Rapid Iodine Oxoacids Nucleation Enhanced by Dimethylamine in Broad Marine Regions

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Abstract. Recent experiments revealed a vital nucleation process of iodic acid (HIO_3) and iodous acid (HIO_2) under the marine boundary layer conditions. However, HIO_3-HIO_2 nucleation may not effectively drive the observed rapid new particle formation (NPF) in certain coastal regions influenced by urban air masses. Dimethylamine (DMA) is a promising basic precursor to enhance nucleation considering its strong ability to stabilize acidic clusters and the wide distribution in marine atmosphere, while its role in HIO_3-HIO_2 nucleation remains unrevealed. Hence, a method combining quantum chemical calculations and Atmospheric Cluster Dynamics Code (ACDC) simulations was utilized to study the HIO_3-HIO_2-DMA nucleation process. We found that DMA can preferentially accept the proton from HIO_3 as a basic precursor in the most stable configurations of HIO_3-HIO_2-DMA clusters. Kinetically, the participation of DMA in the cluster formation pathways of iodine oxoacids system could be significant at 10^{-1} - 1 pptv level of [DMA]. Furthermore, DMA can enhance the cluster formation rates of the HIO_3-HIO_2 system in marine and polar regions near DMA sources for more than 10^3-fold. Compared to the classical nucleation mechanism, the HIO_3-HIO_2-DMA mechanism exhibits strong nucleation ability, worthy of consideration as a promising mechanism in marine and polar regions rich in amine sources. The newly proposed HIO_3-HIO_2-DMA ternary mechanism might provide an explanation for some missing fluxes of atmospheric iodine particles.

1 Introduction

Atmospheric aerosols, the intricate suspension formed by fine particles in the atmosphere, exert far-reaching influences on global climate (Haywood and Boucher, 2000; Murphy and Ravishankara, 2018; Lee et al., 2019), radiation balance (Haywood and Boucher, 2000), and human health (Pope and Dockery, 2006; Gong et al., 2014). A significant source of atmospheric aerosols on the world-wide scale is the new particle formation (NPF), encompassing nucleation and subsequent growth (Zhang, 2010). The nucleation is identified as the key process of NPF events. Therefore, understanding the nucleation mechanism is vital for comprehending the behavior of aerosols (Zhang et al., 2012; Kalivitis et al., 2015).

Sulfuric acid (H_2SO_4) is considered a crucial precursor for the nucleation in continental regions. However, under actual atmospheric conditions, the H_2SO_4-Water (W) binary nucleation is far from sufficient to explain the observed strong NPF events (Elm, 2021a). Therefore, additional components are essential for nucleation. Specifically, abundant atmospheric bases, such as ammonia (A) and alkylamines [methylamine (MA), dimethylamine (DMA), trimethylamine (TMA), and ethylenediamine (EDA)] (Weber et al., 1996; Kurtén et al., 2008; Kirkby et al., 2011; Elm et al., 2017; Xie and Elm, 2021), are recognized as important stabilizers for H_2SO_4-driven nucleation. Computational work by Kurtén et al. (Kurtén et al., 2008) and experimental studies by Almeida et al. (Almeida et al., 2013) indicated that, despite the lower atmospheric concentration of DMA (few pptv.), the promoting effect of DMA on the H_2SO_4-driven nucleation rate is several orders of magnitude higher than that of A. Moreover, nitric acid (NA) is also a potential precursor in the nucleation process (Knattrup and Elm, 2022). Liu et al. (Liu et al., 2018; Liu et al., 2021a) showed the significant promoting effect of NA on the classical H_2SO_4-A and H_2SO_4-DMA nucleation mechanisms by theoretical methods. Additionally, Wang et al. (Wang et al., 2020) studied the nucleation process of mixed vapor of NA and A under atmospheric conditions in the CLOUD chamber at the European Organization for Nuclear Research, and subsequently considered the promoting effect of H_2SO_4 on NA-A system (Wang et al., 2022).

Given the vast expanses of the ocean, marine aerosols play an indispensable role in the global aerosol system (O'Dowd and de Leeuw, 2007). Over the oceans, H_2SO_4 and methanesulfonic acid (MSA), the oxidation products of dimethylsulfide (DMS), is considered as important nucleation precursors over the oceans (Elm, 2021b). Theoretical calculations (Chen et al., 2020a; Chen et al., 2020b; Shen et al., 2020) have indicated that basic precursors such as A, MA, and DMA can promote MSA-based nucleation processes. However, a recent study on aerosol acidity showed that global models substantially overestimate the concentrations of A, especially in polar regions (Nault et al., 2021). This may slightly weaken the influence of H_2SO_4-based and MSA-based nucleation in marine atmosphere (He et al., 2023). In recent years, the iodine species, originate from biological emissions of marine macroalgae (O'Dowd et al., 2002c; O'Dowd et al., 2002b; Zhang et al., 2012; O'Dowd et al., 2002a), are also thought to be important precursors of the frequent NPF events in marine and polar regions (Hoffmann, O'Dowd and Seinfeld, 2001; Ehn et al., 2010; McFiggans et al., 2010; Mahajan et al., 2011; Baccarini et al., 2020). Several studies have consistently highlighted the pivotal role of iodic acid (HIO_3) in marine nucleation processes (Yu et al., 2019; Baccarini et al., 2020; Rong et al., 2020; Xia et al., 2020; He et al., 2021; Sipilä et al., 2016). Molecular-level observations conducted at the Mace Head coastal station in Ireland have provided evidence that the nucleation process is predominantly driven by HIO_3 with high concentration of 10^8 molecules cm^{-3} (Sipilä et al., 2016). Iodous acid (HIO_2) was also detected in both gas (up to 2×10^6 molecules cm^{-3}) and particle phases during the NPF events together with the HIO_3 (Yu et al., 2019; Sipilä et al., 2016). Recently, HIO_2 has been confirmed to play an important role in stabilizing the neutral HIO_3 clusters in the Cosmics Leaving OUtdoor Droplets (CLOUD) chamber in European Organization for Nuclear Research (CERN) (He et al., 2021). This was found to be concerned with the base-like behavior of HIO_2 in HIO_3-HIO_2 clusters by subsequent theoretical studies (Zhang et al., 2022a; Liu et al., 2023). In short, the iodine oxoacids (HIO_x, x = 2, 3) can drive rapid particle formation, and they may play an important role in marine and polar NPF process. However, in certain coastal areas influenced by urban air masses, such as the Zhejiang region, former studies indicated that iodine species could drive nucleation processes, while the HIO_3-HIO_2 nucleation mechanism may not sufficiently explain the field observation results (Yu et al., 2019; Ma et al., 2023; Zu et al., 2024; Xia et al., 2020), which indicates that other nucleation precursors may be involved.

In addition to iodine species, dimethylamine (DMA) is also a common nucleation precursor in the oceanic atmosphere (Facchini et al., 2008). DMA can originate from plankton and bacteria in seawater (Müller et al., 2009; Hu et al., 2015; Chen et al., 2021). Ice-influenced ocean may also be important sources of DMA (Dall'Osto et al., 2017; Dall'Osto et al., 2019). Moreover, the industrial activities also generate a large amount of DMA-containing pollutants (Corral et al., 2022). Hence, DMA is widely distributed and abundant under the different oceanic atmospheric conditions, displaying a spatial distribution remarkably akin to that of iodine species in mid-latitudes coastal and high-latitudes polar regions (Vanneste, Duce and Lee, 1987; Gronberg, Lovkvist and Jonsson, 1992; Gibb, Mantoura and Liss, 1999; Quéléver et al., 2022). DMA has strong base-stabilization effect on the H_2SO_4-based nucleation process (Almeida et al., 2013; Yao et al., 2018) since it possesses relatively strong basicity. Therefore, DMA may participate in and facilitate the iodine oxoacids nucleation through similar acid-base interactions with H_2SO_4-DMA system. However, previous studies have not adequately explored the influence of DMA on the iodine oxoacids (HIO_3 and HIO_2) nucleation in marine regions, and the ternary nucleation mechanism of HIO_3-HIO_2-DMA remains to be disclosed.

In the present study, the nucleation mechanism of HIO_3-HIO_2 enhanced by DMA under atmospheric conditions of different marine regions (mid-latitudes coastal and high-latitudes polar regions) were studied by a method combining quantum chemical calculation and Atmospheric Cluster Dynamics Code (ACDC) model. The simulated system contains $(HIO_3)_x\cdot(HIO_2)_y\cdot(DMA)_z$ ($1 \le x + y + z \le 6$; $x + y \ge z$) clusters. The largest clusters with a mobility diameter (Almeida et al., 2013) up to 1.3 nm in the size range of nucleation clusters (Zhang et al., 2012) are stable enough to resist evaporation at the studied temperature, and clusters with more DMA molecules ($x + y < z$) are usually unstable. This study aims to reveal the potential role of DMA in the HIO_3-HIO_2 nucleation and help to better understand the intensive NPF events in broad marine regions.

2 Method

2.1 Quantum chemical calculations

The HIO_3-HIO_2-DMA system is composed of ternary clusters (HIO_3-HIO_2-DMA), binary clusters (HIO_3-HIO_2, HIO_3-DMA, HIO_2-DMA) and the pure HIO_x (x = 2, 3) clusters. The most stable configuration of HIO_3-HIO_2-DMA ternary clusters and HIO_2-DMA binary clusters were proposed in this study for the first time. Additionally, the structures of HIO_3-HIO_2/DMA clusters and pure-HIO_x (x = 2, 3) clusters presented in this work were adopted from the stable configurations with the lowest Gibbs free energy of formation in previous studies (Rong et al., 2020; Ning et al., 2022; Zhang et al., 2022b; Liu et al., 2023) at the same level of theory. A multi-step searching progress that can systematically screen the structures of clusters was adopted in this research. Firstly, the ABCluster program (Zhang and Dolg, 2015) was performed to generate up to 120000 initial isomer structures using the artificial bee algorithm (details in Section S1 of Supporting Information). The universal force field (UFF) (Rappé et al., 1992) was chosen to select up to 1000 structures with lower energies from the initial isomer structures. Due to the inability of the UFF force field to effectively handle bond breaking issues, we also utilized ion monomers for sampling during the configuration search of ternary clusters (Kubecka et al., 2019). From the most stable configuration of binary HIO_2-DMA clusters (Figure S3), it showed that the proton transfer from HIO_2 to DMA is forbidden in all cluster except for $(HIO_2)_1(DMA)_1$, indicating that this process is difficult to occur spontaneously. Hence, we only considered the ion monomers where HIO_3 donates protons or HIO_2/DMA accept proton. Secondly, 1000 structures for each cluster were pre-optimized by the PM7 semi-empirical method (Stewart, 2013) with Mopac 2016 program (Stewart, 2016) to choose 100 structures with relatively low energies. Then 100 structures were optimized at the ωB97X-D/6-31+G* (for H, C, N and O atoms) + Lanl2DZ (for I atom) level of theory (Yang, Weaver and Merz, 2009; Elm, 2013) to find out 10 relatively stable structures of all. Finally, 10 stable structures were reoptimized at the ωB97X-D/6-311++G (3df, 3pd) (for H, C, N and O atoms) + aug-cc-pVTZ-PP (for I atom) level of theory (Frisch, Pople and Binkley, 1984; Peterson, 2003; Chai and Head-Gordon, 2008; Elm and Kristensen, 2017) together with the calculations of vibrational frequencies. Notably, even though we try our best to search for the global minimum configurations of clusters considering the computational cost, saving 1000 local minima from the ABCluster search and selecting the lowest 100 cluster configurations based on PM7 may lead to the global minimum cluster being missed (Kurfman, Odbadrakh and Shields, 2021). Additionally, we manually constructed some potential stable clusters with multiple hydrogen/halogen bonding sites based on the chemical intuition. All quantum chemical calculations were performed using the Gaussian 09 package (Frisch et al., 2009) to identify the most stable conformations of each cluster.

Afterwards, the single-point energy correction was carried out by the RI-CC2/aug-cc-pVTZ (for H, C, N and O atoms) + aug-cc-pVTZ-PP with ECP28MDF (for I atom) using the Turbomole program (Ahlrichs et al., 1989), because of the good agreement between simulated results (e.g., the cluster formation rates) at the this theoretical level with the experimental results or field measurements through a random cancellation of errors (Almeida et al., 2013; Lu et al., 2020; Kürten et al., 2018). To assess the reliability of RI-CC2 method, we compared the simulated cluster formation rates obtained at ωB97X-D/6-311++G(3df,3pd), RI-CC2/aug-cc-pVTZ, and DLPNO-CCSD(T)/aug-cc-pVTZ level of theory with the CLOUD experiment results (He et al., 2021) (Figure 1 and details can be found in Section S2). As shown in Figure 1, without performing single-point energy correction, the cluster formation rates simulated at ωB97X-D/6-311++G(3df,3pd) level of theory (the diamond points) are significantly lower than the experimental results (the circular points). Therefore, we chose to perform the single-point correction to obtain simulated cluster formation rates that agree more with the experimental results. Compared to the results of DLPNO-CCSD(T) method, the simulated cluster formation rates based on RI-CC2 method are more consistent with the experimental results at T = 263 K. Moreover, at T = 283 K, the RI-CC2 results are closer to lower cluster formation rates from the experiments, and overestimate higher cluster formation rates from the experiments by less than two orders of magnitude. Considering that the results based on RI-CC2 method agree the most with experimental results while saving computational resources, we finally chose the RI-CC2 method for single-point correction. It is important to note that this does not imply RI-CC2 results are inherently more accurate than those obtained using DLPNO-CCSD(T) method. We cautiously state that the choice of the RI-CC2 method in this study is due to its ability to effectively match the experimental results through a random cancellation of errors (details can be found in Section S2) while saving computational resources.

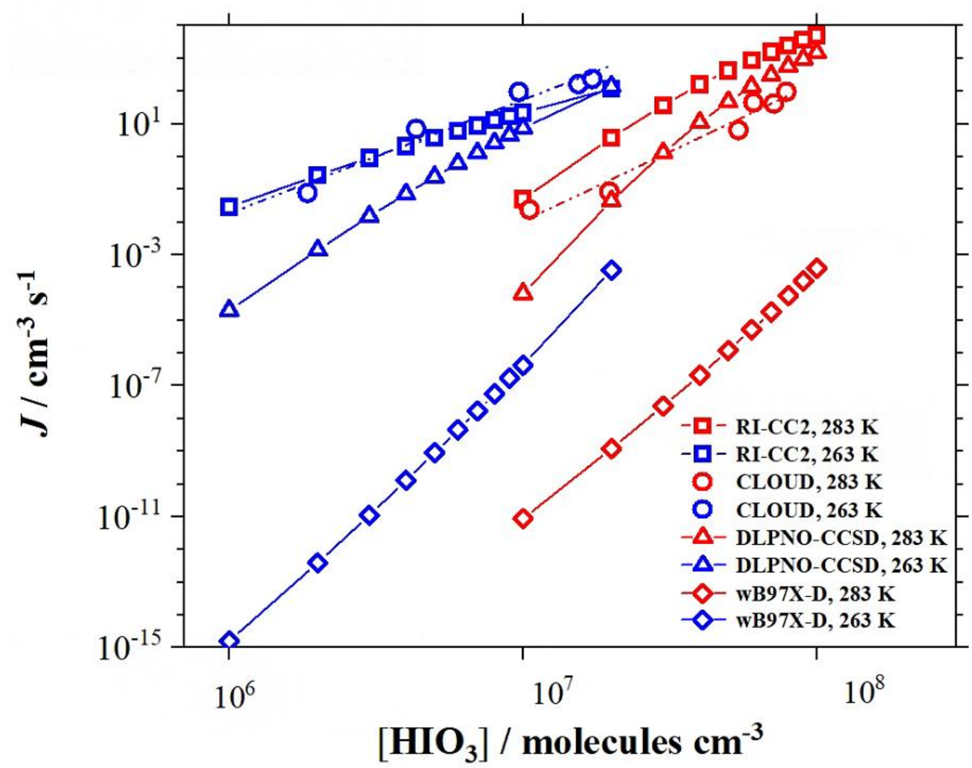

Figure 1. The cluster formation rates (J, cm^{-3} s^{-1}) of HIO_3-HIO_2 system obtained from experiment (CLOUD) and theoretical results at RI-CC2 and DLPNO-CCSD level of theory. The simulation was performed under the same conditions of [HIO_3] = 10^6 - 10^8, [HIO_2] = 2×10^4 - 2×10^6, T = 283 (red) / 263 (blue) K, and CS = 2.2×10^{-3} s^{-1}. The circles represent the experimental results, the squares represent the theoretical results at RI-CC2/aug-cc-pVTZ (for H, C, N and O atoms) + aug-cc-pVTZ-PP with ECP28MDF (for I atom) level of theory, the triangles represent the theoretical results at DLPNO-CCSD(T)/aug-cc-pVTZ (for H, C, N and O atoms) + aug-cc-pVTZ-PP with ECP28MDF (for I atom) level of theory, and the diamonds represent the theoretical results at ωB97X-D/6-311++G(3df,3pd) (for H, C, N and O atoms) + aug-cc-pVTZ-PP with ECP28MDF (for I atom) level of theory.

In the present study, the Gibbs free energy of formation (ΔG, kcal mol^{-1}) of clusters was calculated as:

$$\Delta G = \Delta E_{\mathrm{RI-CC2}} + \Delta G^{\omega\mathrm{B97X-D}}_{\mathrm{thermal}}$$

where $\Delta E_{\mathrm{RI-CC2}}$ is the electronic contribution obtained at the RI-CC2/aug-cc-pVTZ (for H, C, N and O atoms) + aug-cc-pVTZ-PP with ECP28MDF (for I atom) level of theory, and $\Delta G^{\omega\mathrm{B97X-D}}_{\mathrm{thermal}}$ is the thermal contribution calculated at the ωB97X-D/6-311++G(3df,3pd) (for H, C, N and O atoms) + aug-cc-pVTZ-PP with ECP28MDF (for I atom) level of theory.

2.2 Atmospheric Cluster Dynamics Code (ACDC) simulations

In order to investigate the effect of DMA on HIO_3-HIO_2 nucleation in marine areas, a series of ACDC simulations (McGrath et al., 2012) were performed under atmospheric conditions corresponding to mid-latitudes coastal and high-latitudes polar regions. By solving the birth-death equation, the ACDC simulations can obtain the cluster formation rates and formation pathways of clusters using the MATLAB program (Shampine and Reichelt, 1997). The birth-death equation can be written as follows:

$$\frac{dc_i}{dt} = \frac{1}{2}\sum_{j<i}\beta_{j,(i-j)}c_jc_{i-j} + \sum_j \gamma_{(i+j)\to i}c_{i+j} - \sum_j \beta_{i,j}c_ic_j - \frac{1}{2}\sum_{j<i}\gamma_{i\to j}c_i + Q_i - S_i$$

where c_i is the concentration of cluster i, $\beta_{i,j}$ is the collision coefficient between cluster i and cluster j, $\gamma_{(i+j)\to i}$ is the evaporation coefficient of the cluster $(i+j)$ evaporating into cluster i and cluster j, Q_i is the external source term of cluster i, and S_i is the potential sink term for cluster i.

The collision coefficient $\beta_{i,j}$ can be written as:

$$\beta_{i,j} = \left(\frac{3}{4\pi}\right)^{\frac{1}{6}}\left(\frac{6k_{\mathrm{B}}T}{m_i}+\frac{6k_{\mathrm{B}}T}{m_j}\right)^{\frac{1}{2}}\left(V_i^{\frac{1}{3}}+V_j^{\frac{1}{3}}\right)^2$$

where k_{B} is the Boltzmann constant, T is the temperature, m_i is the mass of cluster i, and V_i is the van der Waals volume of cluster i, which is calculated by the improved Marching Tetrahedra (MT) approach (Lu and Chen, 2012b) using Multiwfn 3.7 program (Lu and Chen, 2012a).

The evaporation coefficient $\gamma_{(i+j)\to i}$ of the cluster was obtained from the collision coefficient and the specific balance between cluster formation via the collision and cluster loss via the evaporation:

$$\gamma_{(i+j)\to i} = \beta_{i,j}c_{\mathrm{ref}}\exp\left(\frac{\Delta G_{i+j}-\Delta G_i-\Delta G_j}{k_{\mathrm{B}}T}\right)$$

where c_{ref} is the monomer concentration under the reference pressure of 1 atm, and ΔG_i is the Gibbs free energy of the formation of cluster i.

The formation of clusters is accompanied by the competition between collision and evaporation. The clusters with a collision frequency higher than the total evaporation frequency ($\beta c/\Sigma\gamma>1$) are considered to be stable in the perspective of nucleation kinetics. The detailed collision and total evaporation frequencies of the HIO_3-HIO_2-DMA system at all simulated temperatures and condensation sinks are listed in Tables S1-S4. The boundary conditions of the ACDC simulations are closely related to the ratio of the collision frequency between the clusters and monomer molecules at the concentration c to the total evaporation frequency of clusters. Moreover, the size of clusters in the simulation system also affects the accuracy of the simulation results (Figure S1). We will discuss the issues related to the size of clusters and the settings of boundary clusters in detail in Section S3 of Supporting Information.

3 Results

3.1 Cluster stable configurations

The most stable configurations of the HIO_3-HIO_2-DMA ternary clusters at the ωB97X-D/6-311++G(3df,3pd) (for H, C, N, and O atoms) + aug-cc-pVTZ-PP with ECP28MDF (for I atom) level of theory are shown in Figure 2. The structures of the HIO_2-DMA clusters can be found in Figure S3 of the Supporting Information, and the cartesian coordinates of all HIO_3-HIO_2-DMA and HIO_2-DMA clusters are shown in Table S7. The electrostatic potential (ESP) distribution (details in Section S4 of Supporting Information) showed that the -NH group of DMA molecules can act as both donor and acceptor of non-covalent interactions. Hence, DMA can form stable ternary clusters through the space network formed by HBs and XBs. Moreover, acid-base proton transfer can be found in all ternary clusters except for the $(HIO_3)_1(HIO_2)_2(DMA)_1$ and $(HIO_3)_1(HIO_2)_3(DMA)_2$ clusters. It has been shown in the previous study on HIO_3-DMA and HIO_3-HIO_2 systems that acid-base proton transfer occurred between HIO_3 and HIO_2/DMA (Zhang et al., 2022a; Ning et al., 2022; Liu et al., 2023). The gas-phase basicity of DMA is strong (896.5 kJ mol^{-1}) (Yang et al., 2018). Hence, DMA is capable to efficiently stabilize acidic precursors through acid-base interactions. Moreover, amphoteric HIO_2 molecules, the acid dissociation constant (pK_a) of which is 6.0 (Schmitz, 2008), can also exhibit base-like behavior in the neutral nucleation process of HIO_3-HIO_2 (Zhang et al., 2022a; Liu et al., 2023). This indicates that DMA may play a role similar to HIO_2 in the neutral nucleation process driven by HIO_3.

In order to assess the effect of DMA on the proton transfer process, the analysis of the proton transfer was performed based on the change of bond length at corresponding positions that conduct acid-base reaction. The number of proton transfer between different precursors in ternary clusters and the total number of proton transfer are summarized in Table S8. As shown in Table S8, among most of the ternary clusters, HIO_3 will preferentially interact with DMA, which possesses strong basicity, in the process of proton transfer. Afterwards, the remaining HIO_3 can perform proton transfer with the amphoteric HIO_2, which can also exhibit base-like behavior under this circumstance. It is worth noting that, in terms of the stability (evaluated by ΔG) of clusters, the proton transfer plays a crucial role. Taking two 3-molecule clusters, $(HIO_3)_2(HIO_2)_1$ (ΔG = -30.05 kcal mol^{-1}) and $(HIO_3)_1(HIO_2)_1(DMA)_1$ (ΔG = -35.19 kcal mol^{-1}), as an example, we observed that the $(HIO_3)_2(HIO_2)_1$ cluster with higher energy is formed through three XBs and one HB, while $(HIO_3)_1(HIO_2)_1(DMA)_1$ cluster with lower energy is formed through three HBs after proton transfer. Additionally, when the number of proton transfers is the same, clusters with more halogen bonds formed by HIO_2 generally have lower ΔG, which can be seen from $(HIO_3)_1(HIO_2)_2(DMA)_1$ (ΔG = -50.07 kcal mol^{-1}, formed by three XBs and two HBs) and $(HIO_2)_4$ (ΔG = -58.08 kcal mol^{-1}, formed by four XBs) clusters. Similar results can also be observed in other ternary clusters. As for the water (H_2O) molecules, they are indispensable in the formation process of marine aerosols. However, previous studies have indicated that H_2O contributes less significantly to strong acid-base systems dominated by proton transfer, such as the H_2SO_4-DMA system (Kürten et al., 2018; Olenius et al., 2017; Liu et al., 2021b). The HIO_3-HIO_2-DMA system exhibits clustering pattern similar to the H_2SO_4-DMA system, with proton transfer processes in almost all ternary clusters. Hence, we speculate that the contribution of H_2O to the HIO_3-HIO_2-DMA system is relatively weak similar with contribution of H_2O to the H_2SO_4-DMA system. In addition, considering that the introduction of hydrated clusters requires large amount of additional quantum chemical calculations, which are time-consuming in current workflow, the impact of H_2O is not considered in the present study.

In summary, the structural analysis shows that DMA can form stable clusters with iodine oxoacids via HBs, XBs and proton transfer, laying the foundation for promoting HIO_3-HIO_2 nucleation. Moreover, DMA can preferentially accept the proton from HIO_3 in the most stable configurations of HIO_3-HIO_2-DMA clusters, while the amphoteric HIO_2 can also exhibit similar behavior.

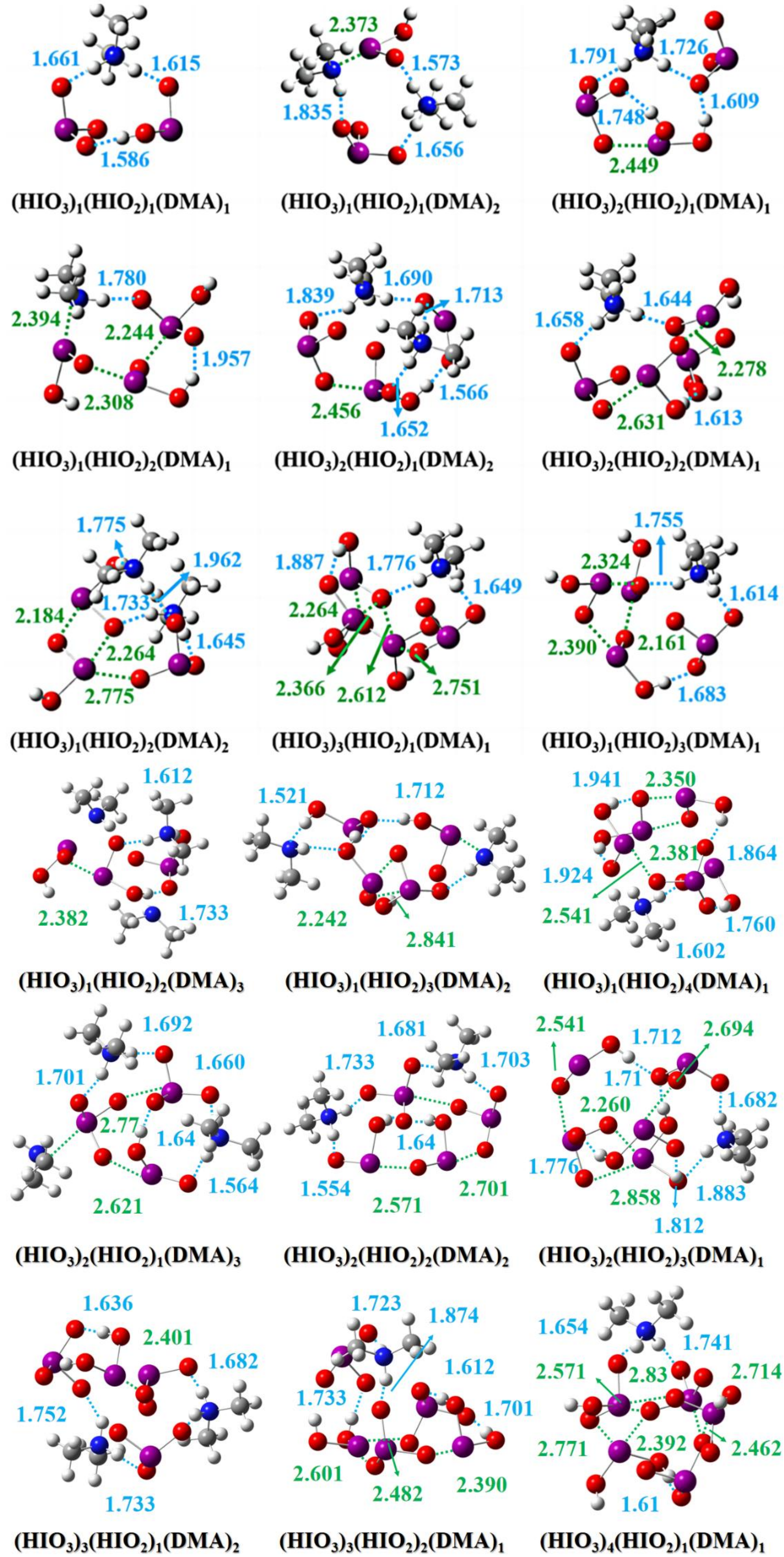
1.661
1.615
1.586
$(HIO_3)_1(HIO_2)_1(DMA)_1$
2.373
1.573
1.835
1.656
$(HIO_3)_1(HIO_2)_1(DMA)_2$
1.791
1.726
1.609
1.748
2.449
$(HIO_3)_2(HIO_2)_1(DMA)_1$
1.780
2.394
2.244
1.957
2.308
$(HIO_3)_1(HIO_2)_2(DMA)_1$
1.839
1.690
1.713
1.566
2.456
1.652
$(HIO_3)_2(HIO_2)_1(DMA)_2$
1.658
1.644
2.278
2.631
1.613
$(HIO_3)_2(HIO_2)_2(DMA)_1$
1.775
1.962
1.733
2.184
1.645
2.264
2.775
$(HIO_3)_1(HIO_2)_2(DMA)_2$
1.887
1.776
1.649
2.264
2.366
2.612
2.751
$(HIO_3)_3(HIO_2)_1(DMA)_1$
1.755
2.324
1.614
2.390
2.161
1.683
$(HIO_3)_1(HIO_2)_3(DMA)_1$
1.612
2.382
1.733
$(HIO_3)_1(HIO_2)_2(DMA)_3$
1.521
1.712
2.242
2.841
$(HIO_3)_1(HIO_2)_3(DMA)_2$
1.941
2.350
2.381
1.864
1.924
2.541
1.760
1.602
$(HIO_3)_1(HIO_2)_4(DMA)_1$
1.692
1.701
1.660
2.77
1.64
2.621
1.564
$(HIO_3)_2(HIO_2)_1(DMA)_3$
1.681
1.733
1.703
1.64
1.554
2.571
2.701
$(HIO_3)_2(HIO_2)_2(DMA)_2$
2.541
1.712
2.694
1.71
1.682
2.260
1.776
2.858
1.883
1.812
$(HIO_3)_2(HIO_2)_3(DMA)_1$
1.636
2.401
1.682
1.752
1.733
$(HIO_3)_3(HIO_2)_1(DMA)_2$
1.723
1.874
1.612
1.733
1.701
2.601
2.482
2.390
$(HIO_3)_3(HIO_2)_2(DMA)_1$
1.654
1.741
2.571
2.83
2.714
2.771
2.392
2.462
1.61
$(HIO_3)_4(HIO_2)_1(DMA)_1$

Figure 2. The most stable structures of HIO_3-HIO_2-DMA clusters identified at the ωB97X-D/6-311++G(3df,3pd) (for H, C, N and O atoms) + aug-cc-pVTZ-PP with ECP28MDF (for I atom) level of theory. The white, grey, blue, red, and purple balls represent the H, C, N, O, and I atoms, respectively. The hydrogen bonds and halogen bonds are shown in blue and green dashed lines, respectively. The values of bond lengths are given in Å.

3.2 Cluster formation pathways

To further study the kinetic behavior of DMA in nucleation process, the ACDC was used to simulate the nucleation pathways under marine atmospheric conditions. Firstly, a specific simulation was performed under atmospheric conditions reported in Zhejiang, an intersection of high [DMA] pollution air masses and marine iodine air masses at the east coast of China (Zhu et al., 2019; Zhang et al., 2023). The main cluster formation pathways, which contributes more than 5% to the total cluster formation rates, at [HIO_3] of 1.0×10^7 molecules cm^{-3}, [HIO_2] of 2.0×10^5 molecules cm^{-3} and T = 293 K are shown in Figure 3. The average condensation sink (CS) was estimated and set to be 1.0×10^{-2} s^{-1} for polluted coastal regions (Ning et al., 2022). In Figure 3, we present the simulation results under three different [DMA] conditions ([DMA] = 0, 0.04, and 4 pptv) to evaluate the influence of DMA on the nucleation process of iodine oxoacids. As shown in Figure 3, with the increase of [DMA], the cluster formation pathways in the simulated system undergo continuous changes. The primary pathway shifts from the binary HIO_3-HIO_2 pathway to the ternary HIO_3-HIO_2-DMA pathway, and further to the binary HIO_3-DMA pathway. Hence, DMA might be involved in the nucleation process of the HIO_3-HIO_2 system in coastal regions, especially in those regions affected by high [DMA].

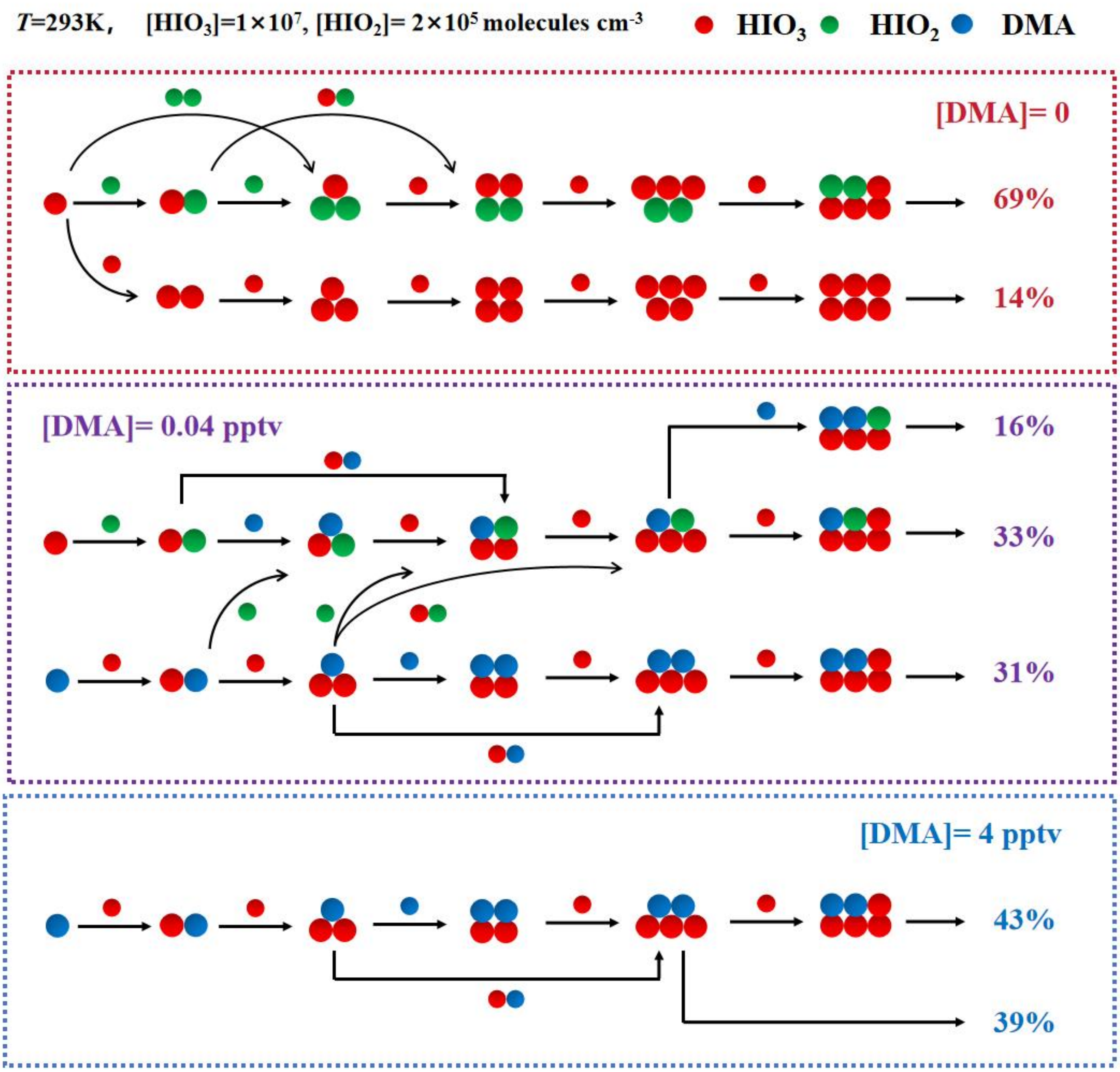

Figure 3. The cluster formation pathways and the contribution of main pathways to the total cluster formation rates under field conditions of Zhejiang at [HIO_3] of 1.0×10^7 molecules cm^{-3}, [HIO_2] of 2.0×10^5 molecules cm^{-3}, [DMA] of 0 (red), 0.04 (purple), and 4 (blue) pptv, $T = 293$ K, and CS = 1.0×10^{-2} s^{-1}. The red, green, and blue balls represent the HIO_3, HIO_2, and DMA molecules, respectively.

The simulated nucleation pathway under the specific condition has proved the participation of DMA in HIO_3-HIO_2 nucleation. However, since HIO_x (x = 2, 3) and DMA originate from different sources, the concentrations of precursors should be changed to better represent the situation of regions with different iodine and amine emission intensities. Therefore, to further study the involvement of DMA in nucleation pathways under various oceanic atmospheric conditions, the contribution of the main cluster formation pathways at different concentrations are simulated and the results are shown in Figure 4. It is worth noting that the concentration of HIO_2 changes together with that of HIO_3 from low to high since HIO_2 and HIO_3 are homologous iodine species. The ratio of [HIO_3] to [HIO_2] is about 20 to 100 depending on the concentration of iodine vapor (Yu et al., 2019; Baccarini et al., 2020; Rong et al., 2020; Xia et al., 2020; He et al., 2021; Sipilä et al., 2016). The ratio used in Figure 4 was 50 according to the former field observations in Mace Head (Sipilä et al., 2016) and the other results obtained from two different ratios (20 and 100) of [HIO_3] and [HIO_2] can be seen from the Section S5 of Supporting Information.

As can be seen from Figure 4, the contribution of DMA to the nucleation increases with [DMA] rising from 10^{-3} to 1 pptv, and the dominating mechanism varies similarly with Figure 3 from HIO_3-HIO_2 nucleation to HIO_3-HIO_2-DMA nucleation and then to HIO_3-DMA nucleation. Moreover, combining Figures S4 and S5, an opposite trend in the dominant mechanism becomes apparent with the increase of [HIO_2]. Specifically, the primary nucleation mechanism shifts from HIO_3-DMA to HIO_3-HIO_2-DMA, or from HIO_3-HIO_2-DMA to HIO_3-HIO_2 as [HIO_2] increase. Notably, the HIO_3-HIO_2-DMA ternary mechanism is more significant when [HIO_2] and [DMA] are similar. In contrast, when DMA (HIO_2) is much more abundant than HIO_2 (DMA), the pathways are overwhelmingly dominated by rapid binary nucleation involving HIO_3 and DMA (HIO_2) with higher concentration. This phenomenon may be attributed to the similar stabilizing effects of DMA and HIO_2 on HIO_3 nucleation, where the component with a higher concentration plays a more significant role. Consequently, the component with a lower concentration exerts less influence, primarily due to the limited availability of HIO_3. This indicates that when [DMA] reaches 10^{-1} to 1 pptv, the proportion of DMA-containing pathways will approach 100% (Figure 4), indicating significant involvement of DMA on HIO_3-HIO_2 system. As mentioned in the introduction, marine regions are not lacking in high-intensity sources of DMA, especially in polluted coastal areas. However, currently reported experiments and model simulations seem to have not yet focused on the ternary HIO_3-HIO_2-DMA mechanism. Therefore, in the next section, we will evaluate the nucleation ability of the newly proposed HIO_3-HIO_2-DMA mechanism through comparison with classical nucleation mechanism or observation results to comprehensively assess the environmental significance of HIO_3-HIO_2-DMA mechanism in the broad marine regions.

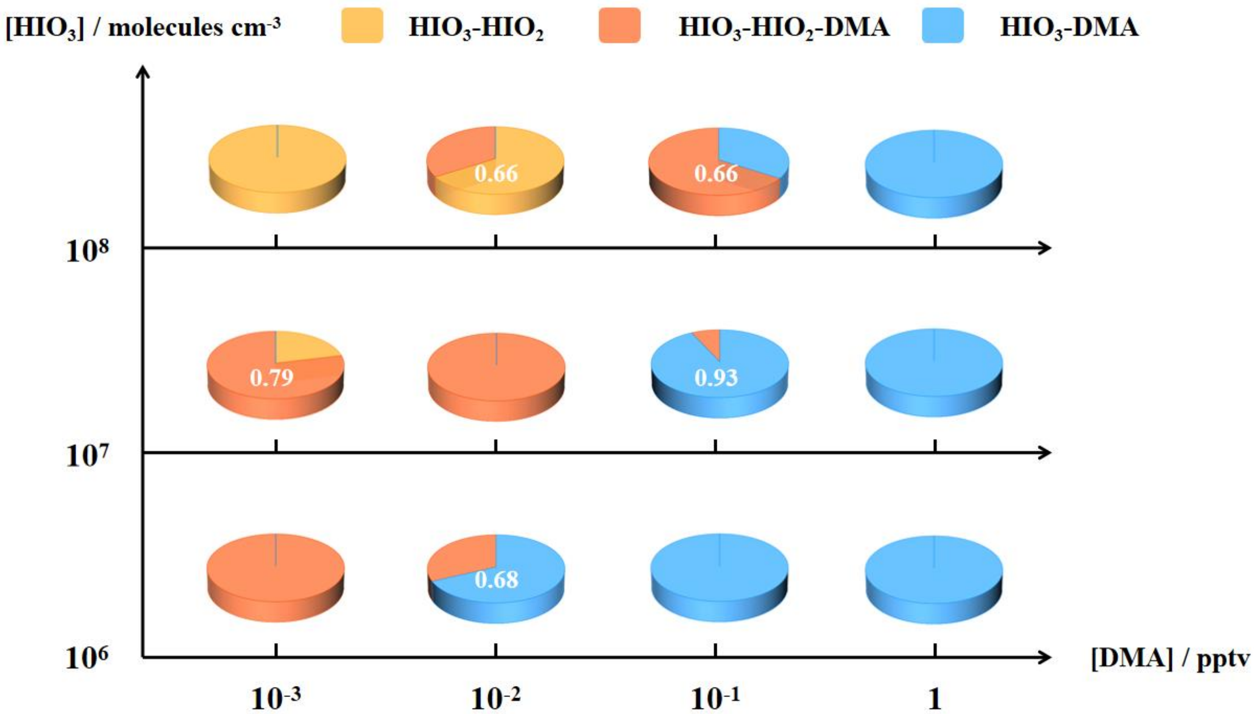

Figure 4. The contribution of main nucleation pathways at different concentrations of precursors. [HIO_3] = 10^6 - 10^8 molecules cm^{-3}, [HIO_2] = 2.0×10^4 - 2.0×10^6 molecules cm^{-3} and [DMA] = 10^{-3} - 1 pptv. The simulated temperature and condensation sink are 283 K and 2.0×10^{-3} s^{-1} as typical values for oceanic atmosphere. The proportion of the contribution of HIO_3-HIO_2, HIO_3-HIO_2-DMA, and HIO_3-DMA are shown in yellow, orange, and blue, respectively.

3.3 Cluster formation rates

The cluster formation pathway showed that DMA may significantly participate in HIO_3-HIO_2 nucleation. However, the influence of DMA on the cluster formation rates (J, cm^{-3} s^{-1}) of the HIO_3-HIO_2 nucleation is still unknown. To evaluate the influence of DMA on HIO_3-HIO_2 system and the environmental significance of HIO_3-HIO_2-DMA system, we compared the *J* of HIO_3-HIO_2 (red), HIO_3-HIO_2-DMA (purple), HIO_3-HIO_2-H_2SO_4 (yellow), HIO_3-HIO_2-MSA (pink), and H_2SO_4-DMA (blue) systems under the simulated conditions of typical marine and polar regions. The results of HIO_3-HIO_2-H_2SO_4 (Zu et al., 2024) and HIO_3-HIO_2-MSA systems (https://doi.org/10.5194/egusphere-2023-2084) were obtained from former studies at the same level of theory with HIO_3-HIO_2-DMA system. The configurations of H_2SO_4-DMA clusters were obtained from the Atmospheric Cluster Database (ACDB) (Elm, 2019). Subsequently, geometric optimizations and frequency calculations were performed at the same (ωB97X-D/6-311++G(3df,3pd)) level of theory with HIO_3-HIO_2-DMA system. Notably, we believe that the influence of other mechanisms (HIO_3-HIO_2-A, etc.) is widespread and significant. However, due to the lack of available data, other mechanisms are not discussed in this study and will be considered in further studies.

The Zhejiang region experiences the frequent NPF events, closely associated with a high-intensity iodine-driven nucleation process (Yu et al., 2019). However, our simulation results under the conditions of Zhejiang (Xia et al., 2020; Yu et al., 2019) indicate that relying solely on HIO_3-HIO_2 nucleation (red curve in Figure 5(a)) appears insufficient to explain the rapid formation rates of ambient environment (gray shaded area). It is noteworthy that the NPF events in the local area is found to be influenced not only by marine components but also by urban pollutants (Zhu et al., 2019; Liu et al., 2022). During polluted periods, the emission capacity of gas-phase DMA is exceptionally strong, and high concentrations of DMA can further enhance the *J* of HIO_3-HIO_2, resulting in a significant enhancement of up to 10^8 times at [DMA] = 4 pptv. Notably, the increase of the concentrations of HIO_2 and DMA can both enhance the *J* to match the field observations, indicating that HIO_2 and DMA molecules exhibit a synergistic effect on HIO_3 nucleation, which may have significant contributions to NPF events in the polluted coastal areas where marine iodine species intersect with high concentrations of DMA. Moreover, the urban pollution also leads to an abundant concentration of gas-phase H_2SO_4. This renders the impact of the HIO_3-HIO_2-H_2SO_4 and H_2SO_4-DMA mechanisms non-negligible. As shown in Figure 5(a), the simulated *J* of H_2SO_4-DMA and HIO_3-HIO_2-H_2SO_4 systems (blue dashed line) is about one or four orders of magnitude lower than that of HIO_3-HIO_2-DMA system, respectively. This indirectly indicates that the HIO_3-HIO_2 system promoted by DMA possesses remarkable nucleation ability and might make unexpected contributions in specific regions, thereby providing an explanation for some missing fluxes of particles in the atmosphere.

In contrast, the results from the Mace Head region present a different situation. Previous studies have demonstrated that local nucleation is primarily driven by high concentrations of HIO_3 (Sipilä et al., 2016). The simulated results showed that the *J* of HIO_3-HIO_2 system can reach up to levels of 10^4 cm^{-3} s^{-1}, which is consistent with the upper limit of formation rates reported in the field observation (Sipilä et al., 2016). Furthermore, we evaluated the potential impact of DMA and other precursors on the *J* of HIO_3-HIO_2 system based on the concentrations from model simulations or gas-phase measurements reported at Mace Head (Yu and Luo, 2014; Sipilä et al., 2016). The results indicate that DMA can promote the *J* significantly only at lower iodine concentrations. As the increases of iodine oxoacids, the *J* of HIO_3-HIO_2-DMA system gradually approaches that of HIO_3-HIO_2 system, indicating a less significant enhancement by DMA. Similar patterns about the enhancement by H_2SO_4 and MSA can also be shown. This indicates that in primitive regions with abundant iodine sources, even if the precursors (DMA, H_2SO_4, and MSA) can reach the high concentrations used in the simulation in this study, their corresponding enhancement is limited. The primary nucleation mechanism is likely to be the HIO_3-HIO_2 mechanism, which is supported by the on-site measurements of the components of nanoparticles (Sipilä et al., 2016).

Recent research has shown that the ice-influenced ocean may also be important sources of DMA (Dall'Osto et al., 2017; Dall'Osto et al., 2019). Hence, we also evaluate the environmental significance of HIO_3-HIO_2-DMA system in the ice-covered polar regions. As shown in Figure 5(c), we performed a simulation under the conditions of Aboa station. The simulation results indicate that HIO_3-HIO_2-H_2SO_4 and H_2SO_4-DMA are more efficient nucleation mechanisms than HIO_3-HIO_2-DMA system in the local area. Moreover, the simulated *J* of HIO_3-HIO_2-DMA system is also slightly lower than the formation rates (0.05 - 0.12 cm^{-3} s^{-1}) of ion-induced H_2SO_4-A system reported by field observations (Jokinen et al., 2018). Hence, due to the overall lower concentrations of iodine and amine components, the nucleation process is predominantly driven by H_2SO_4 molecules. This suggests that in regions with scarce iodine and amine sources, the contribution of the DMA-enhanced HIO_3-HIO_2 mechanism to the particle formation is limited. In contrast, in the Marambio region with relatively abundant DMA and scarce iodine oxoacids (Quéléver et al., 2022; Wang et al., 2023), HIO_3-HIO_2-DMA system may also have significant contributions [Figure 5(d)]. The [HIO_3] used in the simulation is still about an order of magnitude lower than [H_2SO_4] and [MSA]. However, [DMA] is about an order of magnitude higher than that in the Aboa region. In this case, the J of HIO_3-HIO_2 system is significantly enhanced for more than 10^3-fold by the relatively abundant DMA. Compared to the acidic components such as H_2SO_4 and MSA, DMA elevates the J of the HIO_3-HIO_2 system to the range of 10^{-1} to 10^1 cm^{-3} s^{-1}, matching the field observation results, while [DMA] is only one-tenth of [H_2SO_4] and [MSA]. This indicates that, considering nucleation ability, the enhancement effect of DMA on the HIO_3-HIO_2 system may be superior to H_2SO_4 and MSA, which we speculate that is likely related to the base stabilization effect of DMA within acidic clusters. Additionally, our results demonstrate that the nucleation ability of HIO_3-HIO_2-DMA is stronger than that of H_2SO_4-DMA. This means that the HIO_3-HIO_2-DMA ternary mechanism may be an important contributor to iodine-containing particles, especially in regions where there are sufficient iodine and amine sources.

In summary, the results show that HIO_3-HIO_2-DMA ternary nucleation mechanism may have significant contributions to the formation of nanoparticles, especially in those regions with abundant iodine and amine sources. This previously overlooked mechanism may provide an explanation for some missing fluxes of atmospheric iodine particles. Moreover, the observed formation rates in the field can result from multiple rapid nucleation systems or may be solely attributed to a specific system, depending significantly on the variations of precursor concentrations in different regions. The nucleation process in real atmosphere is complex. Hence, the simulation of scenarios where various components participate simultaneously is needed in the future study to accurately assess the roles of different components such as H_2SO_4, MSA, A, and DMA in the iodine oxoacids nucleation. This may contribute to a fundamental understanding of atmospheric particle formation, providing a comprehensive insight into the entire evolution process of atmospheric aerosols.

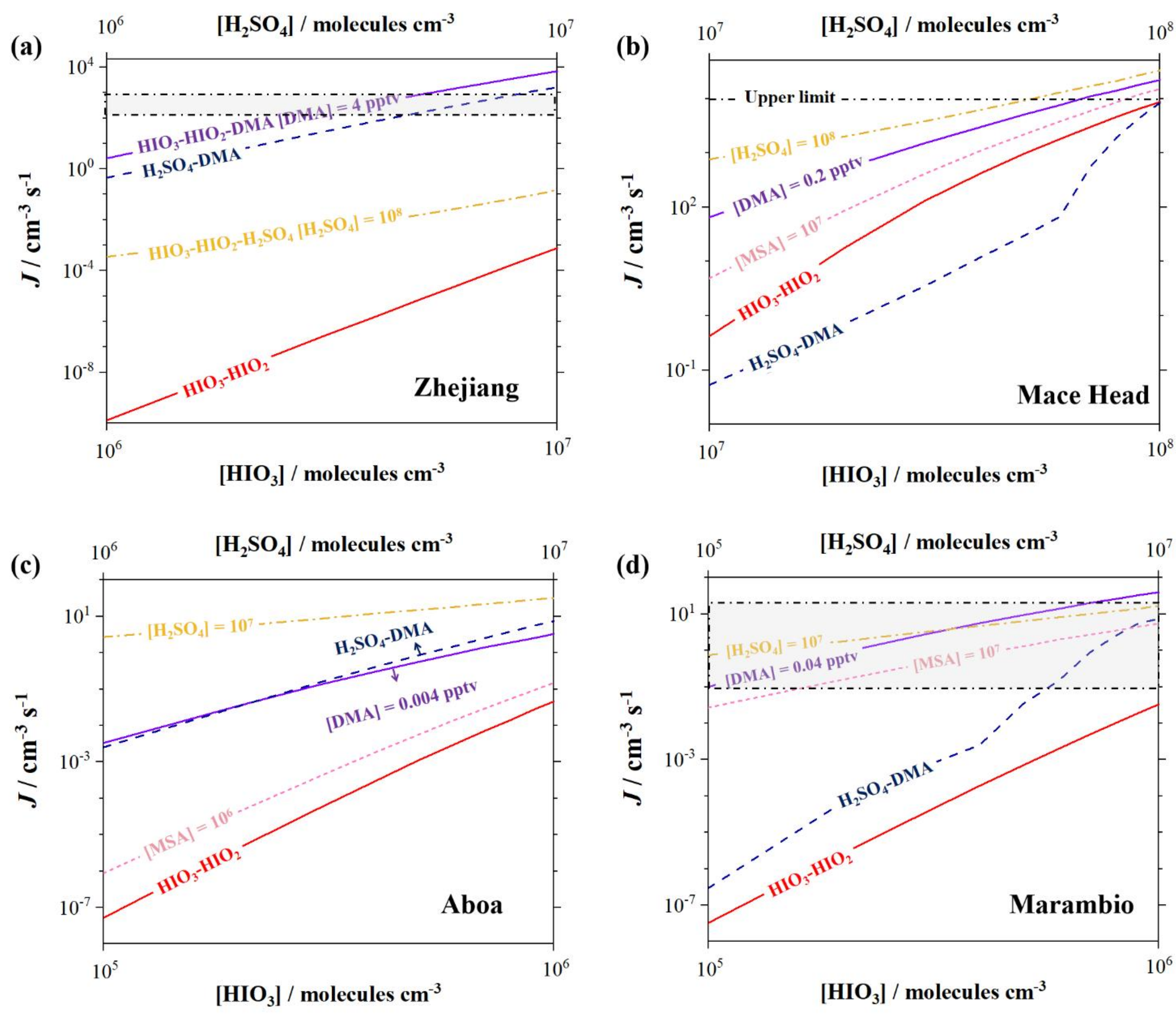

Figure 5. The cluster formation rates (J, cm^{-3} s^{-1}) of HIO_3-HIO_2 (red), HIO_3-HIO_2-DMA (purple), HIO_3-HIO_2-

H_2SO_4(yellow), HIO_3-HIO_2-MSA (pink), and H_2SO_4-DMA (blue) systems under the simulated conditions of (a) Zhejiang: $[HIO_3] = 10^6$ - 10^7, $[HIO_2] = 2\times10^4$ - 2×10^5, $[H_2SO_4] = 10^6$ - 10^8 molecules cm^{-3}, and [DMA] = 4 pptv, (b) Mace Head: $[HIO_3] = 10^7$ - 10^8, $[HIO_2] = 2\times10^5$ - 2×10^6, $[H_2SO_4] = 10^7$ - 10^8, $[MSA] = 10^7$ molecules cm^{-3}, and [DMA] = 0.2 pptv, (c) Aboa: $[HIO_3] = 10^5$ - 10^6, $[HIO_2] = 2\times10^3$ - 2×10^4, $[H_2SO_4] = 10^6$ - 10^7, $[MSA] = 10^6$ molecules cm^{-3}, and [DMA] = 0.004 pptv, and (d) Marambio: $[HIO_3] = 10^5$ - 10^6, $[HIO_2] = 2\times10^3$ - 2×10^4, $[H_2SO_4] = 10^5$ - 10^7, $[MSA] = 10^7$ molecules cm^{-3}, and [DMA] = 0.04 pptv. The shaded area (grey) represents the actual nucleation rates observed locally.

4 Atmospheric significance and conclusion

The present study investigated the iodine oxoacids nucleation enhanced by DMA under broad oceanic atmospheric conditions by the quantum chemical calculations combined with ACDC simulations. As a basic precursor to stabilize acid, DMA can form the stable ternary clusters with HIO_3 and HIO_2, in which DMA can preferentially accept the proton from HIO_3. Kinetically, the participation of DMA in the participation of DMA in the cluster formation pathways of iodine oxoacids system be significant at 10^{-1} - 1 pptv level of [DMA]. Furthermore, DMA can enhance the cluster formation rates of the HIO_3-HIO_2 system in marine and polar regions near DMA sources for more than 10^3-fold. Compared to the classical nucleation mechanism, the HIO_3-HIO_2-DMA mechanism exhibits strong nucleation ability, worthy of consideration as a promising mechanism in marine and polar regions rich in amine sources. The nucleation mechanism in real atmosphere is more complex and may result from multiple rapid nucleation systems, depending significantly on the variations of precursor concentrations in different regions. Hence, there is an urgent need to develop atmospheric models that comprehensively consider the coupling effects of multiple mechanisms.

Data availability

The data in this article can be available from the corresponding author upon request (lingliu@bit.edu.cn and zhangxiuhui@bit.edu.cn).

Supplement

The supplement related to this article is available online at: XXXXXXXX.

Author contributions

XZ designed and supervised the research. HZ performed the quantum chemical calculations and the ACDC simulations. HZ and LL analyzed data. HZ, LL and XZ wrote the paper. XZ, LL, BC, and YL reviewed and edited the paper. All authors commented on the paper.

Competing interests

The contact author has declared that neither they nor their co-authors have any competing interests.

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