Article

Degradation Kinetics and Disinfection By-Product Formation of Iopromide during UV/Chlorination and UV/Persulfate Oxidation

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Abstract: As the detection of micropollutants in various water resources is commonly reported, developing an efficient technology to remove them to maintain water safety has become a major focus in recent years. The degradation kinetics of iopromide, one of a group of iodinated X-ray contrast media (ICM), using advanced oxidation processes of ultraviolet/chlorination (UV/Cl₂) and UV/persulfate (UV/PS) oxidation were investigated in this research. The results show that iopromide degradation fitted pseudo-first-order kinetics, and the rate constants were calculated as $2.20 (\pm 0.01) \times 10^{-1} \text{ min}^{-1}$ and $6.08 (\pm 0.10) \times 10^{-2} \text{ min}^{-1}$ in UV/Cl₂ and UV/PS, respectively. In the two systems, the degradation rates were positively correlated with the initial concentrations of HOCl and PS, respectively. In the UV/Cl₂ system, the degradation rate of iopromide reached a maximum at pH 7, while in the UV/PS system, pH had only a slight effect on the degradation rate. Chloride in water had a negligible effect on iopromide degradation, whereas bromide inhibited iopromide degradation in the UV/Cl₂ system. The contributions of UV irradiation, •OH, and RCS to iopromide degradation during UV/Cl₂ treatment were calculated as 20.8%, 54.1%, and 25.1%, respectively. One carbonated and three nitrogenated disinfection by-products (C-DBP (chloroform) and N-DBPs (dichloroacetonitrile, trichloronitromethane, and trichloroacetone)) were detected at relatively high levels, along with three emerging iodinated DBPs (dichloriodomethane, monochlorodiodomethane, and triiodomethane). More C- and N-DBPs were generated in the UV/Cl₂ and UV/PS systems than in UV irradiation, while considerably higher I-DBPs were generated in UV irradiation than in the other two systems. Thus, it is essential to pay attention to DBP formation when UV/Cl₂ or UV/PS is used to treat iopromide in water. In order to better control the generation of carcinogenic and toxic I-DBPs, Cl₂ or PS combined with UV should be adopted for iopromide degradation, instead of UV alone, for providing safe drinking water to the public.

Keywords: iodinated X-ray contrast media (ICM); kinetics; UV/chlorination; UV/persulfate oxidation; contribution of radicals; disinfection by-products (DBPs)

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1. Introduction

Iodinated X-ray contrast media (ICM) such as iohexol, iopromide, iopamidol, iomeprol, and diatrizoate are widely used in radiological investigations for imaging body organs or blood vessels [1,2]. ICM cannot be effectively removed by conventional wastewater treatment processes and is discharged into the aqueous environment. Therefore, ICM have been detected in many rivers and streams (up to $\mu\text{g L}^{-1}$ in many countries) [3,4]. Iopromide is one of the most commonly used X-ray contrast media, and it remains almost unchanged

after entering the body [5]. Iopromide has been detected in many water bodies [6], in concentrations ranging from ng L^{-1} to $\mu\text{g L}^{-1}$ in wastewater and surface water [7]. It is reported that disinfectants can react with natural organic matter (NOM), bromide, and iodide during drinking-water treatment to form various disinfection by-products (DBPs) [8]. Although ICM themselves have no adverse effects on living creatures, they are thought to produce iodine, which results in the formation of emerging iodinated DBPs (I-DBPs), mainly including iodinated trihalomethanes (I-THMs) and iodo-acids (I-Acids) [9]. I-DBPs are of higher cytotoxicity and genotoxicity than their chlorinated and brominated analogues, and therefore they have attracted widespread attention [10,11]. Moreover, I-DBPs in drinking water can cause taste and odor problems, especially CHI_3 which has a sensory threshold concentration of $1 \mu\text{g L}^{-1}$ [12]. A study indicated that iopamidol can react with chlorine to form trichloroacetic acid (TCAA), chloroform (CHCl_3), and dichloriodomethane (CHCl_2I) [13]. Therefore, it is essential to remove ICM from source water. The physical properties of iopromide are summarized in Table 1.

Table 1. The physical properties of iopromide.

Compound	Molecular Formula	Chemical Structure	Molecular Weight
Iopromide	$\text{C}_{18}\text{H}_{24}\text{I}_3\text{N}_3\text{O}_8$		791.11

According to the previous literature, the degradation efficiency of the traditional oxidation process for ICM is not ideal [14–16]. With the development of advanced oxidation processes (AOPs), UV/chlorine (UV/Cl_2) has been successfully applied for degrading micropollutants in recent years [17]. Other AOPs including $\text{UV/H}_2\text{O}_2$, UV/persulfate (UV/PS), and $\text{UV/peroxymonosulfate}$ can also effectively degrade ICM due to the generation of $\bullet\text{OH}$ and $\bullet\text{SO}_4^-$ possessing high redox potentials (1.8–2.7 and 2.5–3.1 V, respectively) [16]. Wu et al. investigated diatrizoate degradation by UV/Cl_2 and found that the reactive chlorine species (RCS) are major contributors to diatrizoate degradation [1]. Compared with UV/Cl_2 , both iopamidol and diatrizoate could be degraded effectively by $\text{UV/H}_2\text{O}_2$ [18]. UV/PS has been proven to be more efficient than $\text{UV/H}_2\text{O}_2$ for diatrizoate degradation, and $\bullet\text{SO}_4^-$ is the dominant reactive species in UV/PS oxidation. The second-order rate constant of $\bullet\text{SO}_4^-$ with diatrizoate was calculated as $1.90 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [19,20]. However, to the best of our knowledge, there is currently no literature reporting the degradation kinetics of iopromide during UV/Cl_2 and UV/PS AOPs.

Therefore, the purpose of this research was: (1) to investigate the degradation kinetics of iopromide during chlorination, UV photolysis, UV/Cl_2 , and UV/persulfate , (2) to investigate the effects of different oxidant concentrations, pH values, and chloride and bromide concentrations on iopromide degradation, (3) to investigate the contribution of various radicals to the degradation of iopromide by UV/Cl_2 , and (4) to evaluate the C-, N-, and I-DBPs formed in the sequential chlorine disinfection process.

2. Materials and Methods

2.1. Chemicals and Regents

All reagents used were at least analytical grade in this study. Iopromide ($\geq 99\%$) was obtained from Pharmacopeia (Rockville, MD, USA). Sodium hypochlorite solution (NaClO , available chlorine: 4.00–4.99%) was purchased from Sigma-Aldrich (St. Louis, MO, USA).

Sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) was purchased from Aladdin (Shanghai, China). Sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), potassium dihydrogen phosphate (KH_2PO_4), sodium acetate trihydrate ($\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$), sodium chloride (NaCl), sodium bromide (NaBr), sodium bicarbonate (NaHCO_3), sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), tert-butanol (TBA), and ethanol (EtOH) were obtained from the Pharmaceutical Group Chemical Reagent Co., Ltd. (Shanghai, China). Chromatographically pure reagent grade methanol (CH_3OH) and methyl tert-butyl ether (MtBE) were acquired from J.T. Baker (Carpinteria, CA, USA). The I-THM standards including dichloriodomethane (CHCl_2I), chlorodiodomethane (CHClI_2), and triiodomethane (CHI_3) were obtained from CanSyn Chemical Corp. (Toronto, ON, Canada). Mixed C- and N- DBP standards including chloroform (CF), trichloroethane, trichloroethylene, tetrachloroethylene, dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), trichloronitromethane (TCNM), and 1,1,1-trichloroacetone (1,1,1-TCP) were obtained from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Experimental Procedures

A bench-scale reactor equipped with a low-pressure Hg UV mercury lamp (11 W, 254 nm, 4P-SE, Philips, Shanghai, China) was used to conduct the experiments. The UV intensity was determined as 1.12 mW/cm^2 using a UV radiometer (UV-C luxometer, Photoelectric Instrument Factory of Beijing Normal University, Beijing, China). Before the beginning of each experiment, the UV lamp was warmed up for 30 min to obtain a stable UV emission. A total of 100 mL of iopromide solution ($10 \mu\text{M}$) was prepared for UV/ Cl_2 and UV/PS oxidation experiments, with the pH adjusted to 7.0. Then, an appropriate amount of NaClO (100 mM) or PS (1 M) was added into the reactor to achieve the desired dosage (25–200 μM for NaClO and 1–5 mM for PS). During each experiment, 1 mL of sample was withdrawn at certain time intervals and transferred to a high-performance liquid chromatography vial containing 30 μL of $\text{Na}_2\text{S}_2\text{O}_3$ (0.1 M for UV/ Cl_2) or excess methanol (for UV/PS) to terminate the reaction. All samples were analyzed using HPLC. Duplicate experiments were performed.

The contribution of radicals to the degradation of iopromide by UV/ Cl_2 was examined by adding TBA or EtOH as a radical scavenger for the reaction, with an oxidant (100 μM)/iopromide (10 μM) molar ratio of 10 at pH 7.

The experiments for DBP formation were conducted in 45 mL screw-cap glass vials with PTFE Sep under a headspace-free condition in a dark environment at $25 \pm 1^\circ\text{C}$. After 3 d, the samples were quenched using $\text{Na}_2\text{S}_2\text{O}_3$ (for UV/ Cl_2) or excess methanol (for UV/PS) and extracted using MtBE for DBP analysis using gas chromatography (GC).

2.3. Analytical Methods

The concentration of iopromide was analyzed using an HPLC system (Agilent 1200, Palo Alto, CA, USA) equipped with an XTerra MS column (5 μm , $250 \text{ mm} \times 4.6 \text{ mm}$, Waters, Milford, CT, USA) and a UV spectrophotometer at the 242 nm wavelength. A 10 μL sample was injected with 88% mobile phase and 12% acetic acid in ultra-pure water (pH 4) at a flow rate of 1.0 mL/min at 30°C . The detection limit of iopromide was 1 μM .

The pH values of the solutions were detected by using a regularly calibrated pH meter (FE20 FiveEasy, Mettler Toledo, Switzerland). The concentration of chlorine was measured using the N, N-diethyl-p-phenylenediamine (DPD) colorimetric method [21]. The concentration of persulfate was determined with a spectrophotometer (UV-2800, Unicoinstruments Co., Ltd., Shanghai, China) at a wavelength of 352 nm [22].

The formation of DBPs was analyzed according to the US EPA Method 551.1 [23]. Samples were quenched and extracted using MtBE for the analysis using a GC (GC-2010 Plus, Shimadzu, Japan) equipped with an Rtx-5 column (30 m $\times$ 0.25 mm internal diameter, 0.25 μm film thickness, J&W, Palo Alto, CA, USA).

3. Results and Discussion

3.1. Kinetics of Iopromide Degradation during UV Photolysis, UV/Cl₂, and UV/PS Oxidation

In order to elucidate the correlation between iopromide degradation and time, different reaction systems including UV photolysis, chlorination, persulfate, UV/Cl₂ and UV/persulfate systems were investigated. As shown in Figure 1, UV/Cl₂ could degrade iopromide most effectively, followed by UV/PS and UV photolysis, but not chlorination and persulfate alone. The degradation fitted pseudo-first-order kinetics well, as expressed in Equation (1):

$$\frac{-d[\text{iopromide}]}{dt} = k_{\text{obs}}[\text{iopromide}]_t \quad (1)$$

Figure 1. Pseudo-first-order kinetics plot of iopromide degradation during chlorine, persulfate, UV photolysis, UV/Cl₂, and UV/PS oxidation. Experimental conditions: [iopromide]₀ = 10 μM, [HOCl]₀ = [persulfate]₀ = 100 μM, UV intensity = 1.12 mW cm^{−2}, [phosphate buffer]₀ = 10 mM, pH = 7, and temperature = 25 °C.

By using the data in Figure 1, the k_{obs} values of iopromide degradation during UV photolysis, UV/Cl₂, and UV/PS can be calculated as $4.58 (\pm 0.02) \times 10^{-2}$, $2.20 (\pm 0.01) \times 10^{-1}$, and $6.08 (\pm 0.10) \times 10^{-2} \text{ min}^{-1}$, respectively. The k_{obs} values for UV/Cl₂ and UV/PS were greater than the value for UV irradiation alone due to the generation of $\bullet\text{OH}$, $\bullet\text{SO}_4^-$, and RCS [24].

3.2. Effects of Different Initial HOCl and PS Concentrations on Iopromide Degradation by UV/Cl₂ and UV/PS Oxidation

The effects of oxidant concentration on the degradation of iopromide in the UV/Cl₂ and UV/PS processes were studied (Figure S1). As displayed in Figure 2a, the degradation of iopromide with different initial chlorine concentrations during UV/Cl₂ fitted a pseudo-first-order kinetics model well ($R^2 > 0.99$). The k_{obs} of iopromide increased from $4.58 (\pm 0.20) \times 10^{-2}$ to $3.47 (\pm 0.11) \times 10^{-1} \text{ min}^{-1}$ as the chlorine concentration increased from 0 (UV alone) to 200 μM. The lower-left insert in Figure 2a shows a linear relationship between k_{obs} and the chlorine concentration, with $R^2 = 0.973$, which indicates that the rate of iopromide degradation during UV/Cl₂ is first order with respect to chlorine concentration. As the chlorine concentration increases, free chlorine can produce a series of radicals including $\bullet\text{OH}$ and RCS under UV irradiation, enhancing the rate of iopromide degradation, as expressed in Equations (2) and (3):

$$\begin{aligned} \frac{-d[\text{iopromide}]}{dt} &= k_{\text{UV/chlorine}}[\text{iopromide}]_t \\ &= k_{\text{UV}}[\text{iopromide}]_t + k_{\bullet\text{OH}}[\text{iopromide}]_t + k_{\text{RCS}}[\text{iopromide}]_t \end{aligned} \quad (2)$$

$$k_{\text{UV/chlorine}} = k_{\text{UV}} + k_{\bullet\text{OH}} + k_{\text{RCS}} \quad (3)$$

where $k_{\text{UV/chlorine}}$ and k_{UV} represent the observed pseudo-first-order reaction rate constants of iopromide degradation during UV/ Cl_2 and UV photolysis, respectively, and $k_{\bullet\text{OH}}$ and k_{RCS} represent the pseudo-first-order reaction rate constants of iopromide degradation by $\bullet\text{OH}$ and RCS, respectively.

Figure 2. Effects of different oxidant concentrations on iopromide degradation during (a) UV/ Cl_2 and (b) UV/PS oxidation. Experimental conditions: [iopromide] $_0$ = 10 μM , UV intensity = 1.12 mW cm^{-2} , [phosphate buffer] $_0$ = 10 mM , pH = 7, and temperature = 25 $^\circ\text{C}$. Error bars represent one standard deviation of duplicate measurements.

On the other hand, iopromide degradation also fitted pseudo-first-order kinetics well at different PS concentrations, as displayed in Figure 2b. The k_{obs} for iopromide degradation increased considerably from $6.14 (\pm 0.18) \times 10^{-2}$ to $1.09 (\pm 0.02) \times 10^{-1} \text{ min}^{-1}$ as the PS dosage increased from 1 mM to 5 mM , by increasing the formation of oxidizing radicals ($\bullet\text{OH}$ and $\bullet\text{SO}_4^-$), as shown in Equations (4) and (5) [25].

3.3. Contributions of Radicals to Iopromide Degradation by UV/ Cl_2

It has been reported that during UV/ Cl_2 , $\bullet\text{OH}$ and $\bullet\text{Cl}$ were the dominant radicals for the degradation of benzoic acid, while the effects of other reactive species such as $\bullet\text{Cl}_2^-$ and $\bullet\text{O}^-$ were negligible [26]. To determine the contributions of radicals in iopromide degradation in the UV/ Cl_2 system, radical scavenging experiments were performed with the addition of excessive TBA and EtOH. TBA reacts with $\bullet\text{Cl}$ with a rate constant of $1.8 \times 10^{10} \text{ M}^{-1} \text{ min}^{-1}$, whereas the rate constant for the reaction of TBA with $\bullet\text{Cl}_2^-$ is $2.1 \times 10^4 \text{ M}^{-1} \text{ min}^{-1}$ [27,28]. As shown in Figure 3, the k_{obs} values of iopromide during UV/ Cl_2 decreased to $1.64 (\pm 0.06) \times 10^{-1}$ and $1.01 (\pm 0.02) \times 10^{-1} \text{ min}^{-1}$ in the presence of 100 mM TBA and EtOH, respectively, while the degradation of iopromide dropped from 84.2% to 74.7% and 56.7%, respectively, after 8 min of reaction time. As displayed in Figure 4, the calculated contributions of UV irradiation, $\bullet\text{OH}$, and RCS to the degradation of iopromide were 20.8%, 54.1%, and 25.1%, respectively (Equations (6)–(8)). The radicals formed in the UV/ Cl_2 system enhanced the iopromide degradation. It has been reported that the rate constant of the reaction of $\bullet\text{OH}$ with iopromide was $3.34 \pm (0.14) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ using γ -irradiation [29], while there has been little research on the rate constant of $\bullet\text{Cl}$

with iopromide. Therefore, the role of $\bullet\text{Cl}$ should not be neglected in the degradation of iopromide.

$$(k_{\text{obs,UV}}/k_{\text{obs,UV/Cl}_2}) \times 100\% \quad (6)$$

$$(k_{\text{obs,UV/Cl}_2} - k_{\text{obs,EtOH}})/k_{\text{obs,UV/Cl}_2} \times 100\% \quad (7)$$

$$(1 - (k_{\text{obs,UV}}/k_{\text{obs,UV/Cl}_2}) - (k_{\text{obs,UV/Cl}_2} - k_{\text{obs,EtOH}})/k_{\text{obs,UV/Cl}_2}) \times 100\% \quad (8)$$

Figure 3. Effects of two radical scavengers on iopromide degradation during UV/Cl₂. Experimental conditions: [iopromide]₀ = 10 μM, [HOCl]₀ = 100 μM, [TBA]₀ = [EtOH]₀ = 100 mM, UV intensity = 1.12 mW cm^{−2}, [phosphate buffer]₀ = 10 mM, pH = 7, and temperature = 25 °C.

Figure 4. Contribution rates of different radicals to iopromide degradation during UV/Cl₂. Experimental conditions: [iopromide]₀ = 10 μM, [HOCl]₀ = 100 μM, [TBA]₀ = [EtOH]₀ = 100 mM, UV intensity = 1.12 mW cm^{−2}, [phosphate buffer]₀ = 10 mM, pH = 7, and temperature = 25 °C.

3.4. Effects of Solution pH on Iopromide Degradation by UV/Cl₂ and UV/PS

As illustrated in Figure 5a, at pH 7 the rate of iopromide degradation in UV/Cl₂ reached a maximum and then decreased as the pH increased further to pH 9. In the UV/Cl₂ system, chlorine is dissociated into OCl[−], which can form $\bullet\text{OH}$ and $\bullet\text{Cl}$ under UV irradiation (Equations (9) and (10)) [26,30]. As the solution pH changed, chlorine speciations were affected [31]. The acid dissociation constant (pK_a) of HOCl is 7.5, so the solution was dominated by HClO at pH ≤ 7.5. Compared to OCl[−], HOCl is more effective for inactivating *Escherichia coli* and other pathogens in drinking water [32]. However, in the previous experiments, chlorination could not degrade iopromide effectively (Figure 1 at pH 7). Although HOCl has no degradation effect on iopromide, the difference in HOCl/OCl[−]

distribution in water can affect the UV absorbance and quantum yield of the solution. [33]. Under 254 nm irradiation, the quantum yields of HOCl and OCl[−] photolysis at room temperature were determined to be 1.45 and 0.97, respectively [34].

Figure 5. Effects of different pH values on iopromide degradation during (a) UV/Cl₂ and (b) UV/PS oxidation. Experimental conditions: [iopromide]₀ = 10 μM, [HOCl]₀ = [PS]₀ = 100 μM, UV intensity = 1.12 mW cm^{−2}, [phosphate buffer]₀ = 10 mM, and temperature = 25 °C.

In Figure 5b, pH had a minor effect on the degradation of iopromide via UV/PS oxidation, which can be explained as follows. (1) According to the literature, under acidic and neutral conditions $\bullet\text{SO}_4^-$ is the predominant radical [35]. (2) At pH ≥ 7, the $\bullet\text{SO}_4^-$ can be converted to $\bullet\text{OH}$ according to Equations (11) and (12) [36]. The redox potential of $\bullet\text{SO}_4^-$ and $\bullet\text{OH}$ is 2.5–3.1 V and 1.8–2.7 V, respectively [37]. Although the difference from Figure 5b is not significant, the reaction rate constant under alkaline conditions is smaller.

3.5. Effects of Inorganic Ions on Iopromide Degradation by UV/Chlorination

Cl[−] exists widely in the water matrix, with concentrations ranging from 0 to 20 mM in surface water and wastewater effluent [38]. Thus, in this study, the influence of chloride on the degradation of iopromide was studied at concentrations of 0–20 mM. As seen in Figure 6a, the presence of Cl[−] has a negligible effect on the degradation of iopromide. The explanation for this phenomenon involves the reactions between Cl[−] and $\bullet\text{OH}$ to form $\bullet\text{ClOH}^-$ [39]. In addition, Cl[−] can react with $\bullet\text{Cl}$ to produce $\bullet\text{Cl}_2^-$ [40]. The produced $\bullet\text{ClOH}^-$ and $\bullet\text{Cl}_2^-$ can be decomposed into $\bullet\text{OH}$ and $\bullet\text{Cl}$ in a reversible manner [41].

Figure 6. Effects of (a) chloride and (b) bromide concentrations on the degradation of iopromide during UV/chlorination. Experimental conditions: $[iopromide]_0 = 10 \mu\text{M}$, $[\text{HOCl}]_0 = 100 \mu\text{M}$, UV intensity = 1.12 mW cm^{-2} , $[\text{phosphate buffer}]_0 = 10 \text{ mM}$, pH = 7, and temperature = 25°C .

Br^- can also compete for radicals with the target compounds. The concentration range of Br^- in this study was 0–20 mM. As displayed in Figure 6b, the degradation of iopromide was inhibited due to the presence of Br^- , because bromide can react rapidly with $\bullet\text{OH}$ to form $\bullet\text{BrOH}^-$ and act like a radical scavenger. The rate constant of the reaction of Br^- with $\bullet\text{OH}$ is $6.6 \times 10^{11} \text{ M}^{-1} \text{ min}^{-1}$ [42]. Accordingly, the k_{obs} value decreased from $2.20 (\pm 0.01) \times 10^{-1} \text{ min}^{-1}$ to $6.24 (\pm 0.24) \times 10^{-2} \text{ min}^{-1}$ as the bromide concentration increased from 0 to 20 mM.

3.6. Formation of DBPs during Iopromide Degradation in Different Oxidation Systems

In order to evaluate the formation of DBPs after iopromide oxidation in the sequential chlorine disinfection process, which is the most commonly applied disinfection process, various C-, N-, and I-DBPs were analyzed. The results are displayed in Figure 7. In the three systems, one C-DBP (CHCl_3) and three N-DBPs (dichloroacetonitrile (DCAN), trichloronitromethane (TCNM), and trichloroacetone (TCAN)) were detected at high concentrations. The concentrations of CHCl_3 and TCNM after UV/ Cl_2 were greater than those for UV irradiation alone, while the concentrations of DCAN and TCAN were similar in the UV and UV/ Cl_2 systems. In the UV/ Cl_2 system, the amounts of TCM and TCNM were greater than for UV irradiation. A similar phenomenon was also observed in the research of Qin et al. for the treatment of ronidazole in a UV/ Cl_2 system [43]. The concentrations of C- and N-DBPs in the UV/PS system were lower than those for UV irradiation and the UV/ Cl_2 system. On the other hand, three I-DBPs were detected (dichloromonoiodomethane (CHCl_2I), chlorodiiodomethane (CHClI_2), and triiodomethane (CHI_3)), and much higher amounts were formed in the system with UV alone compared to the UV/ Cl_2 and UV/PS oxidation systems. Because the benzene ring of iopromide contains iodine atoms, the organic iodine can be a precursor of I-DBPs in the drinking-water chlorine disinfection process [44]. The reason for the higher amounts of I-DBPs formed with UV alone than in UV/ Cl_2 and UV/PS can be explained by the conversion of I^- into stable IO_3^- in UV/ Cl_2 and UV/PS [45]. Accordingly, UV/ Cl_2 and UV/PS oxidation can reduce the generation of toxic I-DBPs effectively in the sequential chlorine disinfection process after iopromide degradation compared to UV irradiation, which is beneficial for providing safe drinking water to the public.

Figure 7. Formation of DBPs after UV irradiation, UV/Cl₂, and UV/PS oxidation of iopromide. Experimental conditions: [iopromide]₀ = 10 µM, [chlorine]₀ = [persulfate]₀ = 100 µM, UV intensity = 1.12 mW cm^{−2}, [phosphate buffer]₀ = 10 mM, pH = 7, incubation time = 3 d, and temperature = 25 °C. Error bars represent one standard deviation of duplicate measurements.

4. Conclusions

Iopromide could not be degraded by Cl₂ or PS oxidation alone, but could be degraded by UV irradiation, UV/Cl₂, and UV/PS oxidation. The degradation of iopromide fitted pseudo-first-order kinetics with the rate constants calculated as $4.58 (\pm 0.02) \times 10^{-2}$, $2.20 (\pm 0.01) \times 10^{-1}$, and $6.08 (\pm 0.10) \times 10^{-2} \text{ min}^{-1}$, in UV, UV/Cl₂, and UV/PS systems, respectively. In UV/Cl₂, k_{obs} was positively correlated with the initial concentration of HOCl. The presence of Cl[−] had only a slight effect on iopromide degradation, while Br[−] inhibited it. The contributions of UV irradiation, •OH, and RCS to the degradation of iopromide were estimated to be 20.8%, 45.9%, and 33.3%, respectively. The degradation rate of iopromide first increased and then decreased with increasing pH, with a maximum at pH 7. During UV/PS oxidation, the rate constant of iopromide degradation increased significantly with an increase in PS concentration, while the pH had a negligible effect. Compared with UV irradiation, more C- and N-DBPs were produced in the UV/Cl₂ and UV/PS systems, while much higher amounts of I-DBPs were produced in UV irradiation than in the other two systems. In order to better control the generation of carcinogenic and toxic I-DBPs, Cl₂ or PS in combination with UV should be adopted for iopromide degradation, instead of UV alone, for providing safe drinking water to the public.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w14030503/s1>, Figure S1: UV visible spectrum of iopromide degradation during chlorine.

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Abbreviations

ICM: iodinated X-ray contrast media; UV/Cl₂: ultraviolet/chlorination; UV/PS: UV/persulfate; DBPs: disinfection by-products; C-DBPs: carbonated DBPs; N-DBPs: nitrogenated DBPs; I-DBPs: iodinated DBPs; I-THMs: iodinated trihalomethanes; I-Acids: iodo-acids; AOPs: advanced oxidation processes; TBA: tert-butanol; EtOH: ethanol; MtBE: methyl tert-butyl ether; CF: chloroform; DCAN: dichloroacetonitrile; TCAN: trichloroacetonitrile; TCNM: trichloronitromethane; 1,1,1-TCP: 1,1,1-trichloroacetone; HPLC: high-performance liquid chromatography; GC: gas chromatography; DPD: N, N-diethyl-p-phenylenediamine.

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