Formation of iodo-trihalomethanes, iodo-acetic acids, and iodo-acetamides during chloramination of iodide-containing waters: Factors influencing formation and reaction pathways

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HIGHLIGHTS

- Kinetic model for HOI/I₂ evolution during chloramination was developed.
- Maximum I-DBPs formation and HOI/I₂ consumption occurred at pH 8.0.
- I-HAcAms, once formed, could be further hydrolyzed to corresponding I-HAAs.
- Low-SUVA₂₅₄ NOM favored I-DBPs formation compared to high-SUVA₂₅₄ NOM.
- Reaction pathways for I-DBPs formation during chloramination were proposed.

GRAPHICAL ABSTRACT

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ABSTRACT

This study investigated systematically the factors influencing the formation of iodinated disinfection by-products (I-DBPs) during chloramination of I⁻-containing waters, including reaction time, NH₂Cl dose, I⁻ concentration, pH, natural organic matter (NOM) concentration, Br⁻/I⁻ molar ratio, and water matrix. Among the I-DBPs detected, iodoform (CHI₃), iodoacetic acid (IAA), diiodoacetic acid (DIAA), triiodoacetic acid (TIAA), and diiodoacetamide (DIACAm) were the major species produced from reactions between reactive iodine species (HOI/I₂) and NOM. A kinetic model involving the reactions of NH₂Cl auto-decomposition, iodine species transformation and NOM consumption was developed, which could well describe NH₂Cl decay and HOI/I₂ evolution. Higher concentrations of CHI₃, IAA, DIAA, TIAA, and DIACAm were observed in chloramination than in chlorination, whereas IO₃⁻ was only formed significantly in chlorination. Maximum formation of I-DBPs occurred at pH 8.0, but acidic conditions favored the formation of iodinated haloacetic acids and DIACAm. Increasing Br⁻/I⁻ molar ratio from 1 to 10 did not increase the total amount of I-DBPs, but produced more bromine-substituting species. In addition, chloramination of 18 model compounds indicated that

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low-SUVA₂₅₄ (specific ultraviolet absorbance at 254 nm) NOM generally favored the formation of I-DBPs compared to high-SUVA₂₅₄ NOM. Finally, potential pathways for I-DBPs formation from chloramination of NOM were proposed.

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1. Introduction

The formation of disinfection by-products (DBPs) during water treatment is of great concern because of their potential adverse health effects. To comply with the increasingly stringent regulatory limits for trihalomethanes (THMs) and haloacetic acids (HAAs) [1], many water utilities have switched from free chlorine to monochloramine (NH₂Cl) as a secondary disinfectant, because the latter leads to lower concentrations of regulated THMs and HAAs. However, the use of NH₂Cl can promote the formation of a large number of other potentially harmful DBPs, such as haloacetanitriles (HANs), *N*-nitrosodimethylamine, and iodinated disinfection by-products (I-DBPs) [2,3]. Therefore, DBPs formation can still be problematic during chloramination of drinking water.

During the disinfection processes, iodide (I[−]) in source waters is rapidly oxidized to hypiodous acid (HOI), which can either react with natural organic matter (NOM) to form various I-DBPs, or be further oxidized to iodate (IO₃[−]) [4–6]. Apart from iodinated trihalomethanes (I-THMs) [7], many other I-DBPs have also been found in disinfected drinking water in recent years, including iodinated haloacetic acids (I-HAAs) [2], polar I-DBPs [8], and iodinated haloacetamides (I-HAcAms) [9]. The I-DBPs are generally more toxic than their chlorinated and brominated analogues [10], and recent mammalian cell toxicity results have shown that iodoform (CHI₃) is 60 and 146 times more cytotoxic than bromoform (CHBr₃) and chloroform (CHCl₃), respectively [11,12]. I-HAAs are frequently found in chloraminated water, which represent a new class of highly toxic DBPs in drinking water [2,13]. In addition, new nitrogenous I-DBPs, such as I-HAcAms [e.g., chloriodoacetamide (ClIAcAm), diiodoacetamide (DIAcAm), and iodoacetamide (IAcAm)], are believed to be more toxic than their carbonaceous analogues [14]. By comparing the I-DBPs formed in oxidative treatments of I[−]-containing waters using chlorine [8,15–17], NH₂Cl [3,7], chlorine dioxide [18,19], ozone [20], and potassium permanganate [21], it turns out that NH₂Cl favors the formation of I-DBPs [4,22,23]. However, most previous studies on I-DBPs in drinking water have only focused on I-THMs, while little is known about the formation and speciation of I-HAAs and I-HAcAms during chloramination.

In this study, we systematically investigated the factors influencing the formation of three typical classes of I-DBPs (i.e., I-THMs, I-HAAs, and I-HAcAms) during chloramination of I[−]-containing waters, including reaction time, NH₂Cl dose, I[−] concentration, pH, NOM concentration, Br[−]/I[−] molar ratio, and water matrix. A kinetic model, which involved the reactions of NH₂Cl auto-decomposition, iodine species transformation and NOM consumption, was developed to describe NH₂Cl decay and HOI/I₂ evolution. Moreover, 18 model compounds (i.e., amino acids, carboxylic acids, and aromatic compounds) were chloraminated to help clarify the reaction mechanisms for I-DBPs formation.

2. Materials and methods

2.1. Chemicals

All chemicals were of the highest purity available. Individual I-THMs including bromodiodomethane (CHBrI₂), bro-

mochloriodomethane (CHBrClI), chlorodiodomethane (CHClI₂), dibromiodomethane (CHBr₂I) and dichloriodomethane (CHCl₂I), I-HAAs including bromiodoacetic acid (BrIAA), chloriodoacetic acid (ClIAA), diiodoacetic acid (DIAA) and iodoacetic acid (IAA), and I-HAcAms including bromiodoacetamide (BrIAcAm), ClIAcAm, DIAcAm and IAcAm were all purchased from CanSyn Chem. Co. (New Westminster, BC, Canada). A standard mixture of four regulated THMs [THM4, including bromodichloromethane (CHCl₂Br), CHBr₃, CHCl₃ and dibromochloromethane (CHClBr₂)] and an internal standard of 1,2-dibromopropane were purchased from J&K Chemical Co. (Beijing, China). CHI₃ (99%), dichloroacetamide (DCIAcAm, 99%), dichloroacetanitrile (DCIAN, 99%), iodoacetanitrile (IAN, 99%), *o*-iodophenol (99.8%), *p*-iodophenol (99.8%) and triiodoacetic acid (TIAA, 90%) were obtained from Sigma Aldrich (St. Louis, MO, USA). Suwannee River NOM isolate (2R101N) was obtained from the International Humic Substances Society. Ammonium sulfate (99%), potassium bromide (99%), potassium iodide (99%) and NaOCl (5% of active chlorine) were obtained from Sinopharm Chemical Reagent Co. (Shanghai, China). In addition, 18 model compounds (Sinopharm Chemical Reagent Co.) were used to mimic the reactivity of a variety of NOM moieties during disinfection, whose chemical structures and molecular formulae are listed in Table S1. All reaction solutions were prepared with ultrapure water produced by a Milli-Q system (Advantage A10, Millipore, Billerica, MA, USA).

2.2. Experimental procedures

The formation of I-DBPs during chloramination of I[−]-containing waters was studied as a function of reaction time, NH₂Cl dose, I[−] concentration, pH, NOM concentration, Br[−]/I[−] molar ratio, and water matrix. All experiments were performed in triplicate using 40-mL amber glass bottles with polytetrafluoroethylene-lined septum screw-caps under headspace-free conditions. The pH of all reaction solutions was controlled at 7.0 ± 0.1 with 5 mM phosphate buffer except when the effect of pH was examined. Prior to each experiment, preformed NH₂Cl solution was freshly prepared by adding a desired amount of NaOCl stock solution to an (NH₄)₂SO₄ solution (10 mM bicarbonate buffer, pH 8.5) at a Cl/N molar ratio of 0.7:1 according to previously published procedures [24]. For comparison, a set of experiments using free chlorine was also conducted under the same conditions. Similar experimental procedures were adopted when testing the formation of I-DBPs during chloramination of the model compounds. After certain reaction times, water samples were withdrawn and added to an acidified sulfite solution ([HSO₃[−]]:[NH₂Cl] molar ratio = 1.5) to quench the residual oxidant. To prevent potential hydrolytic loss of byproducts during storage, water samples were extracted immediately after quenching.

2.3. Analytical methods

Reactive iodine species (i.e., HOI/I₂) in aqueous solutions were quenched with an excess of phenol and then analyzed as iodophenols by high-performance liquid chromatography (HPLC) as previously described [5]. Dissolved organic carbon (DOC) concentration was measured with a TOC-VCPN analyzer (Shimadzu, Japan). Br[−], I[−], and IO₃[−] concentrations were analyzed by an

Table 1
Main characteristics of three real waters.

Real water	DOC(mg/L)	UV ₂₅₄ (1/cm)	SUVA ₂₅₄ ^a [L/(mg·m)]	Br ⁻ (μg/L)	I ⁻ (μg/L)
WTP	2.6	0.021	0.81	27.5	ND ^b
MYW	4.2	0.060	1.43	60.2	ND
WWTP	5.8	0.107	1.84	100.5	ND

^a SUVA₂₅₄ = UV₂₅₄ × 100/DOC.

^b ND: not detected.

ICS-3000 ion chromatograph (Dionex, USA) equipped with an AS19-HC anion separation column. The limits of quantification (LOQs) for Br⁻, I⁻ and IO₃⁻ were all about 10 μg/L. NH₂Cl concentration was measured using the *N,N*-diethyl-*p*-phenylenediamine (DPD) method [25]. Prior to analysis, free chlorine in chloraminated samples was quenched with an excess of phenol, because the presence of free chlorine causes interference with the DPD method. I-THMs and I-HAAs were quantified according to USEPA Methods 551.1 and 552.2 with minor modifications, respectively. I-THMs were analyzed using a gas chromatograph (Thermo-electron Finnigan, Waltham, MA, USA) equipped with an electron capture detector (ECD) and an HP-5MS column (30 m × 0.25 mm, 0.25 μm film thickness, Agilent Technologies, USA). I-HAAs were analyzed by liquid/liquid extraction with methyl-*tert*-butyl-ether (MtBE), derivatization with acidified methanol, and quantification by GC/ECD with the same capillary column. I-HAcAms were determined by ultra-high performance liquid chromatography-tandem mass spectrometry (UPLC-MS/MS, Waters, USA) as previously described [9]. The LOQs were in the range of 0.1–1.0 μg/L for I-THMs and I-HAAs, and 0.02–0.04 μg/L for I-HAcAms (Table S2). Other byproducts formed in the reactions between NOM and NH₂Cl were identified by triple quadrupole gas chromatography-tandem mass spectrometry (GC-MS/MS, Bruker, Fremont, CA, USA), and their chemical structures were determined by referring to the mass spectral database of National Institute of Standards and Technology.

2.4. Formation of I-DBPs in real waters

To evaluate the effect of water matrix on I-DBPs formation during chloramination, 200 μg/L I⁻ was spiked into three real waters including the surface water from Miyun reservoir (MYR), activated carbon-filtered water from Beijing No. 9 drinking water treatment plant (WTP), and secondary effluent from Qinghe wastewater treatment plant (WWTP), whose major quality parameters are summarized in Table 1. These water samples were filtered through 0.45-μm membranes and stored at 4 °C until use.

3. Results and discussion

3.1. Evolution of reactive iodine species during chloramination

To understand iodide transformation during chloramination of I⁻-containing waters, it is essential to assess the evolution of HOI/I₂. Fig. 1 shows the time-dependent changes of HOI/I₂ concentration during chloramination at pH 7.0 for various initial I⁻ concentrations (10–100 μM). As expected, increasing the initial I⁻ concentration could significantly enhance the formation of HOI/I₂. Meanwhile, the inset in Fig. 1 shows HOI/I₂ evolution along with NH₂Cl decay as a function of reaction time at an initial I⁻ concentration of 100 μM. HOI/I₂ were produced quickly, reaching a maximum of 56 μM at 1 min, and then decreased gradually. The NH₂Cl concentration decreased rapidly within the first 15 min, and thereafter decreased slowly. It is known that NH₂Cl can quickly oxidize I⁻ to HOI/I₂, but cannot further oxidize HOI/I₂ to IO₃⁻. However, HOI can be oxidized to IO₃⁻ by free chlorine and free bromine, which have a higher oxidation potential than NH₂Cl [4,15]. Consequently, the

Fig. 1. Measured and modeled evolutions of reactive iodine species (HOI/I₂) as a function of reaction time and initial I⁻ concentration during chloramination. Experimental conditions: [NH₂Cl]₀ = 100 μM, [DOC]₀ = 3.0 mg/L, 5 mM phosphate buffer, pH 7.0, 25 °C. Symbols and curves represent experimental data and model predictions, respectively.

formation of IO₃⁻, which can only result from the disproportion of HOI during chloramination, is much lower than that during chlorination. Hence, IO₃⁻ was not detected in the reaction solution, and HOI/I₂ were the major reactive iodine species.

A kinetic model was developed based on the Kintecus software [26], which could fit well the experimental data using a set of reactions listed in Table S3 (i.e., NH₂Cl auto-decomposition, iodine species transformation, and NOM consumption), as shown in Figs. S1 and S2. Previous studies have shown that the second-order rate constants for the reaction of NOM with HOI and I₂ were in the ranges of 0.1–0.4 M⁻¹ s⁻¹ and (0.4–1.5) × 10⁻⁴ M⁻¹ s⁻¹, respectively [5,27], which thus accounts for the rapid decrease in HOI/I₂ after 1 min (Fig. 1). Although HOI may be disproportionated to I⁻ and IO₃⁻ [5], it could react much faster with NOM, so little IO₃⁻ was detected in the reaction solution.

3.2. Evolution of I-DBPs during chloramination and chlorination

Fig. 2a and b compare the evolution of I-DBPs during chloramination and chlorination of I⁻-containing waters. The formation of CHI₃ was far higher than those of IAA, DIAA, and DIACAm during chloramination (Fig. 2a). It is noted that other Cl-containing I-DBPs (e.g., CHClI₂, CHCl₂I, ClIAA, ClIAcAm) were also detected (5.87–22.39 nM). The concentrations of CHI₃, IAA, DIAA and TIAA increased with increasing time, but the rates of increase were different for different compounds. At a reaction time of 12 h, 809 nM CHI₃, 45 nM IAA, 71 nM DIAA, and 321 nM TIAA were formed. By contrast, the concentration of DIACAm reached a maximum of 90 nM at 1 h and then decreased gradually with increasing time. This probably results from the rapid reaction of HOI (formed by the transformation of I₂ in water) with NOM to form DIACAm, which was then further hydrolyzed to form DIAA (Fig. S3). Furthermore, it appears that NOM contained fast- and slow-reacting moieties, similar to those involved in CHCl₃ formation [28].

Fig. 2. Evolution of I-DBPs as a function of reaction time during chloramination (a) and chlorination (b). Experimental conditions: $[\text{NH}_2\text{Cl}]_0$ (or $[\text{Cl}_2]_0$) = 100 μM , $[\text{I}^-]_0$ = 100 μM , $[\text{DOC}]_0$ = 3.0 mg/L, 5 mM phosphate buffer, pH 7.0, 25 °C.

During chlorination, CHI_3 , IO_3^- , and TIAA showed the highest yields which reached a plateau after 2 d (Fig. 2b). The formation of DIACAm was rapid and reached a maximum of 43.2 nM at 30 min, whereas the maximum concentration of IAA (30.2 nM) occurred at 12 h; both then decreased with extended time. The decrease of IAA concentration as a function of time suggests that it could be partially transformed into ClIAA in the presence of excess free chlorine, as demonstrated in Fig. S4. Therefore, the different IAA and DIACAm concentrations formed during chloramination and chlorination were associated with their relative stabilities in the presence of free chlorine and NH_2Cl (Fig. S4). For the stability of DIACAm, a similar trend to that of ClIAA was reported previously [29].

Overall, most of the measured I-DBPs (i.e., CHI_3 , IAA, DIAA, TIAA, and DIACAm) showed higher concentrations during chloramination than during chlorination, while IO_3^- was only formed significantly during chlorination; which is consistent with previous studies [13,30]. This can be partly explained by free chlorine oxidizing I^- to IO_3^- , which acted as a sink for I^- , and thus decreased the formation of all other I-DBPs.

3.3. Effect of NH_2Cl dose on I-DBPs formation

The effect of NH_2Cl dosage (0.01–0.4 mM) on I-DBPs formation is shown in Fig. 3. The CHI_3 , TIAA, and DIACAm concentrations significantly increased with increasing NH_2Cl dose in the range of 0.01–0.1 mM, and then decreased with higher NH_2Cl doses. In contrast, the IAA and DIAA concentrations increased progressively with increasing NH_2Cl dose. The decrease in the CHI_3 , IAA, and DIACAm concentrations at relatively high NH_2Cl doses (0.1–0.4 mM) suggests that more I^- could be directly oxidized to IO_3^- by free chlorine produced from NH_2Cl hydrolysis, thus resulting in less organic I-DBPs formation. The enhanced formation of free chlorine at high NH_2Cl doses (0.1–0.4 mM) was also confirmed by the increased concentrations of Cl-DBPs (e.g., CHCl_2 and ClIAA, Fig. S5) formed in the reaction solution.

3.4. Effect of I^- concentration on I-DBPs formation

The effect of I^- concentration on the formation of I-DBPs during chloramination is shown in Fig. 4. The concentrations of CHI_3 , TIAA, and DIACAm increased significantly as the initial I^- concentration increased from 10 to 200 μM , and then decreased slightly at a higher I^- concentration (i.e., 300 μM). The DIAA concentration increased progressively with increasing I^- concentration. Meanwhile, the IAA concentration decreased from 120 to 50 nM in this I^- concentration range. This result suggests the competition of excess I^- for NH_2Cl against NOM. Thus, although increasing I^- concentration was likely to increase the production of HOI/ I_2 , a large excess of I^- (i.e., 200–300 μM) could consume more NH_2Cl and thus reduce the subsequent formation of I-DBPs. Furthermore, increasing I^- concentration could also induce the transformation of HOI/ I_2 to I_3^- , which is relatively less reactive [31], thereby decreasing I-DBPs formation. Therefore, the molar ratio of I^- to NH_2Cl is critical for the iodine sink during chloramination.

Fig. 3. Effect of NH_2Cl dose on the formation of I-DBPs during chloramination. Experimental conditions: $[\text{I}^-]_0$ = 100 μM , $[\text{DOC}]_0$ = 3.0 mg/L, 5 mM phosphate buffer, pH 7.0, 25 °C, reaction time = 3 d.

Fig. 4. Effect of I^- concentration on the formation of I-DBPs during chloramination. Experimental conditions: $[\text{NH}_2\text{Cl}]_0$ = 100 μM , $[\text{DOC}]_0$ = 3.0 mg/L, 5 mM phosphate buffer, pH 7.0, 25 °C, reaction time = 3 d.

tration increased from 10 to 200 μM , and then decreased slightly at a higher I^- concentration (i.e., 300 μM). The DIAA concentration increased progressively with increasing I^- concentration. Meanwhile, the IAA concentration decreased from 120 to 50 nM in this I^- concentration range. This result suggests the competition of excess I^- for NH_2Cl against NOM. Thus, although increasing I^- concentration was likely to increase the production of HOI/ I_2 , a large excess of I^- (i.e., 200–300 μM) could consume more NH_2Cl and thus reduce the subsequent formation of I-DBPs. Furthermore, increasing I^- concentration could also induce the transformation of HOI/ I_2 to I_3^- , which is relatively less reactive [31], thereby decreasing I-DBPs formation. Therefore, the molar ratio of I^- to NH_2Cl is critical for the iodine sink during chloramination.

3.5. Effect of pH on I-DBPs formation

Fig. 5 shows the formation of CHI_3 , IAA, DIAA, TIAA, and DIACAm together with the consumption of HOI/ I_2 during chloramination in the pH range of 5.0–9.0. CHI_3 was at a minimum of 1.2 μM at pH 5.0, increased to a maximum of 1.6 μM at pH 8.0, and then decreased to 1.5 μM at pH 9.0 (Fig. 5a). The concentrations of IAA, DIAA, TIAA, and DIACAm decreased from 110, 183, 382, and 90 nM at pH 5.0 to 58, 72, 364, and 20 nM at pH 9.0, respectively, although the highest yields of IAA and TIAA were observed at pH 6.0. In general, acidic conditions favored the formation of I-HAAs, which is similar to the formation of the regulated THMs and HAAs at various pH values [32].

Fig. 5. Effect of pH on I-DBPs formation and HOI/I₂ consumption during chloramination. Experimental conditions: $[\text{NH}_2\text{Cl}]_0 = 100 \mu\text{M}$, $[\text{I}^-]_0 = 100 \mu\text{M}$, $[\text{DOC}]_0 = 3.0 \text{ mg/L}$, 5 mM phosphate buffer, 25 °C, reaction time = 3 d.

The pH-dependent change in the concentrations of I-DBPs can be mainly attributed to the following aspects:

First, the speciation of HOI/I₂ and the reactions between iodine and NOM are pH dependent [27]. Generally, at acidic pH conditions, I₂ is the dominant species, while HOI becomes predominant at neutral to slightly alkaline conditions (Fig. S6). I₃[−] was insignificant under our experimental conditions based on calculations using published equilibrium data [26,33]. Further experiments confirmed that the maximum HOI/I₂ consumption (65.3 μM) occurred at pH 8.0 (Fig. 5b), where the dominant HOI/I₂ reacted rapidly with NOM resulting in the highest yield of total I-DBPs.

Second, pH affects the speciation of chloramines and the hydrolysis of NH₂Cl to form free chlorine. Under acidic conditions, NH₂Cl is hydrolyzed to form HOCl and NH₃; as a result more free chlorine is released at pH 6.0 than at pH 7.0–8.0 [34]. Thus, the present experimental result was expected, because a small proportion of free chlorine in equilibrium with NH₂Cl could play a significant role in I-DBPs formation.

Finally, pH also affects the stability of I-DBPs. Unlike THMs and HAAs, HACams usually undergo base-catalyzed decomposition. It was reported that HACams were unstable in aqueous solutions and could decompose quickly in alkaline conditions [29]. Our additional experiments on the stability of DIACAm confirmed that its decomposition rate increased at higher pH values (Fig. S7). The pseudo-first-order rate constant (k'_{obs}) for hydrolysis of DIACAm was $3.44 \times 10^{-2} \text{ h}^{-1}$ at pH 9.0, which is about twice that at pH 5.0 ($1.78 \times 10^{-2} \text{ h}^{-1}$). Therefore, the net DIACAm concentration was lower at a higher pH value, and its highest concentration at pH 5.0 could be explained by fast formation and slow hydrolysis at this pH.

3.6. Effect of NOM concentration on I-DBPs formation

The effect of NOM concentration (expressed as DOC) on I-DBPs formation is shown in Fig. 6. The concentrations of CHI₃ and TIAA increased significantly with increasing DOC concentration from 1.0 to 5.0 mg/L, and then decreased at a higher DOC concentration (i.e., 7.0 mg/L). The concentrations of DIAA and DIACAm kept increasing over the studied NOM concentration range, whereas the IAA concentration remained nearly constant. The decrease in the CHI₃

Fig. 6. Effect of NOM concentration on the formation of I-DBPs during chloramination. Experimental conditions: $[\text{NH}_2\text{Cl}]_0 = 100 \mu\text{M}$, $[\text{I}^-]_0 = 100 \mu\text{M}$, 5 mM phosphate buffer, pH 7.0, 25 °C, reaction time = 3 d.

Fig. 7. Effect of Br[−]/I[−] molar ratio on the formation of I-DBPs during chloramination. Experimental conditions: $[\text{NH}_2\text{Cl}]_0 = 100 \mu\text{M}$, $[\text{I}^-]_0 = 100 \mu\text{M}$, 5 mM phosphate buffer, pH 7.0, 25 °C, reaction time = 3 d.

and TIAA concentrations at 7.0 mg/L DOC was attributable to the fact that triiodo-DBPs were less likely to be formed when excess reaction sites of NOM were available. In addition, a previous study reported that NH₂Cl could act as a nitrogen source to some extent for DCIAcAm formation, because MS analysis revealed that >50% of the nitrogen present in dichloroacetonitrile (DCIAN) and DCIAcAm came actually from NH₂Cl [35]. Similarly, NH₂Cl may also contribute nitrogen to the formation of DIACAm.

3.7. Effect of Br[−]/I[−] molar ratio on I-DBPs formation

The molar ratio of Br[−]/I[−] can vary in source waters and thus affect I-DBPs formation. Fig. 7 shows the speciations and concentrations of I-THMs, I-HAAs and I-HACams during chloramination at various Br[−]/I[−] molar ratios in the synthetic (NOM) and WTP waters. Generally, increasing the Br[−]/I[−] molar ratio from 1 to 10 did not increase the total amount of I-DBPs, but changed the proportions of the mixed Br- and I-DBPs. For I-THMs, CHI₃ was always the dominant species in the two waters, even when the concentration of Br[−] was 10 times that of I[−]. However, increasing Br[−] concentration notably shifted the I-THMs towards those containing more bromine (e.g., CHBrI₂ and CHBrI). For I-HAAs, TIAA was the dominant species, and the DIAA and TIAA concentrations decreased while the BrIAA concentration increased with increasing Br[−]/I[−] molar ratio. Di-HACams (e.g., DIACAm and BrIAcAm) accounted for the majority of I-HACams observed after chloramination of both

Fig. 8. Effect of water matrix on the formation of I-DBPs normalized by DOC concentration. Experimental conditions: $[\text{NH}_2\text{Cl}]_0 = 50 \mu\text{M}$, spiked $[\text{I}^-]_0 = 200 \mu\text{g/L}$, 5 mM phosphate buffer, pH 7.0, 25 °C, reaction time = 3 d.

waters. Moreover, the concentration of BrIAcAm increased substantially with increasing Br^-/I^- molar ratio. Overall, the formation patterns of I-DBPs in the two waters were quite similar. There are two reasons for the enhanced formation of bromine-substituting I-DBPs (e.g., BrIAA and BrIAcAm) at high Br^- concentrations: (1) mixed interhalogen compounds (e.g., ICl , ICl_2^- , I_2Cl^- , IBr , IBr_2^- , I_2Br^-) could be formed from HOI and I^- in the presence of Cl^- and Br^- [36,37]; and (2) NH_2Cl could oxidize a small amount of Br^- to bromochloramine, which is more reactive toward NOM than NH_2Cl [38].

3.8. Effect of water matrix on I-DBPs formation

To assess the effect of water matrix on I-DBPs formation, samples of various water sources spiked with $200 \mu\text{g/L I}^-$ were tested. Because of their different DOC contents, the concentrations of I-THMs, THM4, I-HAAs and I-HAcAms were normalized by the DOC concentration (mg/L) (Fig. 8). For I-THMs, CHI_3 and CHBrCl_2 were always the first and second abundant species for all the three waters, respectively. A considerable amount of CHCl_2I was only detected in the WWTP water. For I-HAAs, DIAA was the most abun-

dant I-HAA species, except for the WWTP water. For I-HAcAms, BrIAcAm and DIAcAm were two major species detected. The concentration of DIAcAm was always higher than that of BrIAcAm for all waters, which agrees with a previous study [39]. Overall, the DOC-normalized total yield of I-DBPs in the three real waters followed the descending order of $\text{WTP} > \text{MYR} > \text{WWTP}$, which was mainly attributable to their increasing DOC contents (Table 1).

The specific ultraviolet absorbance at 254 nm (SUVA_{254}) has been widely used as an indicator of aromatic content and DBP formation potential of NOM [40], and a high SUVA_{254} value generally indicates a high aromatic content. From the limited data set in the present study, it appears that low- SUVA_{254} NOM was more reactive in the formation of I-DBPs during chloramination than high- SUVA_{254} NOM, which is consistent with previous findings [41,42]. In addition, the formation of the regulated THM4 showed a similar trend to that of I-THMs for various real waters after chloramination.

3.9. I-DBPs formation during chloramination of model compounds

To compare the reactivity of various organic precursors with iodine during chloramination, the speciation and yields of I-DBPs produced from 18 model compounds were evaluated. These compounds (i.e., amino acids, carboxylic acids, and aromatics), whose chemical structures and major characteristics are shown in Table S1, are present in the NOM structure and are known to react with free halogens. The highest I-DBPs/DOC value (0.482%) was found with citric acid, followed by L-aspartic acid (0.430%) and pyruvic acid (0.188%) (Table 2). By contrast, chloramination of aromatic compounds contributed little to the formation of I-DBPs (3.6–8.1 nM only), exhibiting very low I-DBPs/DOC values (0.0001–0.0011%). This could probably be ascribed to the influence of electron-donating groups (e.g., methyl and hydroxyl) on the reactivity of aromatic compounds toward electrophilic substitutions [43]. The I-DBPs/DOC value was much lower for *p*-cresol (0.0001%) than for other aromatic compounds, because *para*-arrangement of the phenolic group caused a more homogeneous distribution of electron density over all aromatic carbons. Taking into account the relationship between the I-DBPs/DOC and SUVA_{254} values (Table

Table 2
Formation of I-DBPs during chloramination of 18 model compounds^a.

Model compound	CHI_3 (nM)	IAA (nM)	DIAA (nM)	TIAA (nM)	DIAcAm (nM)	I-DBPs (nM)	I-DBPs/DOC (%)
Amino acids							
L-Aspartic acid	362 (19) ^b	ND ^c	17.9 (1.3)	327 (16)	2.8 (0.3)	709	0.430
L-Proline	10.4 (0.5)	ND	6.4 (0.3)	14.1 (1.5)	0.6 (0.3)	17.4	0.004
Tyrosine	4.8 (0.5)	2.2 (0.5)	ND	ND	14.8 (1.0)	21.8	0.012
Histidine	21.1 (0.8)	21.5 (1.1)	10.6 (0.6)	21.3 (1.5)	2.9 (0.3)	56.1	0.011
Phenylalanine	79.4 (0.8)	ND	20.5 (1.0)	52.2 (3.0)	4.5 (0.3)	104	0.014
Alanine	26.9 (0.5)	ND	7.7 (0.5)	15.2 (1.0)	12.2 (1.0)	46.8	0.017
Glycine	14.2 (3.0)	ND	3.5 (0.3)	10.3 (0.2)	1.3 (0.6)	29.3	0.016
Carboxylic acids							
Salicylic acid	10.9 (2.8)	ND	9.0 (0.3)	9.2 (0.3)	10.0 (0.6)	39.1	0.005
Citric acid	1580 (20)	561 (8)	510 (20)	190 (10)	13.5 (1.0)	2854	0.482
Lactic acid	23.9 (3.8)	ND	4.2 (0.4)	14.2 (0.5)	7.1 (0.6)	49.4	0.011
Propionic acid	31.5 (4.6)	ND	12.2 (0.6)	27.9 (0.5)	4.8 (0.3)	76.4	0.026
Pyruvic acid	397 (23)	108 (4)	0.6 (0.3)	269 (0.2)	ND	777	0.188
Aromatic compounds							
Phenol	3.0 (0.9)	1.6 (0.5)	3.5 (0.6)	ND	ND	8.1	0.0010
<i>m</i> -cresol	5.6 (0.5)	ND	0.3 (0.3)	1.6 (0.2)	ND	7.5	0.0009
<i>p</i> -cresol	3.8 (0.3)	ND	ND	ND	ND	3.8	0.0001
Catechol	3.6 (0.3)	ND	ND	ND	ND	3.6	0.0007
Resorcinol	4.1 (0.5)	ND	ND	2.3 (0.3)	ND	6.4	0.0011
Hydroquinone	3.1 (0.5)	ND	ND	0.5 (0.2)	ND	3.6	0.0007

^a Experimental conditions: $[\text{I}^-]_0 = 25 \mu\text{M}$, $[\text{NH}_2\text{Cl}]_0 = 50 \mu\text{M}$, 100 μM each model compound, 5 mM phosphate buffer, pH 7.0, 25 °C, reaction time = 3 d.

^b Mean (standard deviation), $n = 3$.

^c ND: not detected.

Scheme 1. Proposed formation pathways of CHI_3 , IAA, DIAA, TIAA, and DIACAm during chloramination of I^- -containing waters in the presence of NOM. Solid and dashed lines represent major and minor pathways, respectively.

S1), it is seen that the model compounds with low-SUVA₂₅₄ values (e.g., L-aspartic acid and citric acid) were generally more favorable in the formation of I-DBPs than those with high-SUVA₂₅₄ values (e.g., aromatics) during chloramination.

3.10. Proposed pathways for I-DBPs formation from NOM

NOM contains various types of carboxylic, aromatic, amino, and hydroxyl functional groups. Based on the present study and previous publications [40,42,44,45], a reaction scheme involving two possible formation pathways for CHI_3 , IAA, DIAA, TIAA, and DIACAm is proposed (Scheme 1):

It is known that NH_2Cl can quickly oxidize I^- to HOI/I_2 , but cannot further oxidize HOI/I_2 to IO_3^- due to its relatively weak oxidation potential. Under our experimental conditions (i.e., pH 7.0), HOI is the dominant form among various reactive iodine species (i.e., I_2 , HOI , OI^-) (Fig. S6). In Pathway (1), HOI cannot react directly with the carbonyl groups but only with their enolic forms, and either enolization or iodine addition to the enol can be rate-determining. Further iodination of an α -iodomethyl carbonyl group proceeds in two sequential steps until the methyl has been completely converted to triiodomethyl ($-CHI_3$). Then, the triiodocarbonyl compound ($R-CO-Cl_3$) can either be hydrolyzed to CHI_3 and a corresponding acid ($R-COOH$) or be oxidized to TIAA if the $R-$ is an oxidizable group. The detection of CHI_3 (Fig. S8) and TIAA (Fig. S9) in this study could support this pathway.

In Pathway (2), there are two main routes for the formation of I-HAcAms: IAcAm (Route 1) and DIACAm (Route 2). Trehy et al. [44] proposed that seven out of 20 basic amino acids during chlorination could form DCIACAm through a series of substitution, elimination, and decarboxylation reactions followed by further substitution. Similarly, iodine will substitute one hydrogen atom of the inter-

mediate $R-CH_2-CN$ to form $R-CHI-CN$, whose hydrolysis yields iodoacetoneitrile (IAN) (Route 1), which was frequently detected during chloramination of NOM and L-aspartic acid in this study (Fig. S8). Then, the sequential reactions of IAN with water lead to the formation of IAcAm and IAA. It is noted that the IAN concentration increased with increasing time during chloramination, and the yield of IAcAm was much lower than that of DIACAm because IAN is relatively more stable than diiodoacetoneitrile (DIAN). Based on the quantitative structure-property relationship analysis model, the half-life of IAN is predicted to be 451 d, which is longer than those of DIAN and triiodoacetoneitrile [46]. Moreover, if HOI is abundant, iodine will substitute both hydrogen atoms of the intermediate $R-CH_2-CN$ to form $R-CHI_2-CN$, whose hydrolysis yields DIAN (Route 2). Unfortunately, DIAN could not be quantified in this study because of a lack of its authentic standard. The sequential reactions of DIAN with water lead to the formation of DIACAm and DIAA. Our previous experiment has also demonstrated that IAcAm and DIACAm could be hydrolyzed to IAA and DIAA, respectively (Fig. S3).

In addition to the I-DBPs, Cl-N-DBPs (e.g., DCIAN, DCIACAm) were also detected during chloramination of NOM, although with much less concentrations (1.9–2.1 $\mu g/L$). It is also noted that besides the measured I-THMs, I-HAAs and I-HAcAms, the carboxylic and amino groups in the NOM structure were also likely to undergo oxidation and iodination reactions to form other unknown I-DBPs, which would increase the total organic iodine.

4. Conclusions

In reaction systems containing NH_2Cl , I^- and NOM, CHI_3 , IAA, DIAA, TIAA, and DIACAm were the major species detected, and HOI and I_2 were the reactive iodine species that contributed to the formation of I-DBPs.

Solution pH showed a significant impact on the formation of I-DBPs in synthetic I⁻-containing waters. Increasing Br⁻/I⁻ molar ratio from 1 to 10 did not increase the total amount of I-DBPs, but shifted their composition to more brominated species.

Among the 18 model compounds studied, L-aspartic acid, citric acid, and pyruvic acid exhibited the highest yields of I-DBPs during chloramination. The model compounds with low-SUVA₂₅₄ values were generally more favorable in the formation of I-DBPs than those with high-SUVA₂₅₄ values.

Potential pathways for the formation of I-THMs, I-HAAs, and I-HACams during chloramination were proposed in this study. However, it should be pointed out that the present conclusions are only drawn from laboratory water samples with high spikes of I⁻, and further measurements under more natural conditions (with respect to Br⁻ and I⁻ concentrations) are needed to assess the formation of I-DBPs during chloramination of natural waters.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2016.08.071>.

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