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## Significance of halogen bonding in the synergistic nucleation of iodine oxoacids and iodine oxides†

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Congeneric iodine oxoacids and iodine oxides, key nucleating vapours in the marine atmosphere, have been reported to nucleate individually. However, whether they can nucleate together remains unknown. Here, we provide molecular-level evidence that I<sub>2</sub>O<sub>4</sub>, the iodine oxide with the highest nucleation potential towards iodine oxoacids, can synergistically nucleate with HIO<sub>3</sub>–HIO<sub>2</sub>. The nucleation rate of HIO<sub>3</sub>–HIO<sub>2</sub>–I<sub>2</sub>O<sub>4</sub> is 1.5 to 6.8 times higher than that of the known most efficient iodine-associated two-component (HIO<sub>3</sub>–HIO<sub>2</sub>) nucleation at 278.15 K, enhancing the role of iodine-containing species in marine atmospheric particle formation. Microscopic analysis of the three-component cluster configurations revealed that an unexpected acid–base reaction between I<sub>2</sub>O<sub>4</sub> and HIO<sub>2</sub>/HIO<sub>3</sub> is a key driver of this efficient synergistic nucleation, besides hydrogen bonds and halogen bonds. We identified halogen bond-induced basicity enhancement as the chemical nature of I<sub>2</sub>O<sub>4</sub> behaving as a base in the nucleation process with HIO<sub>2</sub>/HIO<sub>3</sub>. Such a basicity enhancement effect can be extended to other iodine-containing species, e.g., HIO<sub>2</sub> and the more acidic HIO<sub>3</sub>, suggesting a common feature in interactions between iodine-containing species. Our findings clarify the synergistic nucleation of iodine oxoacids and iodine oxides and highlight the necessity of considering the effect of halogen bond-induced basicity enhancement on the formation of iodine-containing particles.

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## Introduction

New particle formation (NPF) initiated by the nucleation of condensable vapours produces more than half of all atmospheric aerosols.<sup>1–3</sup> These nascent particles act as cloud condensation nuclei (CCN), significantly influencing the earth's atmosphere radiative balance and modulating global climate patterns.<sup>4,5</sup> Marine NPF plays a pivotal role in the global climate model, as marine clouds have high albedo and are susceptible to changes in CCN availability.<sup>6–10</sup> However, the influence of marine NPF on climate remains uncertain, mainly due to the limited understanding of the nucleation process in the marine atmosphere, thus resulting in extensive uncertainty within global models.

Conventional theory has been based on the assumption that sulfuric acid (SA)–ammonia (NH<sub>3</sub>) nucleation is the dominant mechanism in NPF in marine environments.<sup>11,12</sup> However, recent research has highlighted the importance of iodine oxides

(I<sub>x</sub>O<sub>y</sub>) and iodine oxoacids (HIO<sub>z</sub>) as crucial nucleation precursors.<sup>10,13–28</sup> These species are formed mainly by the transformation of iodine (I<sub>2</sub>) and methyl iodide (CH<sub>3</sub>I), which are emitted from the ocean surface.<sup>29–33</sup> Although iodine-initiated NPF events have been frequently observed,<sup>13,34–37</sup> the specific nucleation mechanism is still not fully understood. One study reported that in flow tube experiments, the nucleation of iodine oxides, particularly I<sub>2</sub>O<sub>2</sub>, I<sub>2</sub>O<sub>3</sub>, and I<sub>2</sub>O<sub>4</sub> at high concentrations, is rapid.<sup>14</sup> However, Cosmics Leaving Outdoor Droplets (CLOUD) chamber experiments have shown that nucleation involving iodic acid (HIO<sub>3</sub>) and iodous acid (HIO<sub>2</sub>) can occur rapidly under marine boundary layer conditions.<sup>38</sup> In these CLOUD chamber experiments, the concentration of formed iodine oxides is relatively low when the precursor concentration is low, which could be one of the reasons why iodine oxide nucleation cannot compete with HIO<sub>3</sub>–HIO<sub>2</sub> nucleation. Iodine oxides and iodine oxoacids are known to coexist on the basis of their homology and can form strong halogen bonds (typical halogen bond energies Δ*E* ranging from 1 to 45 kcal mol<sup>−1</sup> calculated by Oliveira *et al.*<sup>39</sup>), which are non-covalent interactions formed between an electrophilic halogen atom and a nucleophilic heteroatom (*i.e.*, with lone-pair electrons).<sup>39,40</sup> Therefore, they may be able to nucleate together, so investigating the joint nucleation mechanism for iodine oxides and iodine oxoacids is important.

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In this study, the multicomponent nucleation mechanism of iodine oxides and iodine oxoacids was investigated *via* quantum chemical calculations and atmospheric cluster dynamic coding. Here, multicomponent nucleation was considered to occur among HIO<sub>3</sub>, HIO<sub>2</sub> and specific iodine oxides since HIO<sub>3</sub> and HIO<sub>2</sub> have been found to be able to nucleate at realistic atmospheric concentration ranges.<sup>38,41</sup> Since dimer can present the foundational intermolecular interaction between iodine oxides and iodine oxoacids, and the computational cost of dimer is low, the dimer formation free energy ( $\Delta G$ ) between iodine oxides (IO, I<sub>2</sub>O<sub>2</sub>, I<sub>2</sub>O<sub>3</sub>, I<sub>2</sub>O<sub>4</sub>, and I<sub>2</sub>O<sub>5</sub>) and iodine oxoacids (HIO<sub>3</sub> and HIO<sub>2</sub>) was used to screen the propensity of specific iodine oxides towards nucleation with iodine oxoacids. I<sub>2</sub>O<sub>4</sub> was found to have the greatest nucleation potential among the selected iodine oxides and can efficiently nucleate with HIO<sub>3</sub>-HIO<sub>2</sub> as a base. Halogen bond-induced basicity enhancement of I<sub>2</sub>O<sub>4</sub> was found to be the chemical nature for I<sub>2</sub>O<sub>4</sub> behaving as a base during the nucleation with HIO<sub>3</sub>-HIO<sub>2</sub>. This study reveals that iodine oxides and iodine oxoacids can synergistically nucleate, breaking through the previous findings of their independent nucleation<sup>14,38</sup> and providing a new chemical mechanism for iodine-containing particles.

## Methods

A multistep sampling scheme was employed to identify the global minimum for all of the studied clusters, including I<sub>x</sub>O<sub>y</sub>-HIO<sub>2-3</sub> dimer clusters and HIO<sub>3</sub>-HIO<sub>2</sub>-I<sub>2</sub>O<sub>4</sub> system clusters. This procedure has been widely used in many previous studies on atmospheric cluster formation.<sup>42-44</sup> First, 5000-8000 initial configurations were generated for each cluster using the ABCluster program<sup>45</sup> and were optimized *via* the semiempirical PM7 method. The single point energy was subsequently calculated at the M06-2X/def2-TZVP level for all the converged geometries. Configurations up to 15 kcal mol<sup>-1</sup> higher than the lowest energy configuration were further fully optimized at the M06-2X/6-31++G(d,p) (for H O atoms) + aug-cc-pVTZ-PP (a basis set with relativistic pseudopotential for I atoms<sup>46</sup>) level. Since there are tens of configurations we have to optimize for each cluster in this step, the adopted larger basis set such as aug-cc-pVTZ(-PP) (aug-cc-pVTZ for H O atoms and aug-cc-pVTZ-PP for I atoms) would lead to the high-cost for the computational time. Hence, we employed the smaller basis set here to reduce computational cost. Our previous study found that the adopted basis set here for optimization presents similar  $\Delta G$  for HIO<sub>3</sub>-HIO<sub>2</sub> clusters to that of the aug-cc-pVTZ(-PP) basis set (Table S1†).<sup>41</sup> Moreover, we also tested several clusters including (HIO<sub>2</sub>)<sub>1</sub>(I<sub>2</sub>O<sub>4</sub>)<sub>1</sub>, (HIO<sub>3</sub>)<sub>2</sub>(I<sub>2</sub>O<sub>4</sub>)<sub>2</sub> and (HIO<sub>3</sub>)<sub>1</sub>(HIO<sub>2</sub>)<sub>1</sub>(I<sub>2</sub>O<sub>4</sub>)<sub>1</sub> with the other basis set def2-TZVP. It was found that the low-energy configurations (within 1-2 kcal mol<sup>-1</sup> of the lowest-energy configuration) from def2-TZVP basis set are the same as those from 6-31++G(d,p) + aug-cc-pVTZ-PP (Fig. S1†). Therefore, the adopted basis set is acceptable for the first-round geometry optimization for HIO<sub>3</sub>-HIO<sub>2</sub>-I<sub>2</sub>O<sub>4</sub> system. Finally, for the lowest-energy configurations within 1-2 kcal mol<sup>-1</sup>, reoptimization was performed at the M06-2X/aug-cc-pVTZ(-PP) level, and the single point energy was refined at the DLPNO-CCSD(T)/

aug-cc-pVTZ(-PP) level. If the calculation results failed during optimization or ended up with imaginary frequencies, the initial configurations were adjusted and reoptimized until a successful optimization without imaginary frequencies was finished. The configuration with the lowest Gibbs free energy ( $G$ ) at 298.15 K and 1 atm was chosen as the global minimum. The  $G$  values at other temperatures and pressures were obtained *via* a GoodVibes Python script.<sup>47</sup> The  $\Delta G$  for the global minimum was calculated by subtracting the  $G$  of the constituent molecules from that of the cluster. We also tested the influence of the dispersion correction by reoptimizing the global minima for selected three clusters ((HIO<sub>2</sub>)<sub>1</sub>(I<sub>2</sub>O<sub>4</sub>)<sub>1</sub>, (HIO<sub>3</sub>)<sub>2</sub>(I<sub>2</sub>O<sub>4</sub>)<sub>2</sub> and (HIO<sub>3</sub>)<sub>1</sub>(HIO<sub>2</sub>)<sub>1</sub>(I<sub>2</sub>O<sub>4</sub>)<sub>1</sub>) using M06-2X/aug-cc-pVTZ(-PP), with Grimme's dispersion correction with ZERO Damping GD3.<sup>48-50</sup> The root-mean-square deviation (RMSD) for optimized structure and difference in  $\Delta G$  from method with and without dispersion correction are 0.001-0.003 Å and -0.004-0.012 kcal mol<sup>-1</sup>, indicating that the dispersion correction causes slight influence on the results of this study (Table S2†). All the PM7 and M06-2X calculations were carried out with the Gaussian 16 program<sup>51</sup> and DLPNO-CCSD(T) calculations were performed with the software ORCA 5.0.3.<sup>52,53</sup> In addition, natural bond orbital (NBO) analysis was carried out by Gaussian 16 program to give a detailed insight into intermolecular interactions.

The cluster formation rate and growth mechanism were analysed *via* Atmospheric Cluster Dynamics Code (ACDC) software, which simulates the cluster kinetics by means of explicit solution of the birth-death equations.<sup>54</sup> Herein, the simulated system was treated as a 3 × 3 box containing (HIO<sub>3</sub>)<sub>0-3</sub>(HIO<sub>2</sub>)<sub>0-3</sub>, (HIO<sub>3</sub>)<sub>0-3</sub>(I<sub>2</sub>O<sub>4</sub>)<sub>0-3</sub>, (HIO<sub>2</sub>)<sub>0-3</sub>(I<sub>2</sub>O<sub>4</sub>)<sub>0-3</sub> and (HIO<sub>3</sub>)<sub>x</sub>(HIO<sub>2</sub>)<sub>y</sub>(I<sub>2</sub>O<sub>4</sub>)<sub>z</sub> ( $x = 1-3, y + z = 2-3$ ) clusters. The boundary cluster settings can be found in the ESI.† The simulation mainly ran at 278.15 K and 1 atm with a coagulation sink rate coefficient ( $k_{\text{coag}}$ ) of  $2 \times 10^{-3}$  s<sup>-1</sup>, a typical value in coastal regions where iodine species are nucleating.<sup>55</sup> Additional simulations were performed at 298.15, 253, 223.15 K to probe the effect of temperature, and further simulations were conducted at 0.5 and 0.1 atm to test the effect of pressure. The concentration of HIO<sub>3</sub> ([HIO<sub>3</sub>]) was set to 10<sup>5</sup> to 10<sup>8</sup> cm<sup>-3</sup> based on the common atmospheric concentration range.<sup>13,36-38</sup> The concentrations of HIO<sub>2</sub> and I<sub>2</sub>O<sub>4</sub> were set to approximately 1/30 [HIO<sub>3</sub>] and 1/100 [HIO<sub>3</sub>], respectively, corresponding to the measured steady-state concentrations in the CLOUD chamber experiment.<sup>38</sup> The detailed discussion on the selection of [I<sub>2</sub>O<sub>4</sub>] was presented in the ESI.† We accounted for the contribution of long-range interactions *via* an enhancement factor of 2.4 for the collision rate coefficient.<sup>44,56</sup> In addition, the cluster formation rate of the SA-HIO<sub>3</sub>-HIO<sub>2</sub> system ((SA)<sub>x</sub>(-HIO<sub>3</sub>)<sub>y</sub>(HIO<sub>2</sub>)<sub>z</sub> ( $0 \leq x + y \leq 3, 1 \leq z \leq 3$ ) clusters) was simulated for comparison, with the concentration of SA ranging from 10<sup>6</sup> to 10<sup>7</sup> cm<sup>-3</sup>.<sup>37,57</sup>

The similar ACDC simulations based on thermodynamics data from the same theoretical methods as ones used here have been employed in the previous studies on SA-HIO<sub>3</sub>-HIO<sub>2</sub> and HIO<sub>3</sub>-HIO<sub>2</sub> nucleation, producing consistent cluster formation rates with those from CLOUD experiments.<sup>26,41</sup> Therefore, it is reasonably believed that adopted computational level of



theories combined with ACDC simulations can be reliable to describe the interactions among the iodine species and predict the cluster formation mechanism for the  $\text{HIO}_3$ - $\text{HIO}_2$ - $\text{I}_2\text{O}_4$  system.

To investigate the correlation between the formation of halogen bonds (XBs) and the change in basicity of  $\text{I}_2\text{O}_4$ , a series of  $\text{I}_2\text{O}_4$ -containing dimer clusters that contain only one XB were manually constructed and optimized at the M06-2X/aug-cc-pVTZ(-PP) level. After optimization, the single point energies ( $E$ ) of these dimer clusters were calculated at the DLPNO-CCSD(T)/aug-cc-pVTZ(-PP) level. The bond energy ( $\Delta E$ ) was calculated to represent the strength of the formed XB:

$$\Delta E = |E(\text{precursor-I}_2\text{O}_4 \text{ dimer}) - E(\text{precursor}) - E(\text{I}_2\text{O}_4)| \quad (1)$$

Previous study has shown that the change in electrostatic potential ( $\Delta\text{ESP}$ ) at specific basic site can be employed to present the change in basicity of the compounds.<sup>58</sup> Herein, we employed  $\Delta\text{ESP}$  for the basic site of  $\text{I}_2\text{O}_4$  to represent the change in basicity of  $\text{I}_2\text{O}_4$  when it forms XBs with various precursors. The computational details for  $\Delta\text{ESP}$  was presented in the ESI.<sup>†</sup> Furthermore, we also directly calculated the gas basicity (GB) of  $\text{I}_2\text{O}_4$  before and after the formation of XBs, which is defined as the Gibbs free energy change ( $\Delta G$ ) for reactions (2) and (3), respectively:



It is noted that the terminal O atom of  $\text{I}_2\text{O}_4$  with the most negative average ESP after forming XB was taken as the basic site for  $\Delta\text{ESP}$  and GB calculation. The geometries of positive precursor- $\text{I}_2\text{O}_4\text{H}^+$  dimers and  $\text{I}_2\text{O}_4\text{H}^+$  were manually constructed by adding  $\text{H}^+$  to the basic site of  $\text{I}_2\text{O}_4$ .

## Results and discussion

### Of all iodine oxides, $\text{I}_2\text{O}_4$ is the precursor with the highest potential towards iodine oxoacids

The nucleation potential of iodine oxides towards iodine oxoacids was checked by their dimerization with  $\text{HIO}_2$  or  $\text{HIO}_3$ . Fig. 1 presents the  $\Delta G$  values and global minimum configurations of the  $\text{HIO}_2$ -containing and  $\text{HIO}_3$ -containing dimer clusters. The  $\Delta G$  values for all dimers except  $\text{IO-HIO}_2$  and  $\text{IO-HIO}_3$  are negative, ranging from  $-9.7$  to  $-21.6 \text{ kcal mol}^{-1}$ . Of all the  $\text{HIO}_2$ -containing and  $\text{HIO}_3$ -containing dimers,  $\text{HIO}_2$ - $\text{I}_2\text{O}_4$  and  $\text{HIO}_3$ - $\text{I}_2\text{O}_4$  exhibit the lowest  $\Delta G$  values, followed by  $\text{HIO}_2$ - $\text{I}_2\text{O}_2$  and  $\text{HIO}_3$ - $\text{I}_2\text{O}_2$ , respectively. Therefore,  $\text{I}_2\text{O}_4$  is expected to have the greatest intrinsic nucleation potential towards iodine oxoacids, followed by  $\text{I}_2\text{O}_2$ . In addition, the  $\Delta G$  values of  $\text{HIO}_2$ - $\text{I}_2\text{O}_4$  and  $\text{HIO}_3$ - $\text{I}_2\text{O}_4$  are even lower than that of  $\text{HIO}_3$ - $\text{HIO}_2$  ( $-16.79 \text{ kcal mol}^{-1}$ ), indicating that  $\text{I}_2\text{O}_4$  has a greater ability to bind with  $\text{HIO}_2$  or  $\text{HIO}_3$  than  $\text{HIO}_3$  and  $\text{HIO}_2$  do with each other. It is noteworthy that Engsvang *et al.* also calculated  $\Delta G$  values for dimers of iodine oxides ( $\text{I}_2\text{O}_4$  and  $\text{I}_2\text{O}_5$ ) with iodine oxoacids in a recent study.<sup>59</sup> They found  $\text{I}_2\text{O}_4$ - $\text{HIO}_{2-3}$  dimers have lower

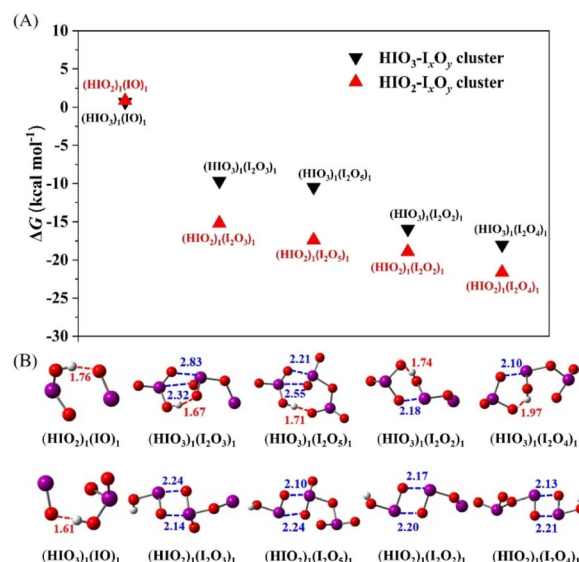


Fig. 1 Formation free energy ( $\Delta G$ ) (A) and global minimum configurations (B) of  $\text{I}_x\text{O}_y$ - $\text{HIO}_{2-3}$  dimers at the DLPNO-CCSD(T)/aug-cc-pVTZ(-PP)//M06-2X/aug-cc-pVTZ(-PP) level of theory at 298.15 K. The red balls represent oxygen atoms, purple ones are for iodine atoms, and white ones are for hydrogen atoms. The red dashed lines in the configurations represent hydrogen bonds (HBs), and the blue dashed lines represent XBs. The red and blue numbers indicate the bond lengths of HBs and XBs, respectively. The bond lengths are given in Å.

$\Delta G$  values than  $\text{I}_2\text{O}_5$ - $\text{HIO}_{2-3}$  dimers, consistent with results predicted here, although the specific  $\Delta G$  values in this study are lower.

Observation of the configurations and NBO analysis of the dimers found that both  $\text{I}_2\text{O}_4$  and  $\text{I}_2\text{O}_2$  accept a proton from  $\text{HIO}_3$  in  $\text{HIO}_3$ - $\text{I}_2\text{O}_4$  and  $\text{HIO}_3$ - $\text{I}_2\text{O}_2$  clusters in addition to forming XBs and hydrogen bonds (HBs). Accordingly, both  $\text{I}_2\text{O}_4$  and  $\text{I}_2\text{O}_2$  behave as bases towards  $\text{HIO}_3$ . However, for dimers of other iodine oxides with  $\text{HIO}_3$ , there is no proton transfer even though XBs and HBs are formed. Therefore, the additional electrostatic interaction caused by the proton transfer reaction is expected to be one reason that  $\text{I}_2\text{O}_4$  and  $\text{I}_2\text{O}_2$  have lower dimer  $\Delta G$  values with  $\text{HIO}_3$  than other iodine oxides do. It is noted that the structure of  $(\text{HIO}_3)_1(\text{I}_2\text{O}_4)_1$  resembles two  $\text{IO}_3$  radicals clustered with a hypiodous acid  $\text{HOI}$ . However,  $(\text{HIO}_3)_1(\text{I}_2\text{O}_4)_1$  could not dissociate into  $\text{HOI} + 2 \cdot \text{IO}_3$  rather than  $\text{HIO}_3 + \text{I}_2\text{O}_4$ , since the  $\Delta G$  value for  $(\text{HIO}_3)_1(\text{I}_2\text{O}_4)_1$  dissociating into  $\text{HOI} + 2 \cdot \text{IO}_3$  ( $76.14 \text{ kcal mol}^{-1}$ ) is much higher than  $\text{HIO}_3 + \text{I}_2\text{O}_4$  ( $18.01 \text{ kcal mol}^{-1}$ ). For the dimers of  $\text{HIO}_2$  with  $\text{I}_2\text{O}_4$  and  $\text{I}_2\text{O}_2$ , two XBs are formed. Two XBs are known to form for the dimers of  $\text{HIO}_2$  with other iodine oxides except for  $\text{IO}$ . The lower dimer  $\Delta G$  values of  $\text{I}_2\text{O}_4$  and  $\text{I}_2\text{O}_2$  with  $\text{HIO}_2$  result from the stronger strength of XBs formed between them, as evidenced by the lower average energy gap between antibonding orbital  $\delta^*(\text{O-I})$  and lone-pair orbital  $\text{LP}(\text{O})$ , which are two critical molecular orbitals for the formation of XBs with  $\text{HIO}_2$  (Table S3<sup>†</sup>). As a representative example, Fig. S2<sup>†</sup> illustrates the  $\delta^*(\text{O-I})$  and  $\text{LP}(\text{O})$  orbitals involved in the  $(\text{I}_2\text{O}_4)_1(\text{HIO}_2)_1$  dimer. Therefore, although  $\text{I}_2\text{O}_5$  has more electronically deficient iodine centers



than  $I_2O_4/I_2O_2$ , the additional electrostatic interaction caused by the proton transfer reaction between  $I_2O_4/I_2O_2$  and  $HIO_3$ , and the stronger average strength of two XBs between  $I_2O_4/I_2O_2$  and  $HIO_2$ , make  $I_2O_4/I_2O_2$  form a more stable complex with iodine oxoacids compared to  $I_2O_5$ .

As discussed above,  $I_2O_4$  is expected to have the highest intrinsic nucleation potential towards iodine oxoacids. In addition, in photochemical reactions of  $I_2$  or  $CH_3I$  with ozone ( $O_3$ ) under laboratory conditions, the gaseous concentration of  $I_2O_4$  produced was higher than that of all other iodine oxides except  $IO$ .<sup>15,60</sup> Therefore,  $I_2O_4$  has the greatest nucleation potential towards iodine oxoacids. In the following section, we describe our detailed investigation of the joint nucleation of  $I_2O_4$  and iodine oxoacids.

### Configurations of $HIO_3$ - $HIO_2$ - $I_2O_4$ clusters featuring halogen-induced acid-base reaction

We present the cluster configurations for the  $HIO_3$ - $HIO_2$ - $I_2O_4$  system in Fig. 2 and S3.† Since  $HIO_3$ - $HIO_2$  configurations have already been investigated in our previous study,<sup>41</sup> we mainly focus on  $HIO_3$ - $I_2O_4$  and  $HIO_2$ - $I_2O_4$  two-component clusters (Fig. S3†) and  $HIO_3$ - $HIO_2$ - $I_2O_4$  three-component clusters (Fig. 2) here. Observation and analysis of the cluster configurations shows that  $I_2O_4$  accepts a proton from  $HIO_3$  and  $HIO_2$  in almost all  $HIO_3$ - $I_2O_4$  and  $HIO_2$ - $I_2O_4$  two-component clusters. Therefore,  $I_2O_4$  behaves as a Brønsted-Lowry base when it clusters with  $HIO_3$  or  $HIO_2$ . To our knowledge, this is the first time that  $I_2O_4$  has been revealed to behave as a base in clustering with  $HIO_3$  or  $HIO_2$ . In  $HIO_3$ - $HIO_2$ - $I_2O_4$  three-component clusters, only  $HIO_3$ , with the greater acidity, can donate

a proton, and  $I_2O_4$  or  $HIO_2$  can accept a proton. In addition,  $I_2O_4$  has a greater ability to accept a proton from  $HIO_3$  than  $HIO_2$  does. Therefore, the behaviour of  $I_2O_4$  as a base is a common feature of  $HIO_3$ - $I_2O_4$  and  $HIO_2$ - $I_2O_4$  two-component clusters and  $HIO_3$ - $HIO_2$ - $I_2O_4$  three-component clusters, in addition to the formation of typical XBs and HBs.

Why  $I_2O_4$  can behave as a base towards  $HIO_{2-3}$  is an interesting topic for discussion. The calculated gas basicity (GB) of  $I_2O_4$  is 199 kcal mol<sup>-1</sup>, close to that of  $NH_3$  (196 kcal mol<sup>-1</sup>), which has been found to be unable to accept a proton from  $HIO_3$  in the  $(HIO_3)_1(NH_3)_1$  dimer.<sup>17,18</sup> Therefore, the GB of  $I_2O_4$  cannot explain its acid-base reaction with  $HIO_2$  and  $HIO_3$ . According to observation of the configurations of  $HIO_3$ - $HIO_2$ - $I_2O_4$  clusters, the occurrence of acid-base reactions with  $I_2O_4$  as a base is always accompanied by the formation of XBs. Therefore, it is reasonable to speculate that the formation of XBs can induce the basicity enhancement of  $I_2O_4$ , further driving the acid-base reaction.

To verify this speculation,  $\Delta ESP$  for the basic site and GB of  $I_2O_4$  when it forms XBs with various precursors, were determined. Here, the selected precursors included amines, carbonyl compounds, sulfides, alcohols, benzothiazole, peroxides and hydroperoxymethyl, which can form XBs with  $I_2O_4$  at various bond strengths. Since  $I_2O_4$  can form two types of XBs *via* its two lowest energy antibonding orbitals  $\delta^*(O-I)$ , the effects of these two types of XBs on  $\Delta ESP$  and GB were considered. Fig. 3A shows that the  $\Delta ESP$  values for the O atom as a basic site are negative when  $I_2O_4$  forms a XB with precursors (identity of selected precursors was presented in Table S4†), which leads to an increased basicity of  $I_2O_4$ . Moreover, a higher XB energy generally results in a greater (more negative)  $\Delta ESP$  value. As shown in Fig. 3B, the GB of  $I_2O_4$ -precursor dimer clusters is significantly greater than that of the  $I_2O_4$  monomer regardless of the type of XBs. In addition, a roughly positive correlation between the formed XB energy and the GB values of  $I_2O_4$ -precursor dimer clusters is observed. More importantly, even when a relatively weak XB (approximately 13 kcal mol<sup>-1</sup>) is formed, the GB of  $I_2O_4$  can be increased to 215 kcal mol<sup>-1</sup>, which is close to that of dimethylamine (DMA) (215 kcal mol<sup>-1</sup>), a typical base for enhancing SA-driven nucleation.<sup>57</sup> Therefore, the formation of XBs indeed increases the basicity of  $I_2O_4$ , increasing it from a level similar to that of  $NH_3$  to a level that is comparable to or even greater than that of DMA.

Notably, the present study and an earlier study also revealed that  $HIO_2$  behaves as a base towards  $HIO_3$ .<sup>41</sup> Similarly, the  $\Delta ESP$  for the basic site of  $HIO_2$  when it forms XBs with various precursors was determined. An effect similar to that of the formed XB on the  $\Delta ESP$  for the terminal O atom as a basic site was also found for the  $HIO_2$  system (Fig. S4†). Therefore, the formation of XBs can greatly increase the basicity of  $I_2O_4$  and  $HIO_2$ . To our knowledge, this is the first study to reveal that XBs induce acid-base reactions in  $HIO_3$ - $HIO_2$  and  $HIO_3$ - $HIO_2$ - $I_2O_4$  nucleation systems.

Since XBs are weak non-covalent interactions, it is interesting to check whether other weak non-covalent interactions like HBs, commonly formed in the acid-base nucleation system, can also induce the basicity enhancement of



Fig. 2 Global minimum configurations of the  $(HIO_3)_x(HIO_2)_y(I_2O_4)_z$  ( $x = 1-3$ ,  $y + z = 2-3$ ) clusters calculated at the DLPNO-CCSD(T)/aug-cc-pVTZ(-PP)//M06-2X/aug-cc-pVTZ(-PP) level of theory. The red balls represent oxygen atoms, purple ones are for iodine atoms, and white ones are for hydrogen atoms. The red dashed lines represent HBs, and the blue dashed lines represent XBs. The red and blue numbers indicate the bond lengths of HBs and XBs, respectively. The bond lengths are given in Å.





Fig. 3 Change in electrostatic potential ( $\Delta\text{ESP}$ ) values ( $\text{kcal mol}^{-1}$ ) for the O atom as a basic site of  $\text{I}_2\text{O}_4$  (A) and the gas basicity (GB) ( $\text{kcal mol}^{-1}$ ) of precursor- $\text{I}_2\text{O}_4$  dimers (B) as a function of the halogen bond energy ( $\text{kcal mol}^{-1}$ ). The purple and red spheres represent two different types of XBs. O-atom 1 is the basic site of  $\text{I}_2\text{O}_4$  when it forms XB type 1 with precursors. O-atom 2 is the basic site of  $\text{I}_2\text{O}_4$  when it forms XB type 2 with precursors.

compounds. Here, possible basicity enhancement effect of the HBs was checked by taking  $\text{NH}_3$  as the test case. It was found that HBs indeed can induce the basicity enhancement of  $\text{NH}_3$  (see  $\Delta\text{ESP}$  values for the N atom as the basic site of  $\text{NH}_3$  when it forms HBs with precursors in Table S5<sup>†</sup>). Still, when XBs and HBs are considered as non-covalent interactions, the correlation of non-covalent interaction energy with  $\Delta\text{ESP}$  is similar to that of XB energy with  $\Delta\text{ESP}$ , *i.e.* a higher non-covalent interaction energy generally results in a greater (more negative)  $\Delta\text{ESP}$  value (Fig. S5<sup>†</sup>). Since the HB energy is weaker than XB energy considered here, the basicity enhancement effect of HBs is much lower than that of the XBs (Fig. S5<sup>†</sup>). If the stronger or more HBs are formed in the SA-base systems, the basicity enhancement effect of HBs could be improved. In view of potential role of HBs in inducing basicity enhancement, future investigation on effect of HB-induced basicity enhancement in different nucleation systems is warranted.

### Low formation free energy of $\text{I}_2\text{O}_4$ -containing clusters

The cluster formation free energy of the  $\text{HIO}_3$ - $\text{HIO}_2$ - $\text{I}_2\text{O}_4$  system at 278.15 K and 1 atm is presented in Fig. S6.<sup>†</sup> As shown in Fig. S6,<sup>†</sup> the  $\Delta G$  values of all  $\text{HIO}_3$ - $\text{I}_2\text{O}_4$  and  $\text{HIO}_2$ - $\text{I}_2\text{O}_4$  two-component clusters are lower than those of the corresponding  $\text{HIO}_3$ - $\text{HIO}_2$  two-component clusters. The  $\Delta G$  values of all  $\text{I}_2\text{O}_4$ -rich clusters are lower than those of the corresponding  $\text{HIO}_3$  or  $\text{HIO}_2$ -rich clusters in these two-component clusters. In addition, the  $\Delta G$  values of the  $\text{I}_2\text{O}_4$ -containing three-component clusters are lower than those of the corresponding  $\text{HIO}_3$ - $\text{HIO}_2$  two-component clusters with the same number of acids ( $\text{HIO}_3$ ) and bases ( $\text{HIO}_2$  and  $\text{I}_2\text{O}_4$ ). All of the aforementioned results indicate that  $\text{I}_2\text{O}_4$  has a greater ability to bind with  $\text{HIO}_2$  or  $\text{HIO}_3$  than  $\text{HIO}_3$  and  $\text{HIO}_2$  do with each other, which is consistent with the conclusion from the  $\Delta G$  analysis of the dimers of  $\text{I}_2\text{O}_4$  with  $\text{HIO}_2$  and  $\text{HIO}_3$ . The higher binding ability of  $\text{I}_2\text{O}_4$  leads to

the high stability of most  $\text{I}_2\text{O}_4$ -containing clusters, as evidenced by their low evaporation rates (Fig. S7<sup>†</sup>). Therefore, the participation of  $\text{I}_2\text{O}_4$  in  $\text{HIO}_3$ - $\text{HIO}_2$  nucleation may be favorable. It is noteworthy that  $(\text{HIO}_2)_3(\text{I}_2\text{O}_4)_3$  and  $(\text{HIO}_2)_3(\text{I}_2\text{O}_4)_2$  clusters own high evaporation rates despite they have low  $\Delta G$  values. It is understandable since the evaporation rate is not only dependent on the  $\Delta G$  value of the individual cluster, but also on the stability of its all possible daughter clusters.<sup>54</sup> The high evaporation rate of  $(\text{HIO}_2)_3(\text{I}_2\text{O}_4)_3$  and  $(\text{HIO}_2)_3(\text{I}_2\text{O}_4)_2$  clusters result from the higher stability of their daughter clusters (*e.g.*  $(\text{HIO}_2)_2(\text{I}_2\text{O}_4)_2$ ). Tables S6 and S7<sup>†</sup> also display the  $\Delta G$  values of the  $\text{HIO}_3$ - $\text{HIO}_2$ - $\text{I}_2\text{O}_4$  system clusters at other temperatures and pressures. The  $\Delta G$  values of most clusters become more negative with decreasing temperature, while they become higher with decreasing pressure.

Previous experimental and theoretical studies have shown that HBs are favorable for new particle formation, particularly for those involving organic acids.<sup>61,62</sup> Herein, we also compared the effects of HBs and XBs on cluster formation by examining the formation free energy of two types of specific dimers: organic acids (benzoic acid, *cis*-pinonic acid, formic acid)- $\text{NH}_3$  dimers formed by HBs,<sup>62</sup> and  $\text{HIO}_2$ - $\text{I}_2\text{O}_4$  and  $\text{HIO}_2$ - $\text{HIO}_2$  dimers formed by XBs.<sup>41</sup> It is found that the formation free energies of  $\text{HIO}_2$ - $\text{I}_2\text{O}_4$  and  $\text{HIO}_2$ - $\text{HIO}_2$  dimers are lower than those of organic acids (benzoic acid, *cis*-pinonic acid, formic acid)- $\text{NH}_3$  dimers (Table S8<sup>†</sup>). This implies that XBs here are stronger than HBs.

### Cluster formation rates of the $\text{HIO}_3$ - $\text{HIO}_2$ - $\text{I}_2\text{O}_4$ system

The variation in the cluster formation rates ( $J$ ) of the three-component  $\text{HIO}_3$ - $\text{HIO}_2$ - $\text{I}_2\text{O}_4$  system with  $[\text{HIO}_3]$  ( $10^5$ - $10^8 \text{ cm}^{-3}$ ) ( $[\text{HIO}_2] = 1/30 [\text{HIO}_3]$ ,  $\text{I}_2\text{O}_4 = 1/100 [\text{HIO}_3]$ ) at 278.15 K, 1 atm and  $k_{\text{coag}} = 0.002 \text{ s}^{-1}$ , along with that of the two-component  $\text{HIO}_3$ - $\text{HIO}_2$  system, is presented in Fig. 4A. The detailed





Fig. 4 Cluster formation rates ( $J$ ) ( $\text{cm}^3 \text{s}^{-1}$ ) of the  $\text{HIO}_3\text{-HIO}_2$  and  $\text{HIO}_3\text{-HIO}_2\text{-I}_2\text{O}_4$  systems and enhancement coefficient ( $R_{\text{I}_2\text{O}_4}$ ) (the ratio of the  $J$  value of the  $\text{HIO}_3\text{-HIO}_2\text{-I}_2\text{O}_4$  system relative to that of the  $\text{HIO}_3\text{-HIO}_2$  system) (A) and comparison coefficient ( $r$ ) (the ratio of the  $J$  value of the  $\text{HIO}_3\text{-HIO}_2\text{-I}_2\text{O}_4$  system relative to that of the  $\text{SA-HIO}_3\text{-HIO}_2$  system) (B) as a function of precursor concentration at 278.15 K, 1 atm and  $k_{\text{coag}} = 0.002 \text{ s}^{-1}$ .

computational methods for  $J$  are presented in ESI.† Note that pure  $\text{I}_2\text{O}_4$  nucleation is not compared with three-component nucleation since its rate is much lower than that of  $\text{HIO}_3\text{-HIO}_2$  nucleation when  $[\text{I}_2\text{O}_4] = 1/100 [\text{HIO}_3]$  (Fig. S8†). As shown in Fig. 4A, the  $J$  values of the  $\text{HIO}_3\text{-HIO}_2\text{-I}_2\text{O}_4$  system increase with  $[\text{HIO}_3]$ . The  $J$  values of the  $\text{HIO}_3\text{-HIO}_2\text{-I}_2\text{O}_4$  system are higher than those of the two-component  $\text{HIO}_3\text{-HIO}_2$  system under the studied conditions, especially at low  $[\text{HIO}_3]$ . Therefore,  $\text{I}_2\text{O}_4$  can enhance  $\text{HIO}_3\text{-HIO}_2$  nucleation. To clearly demonstrate the enhancement effect of  $\text{I}_2\text{O}_4$ , the enhancement coefficient ( $R_{\text{I}_2\text{O}_4}$ ), which is the ratio of the  $J$  value of the  $\text{HIO}_3\text{-HIO}_2\text{-I}_2\text{O}_4$  system relative to that of the  $\text{HIO}_3\text{-HIO}_2$  system, was calculated. The calculated  $R_{\text{I}_2\text{O}_4}$  ranges from 1.5 to 6.8 at 278.15 K, depending on  $[\text{HIO}_3]$ . The lower  $[\text{HIO}_3]$  is, the higher  $R_{\text{I}_2\text{O}_4}$  is. The  $R_{\text{I}_2\text{O}_4}$  of 6.8 applies when the absolute  $J$  is very low and the maximum  $R_{\text{I}_2\text{O}_4}$  for non-negligible absolute  $J$  (around  $7.5 \text{ cm}^3 \text{ s}^{-1}$ ) is about 2–3. The higher enhancement effect of  $\text{I}_2\text{O}_4$  at low  $[\text{HIO}_3]$  decreases the lower limit concentration that  $\text{HIO}_3$ -driven nucleation has a pronounced nucleation rate. The required  $[\text{HIO}_3]$  values are  $3.45 \times 10^6 \text{ cm}^{-3}$  and  $4.35 \times 10^6 \text{ cm}^{-3}$  for  $J$  values of approximately  $1 \text{ cm}^3 \text{ s}^{-1}$  in the systems with and without  $\text{I}_2\text{O}_4$ , respectively. This provides further support for the idea that iodine oxides play a key role in iodine oxoacid nucleation. We also noted that a very recent study by Engsvang and Elm found “oxoacid-assisted oxide” nucleation efficient.<sup>63</sup> In their study, it was found that the predicted rate of  $\text{HIO}_3\text{-HIO}_2$  nucleation is much lower than the experimental rates based on their selected theoretical method.<sup>63</sup> In our early studies, the predicted  $\text{HIO}_3\text{-HIO}_2$  and  $\text{SA-HIO}_3\text{-HIO}_2$  nucleation rates using the same theoretical methods as in this study are comparable to that from CLOUD data.<sup>26,41</sup> Besides, the concentration of iodine oxide is much lower than that of iodine oxoacid in the ambient atmosphere.<sup>38</sup> Hence, we treat  $\text{HIO}_3\text{-HIO}_2\text{-I}_2\text{O}_4$  synergistic nucleation as “oxide-assisted oxoacid” here. In fact, both studies found that iodine oxoacid and iodine oxide can nucleate together.

The  $J$  of  $\text{HIO}_3\text{-HIO}_2\text{-I}_2\text{O}_4$  system and  $R_{\text{I}_2\text{O}_4}$  as a function of temperature at 1 atm are presented in Fig. S9.†  $J$  values rise as temperature declines, while further decreasing temperature exhibits a diminished effect on  $J$  below 253 K. The temperature dependence of  $J$  is more pronounced at lower  $[\text{HIO}_3]$ . As shown in Fig. S9B,† enhancement of  $\text{I}_2\text{O}_4$  on  $\text{HIO}_3\text{-HIO}_2$  nucleation becomes higher at higher temperature (298.15 K). Fig. S10† illustrates the  $J$  and  $R_{\text{I}_2\text{O}_4}$  as a function of pressure at 278.15 K.  $J$  of  $\text{HIO}_3\text{-HIO}_2\text{-I}_2\text{O}_4$  system and  $R_{\text{I}_2\text{O}_4}$  increase slightly as pressure decreases from 1 to 0.5 atm but remain nearly constant when pressure declines from 0.5 to 0.1 atm.

A recent study revealed that SA can also enhance  $\text{HIO}_3\text{-HIO}_2$  nucleation.<sup>26</sup> Therefore, comparing the enhancement potential of  $\text{I}_2\text{O}_4$  with that of SA would be interesting. The variation in the comparison coefficient ( $r$ ), which is the ratio of the  $J$  value of the  $\text{HIO}_3\text{-HIO}_2\text{-I}_2\text{O}_4$  system relative to that of the  $\text{SA-HIO}_3\text{-HIO}_2$  system, with  $[\text{HIO}_3]$  and  $[\text{SA}]$ , is presented in Fig. 4B. At low  $[\text{HIO}_3]$  and therefore lower  $[\text{I}_2\text{O}_4]$ ,  $r$  is much less than 1, indicating that the enhancement potential of  $\text{I}_2\text{O}_4$  is lower than that of SA. When  $[\text{HIO}_3] \geq 5 \times 10^6 \text{ cm}^{-3}$  and the corresponding  $[\text{I}_2\text{O}_4] \geq 5 \times 10^4 \text{ cm}^{-3}$ ,  $r$  becomes approximately 1, *i.e.*, 1.12–1.50 for  $[\text{SA}] = 1 \times 10^6 \text{ cm}^{-3}$ ; 0.20–1.38 for  $[\text{SA}] = 5 \times 10^6 \text{ cm}^{-3}$ , indicating that the enhancement potential of  $\text{I}_2\text{O}_4$  is comparable to or even greater than that of SA for  $\text{HIO}_3\text{-HIO}_2$  nucleation. In most cases for which  $r$  is approximately 1,  $[\text{I}_2\text{O}_4]$  is much lower than  $[\text{SA}]$ . Therefore,  $\text{I}_2\text{O}_4$ , as a base, has a greater enhancement efficiency than SA for  $\text{HIO}_3\text{-HIO}_2$  nucleation.

### Synergistic nucleation mechanism of the $\text{HIO}_3\text{-HIO}_2\text{-I}_2\text{O}_4$ system

The cluster growth pathway for the  $\text{HIO}_3\text{-HIO}_2\text{-I}_2\text{O}_4$  system is shown in Fig. 5. Overall, the cluster growth pathway involves three channels: the (I)  $\text{HIO}_3\text{-HIO}_2$  pathway, (II)  $\text{HIO}_3\text{-I}_2\text{O}_4$  pathway and (III)  $\text{HIO}_3\text{-HIO}_2\text{-I}_2\text{O}_4$  pathway. The contributions of the two-component pathways ( $\text{HIO}_3\text{-HIO}_2$  and  $\text{HIO}_3\text{-I}_2\text{O}_4$ )







Fig. 6 Cluster formation rate ( $J$ ) ( $\text{cm}^{-3} \text{s}^{-1}$ ) of the  $\text{HIO}_3\text{-HIO}_2\text{-I}_2\text{O}_4$  and  $\text{HIO}_3\text{-HIO}_2$  systems and the enhancement coefficient ( $R_{1204}$ ) in different areas with different temperatures ( $T$ ) and  $[\text{HIO}_3]$ . The  $T$  and  $[\text{HIO}_3]$  in different areas were obtained from He *et al.*<sup>38</sup> The  $k_{\text{coag}}$  in Helsinki and Mace Head was set to  $2 \times 10^{-3} \text{ s}^{-1}$ ,<sup>55</sup> and  $k_{\text{coag}}$  in Aboa, Greenland, and Ny-Ålesund was set to  $1 \times 10^{-4} \text{ s}^{-1}$ .<sup>38</sup>

growth. The possible role of such a mechanism in particle growth is worthy of further investigation.

## Conclusions

In this study, quantum chemical methods and ACDC were employed to investigate the nucleation mechanism and kinetics of iodine oxides and iodine oxoacids. Of all iodine oxides,  $\text{I}_2\text{O}_4$  was found to have the strongest nucleation potential towards  $\text{HIO}_3\text{-HIO}_2$ .  $\text{I}_2\text{O}_4$  can synergistically nucleate with  $\text{HIO}_3\text{-HIO}_2$ , breaking through the previous findings that iodine oxoacids and iodine oxides independently nucleate.<sup>14,38</sup> The synergistic nucleation rate of  $\text{HIO}_3\text{-HIO}_2\text{-I}_2\text{O}_4$  is 1.5 to 6.8 times higher than that of the known most efficient iodine-associated two-component ( $\text{HIO}_3\text{-HIO}_2$ ) nucleation at 278.15 K. The high synergistic nucleation rate enhances the role of iodine-containing species in marine atmospheric particle formation. Microscopic analysis of the three-component cluster configurations revealed that an unexpected acid-base reaction between  $\text{I}_2\text{O}_4$  and  $\text{HIO}_2/\text{HIO}_3$  is a key driver of this efficient synergistic nucleation, in addition to traditional HBs and XBs. The halogen bond-induced basicity enhancement was further identified as the chemical nature of  $\text{I}_2\text{O}_4$  behaving as a base in the nucleation with  $\text{HIO}_2$  or  $\text{HIO}_3$ . Such a basicity enhancement effect can be extended to other iodine-containing species, *e.g.*,  $\text{HIO}_2$  and even more acidic  $\text{HIO}_3$ , suggesting that this is a common feature in interactions between iodine-containing species. Our findings clarify the synergistic nucleation of iodine oxoacids and iodine oxides and highlight the importance of halogen bond-induced basicity enhancement in the formation of iodine-containing particles.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Author contributions

H. B. X. and J. S. F. designed the study. R. J. Z. and Y. Y. L. performed the quantum chemical calculation and analyzed data. R. J. Z., Y. Y. L., R. J. Y., F. F. M., H. B. X. and J. S. F. wrote the manuscript. D. M. X., J. W. C., H. B. X. and J. S. F. commented on and revised the manuscript. All coauthors participated in relevant scientific discussion of the manuscript.

## Conflicts of interest

The authors declare no competing financial interest.

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