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Effects of bromide and iodide on the chlorination of diclofenac: Accelerated chlorination and enhanced formation of disinfection by-products

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ABSTRACT

Effects of bromide (Br^-) and iodide (I^-) on chlorination kinetics of diclofenac (DCF) and potential disinfection by-products (DBPs) formation were investigated in this study. The presence of either Br^- or I^- accelerated the chlorination of DCF with different extents. Then species-specific apparent second-order rate constants (k_{app}) of DCF with free chlorine (FC), free bromine (FB), free iodine (FI) were determined. It was found that the reactivity rate of FB with DCF was higher than those of FC and FI. The $k_{app,FB\text{-}DCF}$ at pH 7.0 was determined to be 9320 $M^{-1}\,s^{-1}$, which was 3680 and 3.2 folds of those of FC and FI, respectively. The $k_{app,FC\text{-}DCF}$ were highly pH-dependent, while the k_{app} values of DCF with FB and FI were less influenced by pH than FC. The presence of Br^- and I^- enhanced the formation amounts and altered the speciation of DBPs. The DBPs formation amounts were enhanced from 67.2 to 292.0 $\mu g\,L^{-1}$ and 87.3 $\mu g\,L^{-1}$, respectively, when 50 μM Br^- or I^- was spiked. Meanwhile, the dominant species of formed DBPs shifted from chlorinated DBPs to brominated and iodinated DBPs. At last, the transformation by-products and pathways of DCF under chlorination, chlorination with Br^- and chlorination with I^- were proposed and compared. The DCF transformation pathways mainly proceeded through hydroxylation, decarboxylation and substitution reactions. Although the presence of Br^- and I^- accelerated the chlorination of DCF, the enhanced formation of brominated and iodinated DBPs highlights the necessity to remove Br^- and I^- from source water prior to chlorination for mitigating the formation of toxic DBPs.

1. Introduction

Disinfection is a crucial process in drinking water treatment, which inactivates pathogenic organisms and ensures the water quality for use. However, disinfection by-products (DBPs) usually form during disinfection when chemical disinfectants react with natural organic matter, bromide (Br^-), iodide (I^-) and other pollutants present in source waters. More than 600 DBPs have been identified in chlorinated water since 1970s [1]. Because of their associations with cancer in epidemiological and animal studies, DBPs become a public concern in drinking water [2,3]. Free chlorine (FC) is one of widely adopted disinfectants during disinfection. Due to its pH-dependent aqueous characteristics, various species of chlorine (HOCl, ClO^-, Cl_2, etc.) may coexist in solution, which usually show significant differences in their reactivity with microorganisms and micropollutants. Thus, variability in oxidation and disinfection efficiency were observed depending on the pH of the solution [4].

The worldwide consumption of pharmaceutical provides a continuous release of these substances or their metabolites to aquatic environment. As conventional wastewater treatment processes cannot efficiently remove these pharmaceuticals, they have been widely found in surface water, groundwater and even drinking water [1]. Diclofenac (DCF), which was sold annually approximately up to hundreds of tons, is a common nonsteroidal anti-inflammatory drug [5]. Due to its low biodegradation and small adsorption on sludge, the removal of DCF in wastewater treatment plants (WWTPs) was usually limited [6,7]. The average concentrations detected were in the $\mu g\,L^{-1}$ range in influents and effluents of WWTPs and surface waters in Austria, Pakistan, Germany and the United States [7,8]. The presence of micropollutant in drinking water sources provides the formation possibility of potentially toxic compounds during chlorine disinfection. For example, endocrine-disrupting compounds most often responsible for fish feminization 17β-estradiol, 17α-ethinylestradiol, estrone, and nonylphenol were transformed and low-molecular DBPs may form during chlorine disinfection through reactions with phenolic moieties [9]. The formation of iodinated DBPs was observed during the chlorination of iodinated X-ray contrast media [10].

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Br^- and I^- are ubiquitously observed in the drinking water sources. The concentrations of Br^- and I^- can vary from a few $\mu g\,L^{-1}$ to as much as several $mg\,L^{-1}$, which are impacted by natural processes such as salt water intrusion and/or by special geological circumstances [11-13]. The apparent rate constants for reactions of FC with Br^- and FC with I^- at pH 7 are in the range of 5300–$1.1 \times 10^8\,M^{-1}\,s^{-1}$. Thus during the chlorination of micropollutant in the presence of Br^- or I^-, FC usually reacts with Br^- and I^- firstly, producing free bromine (FB) and free iodine (FI) (Eqs. (1)–(3)) [4]. It was reported that both FB and FI were very reactive with phenolic compounds, with rate constants up to 1000 folds higher than with FC. Meanwhile, formed FB and FI can further react with compound to form brominated and iodinated DBPs (Br/I-DBPs) [14,15]. Br/I-DBPs have been found to be more cytotoxic, mutagenic, and genotoxic to mammalian cells than their chlorinated analogues [16,17].

$$HOCl + Br^- \rightarrow BrCl + OH^- \quad (1)$$

$$BrCl + 2OH^- \rightarrow OBr^- + Cl^- + H_2O \quad (2)$$

$$HOCl + I^- \rightarrow HOI + Cl^- \quad (3)$$

In this work, the effects of Br^- and I^- on the chlorination of DCF were investigated. The chlorination, bromination and iodination kinetics of DCF at pH 5.0–8.5 were investigated and modeled. The DBPs formation during the chlorination of DCF under different Br^- and I^- concentrations was then performed. Finally, the high-molecular-weight transformation by-products (TBPs) and pathways of DCF were compared for chlorination, chlorination with Br^- and chlorination with I^-. It was expected to provide insights for the roles of Br^- and I^- during chlorination of micropollutants, not only on kinetics, but also on potential DBPs formation.

2. Materials and methods

2.1. Materials

All reagents used were of the highest available purity. Chlorodiiodomethane ($CHClI_2$) and dichloroiodomethane ($CHCl_2I$) were purchased from CanSyn Chem. Co. (New Westminster, BC, Canada). A standard mixture of bromodichloromethane ($CHCl_2Br$), bromoform ($CHBr_3$), chloroform ($CHCl_3$), dibromochloromethane ($CHClBr_2$) and an internal standard of 1,2-dibromopropane were purchased from J & K Chemical Co. (Beijing, China). DCF (99%) and iodoform (CHI_3) were obtained from Sigma Aldrich (St. Louis, MO, USA).

High performance liquid chromatography (HPLC) grade methanol was obtained from Thermo Fisher Scientific (Somerset County, NJ, USA), and formic acid (≥99.0%) from Dikma Technologies (Lake Forest, CA, USA). HOBr solution was produced from a chlorine stock solution and Br^- as follows [18]. Briefly, an aliquot of a chlorine stock solution (1.0 M) is added to a solution of Br^- with a slight excess of Br^- compared to chlorine concentration. HOI was prepared by oxidation of I^- with OCl^- [19]. Briefly, 10 mL of 10 mM KI solution was added to 1000 mL pH-buffered (2.5 mM tetraborate buffer, pH 8.0) solution containing 0.1 mM NaOCl.

2.2. Experimental procedures

The effect of Br^- and I^- on the chlorination kinetics of DCF was investigated firstly at pH 7.0. As the occurrence concentrations of Br^- and I^- ranged from a few $\mu g\,L^{-1}$ to several $mg\,L^{-1}$ in the surface water and ground water, 500 $\mu g\,L^{-1}$ Br^- or I^- was spiked to the chlorination of DCF to compare the degradation rates of DCF under chlorination, chlorination with Br^- and chlorination with I^-. Kinetics experiments were performed in aqueous solutions at pH 5.0–8.5 adjusted by 2 mM phosphate buffer around 25 °C. Reactions were initiated by adding FC, FB or FI to 250 mL of buffered solutions containing DCF under pseudo-first-order kinetic conditions, in the presence of an excess of oxidant ($[Oxidant]_o \geq 10\ [DCF]_o$). For the analysis of DCF, samples were collected at different time intervals in vials containing predosed volumes of $Na_2S_2O_3$ to quench residual oxidant. Then the DCF concentration was analyzed by HPLC.

For the analysis of DBPs formation during the chlorination of DCF in the presence and absence of Br^- and I^-, 0–50 μM Br^- or I^- was spiked to the chlorination of DCF at pH 7.0. After 72 h, water samples were withdrawn and quenched with $Na_2S_2O_3$ to quench the residual oxidant. Then the water samples were analyzed as soon as possible to prevent potential hydrolytic loss of DBPs during storage.

Similar experimental procedures were adopted For the analysis of high molecular weight TBPs of DCF under chlorination with Br^- and I^-, 50 μM Br^- or I^- were spiked to the chlorination of DCF at pH 7.0, respectively. After 60 min, the chlorination of terminated with $Na_2S_2O_3$ and the TBPs were analyzed with ultra-performance liquid chromatography-tandem quadrupole time-of-flight mass spectrometry (UPLC-QTOF-MS/MS).

2.3. Analysis

Chlorine stock solution was standardized by the N,N-diethyl−p-phenylenediamine (DPD) method at 510 nm ($\varepsilon_{510nm} = 14550\,M^{-1}\,cm^{-1}$) [20], while bromine stock solution was standardized by measuring the absorbance at 329 nm ($\varepsilon_{329nm} = 332\,M^{-1}\,cm^{-1}$) using a HACH UV–vis. spectrophotometer (DR5000, Loveland, CO, USA) [21]. The concentration of DCF was determined by using an Agilent 1200 HPLC with a diode array detector. Separation was performed by a Waters Atlantis column (3 μm, 150 × 2.1 mm) with elution at $0.5\,mL\,min^{-1}$. The mobile phase consisted of purified water (containing 0.1% formic acid, 25%) and methanol (75%). The sample injection volume was 50 μL and analytical column temperature was controlled at 25 °C. Seven DBPs including $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, $CHBr_3$, $CHICl_2$, CHI_2Cl and CHI_3 were analyzed after samples being extracted with methyl *tert*-butyl ether using a gas chromatograph (7890, Agilent, CA, USA) equipped with an HP 5 capillary column (30 m × 0.25 mm, 0.25 μm, J & W, USA) and an electronic capture detector based on the modified USEPA method 551.1.

The TBPs of DCF were identified by UPLC-QTOF-MS/MS (AcQuity LC, Xevo G2 QTOF MS, Waters, USA) coupled with an Eclipse Plus C18 column (2.1 × 150 mm, 3.5 μm, Agilent). The mobile phase consisted of 0.1% formic acid in water (A) and methanol (B) at a total flow rate of $0.3\,mL\,min^{-1}$. The gradient elution program (time in min, % mobile phase B) was set as follows: (0, 10), (15, 90) and (20, 10). Then the column was equilibrated for 5 min before the next injection. The MS system was operated at ESI^+ mode, cone voltage 30 V, capillary voltage 3 kV, desolvation temperature 280 °C, source temperature 100 °C, desolvation gas $500\,L\,h^{-1}$, and MS/MS collision energy 15–35 eV.

3. Results and discussion

3.1. Accelerated chlorination

The effect of Br^- and I^- on the chlorination kinetics of DCF was investigated firstly. The change of the normalized DCF concentration with reaction time is shown in Fig. 1. During chlorination alone, the removal of DCF after 20 min was < 65%, while in the presence of 500 $\mu g\,L^{-1}$ Br^- or I^-, the transformation of DCF was accelerated obviously. For the chlorination of an organic compound, first-order kinetics was generally observed with respect to each reactant [22]. The good linearity of the fitting curves clearly indicates that DCF was a first-order reactant in this reaction (Eq. (4), $R^2 > 0.99$). The degradation of DCF was promoted to different extents after the addition of Br^- or I^-. The observed pseudo-first-order degradation rate (k_{obs}) of DCF with 500 $\mu g\,L^{-1}$ Br^- ($0.018\,s^{-1}$) was found to be 25.7 folds of that during chlorination alone ($0.0007\,s^{-1}$). Although the k_{obs} value for chlorination with I^- ($0.0023\,s^{-1}$) was lower than that with Br^-, it was 3.3 folds of chlorination alone. Tian et al. also observed the k_{obs} value for the

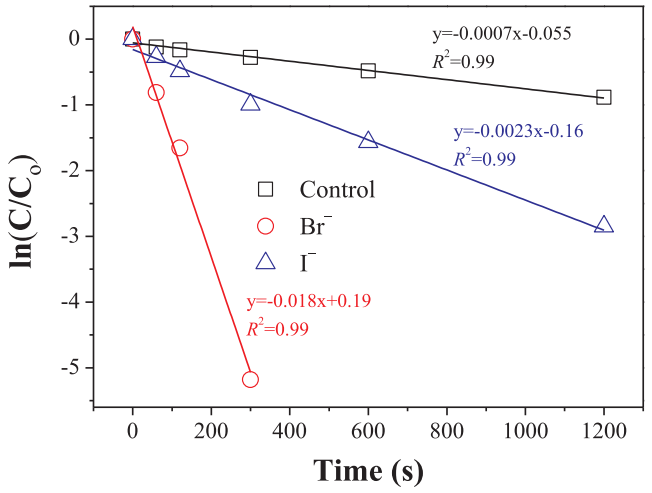

Fig. 1. Effect of Br^- and I^- on transformation kinetics of DCF. Experimental conditions: $[DCF]_o$ = 10 μM, $[HOCl]_o$ = 0.3 mM, $[Br^-$ or $I^-]_o$ = 500 μg L^{-1}, pH = 7.0 adjusted by 2 mM phosphorus buffer, 25 °C. DCF: diclofenac.

chlorination of dimethoate increased linearly with increasing Br^- concentrations (0–5 mg L^{-1}) [23]. Br^- and I^- can be easily oxidized by FC into FB and FI, which was found to oxidize organics at a much faster rate than FC [17]. Furthermore, FB and FI may be reverted to Br^- and I^-, respectively after reaction. The regenerated Br^- or I^- could be oxidized by FC again and participate in additional reactions with DCF. Therefore, Br^- and I^- tended to act as a catalyst during the chlorination of DCF. As pH influences the species distribution of DCF, FC, FB and FI, the measurement of species-specific apparent second-order rate constant (k_{app}) values would be essential for the modeling chlorination, bromination and iodination rates of DCF under different water qualities.

$$d[DCF]_{tot}/dt = k_{obs}[DCF]_{tot} \quad (4)$$

3.2. Kinetics for chlorination, bromination and iodination of DCF

Generally, the second-order rate constant for the chlorination of DCF shows pH-dependence, which could be explained by considering the speciation of both chlorine and DCF species in Eq. (5).

$$d[DCF]_{tot}/dt = k_{app}[Oxidant]_{tot}[DCF]_{tot} = \sum_{\substack{i=1,2 \\ j=1,2}} k_{ij}\alpha_i\beta_j[Oxidant]_{tot}[DCF]_{tot} \quad (5)$$

where k_{app} is the apparent second-order rate constant for the reaction between DCF with FH, $[Oxidant]_{tot}$ = $[HOX]$ + $[OX^-]$, $[DCF]_{tot}$ = $[DCF]$ + $[DCF^-]$, α_i and β_j are the molar fraction of oxidant and DCF, i and j are each of the two oxidant species and two DCF species, respectively, and k_{ij} is the species-specific second-order rate constant for the reaction between the oxidant species i with the DCF species j.

Then the kinetics could be modeled with Eq. (6) and a kinetic model was developed in order to predict the variation in apparent rate constants with the pH values and the expression of $k_{HOX\text{-}DCF}$ during chlorination, bromination and iodination can be formulated as Eq. (7). Then the intrinsic second order rate constant values for each elementary reaction in Table 1 were determined by a nonlinear least-squares regression with SPSS 16.0 Software [24]. As shown in Fig. 2, the calculated values of $k_{app,X\text{-}DCF}$ were modeled by considering the reactions in Table 1 (where X represents Cl, Br or I for chlorination, bromination or iodination experiments).

$$d[DCF]_{tot}/dt = (k_1\alpha_1\beta_1 + k_2\alpha_1\beta_2 + k_3\alpha_2\beta_1 + k_4\alpha_2\beta_2)[Oxidant]_{tot}[DCF]_{tot} \quad (6)$$

Table 1
Elementary reactions considered for chlorination, bromination and iodination of DCF.

Reactions	Chlorination	Bromination	Iodination
HOX → H^+ + OX^-[a]	pK_a = 7.5	pK_a = 8.8	pK_a = 10.4
HOX + DCF → Products	0.18	512	135
HOX + DCF^-→Products	3.52	9504	2816
OX^- + DCF → Products	0.03	85	21.2
OX^- + DCF^-→Products	0.16	414	152

[a] (X indicates Cl, Br or I).

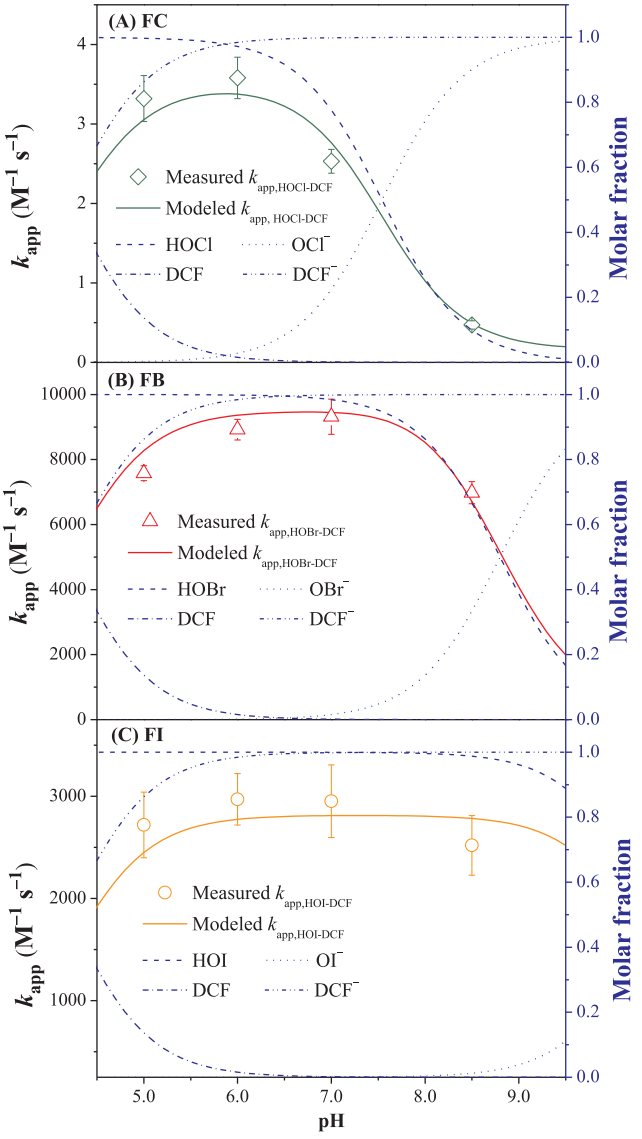

Fig. 2. Measured and modeled pH dependence of the apparent second order rate constants (k_{app}) for the reactions of DCF with free chlorine (A), free bromine (B) and free iodine (C) and pH-dependent speciation of active species.

$$k_{app,oxidant-DCF} = \frac{k_1[H^+]^2 + k_2K_{a2}[H^+] + k_3[H^+]K_{a1} + k_4K_{a1}K_{a2}}{([H^+] + K_{a2})([H^+] + K_{a1})} \quad (7)$$

As shown in Fig. 2, fairly good correlations between measured and modeled values for the reactions of DCF with FC, FB and FI were obtained at pH 5.0–8.5. The results obtained for the chlorination at pH 5.0–8.5 are shown in Fig. 2A. The first order reaction relative to chlorine was checked by varying the initial chlorine concentration. According to these results, the apparent second order rate constants

from 0.47 to 3.58 $M^{-1} s^{-1}$ were obtained for the chlorination of DCF at pH 5.0–8.5. And the values of rate constants obtained from these calculations for reactions between HOCl and DCF, HOCl and DCF^-, OCl^- and DCF, OCl^- and DCF^- were 0.18, 3.52, 0.03 and 0.16 $M^{-1} s^{-1}$ respectively. Rate constants obtained for neutral and acid-catalysed reactions with ionized forms of DCF are larger than the respective constants obtained with neutral form of DCF. The $k_{app,FC\text{-}DCF}$ of FC and DCF decreased when pH was > 6.0, which could be well explained by species-specific reactions between FC and DCF species.

As shown in Fig. 2B, the measured $k_{app,FB\text{-}DCF}$ levels (6890–9320 $M^{-1} s^{-1}$) for bromination of DCF at pH 5.0–8.5 were about three orders of magnitude higher than $k_{app,FC\text{-}DCF}$ for chlorination of DCF. Similarly, the pH profiles of the $k_{app,FB\text{-}DCF}$ can be explained by considering the individual reactions of HOBr/BrO^- with both undissociated and dissociated forms of DCF. The k_{app} value of HOBr with DCF^- are one to four orders of magnitude higher than the other individual reaction rate constants, which controls the overall reaction rate at pH 5.0–8.5. The $k_{app,FB\text{-}DCF}$ was less influenced by pH than FC [25].

Fig. 2C shows the measured and modeled $k_{app,FI\text{-}DCF}$ values for iodination of FI at pH 5.0–8.5, which were in the range of 2000–3000 $M^{-1} s^{-1}$. Similar with the chlorination and bromination, the specific reaction between HOI and DCF^- species control the iodination rate of DCF. The $k_{app,FI\text{-}DCF}$ values were about three orders of magnitude higher than $k_{app,FC\text{-}DCF}$ values at pH 5.0–8.5, which could explain the accelerated chlorination of DCF with I^-. However, the $k_{app,FI\text{-}DCF}$ values were always lower than $k_{app,FB\text{-}DCF}$ values. Meanwhile, chlorination of I^--containing water would usually lead to IO_3^- formation (Eq. (8)) [26], which would consume the formed FI. That is why the chlorination rate of DCF with I^- is always lower than that with Br^- in Fig. 1. After the kinetic comparison of chlorination, bromination and iodination of DCF, it is clear to for the accelerated chlorination of DCF with Br^- or I^-. However, FC, formed FB, and FI may lead to the formation of chlorinated, brominated, iodinated and mixed DBPs.

$$2HOCl + HOI \rightarrow IO_3^- + 2Cl^- + 3H^+ \quad (8)$$

3.3. Enhanced formation of DBPs

In drinking water treatment plants, the high reactivity of bromine with phenol-like organic structures led to the formation of brominated DBPs during chlorination. Using model compounds for the reactive moieties in NOM, previous study reported that rapid production of DBPs over seconds to minutes occurs via chlorination of polyhydroxy aromatic functional groups as well as diketone and keto-carboxylic moieties [27]. Arnold et al. investigated the $CHCl_3$ formation during the chlorination of resorcinol, acetylacetone, acetophenone and lake water. Phenols and other functional groups in NOM are proposed to be chloroform precursors [28]. The molecular structure of DCF has two phenol-like groups, indicating the possibility of DBPs formation during the chlorination of DCF. Moreover, in the presence of Br^- or I^- ions, the formed FB and FI may influence the DBPs species and formation amounts. Thus, the DBPs formation as a function of initial halide concentration during chlorination of DCF was investigated. Fig. 3A illustrates the DBPs formation at varying levels of Br^-. With the increase of Br^- concentration from 0 to 50 μM, the formation amounts of DBPs was increased from 67.2 to 292.0 μg L^{-1}. Meanwhile, increasing Br^- concentration notably shifted the DBPs towards those containing more bromine (e.g., $CHBr_3$ and $CHClBr_2$). $CHBr_3$ became the dominant DBPs when the initial Br^- concentration reached 50 μM. Overall, the formation patterns of DBPs in the presence of Br^- or I^- were quite similar. When the initial I^- concentration was increased from 0 to 50 μM, the formation amounts of DBPs (67.2–87.3 μg L^{-1}) were always higher than that of chlorination alone. However, the formation amounts of DBPs during the chlorination of DCF with I^- were always lower than those with Br^-. There are two reasons for the different enhanced extent with Br^- and I^-: (1) higher reaction rate for FB with DCF than that of

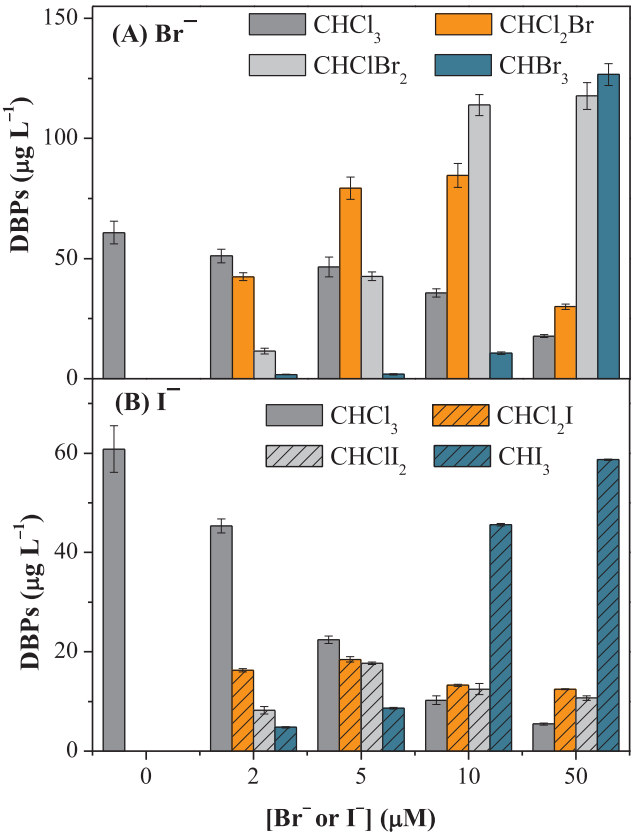

Fig. 3. Effect of initial halide concentration on DBPs formation during chlorination of DCF. Experimental conditions: $[DCF]_o$ = 10 μM, $[HOCl]_o$ = 0.7 mM, pH = 7.0 adjusted by 2 mM phosphrous buffer, reaction time = 72 h, 25 °C.

FI; and (2) HOI could be further oxidized to IO_3^- by FC (Fig. S1) while BrO_3^- formation during the chlorination of Br^- is a very slow process.

3.4. TBPs and pathways

The TBPs of DCF during chlorination, chlorination with Br^- and chlorination with I^- were further analyzed by UPLC-QTOF-MS/MS. The chemical structural of the TBPs were based on the analysis of the total ion chromatogram (TIC) in Figs. S2–4 and the corresponding mass spectra with consideration of isotopic abundance. Due to higher response in positive mode for TBPs, the masses of the different TBPs were determined from the peaks corresponding to the protonated molecule ($[M + H]^+$). In addition to DCF peak, 14 major peaks of TBPs have been tentatively analyzed. The overall retention time (t_R), *m/z*, proposed formula and structure of the 14 TBPs are shown in Table S1.

The transformation pathways of DCF were proposed on the basis of the identified TBPs in Fig. 4A for chlorination, Fig. 4B for chlorination with Br^-, and Fig. 4C for chlorination with I^-. As shown in Fig. 4A, seven TBPs have been identified during chlorination of DCF. The transformation of DCF molecular during chlorination proceeded through three pathways: (1) Hydroxylation reaction of DCF promoted by OH leading to hydroxylated DCF (TBPs 1 and 4) formation, and the oxidation of phenolic hydroxyl group, leading to the formation of TBPs 6 and 7. (2) Decarboxylation reaction resulting with the formation of decarboxy-DCF (TBP 2) as the primary degradation route of DCF with FC. (3) Chlorination reaction with the expected nucleophilic attack of chlorine giving chloro-DCF (TBPs 3 and 5) formation [29,30].

The chlorination of DCF with Br^- exhibited similar pathways. Hydroxylated (TBPs 8 and 10) and decarboxylated TBP (TBP 11) were identified with the presence of Br^-. Brominated TBPs (TBPs 11–13) were observed during the chlorination of DCF with Br^-. In addition to

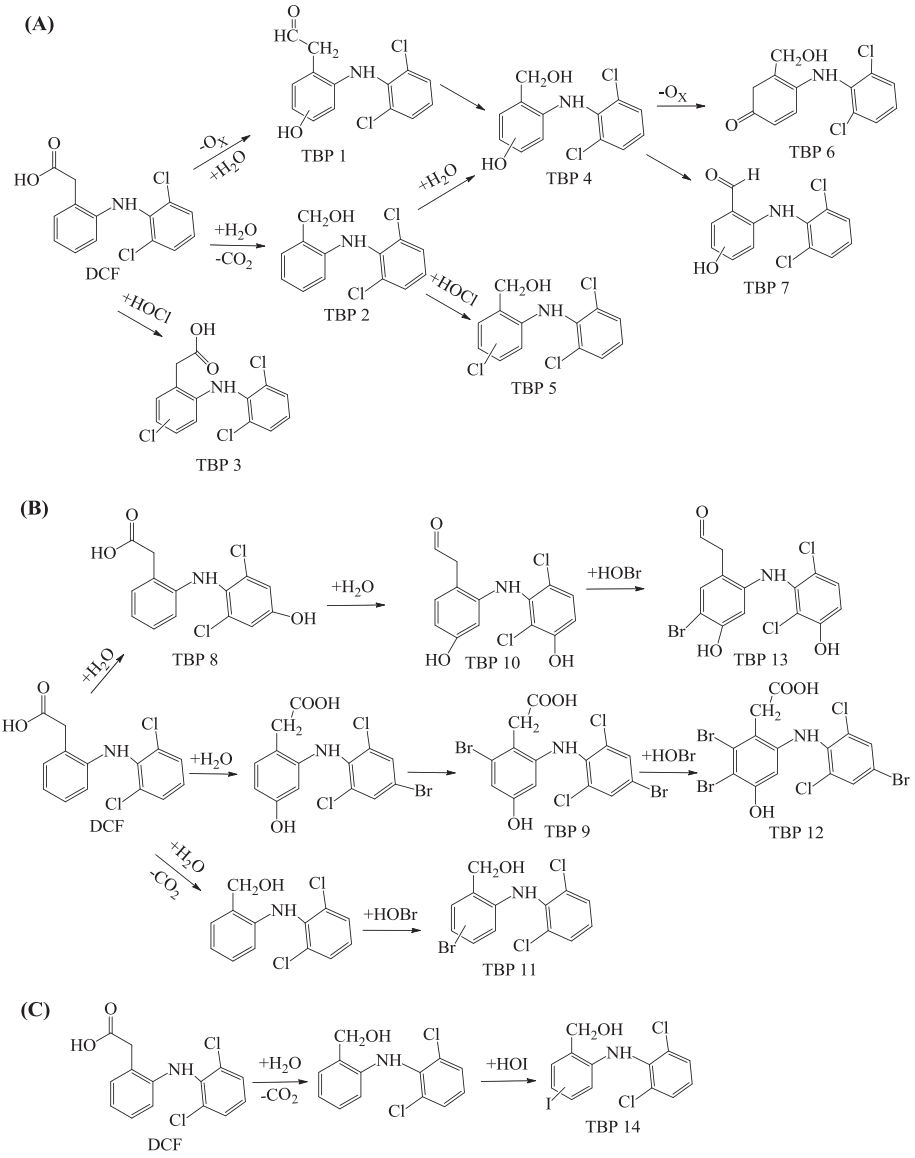

Fig. 4. Proposed transformation pathways of DCF during chlorination (A), chlorination with Br^- (B) and chlorination with I^- (C).

specific reactions on certain moieties bound to the aromatic ring, FB reacts with aromatic compounds mostly by electrophilic substitutions, which occur mainly in ortho or para position to a substituent [4]. The TBPs of chlorination of DCF with I^- was rather limited in this study. Only decarboxylated and iodinated TBP 14 was identified during the reaction. The rapid reaction between FC and I^- may lead the formation of IO_3^- and I-DBPs, which limited the formation of other TBPs. Meanwhile, because of the consuming of FC by I^-, the formation of chlorinated TBPs was lower than those of chlorination and chlorination with Br^-. However, the formation of I-DBPs, which are more cytotoxic, mutagenic, and genotoxic than their chlorinated and brominated analogues, would inevitably increase the toxicity of treated samples [16,17].

4. Conclusions

In this work, the effects of Br^- and I^- on the chlorination of DCF were investigated. Based on the experimental results, the following conclusions can be drawn:

- The presence of Br^- and I^- accelerated the chlorination of DCF with different extents.
- The k_{app} for the reaction of DCF with FB at pH 7.0 was determined to be 9320 $M^{-1} s^{-1}$, which was 3680 and 3.2 folds of the reactions between DCF with FC and FI, respectively.
- The $k_{app,FC\text{-}DCF}$ value was highly pH dependent, while the $k_{app,FB\text{-}DCF}$ and $k_{app,FI\text{-}DCF}$ were less influenced than FC at pH 5.0–8.5.
- Increasing Br^- and I^- concentrations enhanced the formation amounts and altered the speciation of DBPs.
- The DCF transformation pathways mainly proceeded through hydroxylation, decarboxylation and substitution reactions.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.seppur.2017.09.068.

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