



1 **Enhancement Mechanism of Ethylenediamine on Iodine**

2 **Oxoacid-Driven New Particle Formation in Marine Areas**

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16 **Abstract:**

17 The Iodic acid-iodous acid (HIO_3 – HIO_2) binary system is a highly efficient nucleation
18 pathway in marine environments, yet it cannot fully explain observed new particle
19 formation (NPF) events. Combining quantum chemical calculations and kinetic
20 simulations, we demonstrate that ethylenediamine (EDA)—a strong diamine from
21 anthropogenic and marine sources could synergistically enhance HIO_3 – HIO_2
22 nucleation via a ternary mechanism. The result demonstrates that both EDA and HIO_2
23 accept protons from HIO_3 to stabilize initial clusters, and replacing HIO_2 with EDA
24 molecules further reinforces cluster stability. At 278.15 K, EDA concentrations
25 ($[\text{EDA}]$) exceeding 0.1 ppt, both typical of the marine atmosphere, the aerosol
26 formation rate (J) of the HIO_3 – HIO_2 system increases by over one order of magnitude
27 under low iodine oxoacid concentrations. Comparing field observations with
28 simulations using conditions from coastal/polar sites and estimated $[\text{EDA}]$ elsewhere,
29 we find that the HIO_3 – HIO_2 –EDA ternary mechanism significantly contributes to NPF
30 in cold polar and clean coastal regions. Its simulated J values match field
31 measurements better than those of the binary HIO_3 – HIO_2 and HIO_3 –EDA systems,
32 effectively reproducing observed NPF characteristics. This ternary system is expected
33 to be a key contributor to marine NPF in regions with intensive marine industries,
34 carbon capture activities, and coastal agricultural/industrial emissions. These findings
35 broaden our understanding of multicomponent marine aerosol nucleation and
36 highlight the need for future research on strongly basic precursors similar to EDA in
37 promoting HIO_3 – HIO_2 nucleation in complex marine environments.

38 **Keywords:** New particle formation; Iodine oxoacids; Ethylenediamine; Nucleation
39 mechanism; Marine aerosols

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41 1. Introduction

42 Marine atmospheric new particle formation (NPF) serves as a core link in the
43 global aerosol cycle and it is also a critical process that sustains cloud condensation
44 nuclei (CCN) abundance in the marine boundary layer(Andreae and Rosenfeld, 2008;
45 de Jonge et al., 2024; S. Jiang et al., 2026; Lian et al., 2026; Miyakawa et al., 2023;
46 Ning et al., 2022b; Rasmussen et al., 2022; Sipila et al., 2016; Xia et al., 2020; R.
47 Zhang et al., 2025b; Zu et al., 2024a; Zu et al., 2024c), thereby regulating global
48 radiative balance and climate and even influencing human health(Feng et al., 2022;
49 Gordon et al., 2017; J. Merikanto et al., 2009; Jia et al., 2021; Luo, 2009; Prospero,
50 2002; Sun et al., 2023; F. Wang et al., 2023; F. Wang et al., 2024). As a major
51 constituent of aerosols in the marine boundary layer, marine secondary aerosol
52 formation highly relies on stable nucleation systems for their efficient production(Ma
53 et al., 2023; Markku Kulmala et al., 2007; Rong et al., 2020; R. Zhang et al., 2012; R.
54 Zhang et al., 2024; Zhao et al., 2024; Zu et al., 2024a; Zu et al., 2024c). Among
55 various nucleation precursors, the binary nucleation system of iodic acid (HIO_3) and
56 iodous acid (HIO_2) has been demonstrated to be one of the most promising and
57 efficient drivers for marine NPF(de Jonge et al., 2024; Y. Hu et al., 2023; Kirkby et al.,
58 2011a; Kirkby et al., 2011b; Kuang et al., 2008; J. Li et al., 2024b; Liu et al., 2023;
59 Shen et al., 2024; H. Wang et al., 2025; Wei et al., 2026; X-C He et al., 2023; X-C He
60 et al., 2021; R. Zhang et al., 2026; R. Zhang et al., 2025a; R. Zhang et al., 2024; R
61 Zhang. et al., 2022b; Zu et al., 2024a; Zu et al., 2024c). It substantially accelerates the
62 rapid formation of marine secondary aerosols, playing an irreplaceable role in the
63 marine iodine cycle and in atmospheric particle formation. CLOUD experiments
64 combined with theoretical calculations show that HIO_3 and HIO_2 form stable
65 nucleation clusters through strong halogen bonds and acid–base reactions, and that the
66 particle formation efficiency of this system exceeds that of the conventional sulfuric
67 acid–ammonia ($\text{H}_2\text{SO}_4\text{--NH}_3$) nucleation system(Xia et al., 2020; X-C He et al., 2023;
68 X-C He et al., 2021). Furthermore, in coastal regions and polar areas, HIO_3 and HIO_2
69 can act synergistically with species such as H_2SO_4 , methanesulfonic acid (MSA),



70 dimethylamine (DMA), and I_2O_4 to further enhance nucleation rates(Baccarini *et al.*,
71 2020; Beck *et al.*, 2021; J. Li *et al.*, 2024b; Sipila *et al.*, 2016; Xia *et al.*, 2020; X-C He
72 *et al.*, 2023; R. Zhang *et al.*, 2025a; R. Zhang *et al.*, 2025b; Zu *et al.*, 2024a; Zu *et al.*,
73 2024c). However, neither the binary HIO_3 - HIO_2 system alone nor the aforementioned
74 ternary systems can fully account for the high nucleation rates and explosive aerosol
75 growth observed in the marine boundary layer. This indicates that other key
76 precursors may participate in nucleation and improve nucleation efficiency through
77 synergistic effects.

78 Ethylenediamine (EDA) is a highly efficient absorbent and chelating agent
79 widely used in marine carbon capture and storage (CCS) technologies (Cho *et al.*,
80 2025; Güzel Kaya, 2023; E. Hu *et al.*, 2025; Peres *et al.*, 2024). It has also been
81 observed to be emitted from industrial sources such as power plants and
82 petroleum/metallurgical facilities, agricultural sources including livestock farming
83 and crop cultivation, as well as coastal regions and could enhance nucleation(Ayoubi,
84 2023; Elm, 2021a; b; Elm *et al.*, 2016; Jen *et al.*, 2016; Xie and Elm, 2021).
85 Accordingly, EDA has the potential to coexist with HIO_3 and HIO_2 in marine-relevant
86 environments. Our previous study demonstrated that EDA can form stable,
87 low-volatility clusters with HIO_3 , and exhibits prominent nucleation promotion
88 performance even at extremely low concentrations of parts-per-trillion level(Bai *et al.*,
89 2025). Marine atmospheric measurements indicate an average [EDA] of roughly 1 ppt,
90 while putrescine and cadaverine, diamines that share similar properties and sources
91 with EDA, exhibit maximum levels above 10 ppt (Ayoubi, 2023; Elm, 2021a; b; Elm
92 *et al.*, 2016; Jen *et al.*, 2016; Xie and Elm, 2021). On this basis, we assume that [EDA]
93 under marine atmospheric conditions span from 0.01 to 10 ppt Against this
94 background, and considering both the central role of the HIO_3 - HIO_2 binary nucleation
95 system and the nucleation enhancement effect of EDA, we propose that EDA, as an
96 effective precursor for stabilizing HIO_3 -containing clusters, is inferred to synergize
97 with HIO_3 and HIO_2 . This interaction could construct an efficient ternary nucleation
98 system and further accelerate secondary aerosol formation in the marine boundary
99 layer. To date, no systematic study has addressed the synergistic mechanism,



100 nucleation efficiency, and atmospheric implications of the $\text{HIO}_3\text{-HIO}_2\text{-EDA}$ ternary
101 system, and its essential role in marine new particle formation is still poorly
102 understood.

103 Therefore, using quantum chemical calculations and Atmospheric Cluster
104 Dynamics Code (ACDC) simulations, this study investigates the stability, nucleation
105 rate, and formation mechanism of the $\text{HIO}_3\text{-HIO}_2\text{-EDA}$ ternary nucleation system
106 under ambient marine atmospheric temperature and precursor concentration
107 conditions. This work clarifies the regulatory effect of EDA on the $\text{HIO}_3\text{-HIO}_2$ binary
108 nucleation system and elucidates the central role of this ternary system in marine NPF
109 events. This study will enrich the theory of marine atmospheric nucleation and
110 provide critical theoretical support and data reference for global marine aerosol
111 modeling, climate change prediction, and air pollution control.

112 2. Method

113 2.1 Quantum Chemical Calculations

114 This study employed a multi-step automated sampling strategy built on the JKCS
115 workflow (Bai *et al.*, 2025; M Engsvang *et al.*, 2024a; M. Engsvang *et al.*, 2024b; S.
116 Jiang *et al.*, 2026; Kubecka *et al.*, 2019; Kubecka *et al.*, 2023) to systematically
117 identify the global minimum structures of clusters in the $\text{HIO}_3\text{-HIO}_2\text{-EDA}$ system,
118 covering the series $(\text{HIO}_3)_{0-3}(\text{EDA})_{0-3}$, $(\text{HIO}_2)_{0-3}(\text{EDA})_{0-3}$, and $(\text{HIO}_3)_x(\text{HIO}_2)_y(\text{EDA})_z$
119 ($x = 1-3$, $y+z = 2-3$) clusters. The approach enables automated conformational
120 sampling and energy evaluation of nucleation clusters with adjustable precision, and
121 the detailed procedures have been reported in previous studies (Bai *et al.*, 2025; S.
122 Jiang *et al.*, 2026; Kubecka *et al.*, 2019). For $(\text{HIO}_3)_{0-3}(\text{HIO}_2)_{0-3}$, $(\text{HIO}_3)_{4-6}$, $(\text{HIO}_2)_{4-6}$,
123 and $(\text{HIO}_3)_{1-3}(\text{EDA})_{1-3}$ clusters, initial structures were taken from reported studies (Bai
124 *et al.*, 2025; Ning *et al.*, 2022a; R. Zhang *et al.*, 2022b) followed by re-optimization
125 using the identical theoretical framework before conducting single-point energy
126 evaluations. The workflow is as follows. Initial configurations were generated with
127 the artificial bee colony algorithm implemented in ABCluster 3.3 (J. Zhang and Dolg,



2015) to perform global searches for low-energy structures of each cluster. All saved structures were first pre-optimized and screened at the GFN1-xTB level using XTB 6.6.1 (Bannwarth *et al.*, 2020). Duplicate configurations were filtered out according to thresholds for radius of gyration, electronic energy, and dipole moment, and the 1000 lowest-energy structures were retained. Subsequently, single-point energies were computed in Gaussian 16 (Frisch *et al.*, 2016) at the ω B97X-D/aug-cc-pVDZ(-PP) level (aug-cc-pVDZ-PP with ECP28 for I; aug-cc-pVDZ for H, C, N, O atoms) to rank these configurations, and the 100 most stable ones were selected for geometry optimization and frequency analysis at the same level. And the five structures possessing the lowest Gibbs free energies were kept. These were then subjected to final single-point energy calculations in ORCA 5.0.4 (Neese, 2012) at the DLPNO-CCSD(T)/aug-cc-pVTZ(-PP) level (aug-cc-pVTZ-PP with ECP28 for I; aug-cc-pVTZ for H, C, N, O atoms) with the TightPNO and TightSCF settings. The analyses of the optimized global minimum structures of the $(\text{HIO}_2)_{1-3}(\text{EDA})_{1-3}$ and the $(\text{HIO}_3)_x(\text{HIO}_2)_y(\text{EDA})_z$ ($x = 1-3$, $y+z = 2-3$) clusters are presented in Figure 1, Figure S1, and Table S1.

The final Gibbs free energy (G) of each cluster at 298.15 K was obtained as

$$G = E_{\text{DLPNO}} + G_{\text{thermal}}^{\omega\text{B97X-D}} \quad (1)$$

Where E_{DLPNO} is the single-point energy computed at the DLPNO-CCSD(T) level and $G_{\text{thermal}}^{\omega\text{B97X-D}}$ is the thermal correction to the Gibbs free energy evaluated at the ω B97X-D level. Values at other temperatures were recalculated from the enthalpies and entropies. The formation free energy ΔG (kcal mol^{-1}) for each cluster was defined as the difference between the free energy of the cluster and the sum of the free energies of its constituent monomers:

$$\Delta G = G_{\text{cluster}} - \Sigma G_{\text{monomer}} \quad (2)$$

All calculated ΔG values are listed in Table S2.



2.2 Atmospheric Cluster Dynamics Code (ACDC) Simulations

To investigate the nucleation kinetics, the quantum-chemically computed cluster formation free energies (ΔG) were supplied to the ACDC model (S. Jiang *et al.*, 2022; McGrath *et al.*, 2012; Olenius *et al.*, 2013; F. Yu, 2006; F. Yu *et al.*, 2018; F. Yu and Turco, 2001). By solving the birth–death equations for atmospheric clusters, this framework traces how cluster formation rates evolve over time and identifies the dominant growth pathways. The governing equation for the number concentration C_i of cluster i is:

$$\frac{dC_i}{dt} = \frac{1}{2} \sum_{j < i} \beta_{j,(i+j)} C_j C_{(i+j)} + \sum_j \gamma_{(i+j) \rightarrow i} C_{i+j} - \sum_j \beta_{i,j} C_i C_j - \frac{1}{2} \sum_{j < i} \gamma_{i \rightarrow j} C_i + Q_i - S_i \quad (3)$$

Where $\beta_{i,j}$ is the collision coefficient between clusters i and j , $\gamma_{(i+j) \rightarrow i}$ is the evaporation coefficient for cluster $(i+j)$ dissociating into cluster i , and Q_i and S_i represent external sources and sinks, respectively. The collision rate is computed from kinetic gas theory as:

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

And the evaporation rate follows from detailed balance,

$$\gamma_{(i+j) \rightarrow i} = \beta_{i,j} C_{\text{ref}} \exp\left(-\frac{\Delta G_{(i+j)} - \Delta G_i - \Delta G_j}{k_B T}\right) \quad (5)$$

With k_B the Boltzmann constant, m and V the cluster mass and volume, and C_{ref} the monomer reference concentration at standard atmospheric pressure.

All clusters of the HIO_3 - HIO_2 -EDA system were included in the ACDC simulations. On the basis of cluster stability analyses from Figure S2-S5, $(\text{HIO}_3)_4(\text{HIO}_2)_3$, $(\text{HIO}_3)_3(\text{HIO}_2)_4$, $(\text{HIO}_3)_4(\text{HIO}_2)_4$, $(\text{HIO}_3)_7$, $(\text{HIO}_2)_7$, $(\text{HIO}_3)_4(\text{HIO}_2)_1(\text{EDA})_2$, $(\text{HIO}_3)_3(\text{HIO}_2)_2(\text{EDA})_2$, and $(\text{HIO}_3)_3(\text{HIO}_2)_1(\text{EDA})_3$ were set



171 as boundary clusters (see Section S1 of Supporting Information for details). The
172 concentration of HIO_3 ($[\text{HIO}_3]$) was explored over the range 10^6 – 10^8 cm^{-3} , with $[\text{HIO}_2]$
173 fixed at 1/50 of $[\text{HIO}_3]$, which falls within the typical 20–100 range of these
174 homologues observed in field and CLOUD chamber measurements (*Baccarini et al.*,
175 2020; *Rong et al.*, 2020; *Sipila et al.*, 2016; *Xia et al.*, 2020; *X-C He et al.*, 2021; *H.*
176 *Yu et al.*, 2019). To evaluate the influence of EDA on the HIO_3 - HIO_2 binary system,
177 $[\text{EDA}]$ was varied within 0.01–10 ppt. This matches the $[\text{HIO}_3]$ interval recorded at
178 coastal and polar sites (*X-C He et al.*, 2023; *X-C He et al.*, 2021), whereas $[\text{EDA}]$
179 represents an estimated possible range for marine-influenced regions, derived from
180 measurements at other locations (*Elm*, 2021a; b; *Elm et al.*, 2016; *Jen et al.*, 2016; *Xie*
181 *and Elm*, 2021). The baseline conditions were set to 278.15 K and a condensation sink
182 (CS) of 0.002 s^{-1} , representative of typical marine environments (*Dal Maso et al.*, 2002;
183 *S. Jiang et al.*, 2026; *R. Zhang et al.*, 2025a; *R. Zhang et al.*, 2025b; *Zu et al.*, 2024a).
184 To examine the sensitivity of ternary nucleation under a wider range of atmospheric
185 scenarios, additional simulations were carried out across 258.15–298.15 K (Figure
186 S6–S9, S13) and CS values of 0.01, 0.0004, 0.0002, and 0.0001 s^{-1} (Figure S10, S13),
187 corresponding respectively to polluted coastal areas and polar regions (*Baccarini et*
188 *al.*, 2020; *Beck et al.*, 2021; *Qu éver et al.*, 2022; *X-C He et al.*, 2021; *H. Yu et al.*,
189 2019). Additionally, to account for the potential influence of HIO_2 , simulations were
190 performed with $[\text{HIO}_2]$ set to 1/20 and 1/100 of the $[\text{HIO}_3]$ (Figure S11–S12, S14–S15),
191 and the resulting impact on the simulation outcomes was examined.

192 3. Results and Discussion

193 3.1 Global minimum configurations of HIO_3 - HIO_2 -EDA ternary system

194 In the HIO_3 - HIO_2 -EDA ternary system, the configurations of the binary
195 HIO_3 - HIO_2 and HIO_3 -EDA clusters have been comprehensively discussed in previous
196 studies (*Bai et al.*, 2025; *M. Engsvang et al.*, 2024b; *J. Li et al.*, 2024b; *R. Zhang et al.*,
197 2022a). The previously unexplored configurations of the ternary HIO_3 - HIO_2 -EDA
198 clusters are presented in Figure 1, while those of the binary HIO_2 -EDA clusters are



199 shown in Figure S1 of the Supporting Information. All obtained
200 $(\text{HIO}_3)_x(\text{HIO}_2)_y(\text{EDA})_z$ ($x = 1-3$, $y+z = 2-3$) clusters are stabilized by hydrogen bonds
201 (HBs) and halogen bonds (XBs), which is consistent with the structural characteristics
202 of ternary clusters formed by the interactions between HIO_3 - HIO_2 and other
203 precursors including DMA, SA, MSA and I_2O_4 (*J. Li et al.*, 2024b; *R. Zhang et al.*,
204 2025a; *Zu et al.*, 2024a; *Zu et al.*, 2024c). Furthermore, proton transfer reactions occur
205 in all of these HIO_3 - HIO_2 -EDA ternary clusters. Such efficient protonation has also
206 been observed in binary HIO_3 -EDA clusters (*Bai et al.*, 2025), owing to the strong
207 basicity of EDA conferred by its two amino groups. Moreover, previous studies have
208 also confirmed that HIO_2 acts as a base-like species in HIO_3 - HIO_2 binary clusters to
209 accept protons (*Wu et al.*, 2023; *X-C He et al.*, 2023; *X-C He et al.*, 2021; *R. Zhang et al.*,
210 2024; *R. Zhang et al.*, 2022b; *Zu et al.*, 2024b). Therefore, in the HIO_3 - HIO_2 -EDA
211 ternary clusters, both EDA and HIO_2 serve as proton acceptors, receiving protons
212 donated by HIO_3 to further stabilize the ternary cluster configurations, wherein HIO_2
213 and EDA both function as basic molecules. In contrast, as shown in Figure S1, proton
214 transfer from HIO_2 to HIO_2 and EDA also occurs in the binary HIO_2 -EDA clusters,
215 suggesting that HIO_2 exhibits amphoteric behavior. This indicates that the role of
216 HIO_2 can change markedly depending on the nucleation precursors, playing a critical
217 role in stabilizing the cluster configurations.

218 Table S1 summarizes the numbers of HBs, XBs, and proton transfer events
219 formed in the ternary clusters. The results reveal that the total numbers of HBs, XBs
220 and proton transfer processes increase with the rising total molecular number of
221 ternary clusters. Specifically, the number of XBs formed is closely related to the
222 numbers of HIO_3 and HIO_2 molecules. When the number of HIO_3 molecules is no
223 more than two, the number of XBs equals the number of HIO_2 molecules. For ternary
224 clusters containing three HIO_3 molecules, three XBs are formed in
225 $(\text{HIO}_3)_3(\text{HIO}_2)_1(\text{EDA})_1$ and $(\text{HIO}_3)_3(\text{HIO}_2)_2(\text{EDA})_2$ these two cluster configurations,
226 while no XBs are detected in $(\text{HIO}_3)_3(\text{HIO}_2)_1(\text{EDA})_2$ cluster. Notably, in
227 $(\text{HIO}_3)_3(\text{HIO}_2)_1(\text{EDA})_2$ cluster, the two EDA molecules interact with HIO_3 - HIO_2
228 through HBs to form a cage-like structure, leaving abundant unoccupied XBs sites



that facilitate the binding of additional nucleation precursors. A similar phenomenon has been reported in large ternary clusters of the HIO_3 -DMA-AM system (*J. Li et al.*, 2024a), indicating that structurally stable large clusters play an important role in promoting atmospheric cluster nucleation. Likewise, the occurrence of proton transfer is governed by HIO_3 distribution. Except for $(\text{HIO}_3)_3(\text{HIO}_2)_2(\text{EDA})_1$ cluster, single HIO_3 molecules preferentially donate protons to HIO_2 . When the cluster contains two or three HIO_3 molecules, EDA preferentially accepts protons, and residual HIO_3 then protonates HIO_2 . In $(\text{HIO}_3)_3(\text{HIO}_2)_2(\text{EDA})_1$ clusters, one pair of HIO_3 - HIO_2 molecules remains unprotonated, accompanied by extensive XBs formation, rendering this cluster the one with the maximum XBs content. These findings indicate that the diamino structure of EDA within ternary clusters does not exert a dominant basic role upon the incorporation of HIO_2 , as HIO_2 itself displays pronounced basicity. This is likely attributable to the enhanced steric hindrance of EDA molecules resulting from the increased number of molecules.

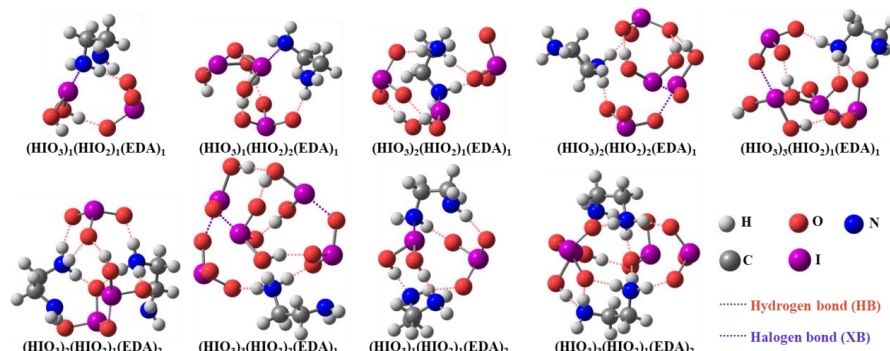


Figure 1 Identified global minimum configurations of $(\text{HIO}_3)_x(\text{HIO}_2)_y(\text{EDA})_z$ ($x = 1-3$, $y+z = 2-3$) clusters at the DLPNO-CCSD(T)/aug-cc-pVTZ(-pp)// ω B97X-D/aug-cc-pVDZ(-pp) level of theory. The dashed red and purple lines indicate HBs and XBs, respectively.

3.2 Cluster Stability of HIO_3 - HIO_2 -EDA ternary system

In this study, the thermodynamic and kinetic stabilities of clusters were evaluated by the cluster formation Gibbs free energy (ΔG) and the total evaporation rate ($\Sigma \gamma$). Lower values of ΔG and $\Sigma \gamma$ indicate that the clusters are more prone to stable existence in the atmosphere (*Ma et al.*, 2024; *Ma et al.*, 2023; *Ning et al.*, 2022a; *R.*



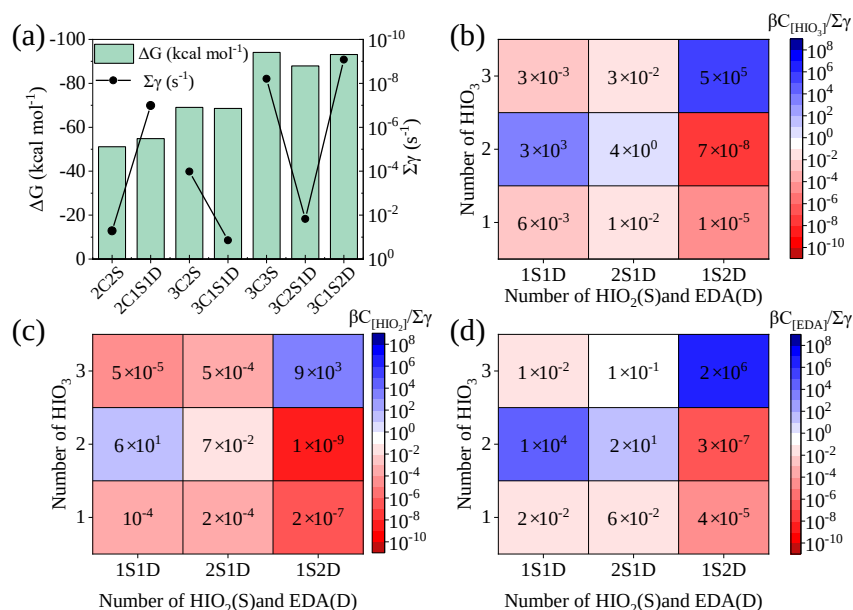
252 *Zhang et al.*, 2025b). Tables S2 and S3 list the ΔG and $\Sigma\gamma$ for HIO_3 - HIO_2 , HIO_2 -EDA
253 binary clusters, and HIO_3 - HIO_2 -EDA ternary clusters at different atmospheric
254 temperatures ($T = 258.15, 268.15, 278.15, 288.15, 298.15$ K). Herein, C, S, and D
255 represent HIO_3 , HIO_2 , and EDA, respectively. At 278.15 K, the ternary clusters
256 $(\text{HIO}_3)_x(\text{HIO}_2)_y(\text{EDA})_z$ ($x = 1-3, y+z = 2-3$) exhibit low ΔG and $\Sigma\gamma$ values. In
257 particular, the $\Sigma\gamma$ of most clusters ranges from 10^{-1} to 10^{-6} s^{-1} , indicating superior
258 stability (*McGrath et al.*, 2012). For the binary systems, the HIO_3 - HIO_2 system
259 possesses higher thermodynamic stability than the HIO_3 -EDA and HIO_2 -EDA systems.
260 All HIO_2 -EDA binary clusters show considerably high $\Sigma\gamma$, suggesting that HIO_2
261 cannot effectively stabilize EDA. Combined with the strong basicity of EDA in the
262 HIO_3 -EDA system, this result further proves that HIO_2 predominantly acts as a base
263 rather than an acid within the HIO_2 -EDA system, leading to instability in binary
264 clusters composed of two basic precursors.

265 Figure 2a evaluates the effect of EDA addition on cluster stability by comparing
266 the ΔG and $\Sigma\gamma$ values of three most stable cluster types from the HIO_3 - HIO_2 binary
267 and HIO_3 - HIO_2 -EDA ternary systems under the condition of equal numbers of acidic
268 and basic molecules. These three types were selected because clusters with the
269 number of acidic molecules greater than or equal to the number of basic molecules
270 exhibit higher stability. After replacing HIO_2 molecules with EDA molecules, the ΔG
271 values of the ternary clusters are comparable to those of the binary clusters. For
272 example, substituting one EDA molecule in 2C2S reduces ΔG from $-51.11 \text{ kcal mol}^{-1}$
273 to $-54.85 \text{ kcal mol}^{-1}$, whereas the ΔG of 3C1S1D, ($-68.60 \text{ kcal mol}^{-1}$) is slightly higher
274 than that of 3C2S ($-69.03 \text{ kcal mol}^{-1}$). Since $\Sigma\gamma$ encompasses all collision and
275 evaporation processes of numerous subclusters (*McGrath et al.*, 2012), significant
276 changes in $\Sigma\gamma$ are observed for the corresponding clusters. The $\Sigma\gamma$ of 2C1S1D
277 (1.03×10^{-7}) decreases by five orders of magnitude compared to 2C2S (0.0521). For
278 3C1S2D (8.33×10^{-10}) and 3C2S1D (0.0149), the $\Sigma\gamma$ values are, respectively, one order
279 of magnitude lower and seven orders of magnitude higher than that of 3C3S
280 (6.23×10^{-9}). In summary, replacing HIO_2 with EDA does not uniformly enhance or
281 reduce cluster stability, but the substitution significantly improves the stability of



282 large-sized structurally stable clusters (e.g., 3C1S2D), which can potentially promote
283 cluster formation and growth. Therefore, EDA molecules have the potential to
284 stabilize the formation of iodine oxoacid-containing clusters.

285 Furthermore, the growth potential of clusters during nucleation is further
286 assessed using the $\beta C/\Sigma\gamma$ ratio (Besel *et al.*, 2020; J. Li *et al.*, 2024a; Ning *et al.*,
287 2022a; Zu *et al.*, 2024a; Zu *et al.*, 2024c), where β is the collision coefficient between
288 the cluster and monomers at a given concentration C in the atmosphere. When $\beta C/\Sigma\gamma$
289 exceeds 1, the cluster favors growth over evaporation. Clusters large enough to
290 nucleate are thus defined as boundary clusters in ACDC simulations, which can grow
291 beyond the simulation system to form larger particles. Figures 2b–2d present the
292 $\beta C/\Sigma\gamma$ values of the $(\text{HIO}_3)_x(\text{HIO}_2)_y(\text{EDA})_z$ ($x = 1-3$, $y+z = 2-3$) ternary clusters after
293 EDA addition at 278.15 K under the observed low atmospheric concentrations of
294 nucleation precursors. The selected concentrations for $[\text{HIO}_3]$, $[\text{HIO}_2]$, and $[\text{EDA}]$ are
295 10^6 cm^{-3} , $2 \times 10^4 \text{ cm}^{-3}$, and 0.1 ppt, respectively. Notably, the 3C1S2D cluster exhibits
296 $\beta C/\Sigma\gamma > 1$ for collisions with HIO_3 , HIO_2 , and EDA monomers, indicating its
297 exceptional stability and eligibility as a boundary cluster, thereby promoting
298 HIO_3 - HIO_2 nucleation. Furthermore, Figures S2–S5 present the $\beta C/\Sigma\gamma$ values for the
299 $(\text{HIO}_3)_x(\text{HIO}_2)_y(\text{EDA})_z$ ($x = 1-3$, $y + z = 2-3$) clusters when interacting with
300 monomers of the three precursors at 258.15, 268.15, 288.15, and 298.15 K. The
301 aforementioned conclusion remains valid: the 3C1S2D cluster exhibits sufficient
302 stability to contribute to nucleation under atmospheric conditions. These results
303 collectively demonstrate that EDA has the potential to enhance HIO_3 - HIO_2 nucleation,
304 warranting further investigation.



305

306 **Figure 2 (a) ΔG and corresponding $\Sigma\gamma$ of selected $(HIO_3)_x(HIO_2)_y(EDA)_z$ ($x = 1-3$, $y+z = 2-3$)**
 307 **clusters and $(HIO_3)_x(HIO_2)_y$ ($x = 1-3$, $y = 1-3$) at 278.15 K and 1 atm at the**
 308 **DLPNO-CCSD(T)/aug-cc-pVTZ(-pp)// ω B97X-D/aug-cc-pVDZ(-pp) level of theory (b) the**
 309 **$(\beta C_{[HIO_3]}/\Sigma\gamma)$ at $C_{[HIO_3]} = 10^6$ cm⁻³ and (c) the $(\beta C_{[HIO_3]}/\Sigma\gamma)$ at $C_{[HIO_3]} = 2 \times 10^4$ cm⁻³ (d) and the**
 310 **$(\beta C_{[EDA]}/\Sigma\gamma)$ at $C_{[EDA]} = 0.1$ ppt at 278.15 K and 1 atm.**

311 3.3 Aerosol formation rate and the enhancement effect of EDA

312 To quantitatively investigate the effect of EDA on HIO₃-HIO₂ nucleation, ACDC
 313 simulations were performed to calculate the variation of cluster formation rate (J) with
 314 $[HIO_3]$ (10^6 - 10^8 cm⁻³) and $[EDA]$ (0.01–10 ppt) in the HIO₃-HIO₂-EDA system at
 315 278.15 K under typical marine conditions with a CS of 0.002 s⁻¹ (Bai et al., 2025; J.
 316 Li et al., 2024b; R. Zhang et al., 2024). The corresponding $[HIO_2]$ concentration range
 317 was 2×10^4 - 2×10^6 cm⁻³. The results were compared with those of the HIO₃-HIO₂
 318 binary system and are presented in Figure 3a. Furthermore, the enhancement factor of
 319 EDA on J (R_{EDA}) is defined as the ratio of J in the ternary system to that of the
 320 HIO₃-HIO₂ system, with the corresponding results shown in Figure 3b. At 278.15 K,
 321 EDA significantly enhances J of the HIO₃-HIO₂ system. The J values of the ternary
 322 system increase markedly with increasing concentrations of all three precursors, while

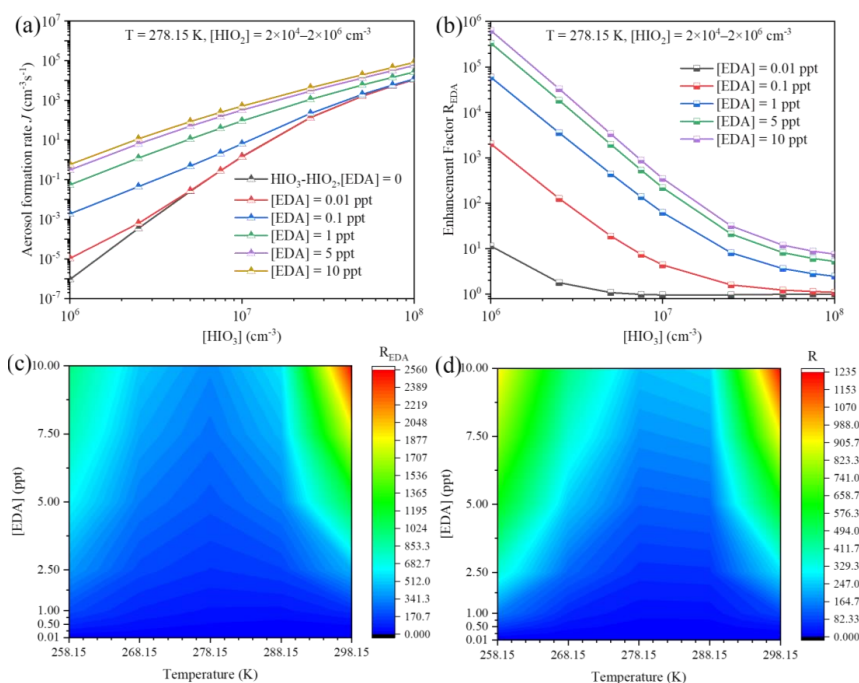


323 R_{EDA} decreases with increasing $[\text{HIO}_3]$ and $[\text{HIO}_2]$. Both J and R_{EDA} rise significantly
324 with increasing $[\text{EDA}]$ (≥ 0.1 ppt) at low iodine oxoacid concentrations ($[\text{HIO}_3] \leq 10^7$
325 cm^{-3} , $[\text{HIO}_2] \leq 2 \times 10^5 \text{ cm}^{-3}$). At $[\text{HIO}_3] \leq 10^7 \text{ cm}^{-3}$, 1 ppt of EDA increases the J of the
326 ternary system to $7.86 \times 10^{-2} - 1.95 \times 10^2 \text{ cm}^{-3} \text{ s}^{-1}$, which is more than one order of
327 magnitude higher than that of the binary system ($2.87 \times 10^{-5} - 1.47 \times 10^1 \text{ cm}^{-3} \text{ s}^{-1}$) under
328 the same environmental conditions, with R_{EDA} ranging from 12.50 to 5469.73.
329 Notably, in the HIO_3 - HIO_2 binary system, a $[\text{HIO}_3]$ of $9.35 \times 10^6 \text{ cm}^{-3}$ is required to
330 achieve a J value of approximately $1 \text{ cm}^{-3} \text{ s}^{-1}$. However, with the addition of 0.1 ppt
331 EDA, the $[\text{HIO}_3]$ required to reach the same J value in the HIO_3 - HIO_2 -EDA ternary
332 system is reduced to $6.15 \times 10^6 \text{ cm}^{-3}$. This indicates that EDA can partially substitute
333 for the role of HIO_3 molecules in nucleation and confirms that EDA can
334 synergistically nucleate with HIO_3 - HIO_2 system.

335 In addition to precursor concentrations, temperature also significantly affects the
336 J and the R_{EDA} of the ternary system. Therefore, Figure 3c further simulates the effects
337 of temperature and $[\text{EDA}]$ variations on the HIO_3 - HIO_2 -EDA ternary system and the
338 HIO_3 - HIO_2 binary system, mainly reflected through R_{EDA} . Considering that our
339 previous study indicated that the HIO_3 -EDA binary system also exhibits strong
340 nucleation potential (Bai *et al.*, 2025), we define R as the ratio of the J value of the
341 HIO_3 -EDA binary system to that of the HIO_3 - HIO_2 binary system to illustrate the
342 effect of EDA on HIO_3 -driven nucleation, with the results shown in Figure 3d. To
343 ensure the environmental relevance of the comparison, we selected simulation results
344 at 278.15 K with $[\text{HIO}_3] = 10^7 \text{ cm}^{-3}$ and the corresponding $[\text{HIO}_2] = 2 \times 10^5 \text{ cm}^{-3}$, under
345 which both the HIO_3 - HIO_2 -EDA ternary system and the HIO_3 - HIO_2 binary system
346 yield J values exceeding $1 \text{ cm}^{-3} \text{ s}^{-1}$. As lower temperatures enhance cluster stability,
347 they consequently increase the J value of the HIO_3 - HIO_2 -EDA, HIO_3 -EDA,
348 HIO_3 - HIO_2 systems, which holds true for all three nucleation systems mentioned
349 above. However, unlike the temperature sensitivity of J , the dependences of R_{EDA} and
350 R on temperature are non-monotonic and exhibit a strong dependence on $[\text{EDA}]$.
351 Compared to temperature variations, R_{EDA} and R are significantly more sensitive to
352 changes in $[\text{EDA}]$. When $[\text{EDA}]$ exceeds 0.1 ppt, the relationship



353 $J(\text{HIO}_3\text{-HIO}_2\text{-EDA}) > J(\text{HIO}_3\text{-EDA}) > J(\text{HIO}_3\text{-HIO}_2)$ holds consistently across all
354 selected marine-relevant temperatures (258.15–298.15 K). When [EDA] decreases to
355 0.1 ppt, a distinct behavior emerges: for $T \geq 278.15$ K, the $\text{HIO}_3\text{-HIO}_2$ system exhibits
356 a slightly higher J value than the $\text{HIO}_3\text{-EDA}$ system. Moreover, when [EDA] is below
357 0.1 ppt, the J value of the $\text{HIO}_3\text{-HIO}_2$ system is higher than that of the $\text{HIO}_3\text{-EDA}$
358 system under almost all conditions. These results indicate that the $\text{HIO}_3\text{-HIO}_2$ binary
359 system exhibits extremely high nucleation efficiency under realistic atmospheric
360 conditions, and EDA significantly enhances $\text{HIO}_3\text{-HIO}_2$ nucleation, making this
361 ternary system one of the most realistic multi-component nucleation systems in the
362 atmosphere.



363
364 **Figure 3** (a) Aerosol formation rate (J , cm³s⁻¹) of $\text{HIO}_3\text{-HIO}_2$ system and $\text{HIO}_3\text{-HIO}_2\text{-EDA}$
365 system and (b) corresponding enhancement factor of EDA (R_{EDA}) for $\text{HIO}_3\text{-HIO}_2\text{-EDA}$
366 system compared with $\text{HIO}_3\text{-HIO}_2$ system at $T = 278.15$ K, 1atm, $\text{CS} = 0.002$ s⁻¹, $[\text{HIO}_3] = 10^6$
367 - 10^8 cm⁻³, $[\text{HIO}_2] = 2 \times 10^4 - 2 \times 10^6$ cm⁻³, [EDA] = 0.01, 0.1, 1, 5, 10 ppt. Variation of (c) R_{EDA}
368 and (d) enhancement factor of EDA (R) for $\text{HIO}_3\text{-EDA}$ system compared with $\text{HIO}_3\text{-HIO}_2$
369 system with precursor concentrations ([EDA] = 0.01–10 ppt) and temperature ($T = 258.15$,
370 268.15, 278.15, 288.15, 298.15 K) at 1atm, $\text{CS} = 0.002$ s⁻¹, $[\text{HIO}_3] = 10^7$ cm⁻³, $[\text{HIO}_2] = 2 \times 10^5$
371 cm⁻³.



3.4 Cluster formation pathway of HIO_3 - HIO_2 -EDA system

From the preceding discussion, it is clear that trace amounts of EDA can significantly promote HIO_3 - HIO_2 nucleation. To further explore the underlying mechanism of EDA involvement in HIO_3 - HIO_2 -EDA ternary nucleation, ACDC simulations were conducted under typical marine atmospheric conditions. Under typical marine atmospheric conditions ($T = 278.15 \text{ K}$, $CS = 0.002 \text{ s}^{-1}$) with moderate concentrations of $[\text{HIO}_3] = 10^7 \text{ cm}^{-3}$ and $[\text{HIO}_2] = 2 \times 10^5 \text{ cm}^{-3}$, cluster formation pathways were simulated at $[\text{EDA}] = 0$ and 0.1 ppt . For clarity, pathways contributing less than 5% to the cluster formation flux are not shown. As shown in Figure 4a, in the absence of EDA, binary HIO_3 - HIO_2 nucleation proceeds primarily via collisions with HIO_3 or HIO_2 monomers and with the $(\text{HIO}_3)_1(\text{HIO}_2)_1$ dimer, as confirmed by previous studies (Liu *et al.*, 2023; X-C He *et al.*, 2021; R. Zhang *et al.*, 2022b). When $[\text{EDA}]$ is increased to 0.1 ppt , the nucleation pathways become diversified, with the emergence of additional HIO_3 -EDA binary and HIO_3 - HIO_2 -EDA ternary nucleation pathways. Due to the prominent contribution of EDA to cluster formation, the relative contribution of binary HIO_3 - HIO_2 clusters growing out of the simulated system is reduced. Instead, most clusters in the binary system combine with EDA molecules, contributing to the ternary pathways. The changes are mainly reflected in two pathways: the formation of $(\text{HIO}_3)_3(\text{HIO}_2)_2(\text{EDA})_1$ via collision of $(\text{HIO}_3)_3(\text{HIO}_2)_2$ with an EDA molecule contributes 22%, and the formation of $(\text{HIO}_3)_3(\text{HIO}_2)_1(\text{EDA})_2$ via collisions of $(\text{HIO}_3)_2(\text{HIO}_2)_1$ with one HIO_3 monomer and EDA monomer contributes 33%. Additionally, the $(\text{HIO}_3)_3(\text{HIO}_2)_2(\text{EDA})_1$ cluster exhibits high stability and accounts for 13% of the total nucleation pathways. Furthermore, the addition of EDA introduces competitive pathways with HIO_2 : EDA can also combine with HIO_3 to form HIO_3 -EDA binary clusters, which subsequently collide with HIO_3 and EDA monomers to generate $(\text{HIO}_3)_3(\text{EDA})_3$, contributing 16% of the cluster growth flux. These results demonstrate that EDA has a strong affinity for HIO_3 monomers and HIO_3 - HIO_2 clusters. Consequently, increasing $[\text{EDA}]$ gradually enhances the contributions of HIO_3 -EDA and HIO_3 - HIO_2 -EDA pathways, while



401 diminishing the contribution of the pure $\text{HIO}_3\text{-HIO}_2$ pathway.

402 Figure 5 investigates the underlying mechanism of the competitive contributions
403 between EDA-involved and Non-EDA nucleation pathways by varying $[\text{HIO}_3]$,
404 $[\text{HIO}_2]$, and $[\text{EDA}]$. It can be seen that when $[\text{HIO}_3]$ is as low as 10^6 cm^{-3} , the
405 $\text{HIO}_3\text{-EDA}$ pathway consistently dominates over the entire range of $[\text{EDA}]$. At an
406 intermediate $[\text{HIO}_3]$ (10^7 cm^{-3}), when $[\text{EDA}]$ exceeds 0.1 ppt, the dominant
407 mechanism shifts from the $\text{HIO}_3\text{-HIO}_2$ pathway to the $\text{HIO}_3\text{-HIO}_2\text{-EDA}$ pathway.
408 However, when $[\text{EDA}]$ surpasses 5 ppt, the dominance reverts to the $\text{HIO}_3\text{-EDA}$
409 pathway. At a high $[\text{HIO}_3]$ of 10^8 cm^{-3} , the dominant mechanism transitions from the
410 $\text{HIO}_3\text{-HIO}_2$ pathway to the $\text{HIO}_3\text{-HIO}_2\text{-EDA}$ pathway for $[\text{EDA}]$ above 0.1 ppt, but it
411 again becomes $\text{HIO}_3\text{-EDA}$ pathway dominated at an extremely high $[\text{EDA}]$ of 10 ppt.
412 Such shifts between HIO_3 -driven binary nucleation and ternary nucleation involving
413 amines are evidently dictated by precursor concentrations. At low $[\text{HIO}_3]$, the $[\text{HIO}_2]$
414 is much lower than $[\text{EDA}]$, resulting in a negligible contribution from the $\text{HIO}_3\text{-HIO}_2$
415 pathway and consequently a similarly weak contribution from the $\text{HIO}_3\text{-HIO}_2\text{-EDA}$
416 pathway. As $[\text{HIO}_3]$ and $[\text{HIO}_2]$ increase, the $\text{HIO}_3\text{-HIO}_2\text{-EDA}$ pathway becomes
417 dominant when $[\text{EDA}]$ is one order of magnitude higher than $[\text{HIO}_2]$. Particularly at
418 extremely high $[\text{HIO}_3]$, comparable levels of $[\text{EDA}]$ and $[\text{HIO}_2]$ result in similar
419 relative contributions from the $\text{HIO}_3\text{-HIO}_2$ binary pathway and the $\text{HIO}_3\text{-HIO}_2\text{-EDA}$
420 ternary pathway. Notably, when $[\text{EDA}]$ reaches 0.1 ppt or higher, the EDA-involved
421 pathways collectively contribute more than 50% to the cluster formation flux,
422 indicating that their influence cannot be neglected. In summary, the effect of EDA on
423 $\text{HIO}_3\text{-HIO}_2$ nucleation pathways is analogous to that of DMA (Zu *et al.*, 2024a).
424 These amines exhibit strong stabilizing effects on HIO_3 -containing clusters,
425 comparable to that of HIO_2 , resulting in transitions between the three dominant
426 nucleation pathways depending on the relative concentrations of HIO_2 and amines.
427 Consequently, in regions with high amine emissions, the contribution of EDA
428 interacting with $\text{HIO}_3\text{-HIO}_2$ to nucleation is expected to be significant.

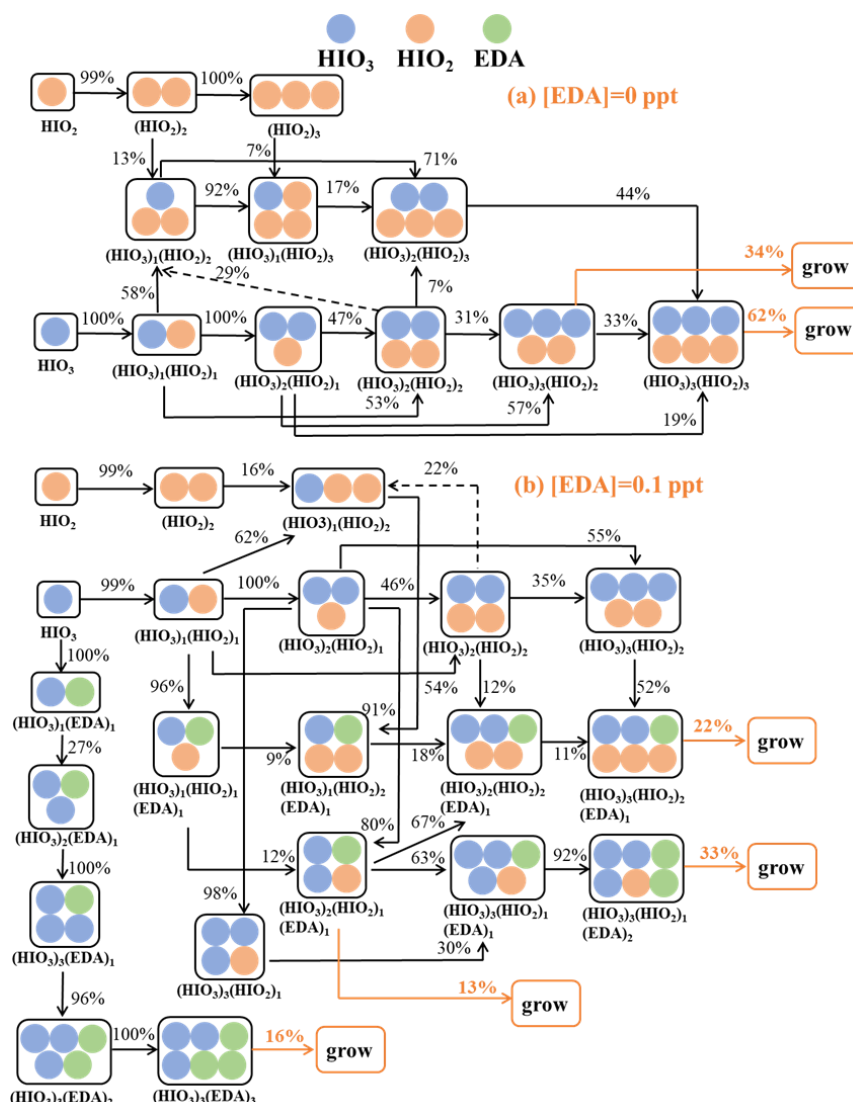


Figure 4 Cluster formation pathways for (a) HIO_3 - HIO_2 system and (b) HIO_3 - HIO_2 -EDA system at 278.15 K, 1atm, $\text{CS} = 0.002 \text{ s}^{-1}$ at $[\text{HIO}_3] = 10^7 \text{ cm}^{-3}$, $[\text{HIO}_2] = 2 \times 10^5 \text{ cm}^{-3}$, and $[\text{EDA}] = 0.1$ ppt. The values of percentages represent the contribution percentage of a small cluster to a larger cluster along the direction of the arrow. For clarity, other pathway that contributes less than 5% to the cluster growing out of the studied system are not shown.

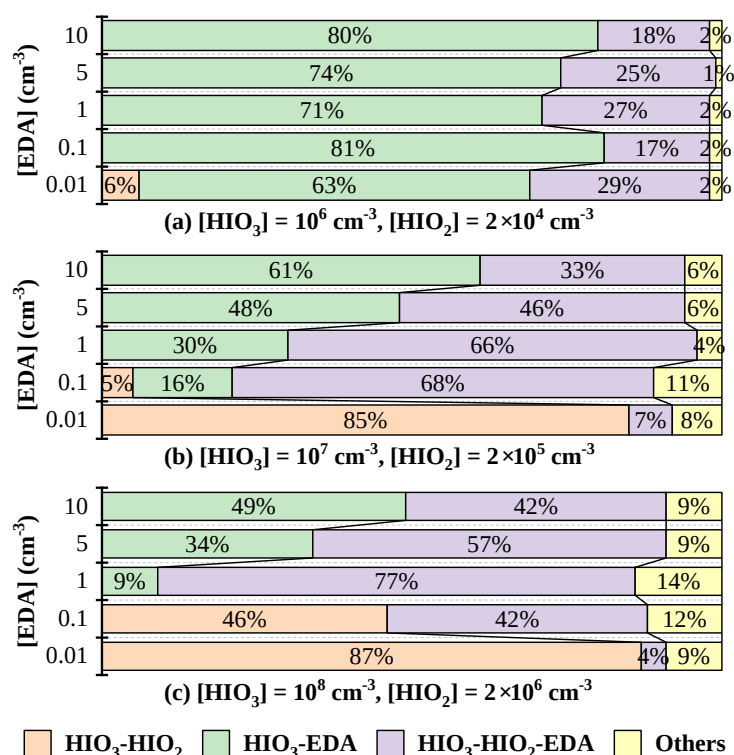


Figure 5 The influence of [EDA] (0.01-10 ppt), [HIO₃] and [HIO₂] ((a) [HIO₃] = 10⁶, [HIO₂] = 2 × 10⁴ cm⁻³, (b) [HIO₃] = 10⁷, [HIO₂] = 2 × 10⁵ cm⁻³, (c) [HIO₃] = 10⁸, [HIO₂] = 2 × 10⁶ cm⁻³ at 278.15 K and CS = 0.002 s⁻¹ on the relative contribution of the HIO₃-HIO₂, HIO₃-EDA, and the HIO₃-HIO₂-EDA clustering route to the system flux. Others indicate that the route contribution of the cluster growing out of the studied system is less than 5%.



3.5 Comparison with field observations

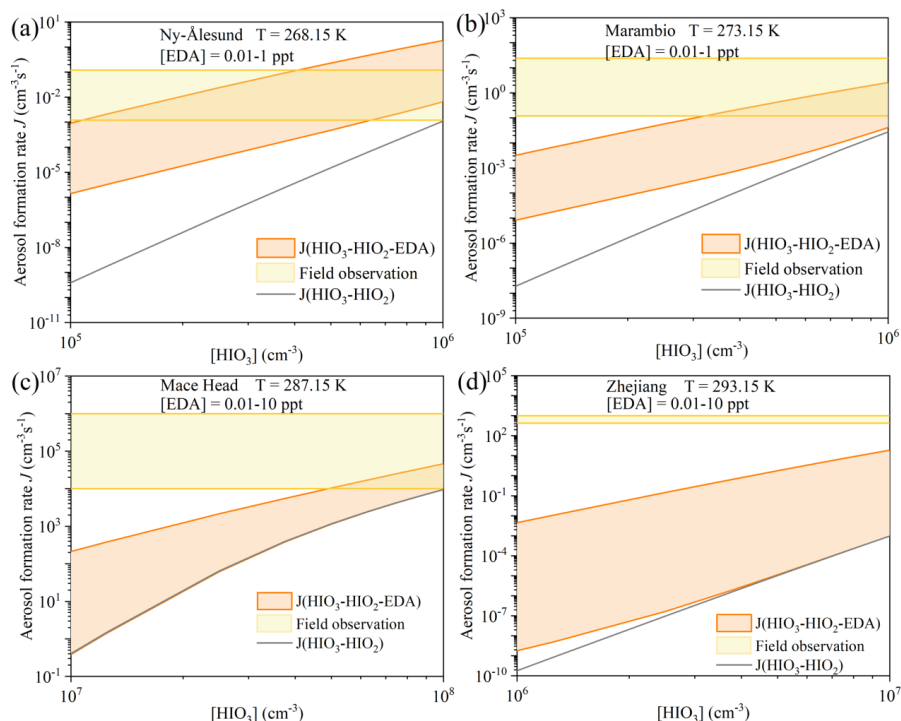


Figure 6 Comparison to the simulated aerosol formation rates for $\text{HIO}_3\text{-HIO}_2\text{-EDA}$ system ($J(\text{HIO}_3\text{-HIO}_2\text{-EDA})$, cm^3s^{-1}) and $\text{HIO}_3\text{-HIO}_2$ system ($J(\text{HIO}_3\text{-HIO}_2)$, cm^3s^{-1}) and field observations under ambient conditions of (a) Ny-Ålesund, (b) Marambio, (c) Mace Head, and (d) Zhejiang with CS as 0.0004, 0.0001, 0.002, and 0.01 s^{-1} , respectively. The orange and yellow areas represent $J(\text{HIO}_3\text{-HIO}_2\text{-EDA})$ and $J(\text{field observation})$, respectively. The grey line represents $J(\text{HIO}_3\text{-HIO}_2)$

To further confirm the role of the $\text{HIO}_3\text{-HIO}_2\text{-EDA}$ ternary nucleation system, we simulated aerosol formation rates (J) for both the $\text{HIO}_3\text{-HIO}_2\text{-EDA}$ ternary system and the $\text{HIO}_3\text{-HIO}_2$ binary system under ambient conditions of polar stations with low $[\text{HIO}_3]$ (Ny-Ålesund (Beck et al., 2021; X-C He et al., 2021) and Marambio (Qu d éver et al., 2022; X-C He et al., 2021) and coastal stations with high $[\text{HIO}_3]$ (Mace Head (Sipila et al., 2016) and Zhejiang (Xia et al., 2020; H. Yu et al., 2019), and compared the simulated J values against field observations at the corresponding sites. The simulated EDA concentration ($[\text{EDA}]$) was set to 0.01–1 ppt for the two polar sites



(Ny-Ålesund and Marambio) and 0.01–10 ppt for the two urban coastal sites (Mace Head and Zhejiang). This range was estimated from field observations at other sites for potential [EDA] in marine-related atmospheres and for diamines with similar sources and properties (Jen *et al.*, 2016; K. Saeki *et al.*, 2024; K Saeki *et al.*, 2022), consistent with previous theoretical studies of marine aerosol nucleation (Ayoubi, 2023; Bai *et al.*, 2025; Elm, 2021a; b; Xie and Elm, 2021). Previous field studies (Jen *et al.*, 2016) have reported a mean atmospheric [EDA] of ~1 ppt across industrial agricultural zones, coastal regions, plains impacted by oil extraction and processing, and urban/power-plant areas. Physicochemically similar diamines (e.g., putrescine, cadaverine) can reach tens of ppt, supporting the assumed 0.01–10 ppt [EDA] range for marine-related atmospheres. At sea-ice-covered polar sites, local biogenic sources emit low concentrations of amines such as DMA (Zu *et al.*, 2024a). In contrast, strong anthropogenic emissions at urban coastal sites can elevate amine levels to several ppt (H. Yu *et al.*, 2019). Given the distinct environmental conditions and emission source profiles of the two site categories, a lower [EDA] range was adopted for polar sites and a higher range for urban coastal sites.

As shown in Figure 6, the HIO₃-HIO₂ binary system alone deviates substantially from the observed J at every site, failing to explain the high measured J values and clearly indicating that additional precursors contribute to nucleation at these sites. With the inclusion of EDA, the simulated J values of the HIO₃-HIO₂-EDA ternary system exhibit markedly better agreement with field observations across all four stations and cover a wider range of measured J values. Notably, the simulated J values of HIO₃-HIO₂-EDA ternary system largely encompass the observed range in the polar regions, demonstrating that basic species such as HIO₂ and EDA play a crucial role in HIO₃-dominated NPF and serve as key drivers of NPF in polar atmospheres with low HIO₃ concentrations. However, for the coastal sites in Ireland and Zhejiang, the high nucleation rates observed under high-temperature conditions still cannot be explained by the HIO₃-HIO₂-EDA ternary system, as there remains a considerable gap between simulations and observations. For the Irish coast, the simulation results barely reach the lower limit of the observed nucleation rates even at extremely high iodine oxoacid



489 concentrations. In Zhejiang, under the observed low iodic acid concentrations, the
490 simulated the simulation results of the HIO_3 - HIO_2 -EDA system are far lower than the
491 actual measured nucleation rates. Therefore, in complex and polluted coastal regions,
492 further investigation are required to identify other factors contributing to the
493 extremely high nucleation rates at high temperatures, which may be caused by
494 additional nucleation precursors or alternative nucleation mechanisms.

495 **4 Atmospheric implications and conclusions**

496 The critical role of HIO_3 in driving marine NPF has been widely established.
497 HIO_3 can undergo synergistic nucleation with amines such as DMA, which are
498 emitted from marine microbial metabolism and coastal industrial/agricultural
499 activities (Ge, 2011; Hellén, 2014; Sipilä *et al.*, 2015). EDA, which exhibits
500 physicochemical properties and nucleation potential similar to DMA (Zu *et al.*,
501 2024a), has been detected in offshore regions and petrochemical industrial areas, and
502 exhibits promising applications in marine carbon capture and storage technologies
503 (Cho *et al.*, 2025; Güzél Kaya, 2023; E. Hu *et al.*, 2025; Jen *et al.*, 2016; Peres *et al.*,
504 2024), suggesting its spatial coexistence with HIO_3 and HIO_2 in the marine
505 atmosphere. Our previous study demonstrated that EDA significantly promotes
506 HIO_3 -driven nucleation, and HIO_3 -EDA binary nucleation partially explains the NPF
507 sources at polar and coastal sites (Bai *et al.*, 2025). This study further reveals the
508 promotion mechanism of EDA on the highly efficient HIO_3 - HIO_2 binary nucleation
509 system. In this ternary system, both EDA and HIO_2 efficiently accept protons from
510 HIO_3 , thereby significantly stabilizing the initial cluster structures. The extent of
511 proton transfer is closely related to the number of HIO_3 molecules, and replacing
512 HIO_2 with EDA also effectively improves cluster stability, further highlighting the
513 unique role of diamines in iodine precursor nucleation. ACDC simulation results
514 show that at 278.15 K, EDA significantly increases the J values of the HIO_3 - HIO_2
515 system. Notably, within typical atmospheric concentration ranges of $[\text{EDA}] \geq 0.1$ ppt,
516 $[\text{HIO}_3] \leq 10^7 \text{ cm}^{-3}$, and $[\text{HIO}_2] \leq 2 \times 10^5 \text{ cm}^{-3}$, the nucleation rate is enhanced by more



517 than an order of magnitude. Compared with temperature effects, changes in [EDA]
518 exert a more sensitive influence on the nucleation enhancement of both $\text{HIO}_3\text{-HIO}_2$
519 and $\text{HIO}_3\text{-EDA}$ systems. When [EDA] exceeds 0.1 ppt, the promotion is primarily
520 achieved by increasing the collision frequency between EDA molecules and
521 $\text{HIO}_3\text{-HIO}_2$ binary clusters and enhancing the cluster formation flux of ternary
522 clusters, thereby directly driving NPF. With variations in $[\text{HIO}_2]$ and [EDA],
523 significant competition and transitions occur among the three dominant nucleation
524 pathways: $\text{HIO}_3\text{-HIO}_2\text{-EDA}$, $\text{HIO}_3\text{-HIO}_2$, and $\text{HIO}_3\text{-EDA}$. These results have
525 important atmospheric implications: in regions with intensive marine industries,
526 marine carbon capture activities, and coastal agricultural/industrial emissions, the
527 synergistic nucleation between EDA and the $\text{HIO}_3\text{-HIO}_2$ system is likely to become a
528 key contributor to atmospheric NPF. Furthermore, comparison with field observations
529 and simulations indicates that the $\text{HIO}_3\text{-HIO}_2\text{-EDA}$ ternary nucleation mechanism
530 contributes more prominently in cold polar regions and clean coastal areas, effectively
531 reproducing NPF characteristics in such environments. However, it remains
532 insufficient to fully explain the extremely high NPF rates observed in
533 high-temperature and polluted urban coastal areas. In summary, compared with the
534 binary $\text{HIO}_3\text{-HIO}_2$ and $\text{HIO}_3\text{-EDA}$ systems, the elevated cluster formation rates (J) of
535 the $\text{HIO}_3\text{-HIO}_2\text{-EDA}$ ternary system show better consistency with field observations
536 at both coastal and polar sites. Therefore, future studies need to consider the
537 contributions of other nucleation precursors in these complex marine environments,
538 especially the promoting effect of strongly basic nucleation precursors similar to EDA
539 on the $\text{HIO}_3\text{-HIO}_2$ nucleation system.

540 **Data availability**

541 All primary data supported this study are available in the Supplement. As the
542 data used in this study have not been previously published, other analyzed data of
543 interest can be further derived from the primary data in the Supplement or obtained
544 from the main text.



545 **Supplement**

546 Selection of boundary clusters, global minimum geometric configurations of
547 $(\text{HIO}_2)_{0-3}(\text{EDA})_{0-3}$ clusters, $\beta C/\sum \gamma$ values for $(\text{HIO}_3)_x(\text{HIO}_2)_y(\text{EDA})_z$ clusters at
548 258.15, 268.15, 288.15 and 298.15 K, aerosol formation rates and EDA enhancement
549 factor of the $\text{HIO}_3\text{-HIO}_2$ and $\text{HIO}_3\text{-HIO}_2\text{-EDA}$ systems under different T, $[\text{HIO}_3]$,
550 $[\text{HIO}_2]$, $[\text{EDA}]$ and CS, relative flux contribution of $\text{HIO}_3\text{-HIO}_2$, $\text{HIO}_3\text{-EDA}$ and
551 $\text{HIO}_3\text{-HIO}_2\text{-EDA}$ clustering pathways affected by T, CS and precursor concentrations,
552 number of HBs, XBs and proton transfer events, ΔG values and total evaporation rate
553 coefficients $\sum \gamma$ for all clusters of the $\text{HIO}_3\text{-HIO}_2\text{-EDA}$ system at 258.15–298.15 K.

554 **Author contributions**

555 XB: Investigation, Conceptualization, Methodology, Software, Formal analysis,
556 Data curation, Writing– original draft, Writing– reviewing and editing. YL:
557 Methodology, Software. RY: Formal analysis. WX: Formal analysis. YJ: Formal
558 analysis. JZ: reviewing and editing. CW: reviewing and editing. JP: Supervision,
559 Funding acquisition. HM: Supervision, Funding acquisition. SJ: Writing– reviewing
560 and editing, Supervision, Funding acquisition.

561 **Competing interests**

562 The authors declare that they have no known competing financial interests or
563 personal relationships that could have appeared to influence the work reported in this
564 paper.

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