

Peer Review Report

Manuscript title: Enhancement Mechanism of Ethylenediamine on Iodine Oxoacid-Driven New Particle Formation in Marine Areas

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Summary

The binary HIO_3 – HIO_2 system is widely recognized as an important pathway to new particle formation in marine and polar environments. Model studies, however, show that this binary system alone is not able to explain the particle formation rates (J) measured in several field campaigns. This manuscript proposes the ternary HIO_3 – HIO_2 –ethylenediamine (EDA) system as a potential pathway to explain the measured particle formation rates. This is done by running Atmospheric Cluster Dynamics Code (ACDC) simulations to obtain particle formation rate estimates of both the binary and ternary system at different monomer concentrations and temperatures. As input, ACDC requires cluster binding free energies, which were obtained from quantum chemistry. The lowest free-energy cluster configurations were found through configurational sampling with ABCluster and GFN1-xTB, followed by $\omega\text{B97X-D/aug-cc-pVDZ(-PP)}$ optimizations and DLPNO-CCSD(T)/aug-cc-pVTZ(-PP) single-point energies.

The authors find that both EDA and HIO_2 accept protons from HIO_3 to stabilize the clusters, and that replacing HIO_2 by EDA can further stabilize them. At 278.15 K, EDA concentrations of 0.1 ppt or higher increase J of the HIO_3 – HIO_2 system by more than an order of magnitude at low iodine oxoacid concentrations. The dominant nucleation pathway shifts between HIO_3 – HIO_2 , HIO_3 – HIO_2 –EDA and HIO_3 –EDA depending on $[\text{HIO}_2]$ and $[\text{EDA}]$. The simulations are then compared to field observations at two polar sites (Ny-Ålesund and Marambio) and two coastal sites (Mace Head and Zhejiang), assuming $[\text{EDA}]$ of 0.01–1 ppt and 0.01–10 ppt, respectively. The authors report that the ternary system agrees better with the measured J than the binary HIO_3 – HIO_2 and HIO_3 –EDA systems, particularly in cold polar and clean coastal regions. They also note that it remains insufficient to explain the high J observed in warm, polluted urban coastal areas. The authors conclude that the HIO_3 – HIO_2 –EDA mechanism is likely to be a key contributor to new particle formation in regions with marine industries, carbon capture activities, and coastal agricultural and industrial emissions, and that future studies should consider strongly basic precursors similar to EDA.

General comments

Since cluster population dynamics codes, such as ACDC, make it possible to calculate particle formation rates, many computational studies have attempted to identify new chemical species that could contribute to new particle formation and explain the (generally higher) rates measured in field campaigns, both continental and marine. In continental regions, the binary sulfuric acid–dimethylamine (DMA) system comes close to the measured rates, and while there is likely a synergistic contribution from many less effective species, to my knowledge no species has yet been found that contributes comparably to DMA. Similarly, in marine environments, the HIO_3 – HIO_2 system comes close to the measured rates at some sites, and other species have yet to close the remaining gap consistently. Studies such as the present one are, therefore, best viewed as proposing species that may contribute synergistically, rather than species that close the gap on their own.

In that context, I believe that EDA is one of the more reasonable suggestions. The manuscript makes a good case that, given sufficiently high concentrations, EDA could bring the simulated particle formation rates closer to the measured ones. The methodology used to obtain the

simulated particle formation rates follows established practice in the field, so the results are reasonably obtained. I do, however, have some concerns about how these results are subsequently framed in the discussion. Given the lack of information about EDA concentrations in marine and polar environments, and the presence of other bases that are considerably more abundant, such as DMA, I think the conclusions need to be adjusted accordingly. These issues are explained in more detail in the comments below. I would support publication in Atmospheric Chemistry and Physics once these comments have been adequately addressed.

Major comments

The results show that EDA can enhance new particle formation in combination with HIO_3 and HIO_2 . My main concern, however, is whether the atmospheric abundance of EDA is sufficient for this to matter, and how EDA fares against other bases that are more abundant, such as DMA.

The manuscript provides several citations to justify the EDA concentrations used in the simulations (L89–93 and L460–474). However, five of these (Ayoubi et al., 2023; Elm, 2021a, b; Elm et al., 2016; Xie and Elm, 2021), as well as Bai et al. (2025), are computational studies that do not report measured concentrations, and therefore cannot be used as evidence for atmospheric EDA levels. The remaining citations do not support the stated range either:

- Jen et al. (2016) report the only EDA-specific value of ~ 1 ppt in their supplement (Table S1). This is the average signal at the EDA mass during acid-scrubber tests in Minneapolis, of which only about 45% could be attributed to EDA. Their field measurements (Oklahoma, Delaware and Atlanta) are explicitly reported as upper limits measured at nominal mass, and none of these sites is marine. At the only coastal site (Lewes, Delaware), the EDA upper limit was typically a few ppt, with occasional peaks up to ~ 10 ppt (Fig. S8), whereas the daily average DMA concentration ranged between 10 and 50 ppt.
- Saeki et al. (2022, 2024) measured diamines in forest air in Japan, emitted by flowering trees. EDA was not among the measured species in either study.
- Yu et al. (2019) is a study of iodine speciation in aerosol particles and contains no gas-phase amine measurements, so it cannot support amine levels of several ppt at urban coastal sites (L471–472).

As a result, the statement that “marine atmospheric measurements indicate an average [EDA] of roughly 1 ppt” (L89) is not supported, and neither is the description of $[\text{EDA}] \geq 0.1$ ppt as typical of the marine atmosphere in the abstract and conclusions. I do not think this disqualifies the robust computational work done in this manuscript, but the results have to be framed correctly. To my knowledge, no EDA measurements exist for marine or polar environments, and only upper limits exist for a single coastal site. The manuscript should state this explicitly and present the [EDA] range as a sensitivity study: it shows which EDA concentrations would be required for EDA to contribute meaningfully to new particle formation. The abstract, the introduction (L89–93), Sect. 3.5 and the conclusions should be revised accordingly.

This also affects the interpretation of Fig. 6. The ternary HIO_3 – HIO_2 –EDA system contains both binary systems, so adding EDA essentially can only increase J (as also reflected by $R_{\text{EDA}} > 1$ throughout). Since the binary HIO_3 – HIO_2 system underestimates the observed J at all sites (L475–477), including EDA at any concentration will, therefore, bring the simulated J closer to the observations. With [EDA] effectively a free parameter, the improved agreement shows that EDA *could* explain part of the gap at these concentrations, but it cannot be taken as evidence that it does. The text, in particular the abstract and Sect. 3.5, should be phrased accordingly.

The manuscript mentions DMA several times and states that EDA has properties and nucleation potential similar to DMA (L499–501), but it does not compare the two directly. DMA has been measured at considerably higher concentrations than EDA (e.g., tens of ppt at Lewes; Jen

et al., 2016) and has already been shown to strongly enhance HIO_3 – HIO_2 nucleation at largely the same field sites (Zu et al., 2024). In iodine oxyacid–amine simulations, DMA-containing clusters also dominate the outgrowing flux (Engsvang and Elm, 2025). Moreover, for sulfuric acid–multi-base clusters, Kubečka et al. (2023) showed that the advantage of EDA lies in its two binding sites stabilizing small clusters, while in larger clusters it effectively acts as two weak bases. Omitting EDA from their five-base simulations, therefore, had only a minor effect on J , as DMA-containing clusters took over its role, even at equal base concentrations. The key question is, therefore, whether EDA-containing clusters still carry a significant fraction of the flux when realistic DMA concentrations are present, or whether DMA takes over. I realize that a full quantum chemical treatment of the HIO_3 – HIO_2 –DMA or HIO_3 – HIO_2 –EDA–DMA systems would require a computational effort comparable to, or larger than, the present study, and I do not consider it a requirement. However, I would like the authors to at least:

- compare their results directly with the HIO_3 – HIO_2 –DMA results of Zu et al. (2024), which cover largely the same field sites, noting the difference in level of theory, and discuss the competition between EDA and DMA in light of the studies mentioned above.
- adjust the conclusions accordingly, making clear that the contribution of EDA in the presence of realistic DMA concentrations remains to be established.

As EDA mainly stabilizes the smallest clusters, a relatively cheap test would be to calculate a limited set of small DMA-containing and mixed EDA–DMA clusters (e.g., $(\text{HIO}_3)_1(\text{DMA})_1$, $(\text{HIO}_3)_1(\text{HIO}_2)_1(\text{DMA})_1$ and $(\text{HIO}_3)_1(\text{EDA})_1(\text{DMA})_1$) at the same level of theory, and compare their stabilities at realistic EDA and DMA concentrations. This would considerably strengthen the conclusions.

Minor comments

- Iodine is treated with an ECP28 pseudopotential. Engsvang et al. (2024) showed that DLPNO-CCSD(T0) with pseudopotentials and triple- ζ basis sets, as used here, overestimates the binding of iodine-containing dimers compared with explicit scalar-relativistic (ZORA) calculations, and Engsvang and Elm (2025) found that pure iodine oxyacid nucleation is considerably weaker when this is accounted for. The dimer formation free energies in Table S2 are indeed considerably more negative than the ZORA-DLPNO-CCSD(T0) values of Engsvang et al. (2024) at the same temperature, e.g., -10.3 vs. -6.3 kcal mol $^{-1}$ for $(\text{HIO}_3)_1(\text{EDA})_1$ and -7.4 vs. -4.4 kcal mol $^{-1}$ for $(\text{HIO}_2)_1(\text{EDA})_1$. Part of this difference may be due to structural or other methodological differences, but differences of this magnitude strongly affect the absolute J values compared with field observations in Fig. 6. I ask the authors to discuss this, and ideally to perform ZORA-DLPNO-CCSD(T) single points on the dominant clusters (e.g., those in Fig. 4b) to show how sensitive J and R_{EDA} are to this choice.
- Please report the ABCluster settings (population size, number of generations, number of runs and structures saved per cluster), and state whether ionic starting configurations (e.g., protonated EDA and IO_3^-) were included, as proton transfer occurs in all ternary clusters.
- After GFN1-xTB preoptimization, the 1000 lowest-energy structures are retained (L129–132). Wu et al. (2023) showed that, while GFN1-xTB gives reasonable geometries, its energies correlate poorly with DFT and should not be used as a cutoff, and instead perform DFT single points on all preoptimized structures. I do not expect this to change the main conclusions, but I recommend this protocol for future work, or a check on a few of the larger ternary clusters that the global minimum does not change.

- The collision coefficients are calculated from hard-sphere kinetic gas theory (Eq. 4). Previous studies of iodine oxyacid clusters applied an enhancement factor of about 2.4 to account for long-range interactions (e.g., Ma et al., 2023; Engsvang and Elm, 2025). Please discuss how this affects the absolute J values compared with field data in Fig. 6.
- The simulation box is limited to clusters of at most three HIO_3 molecules, and EDA-rich compositions such as $(\text{HIO}_3)_3(\text{HIO}_2)_1(\text{EDA})_3$ are treated as stable outgrowing clusters (L169–171), while the authors themselves argue that steric hindrance weakens the role of EDA in larger clusters (L238–242). Kubečka et al. (2023) showed that J decreases with increasing simulation size, also for sulfuric acid–EDA from a 3×3 to a 4×4 scheme, and that this decrease can reach several orders of magnitude for three-component systems at higher temperatures or lower concentrations. In addition, the outgrowing clusters are likely smaller than the sizes at which the field formation rates in Fig. 6 were reported, and only neutral clusters are considered. Please discuss how these factors affect the comparison with field observations, and ideally test the sensitivity of J to the choice of boundary clusters.
- L24–25: The sentence “EDA concentrations ($[\text{EDA}]$) exceeding 0.1 ppt, both typical of the marine atmosphere” is grammatically unclear. It is not clear what “both” refers to.
- L78–80: The cited works are laboratory or early-stage studies of amine-based CO_2 sorbents and membranes, only one of which concerns marine (direct ocean) capture. They do not support that EDA is “widely used” in marine CCS, nor do they show that such applications emit EDA to the atmosphere. As “carbon capture activities” are later named as a setting where the ternary mechanism is likely a key contributor (abstract and L525–527), please rephrase this statement or provide evidence for EDA emissions from CCS.
- L213–215 and L260–264: In the binary HIO_2 –EDA system, HIO_2 is the only species that can donate protons. Accordingly, Fig. S1 shows proton transfer from HIO_2 to EDA and to other HIO_2 molecules, i.e., HIO_2 acts as an acid towards EDA. The high evaporation rates of these clusters indicate that HIO_2 is a weak acid, but they do not necessarily show that HIO_2 “predominantly acts as a base rather than an acid within the HIO_2 –EDA system” (L262–263). Please revise this conclusion.
- L325–332: The numbers in this paragraph do not appear to be consistent. A binary J of up to $14.7 \text{ cm}^{-3} \text{ s}^{-1}$ at $[\text{HIO}_3] \leq 10^7 \text{ cm}^{-3}$ is difficult to reconcile with $J \approx 1 \text{ cm}^{-3} \text{ s}^{-1}$ requiring $[\text{HIO}_3] = 9.35 \times 10^6 \text{ cm}^{-3}$. Please also check the stated range of R_{EDA} (12.50–5469.73). The ratios of the lower and upper ends of the stated J ranges are approximately $2700 (7.86 \times 10^{-2} / 2.87 \times 10^{-5})$ and $13 (1.95 \times 10^2 / 1.47 \times 10^1)$, respectively. A maximum R_{EDA} of about 5470 would therefore require the enhancement to peak at intermediate conditions. Please state at which conditions the minimum and maximum R_{EDA} occur.
- L330–334: The lower $[\text{HIO}_3]$ required to reach $J \approx 1 \text{ cm}^{-3} \text{ s}^{-1}$ in the presence of EDA does not indicate that EDA substitutes for HIO_3 . Rather, EDA (as a base, analogous to HIO_2) stabilizes the HIO_3 -containing clusters and lowers their evaporation rates, so that a lower acid concentration suffices to reach the same J . Please rephrase.
- Fig. 4b and L393–394: In Fig. 4b, the 13% contribution is attributed to $(\text{HIO}_3)_2(\text{HIO}_2)_1(\text{EDA})_1$, whereas the text states $(\text{HIO}_3)_3(\text{HIO}_2)_2(\text{EDA})_1$. Please correct whichever is wrong, and check that all cluster labels and percentages in the text are consistent with the figures.
- Fig. 5: The $[\text{EDA}]$ axes are labeled in cm^{-3} , but the values appear to be in ppt.
- L459: Mace Head is generally considered a clean marine background site rather than an

urban coastal site.

- Table S2: The ΔG of $(\text{HIO}_2)_5$ at 288.15 K is missing a minus sign.

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