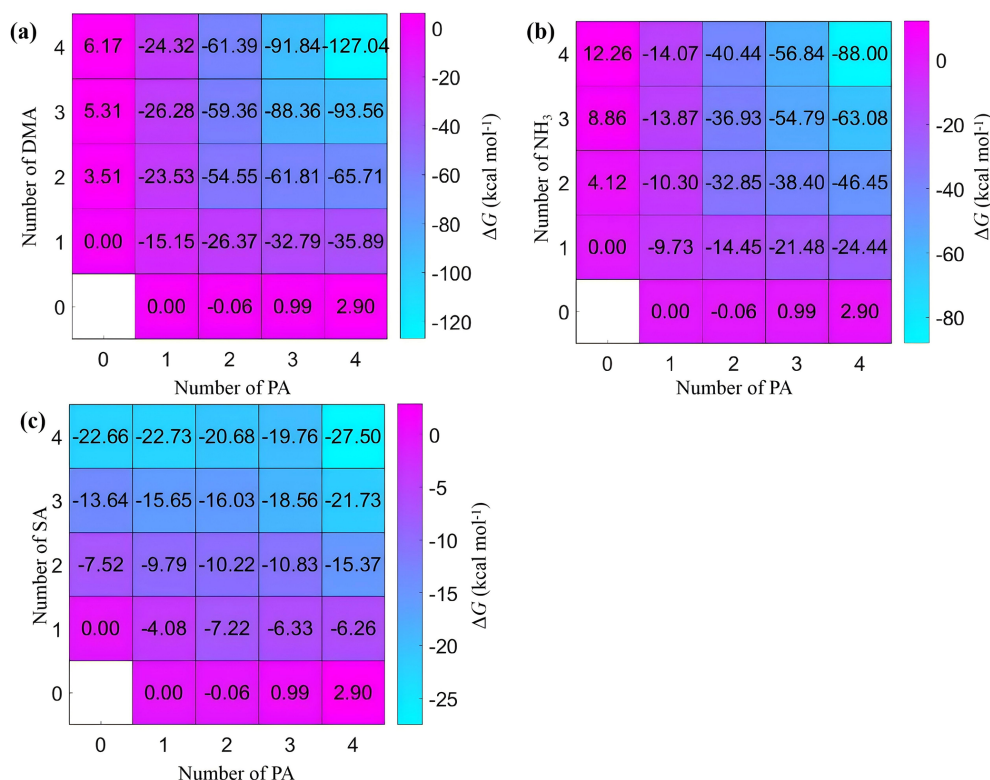


Figure 2. At the DLPNO-CCSD(T)/aug-cc-pVTZ// ω B97X-D/6-31++G(d,p) level of theory, the formation free energy (ΔG) (in kcal mol⁻¹) of (a) $(\text{PA})_{1-4}(\text{DMA})_{1-4}$, (b) $(\text{PA})_{1-4}(\text{NH}_3)_{1-4}$ and (c) $(\text{PA})_{1-4}(\text{SA})_{1-4}$ clusters. The computations are carried out at 1 atm and 278 K.

3.4 Cluster Growth Route

The growth routes of the PA-DMA (a) and PA-NH₃ (b) systems at 278 K, $[\text{PA}] = 10^6 \text{ cm}^{-3}$, $[\text{DMA}] = 3 \text{ ppt}$, and $[\text{NH}_3] = 100 \text{ ppt}$ are shown in Fig. 7. The evaporation rates of $(\text{PA})_2$ and $(\text{DMA})_2$ clusters are 4×10^9 and $2 \times 10^{12} \text{ s}^{-1}$. The higher evaporation rate causes the PA-DMA system to form via the $(\text{PA})_1(\text{DMA})_1$ dimer pathway rather than via the $(\text{PA})_2$ and $(\text{DMA})_2$ cluster pathways. The formation of the $(\text{PA})_1(\text{DMA})_1$ dimer is the initial stage in the PA-DMA system. There is no branching during the growth of clusters of the PA-DMA system, which may be due to the fact that the evaporation rate of clusters on the diagonal (the number of PA molecules is the same as the number of DMA molecules) is much lower than that of clusters off the diagonal (the number of PA molecules is different from the number of DMA molecules). A $(\text{PA})_2(\text{DMA})_2$ cluster complex is then formed by the combination of two $(\text{PA})_1(\text{DMA})_1$ dimer clusters.

$(\text{PA})_2(\text{DMA})_2$ also has only one growth path and further collides with $(\text{PA})_1(\text{DMA})_1$ to form a $(\text{PA})_3(\text{DMA})_3$ cluster. Eventually $(\text{PA})_5(\text{DMA})_5$ clusters is stable enough to grow from the PA-DMA system. Therefore, collision between clusters with PA and DMA monomers is not the main way in the PA-DMA cluster system. Cluster coalescence between a large number of $(\text{PA})_1(\text{DMA})_1$ clusters play an important

role in the growth of PA-DMA clusters, which may be due to the low evaporation rate and high stability of $(\text{PA})_1(\text{DMA})_1$, $(\text{PA})_2(\text{DMA})_2$, $(\text{PA})_3(\text{DMA})_3$, and $(\text{PA})_4(\text{DMA})_4$ clusters. This is a usual property of acid-base clusters (Lu et al., 2020). The growth path of the PA-NH₃ cluster system is very similar to that of the PA-DMA cluster system, in which a PA monomer molecule collides with an NH₃ molecule to form a $(\text{PA})_1(\text{NH}_3)_1$ dimer cluster, and then $(\text{PA})_1(\text{NH}_3)_1$ dimer clusters are continuously added to form $(\text{PA})_4(\text{NH}_3)_4$ cluster.

4 Atmospheric Implications and Conclusion

In this paper, quantum chemical methods are used to study the energy minimum configurations for the formation of atmospheric clusters of PA with DMA, NH₃ and SA in the Arctic boundary layer. The evaporation rates, cluster formation rates and growth paths of the nucleation process of PA with DMA, NH₃ and SA clusters are simulated by inputting ACDC from the thermodynamic data obtained. The following conclusions were drawn:

1. Based on the Gibbs free energies calculated in this study, DMA and NH₃ can strongly interact with PA through hydrogen bonding and proton transfer, thus pro-

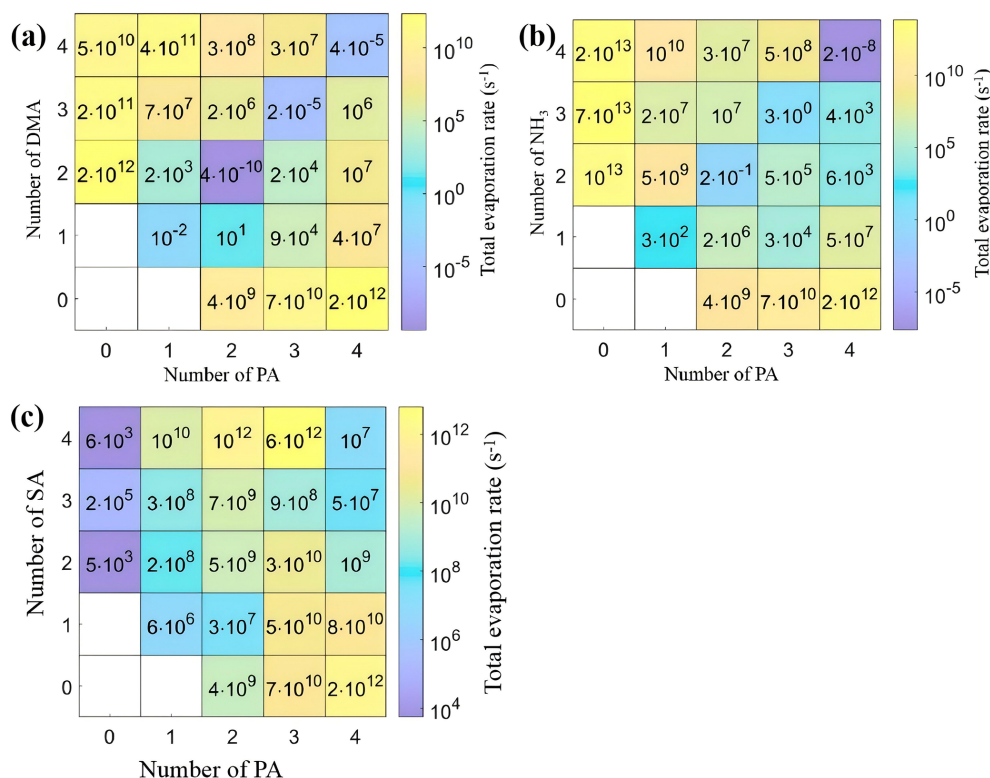


Figure 3. Evaporation rates for (a) (PA)₁₋₄(DMA)₁₋₄ and (b) (PA)₁₋₄(NH₃)₁₋₄ (c) (PA)₁₋₄(SA)₁₋₄ clusters at 278 K and 1 atm.

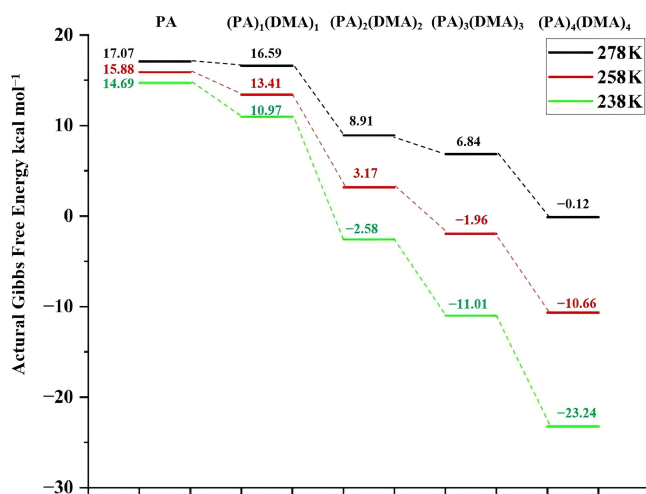


Figure 4. Actual Gibbs free energy of the PA-DMA clusters at 278, 258 and 238 K.

moting the formation of PA-DMA and PA-NH₃ clusters. No halogen bonds are found in PA-DMA and PA-NH₃ clusters.

- Under the condition that the DMA concentration is two orders of magnitude lower than the NH₃ concentration, the formation rate of PA-DMA clusters is much faster

than that of PA-NH₃ clusters. The cluster formation rate of the PA-SA cluster system is the slowest among the three systems. This may be due to the fact that no proton transfer occurs between the PA and SA molecules and only hydrogen bonding stabilizes the clusters.

- The formation rate of pure PA clusters is extremely low. DMA can promote the formation rate of PA clusters to a high level, which reflects the stabilizing effect of DMA on PA clusters. The results suggest that PA can contribute to new particle formation in the Arctic. The formation of (PA)₁(DMA)₁ and (PA)₁(NH₃)₁ dimers are the decisive clusters for the growth of PA-DMA and PA-NH₃ cluster systems.
- PA can form stable binary clusters with DMA, which is an important step in the formation of new particles in the atmosphere. The nucleation mechanism of PA-DMA revealed in this study may contribute to a deeper understanding of the role of marine chlorine-containing components on marine NPF.

Previous views hold that nucleation involving sulfuric acid/iodine oxoacid and amines/ammonia is a key pathway for new particle formation in the polluted boundary layer. The results of this study provide a partial explanation for the “fate” of PA in the Arctic atmosphere: PA can not only be removed via wet and dry deposition but is also

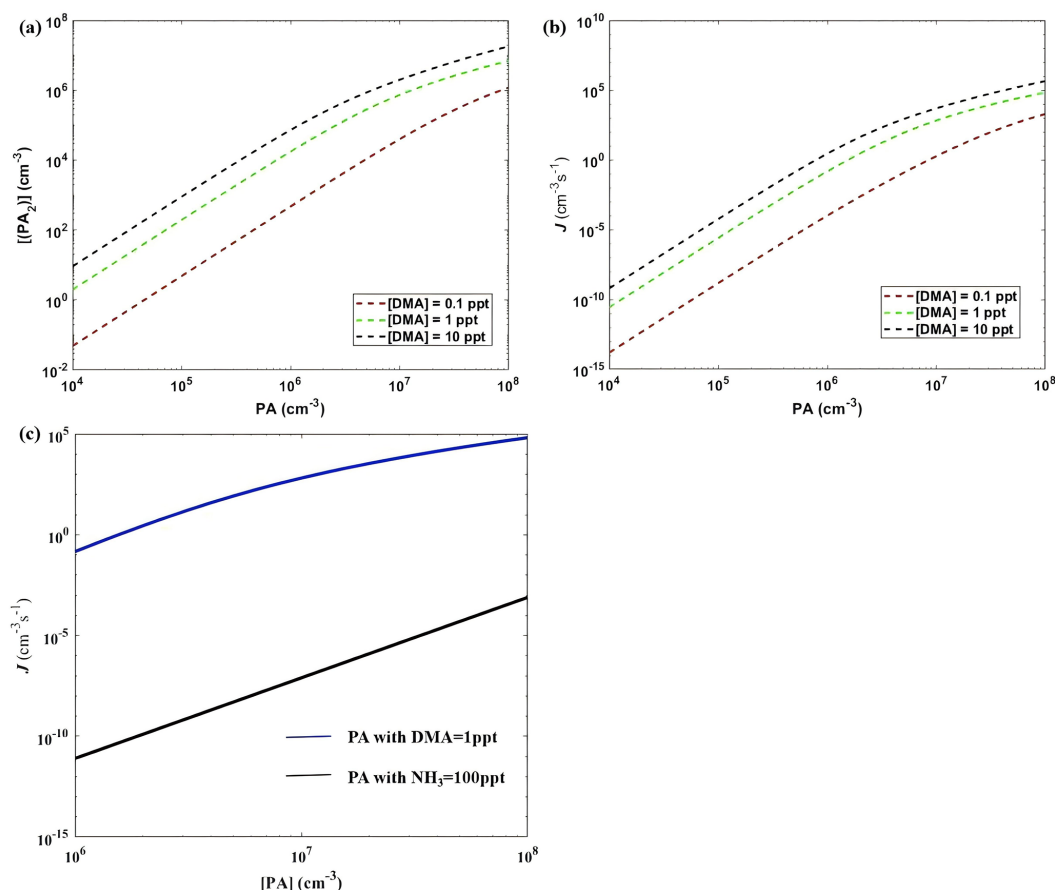


Figure 5. Simulated steady-state PA dimer concentration $\sum[(PA)_2]$ (cm^{-3}) (a) and the cluster formation rates J ($\text{cm}^{-3} \text{s}^{-1}$) of the simulation systems (b) as a function of $[PA]$ at 278 K. (c) Comparison of the cluster formation rates J ($\text{cm}^{-3} \text{s}^{-1}$) of PA-DMA clusters with PA-NH₃ clusters at 278 K; $[PA] = 10^6$ – 10^8 cm^{-3} ; $[DMA] = 1 \text{ ppt}$; $[NH_3] = 100 \text{ ppt}$; and $CS = 2 \times 10^{-3} \text{ s}^{-1}$. The ΔG values at the DLPNO-CCSD(T)/aug-cc-pVTZ// ω B97X-D/6-31++G(d,p) level are used to compute the PA-DMA and PA-NH₃ rates.

likely to participate in new particle formation by reacting with basic gases (especially DMA) to form stable clusters. This provides a theoretical basis for understanding the role of chlorine-containing components, particularly previously overlooked chlorate, in tropospheric aerosol nucleation. In a region where conventional sulfuric acid-amine/ammonia nucleation is often limited by low precursor concentrations, this PA-DMA pathway offers an additional source of ultra-fine particles that can grow into cloud condensation nuclei. This has direct consequences for CCN budgets and, consequently, for cloud microphysical properties and shortwave radiative forcing over the Arctic and other remote marine environments.

This study indicates that perchloric acid has potential in new particle formation in the Arctic marine boundary layer, particularly in the presence of dimethylamine. This finding has significant atmospheric and climatic implications: first, it reveals a potential new and efficient nucleation pathway between active chlorine released from the ocean (via the formation of HClO₄) and nitrogen-containing bases (such as DMA

from marine biogenic sources), which may have important implications for assessing the number of cloud condensation nuclei and cloud radiative forcing in the marine boundary layer. Second, it expands our understanding of the atmospheric chlorine cycle, indicating that, in addition to known deposition processes, gas-to-particle transformations involving basic gases represent an important atmospheric “sink” for HClO₄. This additional sink may influence the atmospheric residence time and vertical profile of HClO₄, with potential ramifications for oxidative capacity and halogen-mediated chemistry in the polar troposphere. These findings underscore the need to revisit how chlorine-containing species are represented in global and regional climate models. Current Earth system models typically neglect HClO₄ and its interaction with amines in aerosol nucleation schemes. Incorporating the PA-DMA nucleation mechanism, especially in high-latitude and marine domains, could improve simulations of aerosol-cloud-climate interactions.

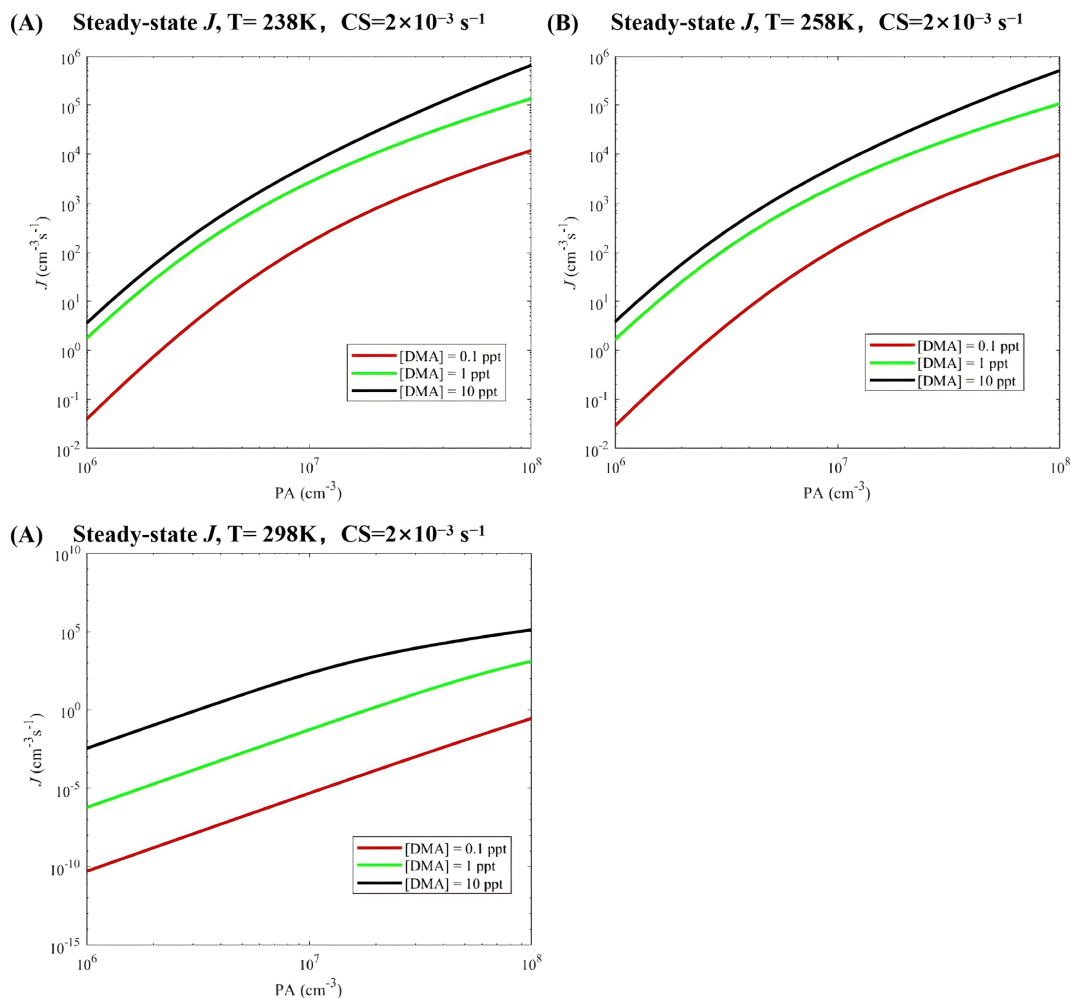


Figure 6. The simulated cluster formation rate J ($\text{cm}^{-3} \text{s}^{-1}$) of the PA-DMA system at different temperatures (A) 238, (B) 258, and (C) 298 K; $[\text{PA}] = 10^6$ – 10^8 cm^{-3} ; $[\text{DMA}] = 0.1, 1$, and 10 ppt ; and $\text{CS} = 2 \times 10^{-3} \text{ s}^{-1}$.

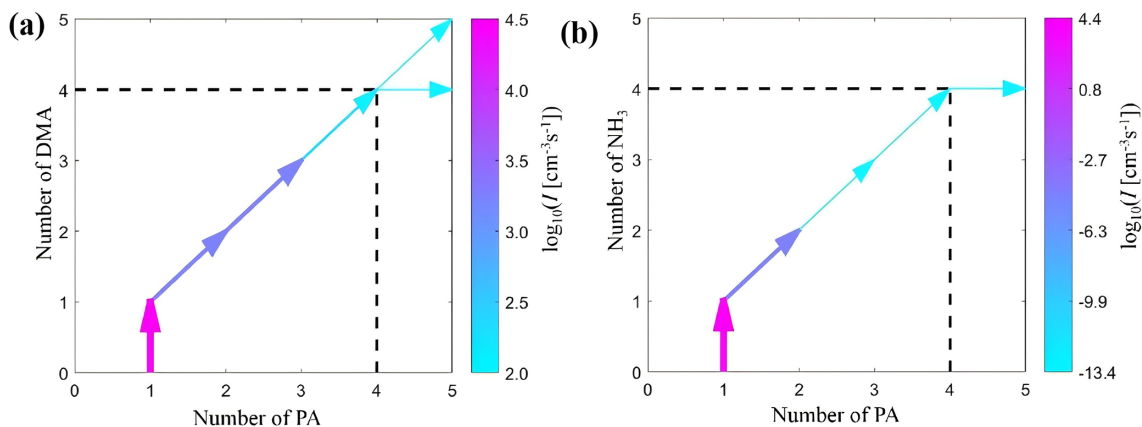


Figure 7. (a) Main clustering routes of $(\text{PA})_{1-4}(\text{DMA})_{1-4}$ clusters at 278 K, $[\text{PA}] = 10^6 \text{ cm}^{-3}$, and $[\text{DMA}] = 3 \text{ ppt}$. (b) Main clustering routes of $(\text{PA})_{1-4}(\text{NH}_3)_{1-4}$ clusters at 278 K, $[\text{PA}] = 10^6 \text{ cm}^{-3}$, and $[\text{NH}_3] = 100 \text{ ppt}$.

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