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

Chenyen Hu 1,2, Qiangbing Wang 1, Yi-Li Lin 3,* , Yeye Zhu 1, Cun Xiong 1, Dandan Huang 1 and Ling Xu 1

1 College of Environmental and Chemical Engineering, Shanghai Engineering Research Center of Energy-Saving in Heat Exchange Systems, Shanghai University of Electric Power, Shanghai 200090, China; huchenyan@126.com (C.H.); 18297422290@163.com (Q.W.); dfisz@outlook.com (Y.Z.); cunxinxiaoniu@163.com (C.X.); 1782615927@163.com (D.H.); XuLing982@163.com (L.X.)
2 Shanghai Institute of Pollution Control and Ecological Security, Shanghai 200092, China
3 Department of Safety, Health and Environmental Engineering, National Kaohsiung University of Science and Technology, Kaohsiung 824, Taiwan
* Correspondence: yilin@nkust.edu.tw

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 (± 0.01) × 10⁻¹ min⁻¹ and 6.08 (± 0.10) × 10⁻² 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 (dichloroiodomethane, monochlorodiiodomethane, and trichloroacetone)) were detected at relatively high levels, along with three emerging iodinated DBPs (dichloroiodomethane, 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)

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 µg 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 μg 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$^-$, and therefore they have attracted widespread attention [10,11]. 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 | C$_{18}$H$_{24}$I$_3$N$_3$O$_8$ | ![Chemical Structure of Iopromide](image) | 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 UV/H$_2$O$_2$, UV/persulfate (UV/PS), and UV/peroxymonosulfate can also effectively degrade ICM due to the generation of $\bullet$OH and $\bullet$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 UV/H$_2$O$_2$ [18]. UV/PS has been proven to be more efficient than UV/H$_2$O$_2$ for diatrizoate degradation, and $\bullet$SO$_4$$^-$$^-$ is the dominant reactive species in UV/PS oxidation. The second-order rate constant of $\bullet$SO$_4$$^-$$^-$ with diatrizoate was calculated as 1.90 × 10$^6$ M$^{-1}$ 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 Regants

All reagents used were at least analytical grade in this study. Iopromide (≥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 (Na$_2$S$_2$O$_8$) was purchased from Aladdin (Shanghai, China). Sodium hydroxide (NaOH), sulfuric acid (H$_2$SO$_4$), potassium dihydrogen phosphate (KH$_2$PO$_4$), sodium acetate trihydrate (CH$_3$COONa·3H$_2$O), sodium chloride (NaCl), sodium bromide (NaBr), sodium bicarbonate (NaHCO$_3$), sodium thiosulfate (Na$_2$S$_2$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$_3$OH) and methyl tert-butyl ether (MtBE) were acquired from J.T. Baker (Carpinteria, CA, USA). The I-THM standards including dichloriodomethane (CHCl$_2$I), chlorodiiodomethane (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, 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 µM) 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 Na$_2$S$_2$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 ± 1 °C. After 3 d, the samples were quenched using Na$_2$S$_2$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 mm × 4.6 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, Unico Instruments 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 × 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):

\[-\frac{d[iopromide]}{dt} = k_{\text{obs}}[iopromide]_t\]

![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, [HOCI]₀ = [persulfate]₀ = 100 μM, UV intensity = 1.12 mW cm⁻², [phosphate buffer]₀ = 10 mM, pH = 7, and temperature = 25 °C.](image)

By using the data in Figure 1, the \(k_{\text{obs}}\) values of iopromide degradation during UV photolysis, UV/Cl₂, and UV/PS can be calculated as \(4.58 \times 10^{-2}\), \(2.20 \times 10^{-1}\), and \(6.08 \times 10^{-2}\) min⁻¹, respectively. The \(k_{\text{obs}}\) 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 HOCI 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 \(k_{\text{obs}}\) of iopromide increased from \(4.58 \times 10^{-2}\) to \(3.47 \times 10^{-1}\) 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 \(k_{\text{obs}}\) 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):

\[-\frac{d[iopromide]}{dt} = k_{\text{UV/chlorine}}[iopromide]_t\]
\[= k_{\text{UV}}[iopromide]_t + k_{\bullet\text{OH}}[iopromide]_t + k_{\text{RCS}}[iopromide]_t\]  
\(k_{\text{UV/chlorine}} = k_{\text{UV}} + k_{\bullet\text{OH}} + k_{\text{RCS}}\)
where \( k_{\text{UV}} \) and \( k_{\text{Cl}} \) 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 \( k_{\text{RCS}} \) 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 °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 \( k_{\text{obs}} \) for iopromide degradation increased considerably from 6.14 (± 0.18) × 10\(^{-2}\) to 1.09 (± 0.02) × 10\(^{-1}\) 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].

\[
\text{S}_2\text{O}_8^{2-} + \text{hv} \rightarrow 2\bullet \text{SO}_4^- 
\]

Equation (4)

\[
\bullet \text{SO}_4^- + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \bullet \text{OH} 
\]

Equation (5)

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 × 10\(^{10}\) M\(^{-1}\) min\(^{-1}\), whereas the rate constant for the reaction of TBA with \( \bullet \text{Cl}_2^- \) is 2.1 × 10\(^4\) M\(^{-1}\) min\(^{-1}\) [27,28]. As shown in Figure 3, the \( k_{\text{obs}} \) values of iopromide during UV/Cl\(_2\) decreased to 1.64 (± 0.06) × 10\(^{-1}\) and 1.01 (± 0.02) × 10\(^{-1}\) 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 ± (0.14) × 10\(^{9}\) M\(^{-1}\) 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 •Cl should not be neglected in the degradation of iopromide.

\[
\left( \frac{k_{\text{obs,UV}}}{k_{\text{obs,UV/Cl}_2}} \right) \times 100\% \quad \text{(6)}
\]

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

\[
(1 - \left( \frac{k_{\text{obs,UV}}}{k_{\text{obs,UV/Cl}_2}} \right) - \left( k_{\text{obs,UV/Cl}_2} - k_{\text{obs,EtOH}} \right) / k_{\text{obs,UV/Cl}_2} ) \times 100\% \quad \text{(8)}
\]

**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 •OH and •Cl under UV irradiation (Equations (9) and (10)) [26,30]. As the solution pH changed, chlorine speciations were affected [31]. The acid dissociation constant (pKa) 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].

\[
\text{HOCl} \leftrightarrow \text{OCl}^- + \text{H}^+ \quad (9)
\]

\[
\text{HOCl/OCl}^- \rightarrow \bullet \text{OH}/\bullet \text{O}^- + \bullet \text{Cl} \quad (10)
\]

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.

\[
\bullet\text{SO}_4^- + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \bullet\text{OH} + \text{H}^+ \quad (11)
\]

\[
\bullet\text{SO}_4^- + \text{OH}^- \rightarrow \text{SO}_4^{2-} + \bullet\text{OH} \quad (12)
\]

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 5](image-url) Effects of different pH values on iopromide degradation during (a) UV/Cl\(_2\) and (b) UV/PS oxidation. Experimental conditions: \([\text{iopromide}]_0 = 10 \mu\text{M}, [\text{HOCl}]_0 = [\text{PS}]_0 = 100 \mu\text{M}, \text{UV intensity} = 1.12 \text{mW cm}^{-2}, [\text{phosphate buffer}]_0 = 10 \text{mM}, \text{and temperature} = 25 ^\circ\text{C}.

![Figure 6a](image-url)
Figure 6. Effects of (a) chloride and (b) bromide concentrations on the degradation of iopromide during UV/chlorination. Experimental conditions: [iopromide]₀ = 10 μM, [HOCl]₀ = 100 μM, UV intensity = 1.12 mW cm⁻², [phosphate buffer]₀ = 10 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 •OH to form •BrOH⁻ and act like a radical scavenger. The rate constant of the reaction of Br⁻ with •OH is 6.6 × 10¹¹ M⁻¹ min⁻¹ [42]. Accordingly, the kₜₐₙ value decreased from 2.20 (± 0.01) × 10⁻¹ min⁻¹ to 6.24 (± 0.24) × 10⁻² 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 (CHCl₂) and three N-DBPs (dichloroacetoneitrile (DCAN), trichloronitromethane (TCNM), and trichloroacetone (TCAN)) were detected at high concentrations. The concentrations of CHCl₂ and TCNM after UV/Cl₂ were greater than those for UV irradiation alone, while the concentrations of DCAN and TCAN were similar in the UV and UV/Cl₂ systems. In the UV/Cl₂ system, the amounts of TCN 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/Cl₂ system [43]. The concentrations of C- and N-DBPs in the UV/PS system were lower than those for UV irradiation and the UV/Cl₂ system. On the other hand, three I-DBPs were detected (dichloromoniiodomethane (CHCl₂I), chlorodiodomethane (CHClI₂), and triiodomethane (CHI₃I)), and much higher amounts were formed in the system with UV alone compared to the UV/Cl₂ 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/Cl₂ and UV/PS can be explained by the conversion of I⁻ into stable IO₃⁻ in UV/Cl₂ and UV/PS [45]. Accordingly, UV/Cl₂ 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.
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 and UV should be adopted for iopromide degradation instead of UV alone, for providing safe drinking water to the public.

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 (± 0.02) × 10⁻², 2.20 (± 0.01) × 10⁻¹, and 6.08 (± 0.10) × 10⁻² min⁻¹, in UV, UV/Cl₂, and UV/PS systems, respectively. In UV/Cl₂, \( k_{\text{obs}} \) 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, \( \bullet \text{OH} \), 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.

Author Contributions: Conceptualization, C.H. and Y.-L.L.; methodology, C.X.; software, Q.W.; validation, D.H. and Q.W.; formal analysis, Y.Z.; investigation, Y.Z.; data curation, Q.W.; writing—original draft preparation, C.H.; writing—review and editing, Y.-L.L., Y.Z. and L.X.; visualization, Q.W.; supervision, C.H. and Y.-L.L.; project administration, C.H.; funding acquisition, C.H. and Y.-L.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Natural Science Foundation of China, China (No. 52170006), the Shanghai Committee of Science and Technology, China (Grant No. 17DZ2282800), and the Ministry of Science and Technology in Taiwan (110-2221-E-992-025).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All analyzed data in this study have been included in the manuscript.
Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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: dichloroacetanilide; TCAN: trichloroacetanilide; TCNM: trichloronitromethane; 1,1,1-TCP: 1,1,1-trichloroacetone; HPLC: high-performance liquid chromatography; GC: gas chromatography; DPD: N, N-diethyl-p-phenylenediamine.

References

1. Wu, Y.; Zhu, S.; Zhang, W.; Bu, L.; Zhou, S. Comparison of diatrizoate degradation by UV/chlorine and UV/chloramine processes: Kinetic mechanisms and iodinated disinfection byproducts formation. Chem. Eng. J. 2019, 375, 121972. [CrossRef] [PubMed]
2. Pérez, S.; Barceló, D. Fate and occurrence of X-ray contrast media in the environment. Anal. Bioanal. Chem. 2007, 387, 1235–1246. [CrossRef] [PubMed]
3. Duirk, S.E.; Lindell, C.; Cornelison, C.C.; Kormos, J.; Ternes, T.A.; Attene-Ramos, M.; Osiol, J.; Wagner, E.D.; Plewa, M.J.; Richardson, S.D. Formation of Toxic Iodinated Disinfection By-Products from Compounds Used in Medical Imaging. Environ. Sci. Technol. 2011, 45, 6845–6854. [CrossRef] [PubMed]
4. Schulz, M.; Löfler, D.; Wagner, M.; Ternes, T.A. Transformation of the X-ray contrast medium iopromide in soil and biological wastewater treatment. Environ. Sci. Technol. 2008, 42, 7207–7217. [CrossRef]
5. Wang, Z.; Wang, X.; Yuan, R.; Xiao, D. Resolving the kinetic and intrinsic constraints of heat-activated peroxysulfate oxidation of iopromide in aqueous solution. J. Hazard. Mater. 2020, 384, 121281. [CrossRef] [PubMed]
6. Müller, J.; Jewell, K.S.; Schulz, M.; Hermes, N.; Ternes, T.A.; Drewes, J.E.; Hübner, U. Capturing the oxic transformation of iopromide—A useful tool for an improved characterization of predominant redox conditions and the removal of trace organic compounds in biofiltration systems? Water Res. 2019, 152, 274–284. [CrossRef]
7. Cui, H.; de Angelis, M.H.; Schröder, P. Iopromide exposure in Typha latifolia L.: Evaluation of uptake, translocation and different transformation mechanisms in planta. Water Res. 2017, 122, 290–298. [CrossRef]
8. Jeong, C.H.; Machek, E.J.; Shakeri, M.; Duirk, S.E.; Ternes, T.A.; Wagner, E.D.; Plewa, M.J. The impact of iodinated X-ray contrast agents on formation and toxicity of disinfection by-products in drinking water. J. Environ. Sci. 2017, 58, 173–182. [CrossRef]
9. Steger-Hartmann, T.; Länge, R.; Schweinfurth, H. Environmental risk assessment for the widely used iodinated X-ray contrast agent iopromide (Ultravist). Ecotox. Environ. Saf. 1999, 42, 274–281. [CrossRef]
10. Plewa, M.J.; Wagner, E.D.; Richardson, S.D.; Thruston, A.D.; Woo, Y.T.; McGauley, A.B. Chemical and biological characterization of newly discovered iodoacetic drinking water disinfection byproducts. Environ. Sci. Technol. 2004, 38, 4713–4722. [CrossRef]
11. Richardson, S.D.; Plewa, M.J.; Wagner, E.D.; Schoeny, R.; Demarini, D.M. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research. Mutat. Res. 2007, 636, 178242. [CrossRef] [PubMed]
12. Xu, Z.; Li, X.; Hu, X.; Yin, D. Distribution and relevance of iodinated X-ray contrast media and iodinated trihalomethanes in an aquatic environment. Chemosphere 2017, 184, 253–260. [CrossRef] [PubMed]
13. Ackerson, N.O.B.; Machek, E.J.; Killinger, A.H.; Crafton, E.A.; Kumkum, P.; Liberatore, H.K.; Plewa, M.J.; Richardson, S.D.; Ternes, T.A.; Duirk, S.E. Formation of DBPs and halogen-specific TOX in the presence of iopamidol and chlorinated oxidants. Chemosphere 2018, 202, 349–357. [CrossRef] [PubMed]
14. Wendel, F.M.; Eversloeh, C.L.; Machek, E.J.; Duirk, S.E.; Plewa, M.J.; Richardson, S.D.; Ternes, T.A. Transformation of iopamidol during chlorination. Environ. Sci. Technol. 2014, 48, 12689–12697. [CrossRef]
15. Velo-Gala, I.; López-Petalver, J.J.; Sánchez-Polo, M.; Rivera-Utrilla, J. Comparative study of oxidative degradation of sodium diatrizoate in aqueous solution by H₂O₂/Fe²⁺, H₂O₂/Fe³⁺, Fe (VI) and UV, H₂O₂/UV, K₂S₂O₈/UV. Chem. Eng. J. 2014, 241, 504–512. [CrossRef]
16. Li, J.; Jiang, J.; Pang, S.; Yang, Y.; Sun, S.; Wang, L.; Wang, P. Transformation of X-ray contrast media by conventional and advanced oxidation processes during water treatment: Efficiency, oxidation intermediates, and formation of iodinated byproducts. Water Res. 2020, 185, 116234. [CrossRef]
17. Dong, H.; Qiang, Z.; Hu, J.; Qu, J. Degradation of chloramphenicol by UV/chlorine treatment: Kinetics, mechanism and enhanced formation of halonitromethanes. Water Res. 2017, 121, 178–185. [CrossRef]
18. Kong, X.; Jiang, J.; Ma, J.; Yang, Y.; Fang, S. Comparative investigation of X-ray contrast medium degradation by UV/chlorine and UV/H₂O₂. Chemosphere 2018, 193, 655–663. [CrossRef]
19. Duan, X.; He, X.; Wang, D.; Mezyk, S.P.; Otto, S.C.; Marfil-Vega, R.; Mills, M.A.; Dionysiou, D.D. Decomposition of iodinated pharmaceuticals by UV-254 nm-assisted advanced oxidation processes. J. Hazard. Mater. 2017, 323, 489–499. [CrossRef]

20. Zhou, L.; Ferronato, C.; Chovelon, J.M.; Sleiman, M.; Richard, C. Investigations of diatrizoate degradation by photo-activated persulfate. Chem. Eng. J. 2017, 311, 28–36. [CrossRef]

21. APHA. Standard Methods for the Examination of Water and Wastewater; American Public Health Association: Washington, DC, USA, 1998.

22. Liang, C.; Huang, C.; Mohanty, N.; Kurakalva, R.M. A rapid spectrophotometric determination of persulfate anion in ISCO. Chemosphere 2008, 73, 1540–1543. [CrossRef][PubMed]

23. USEPA. Determination of Chlorination Disinfection Byproducts, Chlorinated Solvents, and Halogenated Pesticides/herbicides in Drinking Water by Liquid-Liquid Extraction and Gas Chromatography with Electron-Capture Detection; USEPA: Cincinnati, OH, USA, 1995.

24. Zhang, B.; Wang, X.; Fang, Z.; Wang, S.; Shao, C.; Pan, B. Unravelling molecular transformation of dissolved effluent organic matter in UV/H₂O₂, UV/persulfate, and UV/chlorine processes based on FT-ICR-MS analysis. Water Res. 2021, 199, 117158. [CrossRef][PubMed]

25. Lee, M.; Wang, W.; Xu, Z.; Ye, B.; Wu, Q.; Hu, H. The application of UV/PS oxidation for removal of a quaternary ammonium compound of dodecyl trimethyl ammonium chloride (DTAC): The kinetics and mechanism. Sci. Total Environ. 2019, 655, 1261–1269. [CrossRef][PubMed]

26. Fang, J.; Fu, Y.; Shang, C. The Roles of Reactive Species in Micropollutant Degradation in the UV/Free Chlorine System. Environ. Sci. Technol. 2014, 48, 1859–1868. [CrossRef][PubMed]

27. Buxton, G.V.; Greenstock, C.L.; Helman, W.P.; Ross, A.B. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (•OH/•O) in aqueous solution. J. Phys. Chem. Ref. Data 1988, 17, 513–886. [CrossRef]

28. Anipsitakis, G.P.; Dionysiou, D.D. Radical Generation by the Interaction of Transition Metals with Common Oxidants. Environ. Sci. Technol. 2004, 38, 3705–3712. [CrossRef][PubMed]

29. Jeong, J.; Jung, J.; Cooper, W.J.; Song, W. Degradation mechanisms and kinetic studies for the treatment of X-ray contrast media compounds by UV/chlorination processes. Water Res. 2010, 44, 4391–4398. [CrossRef]

30. Zhu, T.; Deng, J.; Zhu, S.; Cai, A.; Ye, C.; Ling, X.; Guo, H.; Wang, Q.; Li, X. Kinetic and mechanism insights into the degradation of venlafaxine by UV/chlorine process: A modelling study. Chem. Eng. J. 2021, 431, 133473. [CrossRef]

31. Merouani, S.; Hamdaoui, O.; Alghyamah, A.; Bouhelassa, M. Influence of processing conditions on the synergism between UV irradiation and chlorine toward the degradation of refractory organic pollutants in UV/chlorine advanced oxidation system. Sci. Total Environ. 2020, 736, 139623.

32. Watts, M.J.; Linden, K.G. Chlorine photolysis and subsequent •OH radical production during UV treatment of chlorinated water. Water Res. 2007, 41, 2871–2878. [CrossRef]

33. Kong, X.; Jiang, J.; Ma, J.; Yang, Y.; Liu, W.; Liu, Y. Degradation of atrazine by UV/chlorine: Efficiency, influencing factors, and products. Water Res. 2016, 90, 15–23. [CrossRef][PubMed]

34. Gao, Z.; Lin, Y.; Xu, B.; Pan, Y.; Xia, S.; Gao, N.; Zhang, T.; Chen, M. Degradation of acrylamide by the UV/chlorine advanced oxidation process. Chemosphere 2017, 187, 268–276. [CrossRef]

35. Chen, L.; Cai, T.; Cheng, C.; Xiong, Z.; Ding, D. Degradation of acetamiprid in UV/H₂O₂ and UV/persulfate systems: A comparative study. Chem. Eng. J. 2018, 351, 1137–1146. [CrossRef]

36. Gao, Y.; Gao, N.; Deng, Y.; Yang, Y.; Ma, Y. Ultraviolet (UV) light-activated persulfate oxidation of sulfamethazine in water. Chem. Eng. J. 2012, 195, 248–253. [CrossRef]

37. Neta, P.; Grodkowski, J.; Ross, A.B. Rate Constants for Reactions of Aliphatic Carbon-Centered Radicals in Aqueous Solution. J. Phys. Chem. Ref. Data 1996, 25, 709. [CrossRef]

38. Liu, H.; Hou, Z.; Li, Y.; Lei, Y.; Xu, Z.; Gu, J.; Tian, S. Modeling degradation kinetics of gemfibrozil and naproxen in the UV/chlorine system: Roles of reactive species and effects of water matrix. Water Res. 2021, 202, 117445. [CrossRef]

39. Grebel, J.E.; Pignatelto, J.J.; Mitch, W.A. Effect of Halide Ions and Carbonates on Organic Contaminant Degradation by Hydroxyl Radical-Based Advanced Oxidation Processes in Saline Waters. Environ. Sci. Technol. 2010, 44, 6822–6828. [CrossRef]

40. Yang, T.; Mai, J.; Wu, S.; Liu, C.; Tang, L.; Mo, Z.; Zhang, M.; Guo, L.; Liu, M.; Ma, J. UV/chlorine process for degradation of benzothiazole and benzotriazole in water: Efficiency, mechanism and toxicity evaluation. Sci. Total Environ. 2021, 760, 144304. [CrossRef]

41. Gao, Y.; Zhang, J.; Li, C.; Tian, F.; Gao, N. Comparative evaluation of metoprolol degradation by UV/chlorine and UV/H₂O₂ processes. Chemosphere 2020, 243, 125325. [CrossRef]

42. Wu, Z.; Guo, K.; Fang, J.; Yang, X.; Xiao, H.; Hou, S.; Kong, X.; Shang, C.; Yang, X.; Meng, F.; et al. Factors affecting the roles of reactive species in the degradation of micropollutants by the UV/chlorine process. Water Res. 2017, 126, 351–360. [CrossRef]

43. Qin, L.; Lin, Y.; Xu, B.; Hu, C.; Tian, F.; Zhang, T.; Zhu, W.; Huang, H.; Gao, N. Kinetic models and pathways of ronidazole degradation by chlorination, UV irradiation and UV/chlorine processes. Water Res. 2014, 65, 271–281. [CrossRef][PubMed]

44. Dong, Z.; Xu, B.; Hu, C.; Zhang, T.; Tang, Y.; Pan, Y.; Mohamed, G.E.D.; Xian, Q.; Gao, N. The application of UV-C laser in persulfate activation for micropollutant removal: Case study with iodinated X-ray contrast medias. Sci. Total Environ. 2021, 779, 146340. [CrossRef][PubMed]

45. Wang, L.; Kong, D.; Ji, Y.; Lu, J.; Yin, X.; Zhou, Q. Transformation of iodide and formation of iodinated by-products in heat activated persulfate oxidation process. Chemosphere 2017, 181, 400–408. [CrossRef][PubMed]