

1 Chloric Acid-Driven Nucleation Enhanced by
2 Dimethylamine and Sulfuric acid in the Arctic:
3 Mechanistic Study

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Abstract

Chlorine radicals are strong oxidizing agents in the atmosphere, and the process of chlorine oxidation results in the formation of chloric acid (HClO_3 , CA). Recent studies have shown that trace amounts of CA have been detected in the Arctic boundary layer. However, the contribution of chlorine-containing species to oceanic new particle formation (NPF) has not been fully revealed. It is speculated that CA is involved in the oceanic nucleation process. In this study, the enhancement of CA-based NPF by dimethylamine (DMA) and sulfuric acid (SA) was comparatively investigated at the molecular level using density-functional theory (DFT) and atmospheric cluster dynamics simulation (ACDC). The results show that DMA can form clusters with CA through hydrogen bonding, halogen bonding and proton transfer, which reduces the energy barrier for CA-based cluster formation and significantly improves the thermodynamic stability of CA clusters. The cluster formation rate of CA-DMA cluster system is higher than that of the CA-SA cluster system. CA-DMA nucleation may not effectively contribute to Arctic NPF. These findings may help to reveal some of the missing sources of the Arctic NPF. The present study contributes to a deeper understanding of the influence of oceanic chlorine-containing constituents on the oceanic NPF.

1 Introduction

Marine aerosols as the main natural aerosol system have a major global impact by regulating the radiative balance and climate of clouds (Moore et al., 2024; Revell et al., 2025). New particle formation (NPF) contributes to more than half of the global cloud condensation nuclei, which in turn contributes to cloud formation (Gordon et al., 2017; Takegawa et al., 2020; Williamson et al., 2019; Zhang et al., 2012; Zhao et al., 2024). Compared with clouds over land, ocean clouds cover a wider area and significantly increase the albedo of the ocean, so ocean clouds contribute more to the climate system (Merikanto et al., 2009; Wood, 2012; Zheng et al., 2021). Sulfuric acid (SA, H_2SO_4), methane sulfonic acid (MSA, CH_3HSO_3), and iodic acid (IA, HIO_3) are generally considered to contribute to the formation of oceanic particles (Hodshire et al., 2019; Yin et al., 2021; Facchini et al., 2008; Perraud et al., 2015; Arquero et al., 2017; Hopkins et al., 2008). However, there is still a significant difference between the particle formation rates observed in the field and those predicted by simulation (Kirkby et al., 2011; Kirkby et al., 2016; Zhang et al., 2004; Ehn et al., 2014; Dawson et al., 2012). Therefore, it is necessary to consider whether other gaseous precursors are involved in NPF to narrow the gap between experiments and simulations.

Compared to the main atmospheric oxidants, hydroxyl radicals, chlorine radicals act as strong oxidants in the polar troposphere at relatively high concentration levels (Stone et al., 2012). The active chlorine cycle in the Arctic boundary layer during the spring after polar sunrise depletes O_3 in the region (Custard et al., 2016; Foster et al.,

2001; Thompson et al., 2015). Chloric acid (CA) has no photoactivity, with concentrations estimated to range from 1×10^5 to 7×10^6 molecules cm^{-3} (Tham et al., 2023). Research by Tham et al. indicates that the CA and perchloric acid (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 CA or PA may form as the final oxidation step of chlorine oxides. CA was not found in the particle phase of the aerosol, thus it is difficult to determine whether CA is involved in the NPF phase.

Many studies have shown that atmospheric bases such as methylamine (MA), dimethylamine (DMA), trimethylamine (TMA) and ammonia can effectively enhance SA-based NPF (Yao et al., 2018; Almeida et al., 2013). Although amines emit 10–20 times less than ammonia in the ocean, amines can effectively form clusters with substances such as SA in the ocean (Myriokefalitakis et al., 2010; Semeniuk and Dastoor, 2018; Almeida et al., 2013). Of these amines, DMA has been found as a component of marine secondary aerosols (Facchini et al., 2008). 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 has been identified as the strongest enhancing atmospheric amine for SA and IA-driven NPF (Olenius et al., 2017; Ning et al., 2022). Thus, DMA may have a higher enhancing potential (EP) than NH_3 for CA-based NPF.

Sulfuric acid (H_2SO_4 , SA) has been detected in both gas and particulate phases in polluted coastal areas of China(Zhu et al., 2019; Yu et al., 2019). It is noteworthy that the concentration of SA is two orders of magnitude higher (up to 10^8 molecules cm^{-3}) in the coastal polluted areas due to urban air pollution compared to the clean marine atmosphere(Zhu et al., 2019). Sulfuric acid is poor nucleating agent in the atmosphere and promotes nucleation processes when combined with bases(Sipilä et al., 2010; Faloona, 2009). This precisely demonstrates the value of studying the CA-DMA system—it may serve as an additional source of acidic substances in the marine atmosphere. The nucleation of iodine species (oxyacids and oxides) is a current hot topic(Li et al., 2024; Ning et al., 2024). Additionally, extensive quantum chemical studies have been conducted on the clustering phenomena of sulfuric acid, methanesulfonic acid, and alkali compounds(Wu et al., 2023; Zhang et al., 2023). Engsvang et al.(Engsvang et al., 2024) has investigated the formation mechanism of CA clusters, concluding that CA did not contribute. The formation rate and mechanism of CA-DMA clusters deserve further investigation.

Using density functional theory (DFT) and the Atmospheric Clusters Dynamic Code (ACDC), the involvement of DMA and SA in the initial phase of CA-based NPF has been investigated. We obtained the minimum free energy structures of the $(\text{CA})_{1-4}(\text{DMA})_{1-4}$ and $(\text{CA})_{1-4}(\text{SA})_{1-4}$ clusters. The temperatures used in this study are within the temperature range of the atmospheric boundary layer in the ordinary range(Miřijovský and Langhammer, 2015). The specific temperature value studied is 238, 258 and 278K. The concentration of CA was estimated to be in the range of 1.0

$\times 10^6 - 1.0 \times 10^8$ molecules cm^{-3} based on measured data. The concentration of CA used is higher than the measured value and is intended solely for testing/prediction purposes. Further study of CA-DMA clusters under Arctic atmospheric conditions and the corresponding thermodynamic data used as input to the ACDC reveals the growth pathways and formation rates of the clusters.

2 Computational methods

Configurational Sampling

We employed a multi-step global minimum sampling scheme to search for the global minimum of $(\text{CA})_{1-4}(\text{DMA})_{1-4}$ and $(\text{CA})_{1-4}(\text{SA})_{1-4}$ clusters. In this study, the initial structures of 1000-10000 $(\text{CA})_{1-4}(\text{DMA})_{1-4}$ and $(\text{CA})_{1-4}(\text{SA})_{1-4}$ clusters were randomly generated using the ABCluster software to determine their global minima (clusters with the lowest Gibbs free energies). In the multistep sampling scheme, the geometry optimization is performed at the PM7, $\omega\text{B97X-D/6-31+G(d,p)}$ and $\omega\text{B97X-D/6-31++G(d,p)}$ levels of theory, and the single-point energy calculations are performed at the DLPNO-CCSD(T)/aug-cc-pVTZ level of theory. Geometry calculations are based on the $\omega\text{B97X-D/6-31++G(d,p)}$ theory level (Li et al., 2024; Ning et al., 2024; Wu et al., 2023). The GAUSSIAN 09 program package (Frisch et al., 2016) was used to perform the PM7 and $\omega\text{B97X-D}$ calculations. DLPNO-CCSD(T) calculations were performed in the ORCA 4.0.0 program (Neese, 2012). For convergence problems and failures such as ending with a false frequency in the optimization of $(\text{CA})_{1-4}(\text{DMA})_{1-4}$ and $(\text{CA})_{1-4}(\text{SA})_{1-4}$ cluster geometries, the initial

structures will be modified and re-optimized until the optimization is successful. The free energy of formation (ΔG) of individual clusters is calculated at different temperatures 238, 258, and 278 K. The structures of (SA)₁₋₄ and (DMA)₁₋₄ clusters were obtained from previous studies and are recalculated here (Xie et al., 2017).

Atmospheric Cluster Dynamics Code (ACDC) Simulation

Cluster formation rates, steady-state concentrations, and growth paths for (CA)₁₋₄(DMA)₁₋₄ and (CA)₁₋₄(SA)₁₋₄ clusters were calculated using ACDC without considering the effects of charge and water (Mcgrath et al., 2012). ACDC simulation conclusions are obtained based on the birth and death equation (Almeida et al., 2013; Lu et al., 2020; Kürten et al., 2018). The (CA)₅(DMA)₅ clusters are set as boundary clusters (see Supporting Information (SI) for details). The concentration ranges of [CA], [SA] and [DMA] were set to $10^6 - 10^8 \text{ cm}^{-3}$, $10^6 - 10^8 \text{ cm}^{-3}$ and 0.1–100 ppt, respectively. Widely dispersed DMA has an atmospheric concentration of 0.4 – 10 ppt 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.

3 Results and discussion

3.1 Cluster Structures and Cluster Formation Free Energy

To evaluate the thermodynamic stability of the formed CA-DMA clusters, the formation free energies (ΔG , kcal mol⁻¹) at 278 K are calculated for the (CA)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. As shown

in Figure. 1, hydrogen bonds play an important role in the formation of CA-DMA clusters. Proton transfer reactions are not observed in the pure (CA)₂ and (CA)₃ clusters, whereas spontaneous proton transfer reactions are observed in all (CA)₁₋₄(DMA)₁₋₄ clusters. For most (CA)₁₋₄(DMA)₁₋₄ clusters, protons are transferred from CA to DMA. Proton transferring wasn't observed in pure (CA)₂ and (CA)₃ clusters, whereas spontaneous proton transfer reactions were present in all (CA)₁₋₄(DMA)₁₋₄ clusters. For most (CA)₁₋₄(DMA)₁₋₄ clusters, protons are transferred from CA to DMA, forming Cl-O...H-N hydrogen bonding, accompanied by the production of ClO₃⁻ negative ions and DMA⁺ ions. In CA-DMA clusters containing two or more chlorine atoms, including (CA)₂(DMA)₁, (CA)₃(DMA)₁, (CA)₃(DMA)₁, (CA)₃(DMA)₁, (CA)₃(DMA)₄, (CA)₄(DMA)₁, (CA)₄(DMA)₂, (CA)₄(DMA)₃, and (CA)₄(DMA)₄ clusters, O-Cl...O-Cl halogen bonds and Cl-O...H-N hydrogen bonds together stabilize these clusters described above. Halogen bonds are not present in clusters containing single Cl atom and in (CA)₂(DMA)₂, (CA)₂(DMA)₃, (CA)₂(DMA)₄, as well as (CA)₃(DMA)₃ clusters. For the CA-SA clusters, the ClO₃⁻ negative ions generated in the CA-DMA cluster system were not found in the CA-SA cluster system because proton transfer do not occur. In contrast to the O-Cl...O-Cl halogen bond found in the CA-DMA cluster system, the CA-SA cluster adds S-O...Cl-O halogen bond (in the Figure S2). It is worth noting that the most stable cluster structure of CA-DMA we obtained exhibits similarities to the findings of Engsvang et al(Engsvang et al., 2024). CA-DMA clusters are primarily stabilized by hydrogen bonds.

The formation Gibbs free energy values of (A) $(\text{CA})_{1-4}(\text{DMA})_{1-4}$ and (B) $(\text{CA})_{1-4}(\text{SA})_{1-4}$ at 278 K and 1 atm are shown in Figure. 2. The Gibbs free energy values for the formation of $(\text{CA})_2$, $(\text{CA})_3$, and $(\text{CA})_4$ clusters in the pure acid system are 1.31, 2.52, and 5.37 kcal mol⁻¹, respectively, implying that at 278 K, pure CA clusters are thermodynamically difficult to form. The difference between the ΔG values of $(\text{CA})_4(\text{DMA})_4$ cluster and $(\text{CA})_4(\text{SA})_4$ cluster is the largest, up to 61.62 kcal mol⁻¹. $(\text{CA})_1(\text{SA})_1$ and $(\text{CA})_1(\text{DMA})_1$ are both very important in their respective cluster systems, and their ΔG values are -2.62 and -10.08 kcal mol⁻¹, respectively⁻¹. The ΔG values of $(\text{CA})_{1-4}$ clusters are 10.08 – 28.16 kcal mol⁻¹ higher than those of the corresponding $(\text{CA})_{1-4}(\text{DMA})_1$ clusters, suggesting that DMA stabilizes the CA clusters. As the size of CA-DMA clusters increases, the clusters gradually form a cage-symmetric structure. The ΔG values of the majority of clusters in the CA-DMA system are 3.55 – 61.62 kcal mol⁻¹ lower than the corresponding ΔG values of the CA-SA system. This indicates that the CA-DMA cluster system is more thermally stable compared to the CA-SA cluster system.

3.2 Evaporation Rates and Cluster Stability

The total evaporation rate ($\sum \gamma$, s⁻¹) of $(\text{CA})_{1-4}(\text{DMA})_{1-4}$ clusters and $(\text{CA})_{1-4}(\text{SA})_{1-4}$ clusters formed at T = 278 K is shown in Figure. 3. The smaller value of $\sum \gamma$ means that the stability of CA-DMA clusters is higher and the clusters shrink further. The clusters with the same number of CA molecules and the number of DMA molecules include $(\text{CA})_1(\text{DMA})_1$, $(\text{CA})_2(\text{DMA})_2$, $(\text{CA})_3(\text{DMA})_3$, and $(\text{CA})_4(\text{DMA})_4$

clusters, which have the values of $\sum\gamma$ of 10^2 , 2×10^{-4} , 5×10^{-1} , and $3 \times 10^1 \text{ s}^{-1}$, respectively. $(\text{CA})_2(\text{DMA})_2$ cluster has the lowest $\sum\gamma$ value, implying that $(\text{CA})_2(\text{DMA})_2$ cluster is the most stable cluster in the “ 4×4 ” box system of CA-DMA clusters. For clusters with different numbers of CA and DMA molecules, the $\sum\gamma$ value of $(\text{CA})_2(\text{DMA})_1$ cluster is significantly lower than that of other clusters, which indicates that $(\text{CA})_2(\text{DMA})_1$ cluster has a high probability of competing for the growth path of nucleation. In this study, we compare the evaporation rates of clusters from the CA-DMA system with those from the CA-SA system at 278K. In contrast to the other clusters, the evaporation rate of $(\text{CA})_1(\text{SA})_4$ clusters is lower than that of the corresponding $(\text{CA})_1(\text{DMA})_4$ clusters. The evaporation rates of most $(\text{CA})_{1-4}(\text{DMA})_{1-4}$ clusters are much smaller than those of the corresponding $(\text{CA})_{1-4}(\text{SA})_{1-4}$ clusters, indicating that the CA-DMA cluster system is kinetically more stable than the CA-SA cluster system.

3.3 Cluster Formation Rates and Steady-State Cluster Concentrations

Cluster formation rate (J) and steady-state CA dimer concentration ($\sum[(\text{CA})_2]$) are important indicators for assessing the enhancement potential of DMA for CA-based nucleation. Figure 4 shows the variation of $\sum[(\text{CA})_2]$ and J values at 278 K with CA concentration ($[\text{CA}] = 10^6 - 10^8 \text{ cm}^{-3}$) and DMA concentration ($[\text{DMA}] = 1, 10 \text{ and } 100 \text{ ppt}$). The J value of the CA-DMA system showed a positive correlation with CA and DMA concentrations as CA and DMA concentrations increased. The dependence of the cluster formation rate on the DMA concentration does not decrease

with increasing CA concentration, which means that the dependence of the system on DMA does not saturate when the CA concentration is high. The $\Sigma[(CA)_2]$ and J of the CA-DMA system with the full range of acid-base concentrations considered (CA: $10^6 - 10^8$ molecules cm^{-3} , DMA: 1, 10 and 100 ppt) were significantly higher than the CA-SA system (Figure. S4). However, at high concentrations of $[CA] = 1 \times 10^7$ molecules cm^{-3} and $[DMA] = 10$ ppt, the J value of the CA-DMA cluster system only reaches $1.39 \times 10^{-11} \text{ cm}^{-3} \text{ s}^{-1}$. The contribution of the CA-DMA cluster system to the NPF is not significant under the atmospheric conditions of 278 K. In addition, 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). Comparative studies indicate that the cluster formation rate of SA-DMA clusters exceeds that of CA-DMA clusters by more than seven orders of magnitude (Zhang et al., 2022). Under temperature and concentration parameters relevant to Arctic environments, the CA-DMA system could be incapable of forming cluster structures. Despite the negative outcome, this represents a significant advancement in advancing research on nucleation mechanisms in marine and Arctic regions.

To further systematically explore the effect of temperature on the J of the CA-DMA cluster system, Figure. 5 shows the simulated J at other temperatures (238 and 258 K), $[CA] = 10^6 - 10^8$ molecules cm^{-3} , $[DMA] = 0.1$ ppt (red line), 1 ppt (green line), 10 ppt (blue line), and 100 ppt (black line). A comparison of the simulations at 258 K (Figure. 5a) and 238 K (Figure. 5b) reveals that the decrease in

temperature further increases the J value of the CA-DMA cluster system to a higher level. However, at a low temperature (258 K), the J values of the CA-DMA cluster system do not reach higher levels at high concentrations of $[CA] = 1 \times 10^7$ molecules cm^{-3} and $[DMA] = 10$ ppt. The J values of the CA-DMA cluster system were further investigated under cold Arctic conditions (238 K). It was found that the J value of CA-DMA cluster system at 238 K atmospheric condition was significantly higher than that of CA-DMA cluster system at other higher temperature conditions, which was mainly due to the fact that the low temperature attenuates the evaporation of CA-DMA clusters.

3.4 Cluster growth pathway

Figure 6 shows the growth paths of CA-DMA and CA-SA clusters at 278 K, $[CA] = 10^6 \text{ cm}^{-3}$, $[DMA] = 1$ ppt, and $[SA] = 10^6 \text{ cm}^{-3}$. The first step in the growth of CA-DMA clusters is the collision of a CA molecule and a DMA molecule to form a $(CA)_1(DMA)_1$ cluster. There are two growth paths for $(CA)_1(DMA)_1$ clusters: a CA molecule collides and combines with a $(CA)_1(DMA)_1$ cluster to form a $(CA)_2(DMA)_1$ cluster, and a DMA molecule is subsequently added to form a $(CA)_2(DMA)_2$ cluster; a $(CA)_1(DMA)_1$ cluster combines with another $(CA)_1(DMA)_1$ cluster to form a $(CA)_2(DMA)_2$ cluster. This growth pattern is mainly due to the high stability of $(CA)_2(DMA)_1$ clusters. After the $(CA)_2(DMA)_2$ clusters, the growth route of the CA-DMA cluster system extends along the direct binding to the $(CA)_1(DMA)_1$ clusters. For $(CA)_3(DMA)_3$ clusters, one route is the addition of acid and base, and the

other route is the direct binding to $(\text{CA})_1(\text{DMA})_1$ clusters to produce $(\text{CA})_4(\text{DMA})_4$ clusters. Compared to the nucleation pathways observed at 278K in the CA-DMA system, pathways at 238K involve in the formation of $(\text{CA})_2(\text{DMA})_2$ to $(\text{CA})_2(\text{DMA})_4$ clusters, as well as the combination of $(\text{CA})_4(\text{DMA})_4$ clusters with a single $(\text{CA})_1(\text{DMA})_1$ cluster to generate $(\text{CA})_5(\text{DMA})_5$ clusters.

The growth pathway of the CA-SA cluster system differs considerably from that of the CA-DMA cluster system. The cluster initially formed in the CA-SA cluster system is the $(\text{CA})_2$ cluster not the $(\text{CA})_1(\text{SA/DMA})_1$ cluster in the CA-DMA system. After the generation of $(\text{CA})_2$ cluster, the system can generate $(\text{CA})_3(\text{SA})_1$ clusters by successive addition of acid molecules. Subsequently, $(\text{CA})_3(\text{SA})_1$ clusters combine with $(\text{CA})_1(\text{SA})_1$ clusters to generate $(\text{CA})_3(\text{SA})_2$ clusters. The final $(\text{CA})_4(\text{SA})_4$ cluster of the system is generated by collision of a $(\text{CA})_3(\text{SA})_2$ cluster with an $(\text{SA})_2$ cluster.

3.5 Atmospheric implications and conclusions

In this paper, combination method of quantum chemistry and ACDC were used to elucidate the molecular structure mechanism of DMA and SA enhancing role of CA nucleation by comparing the CA-DMA and CA-SA nucleation systems. Proton transfer was observed in all $(\text{CA})_{1-4}(\text{DMA})_{1-4}$ clusters while no proton transfer occurred within $(\text{CA})_{1-4}(\text{SA})_{1-4}$ clusters. The ClO_3^- groups generated by the deprotonation of CA are involved in the formation of at least one hydrogen bond. Hydrogen and halogen bonds together stabilize the CA-DMA and CA-SA nucleation

systems. The vast majority of CA-SA cluster systems have higher ΔG values than the corresponding CA-DMA cluster systems. The cluster formation rates of the pure CA-PA and CA-SA nucleation systems are relatively low, and the contribution of DMA to CA nucleation is stronger than that of SA. Clusters with the same number of CA and DMA molecules ((CA)₁(DMA)₁, (CA)₂(DMA)₂, (CA)₃(DMA)₃, and (CA)₄(DMA)₄ clusters) play a key role in the growth path of CA-DMA clusters, which is consistent with the existing literature(Wu et al., 2023; Zhang et al., 2023). This study is important for a deeper understanding of Arctic atmospheric nucleation. The current simulations do not take into account charge effects, the involvement of water molecules, and the influence of complex atmospheric matrices (e.g., organic matter). In the future, it is necessary to validate the simulation results with field observations and extend it to multi-component (e.g., IA/SA/DMA mixing or CA-SA-DMA clusters) nucleation systems in order to quantify the contribution of chlorine-containing substances to the global NPF in a more comprehensive way.

Data availability

All data supported the paper are available from the article, supplementary information, and the corresponding author upon reasonable request.

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309 **Additional information**

310 **Competing interests:** The authors declare no competing financial interests.

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Graphical Abstract

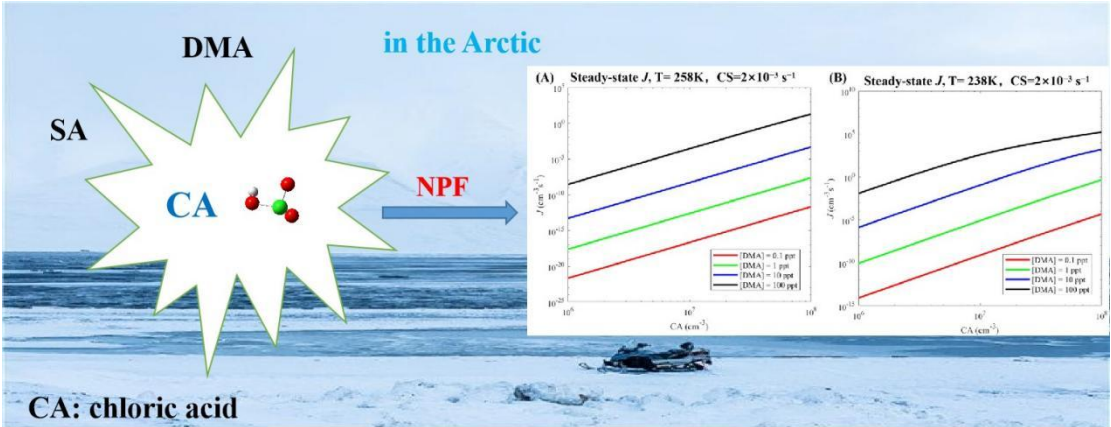


Figure Captions

Figure 1. Identified lowest free energy structures of the $(\text{CA})_{1-4}(\text{DMA})_{1-4}$ clusters at the DLPNO-CCSD(T)/aug-cc-pVTZ// $\omega\text{B97X-D/6-31++G(d,p)}$ level of theory. The red, blue, gray, green and white balls represent oxygen, nitrogen, carbon, chlorine and hydrogen atoms, respectively. The dashed white and black lines indicate hydrogen and halogen bonds, respectively.

Figure 2. The formation free energy (ΔG) (in kcal mol^{-1}) of (A) $(\text{CA})_{1-4}(\text{DMA})_{1-4}$ and (B) $(\text{CA})_{1-4}(\text{SA})_{1-4}$ clusters at the DLPNO-CCSD(T)/aug-cc-pVTZ// $\omega\text{B97X-D/6-31++G(d,p)}$ level of theory. The calculations are performed at 278 K and 1 atm.

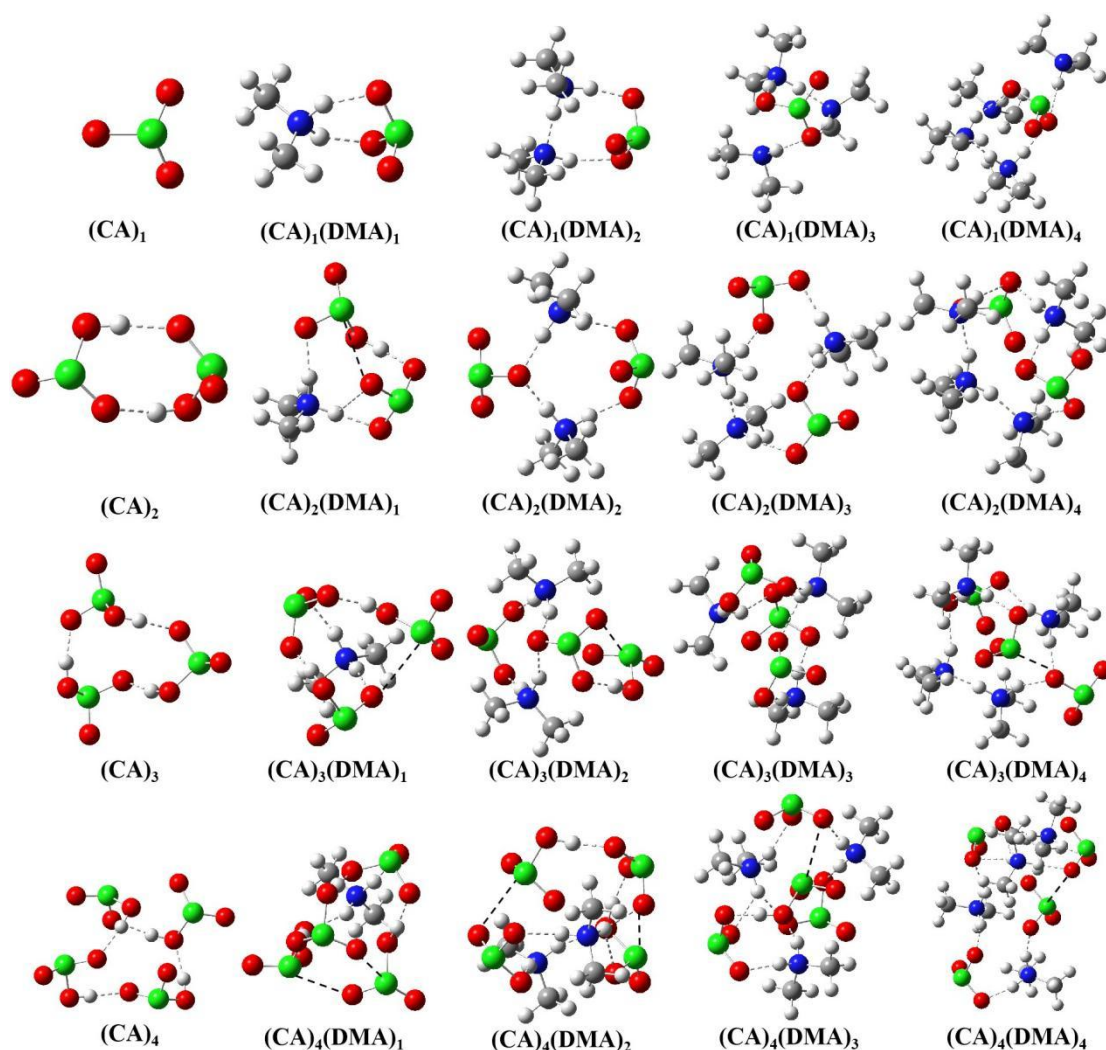
Figure 3. Evaporation rates for (A) $(\text{CA})_{1-4}(\text{DMA})_{1-4}$ and (B) $(\text{CA})_{1-4}(\text{SA})_{1-4}$ clusters at 278 K and 1 atm.

Figure 4. Simulated steady-state CA dimer concentration $\Sigma[(\text{CA})_2]$ (cm^{-3}) (A) and the cluster formation rates J ($\text{cm}^{-3} \text{s}^{-1}$) out of the simulation systems (B) as a function of $[\text{CA}]$ at 278 K.

Figure 5. The simulated cluster formation rate J ($\text{cm}^{-3} \text{s}^{-1}$) of the CA-DMA system at different temperatures (A) 258, and (B) 238 K; $[\text{CA}] = 10^6 - 10^8 \text{ molec. cm}^{-3}$; $[\text{DMA}] = 0.1, 1, 10, \text{ and } 100 \text{ ppt}$; and $\text{CS} = 2 \times 10^{-3} \text{ s}^{-1}$.

Figure 6. (A) Main clustering pathways of $(\text{CA})_{1-4}(\text{DMA})_{1-4}$ clusters at 278 K, $[\text{CA}] = 10^6 \text{ cm}^{-3}$, and $[\text{DMA}] = 5 \text{ ppt}$. (B) Main clustering pathways of $(\text{CA})_{1-4}(\text{SA})_{1-4}$ clusters at 278 K, $[\text{CA}] = 10^6 \text{ cm}^{-3}$, and $[\text{SA}] = 10^6 \text{ cm}^{-3}$. (C) Main clustering pathways of $(\text{CA})_{1-4}(\text{DMA})_{1-4}$ clusters at 238 K, $[\text{CA}] = 10^6 \text{ cm}^{-3}$, and $[\text{DMA}] = 5$

542 ppt.



543

544 **Figure 1.** Identified lowest free energy structures of the (CA)₁₋₄(DMA)₁₋₄ clusters at

545 the DLPNO-CCSD(T)/aug-cc-pVTZ// ω B97X-D/6-31++G(d,p) level of theory. The

546 red, blue, gray, green and white balls represent oxygen, nitrogen, carbon, chlorine and

547 hydrogen atoms, respectively. The dashed white and black lines indicate hydrogen

548 and halogen bonds, respectively.

549

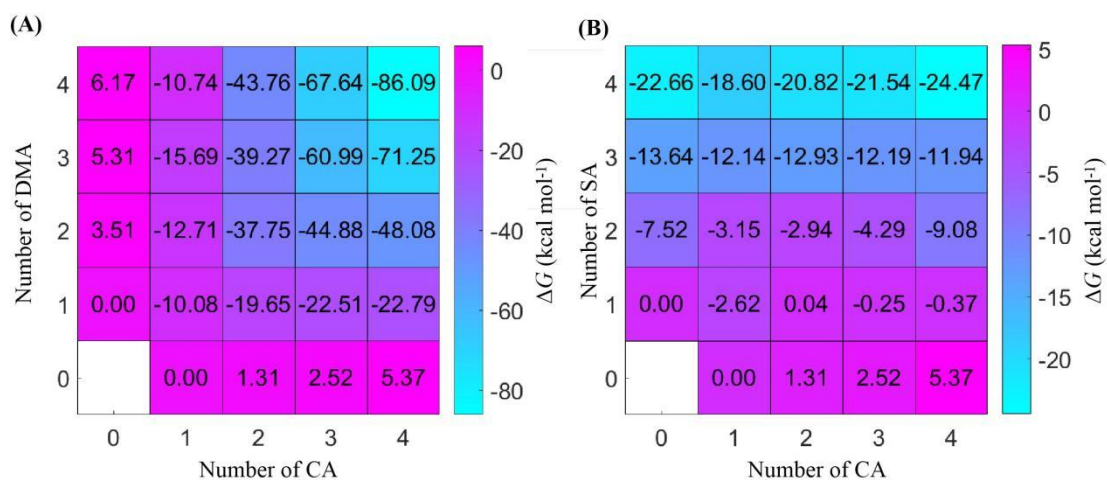


Figure 2. The formation free energy (ΔG) (in kcal mol^{-1}) of (A) (CA)₁₋₄(DMA)₁₋₄ and (B) (CA)₁₋₄(SA)₁₋₄ clusters at the DLPNO-CCSD(T)/aug-cc-pVTZ// ω B97X-D/6-31++G(d,p) level of theory. The calculations are performed at 278 K and 1 atm.

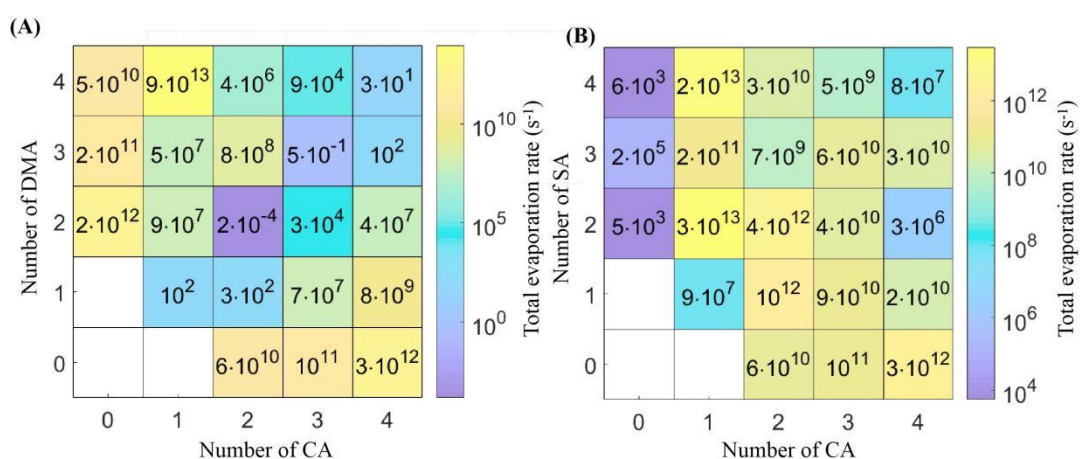


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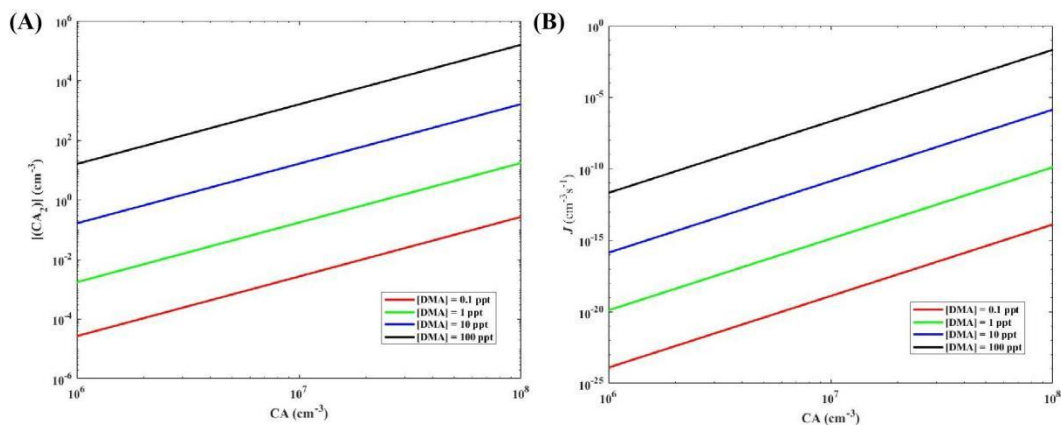


Figure 4. Simulated steady-state CA dimer concentration $\sum[(\text{CA})_2] (\text{cm}^{-3})$ (A) and the cluster formation rates $J (\text{cm}^{-3} \text{s}^{-1})$ out of the simulation systems (B) as a function of $[\text{CA}]$ at 278 K.

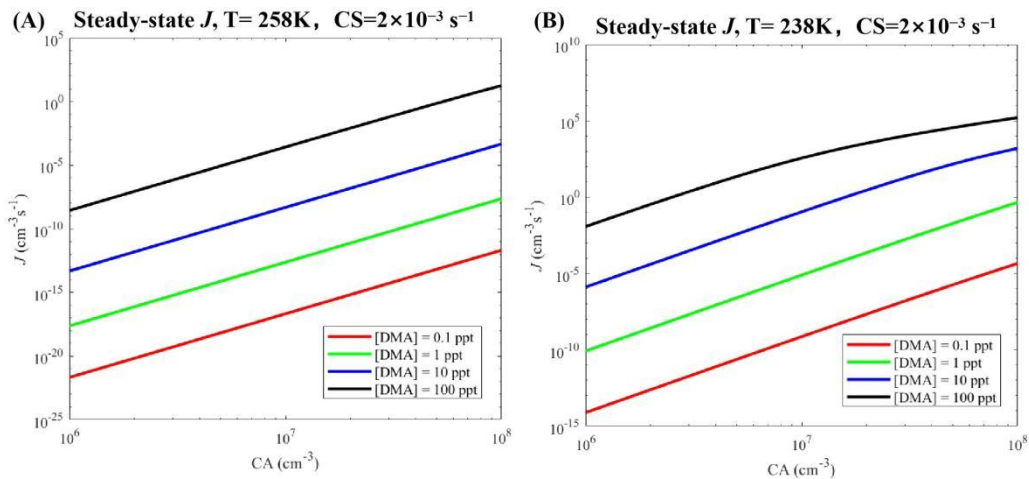


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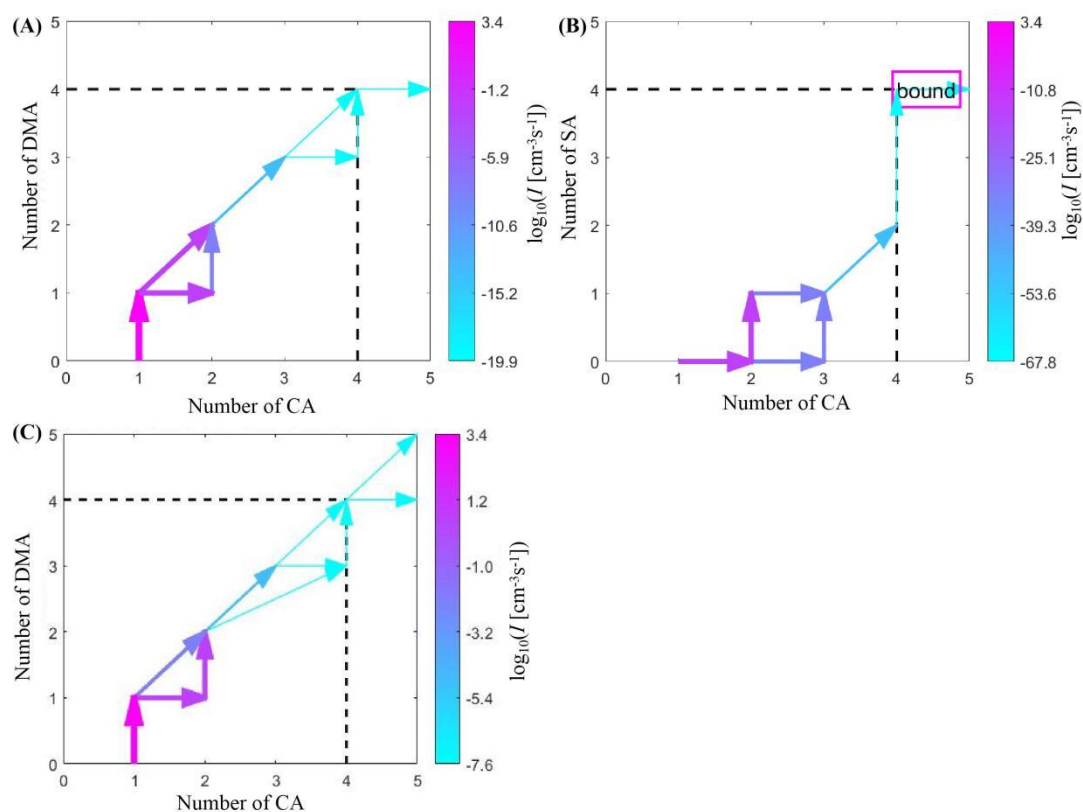


Figure 6. (A) Main clustering pathways of (CA)₁₋₄(DMA)₁₋₄ clusters at 278 K, [CA] = 10^6 cm^{-3} , and [DMA] = 5 ppt. (B) Main clustering pathways of (CA)₁₋₄(SA)₁₋₄ clusters at 278 K, [CA] = 10^6 cm^{-3} , and [SA] = 10^6 cm^{-3} . (C) Main clustering pathways of (CA)₁₋₄(DMA)₁₋₄ clusters at 238 K, [CA] = 10^6 cm^{-3} , and [DMA] = 5 ppt.