



## Degradation of iopromide by combined UV irradiation and peroxydisulfate

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### ABSTRACT

The aqueous degradation of iopromide, an iodinated X-ray contrast media (ICM) compound, by the combination of UV<sub>254</sub> irradiation and potassium peroxydisulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) has been studied in laboratory scale experiments. The influence of various parameters on the performance of the treatment process has been considered, namely the UV irradiation light intensity, the initial concentrations of iopromide and peroxydisulfate, and the initial solution pH. Iopromide degradation increased with UV light intensity and peroxydisulfate concentration, but decreased with initial pH. Under specific conditions complete removal of iopromide was achieved within 30 min, and near-complete mineralisation (loss of solution TOC) within 80 min. Degradation was believed to be caused by a combination of direct photolysis, sulphate radical attack, and, to a minor degree, direct oxidation by peroxydisulfate. Approximate values for the reaction rate constants have been determined and found to be equal to  $1-2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  for sulfate radicals, and  $1-2 \text{ M}^{-2} \text{ s}^{-1}$  for S<sub>2</sub>O<sub>8</sub><sup>2-</sup>. Overall compound degradation was observed to follow first-order kinetics where the rate constant decreased with initial solution pH. During the reaction, the solution pH decreased as a consequence of sulfate radical scavenging.

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### 1. Introduction

There is much interest currently in the occurrence and control of pharmaceutical contaminants in the aqueous environment. One specific group of compounds, iodinated X-ray contrast media (ICM), has become the focus of environmental concern due to the presence of these compounds in wastewaters and potential contamination of, and harm to, the aquatic environment. As halogenated compounds, they are the main contributors to the burden of total adsorbable organic halogen (AOX) in clinical wastewater [1] and several ICM compounds have been measured at relatively high concentrations ( $>1 \mu\text{g L}^{-1}$ ) in many aqueous environments, including water treatment plant effluents, groundwaters, creeks, rivers, and drinking water [2]. At present, it is unclear whether ICM compounds themselves at the concentrations likely to be present pose a significant risk to human health, but iopromide has been shown recently to have estrogen activity [3]. There is also concern about the ecotoxicity of metabolite/transformation products of ICM, whose presence in environmental waters is suspected [4].

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The ICM compounds are derivatives of 2,4,6-tri-iodobenzoic acid possessing polar carboxylic and hydroxyl moieties in their branch chains. Most ICM compounds are non-ionic, such as iopromide, while others are ionic ICM compounds, such as diatrizoate. As a consequence of their physico-chemical nature, they are recalcitrant, and conventional municipal treatment plants are not able to remove them effectively from influent wastewaters [2,4]. In view of this it may be necessary for water utilities to employ an advanced oxidation process (AOP) to control these contaminants.

While some recent studies have reported on the degradation of iopromide by UV photolysis [5], ozone [6] and ozone-sonolysis AOP [7], previous research by the authors [16] has identified the combination of UV irradiation and peroxydisulphate as another potential AOP for the effective treatment of ICM compounds. Peroxydisulphate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup> ion) is a strong oxidant ( $E^\circ = 2.05 \text{ V}$ ) which has been used widely in the petroleum industry for the treatment of hydraulic fluids or as a reaction initiator [8]. The peroxydisulfate is normally available as a salt associated with ammonium, sodium or potassium. Potassium peroxydisulfate (KPS) recently was shown to be an effective disinfectant and/or oxidant for the Norwalk virus, foot-and-mouth disease and Coronaviridae (causing severe acute respiratory syndrome—SARS) [9]. It has also been reported to be effective for degrading organics in hazardous wastewaters in acidic or basic media through direct chemical oxidation [8], where peroxydisulfate is used as a sacrificial reagent [10]. However, since the reactions of peroxydisulfate are generally slow at normal temper-

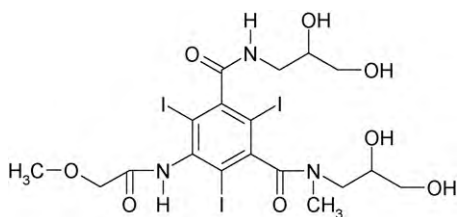
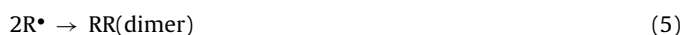
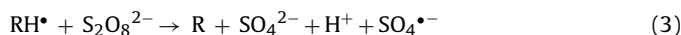
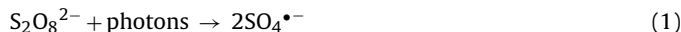


Fig. 1. Chemical structure of iopromide (CAS #73334-07-3; MW 791.12).

atures, the thermal or photochemical activated decomposition of  $S_2O_8^{2-}$  ion to  $SO_4^{\bullet-}$  radical has been proposed as a method of accelerating the process [11], as summarised in the following reactions (Eqs. (1)–(5)):



In the oxidation process, sulfate ions will be generated as the end-product [12], which leads to a decrease in pH and an increase in salt content in the effluent. The  $SO_4^{2-}$  is practically inert and is not considered to be a pollutant; the USEPA has listed it under the secondary drinking water standards with a maximum concentration of 250 mg/L (1.43 mM), based on aesthetic reasons [13]. Theoretically, sulfate ion can be regenerated electrolytically to peroxydisulfate for reuse in water as shown by Balazs et al. [14]. Since peroxydisulfate will start reacting exothermally only at 100 °C [15], it is not recommended for use in conventional water purification processes. The potential use of photo-activated peroxydisulfate at ambient temperature is of interest and has been investigated as a treatment method for the endocrine disruptor chemical, butylated hydroxyanisole (BHA) [16]. At neutral pH, photo-activated ( $UV_{254}$ ) peroxydisulfate achieved a complete degradation of 2 mM BHA within 5 min, and a complete mineralisation within 45 min.

This study has been undertaken to investigate the degradation behaviour of iopromide, as a representative non-ionic ICM compound, with photo-activated potassium peroxydisulfate under various conditions of  $UV_{254}$  light intensity, reactant concentrations, and solution pH. The study has considered the influence of each of these factors and has determined approximate values for the reaction rate constants.

## 2. Experimental methods

### 2.1. Chemicals

All solutions were prepared using 18 M $\Omega$  deionized distilled water produced from a NANO pure water treatment system (Specbiochrom, Milli-Q, LibraS12). All chemicals and solvents were HPLC grade, and they were used without further purification. Potassium peroxydisulfate ( $K_2S_2O_8$ , KPS) was obtained from Sigma-Aldrich at a purity of 99.5% and highly purified iopromide was purchased from Schering AG (Berlin, Germany). The chemical structure of iopromide ( $C_{18}H_{24}I_3N_3O_8$ ) is shown in Fig. 1, and its IUPAC name is as follows: 1-N,3-N-bis(2,3-dihydroxypropyl)-2,4,6-triiodo-5-[(2-methoxyacetyl)amino]-3-N-methylbenzene-1,3-dicarboxamide. From the results of liquid chromatography the iopromide, as supplied, was present in the form of two isomers; Schulz et al. [17] and Putschew et al. [18] also observed two identical main peaks for iopromide in their studies indicating the presence of structural isomers. The chemical structure of the isomers was not

established in this study, and all tests were carried out with both isomers present. For pH adjustment, 0.1 M sulphuric acid and 0.1 M sodium hydroxide were used. The probe compound (iopromide) and standard solutions were stored in a refrigerator prior to use.

### 2.2. Experimental methods

Photodegradation experiments were carried out in a 300 mL (56 mm i.d.  $\times$  130 mm H) quartz beaker with magnetic stirring, where 250 mL of the test solution was placed in the centric of the UV photoreactor, Rayonet<sup>TM</sup> RPR-200 (Southern New England Ultraviolet Co.). The reactor was equipped with two to six phosphor-coated low-pressure mercury lamps (approximately 35 W each), emitting 253.7 nm monochromatic UV at a light intensity of  $1.5 \times 10^{-6}$  Einstein  $L^{-1} s^{-1}$  per lamp. Unless otherwise stated, reactions were carried out with 0.126 mM ( $\sim$ 100 mg  $L^{-1}$ ) iopromide and 2 mM KPS in blank solutions with the requisite amount of  $H_2SO_4$  or NaOH for the desired initial pH. To terminate the reaction, samples were mixed with an excess of sodium azide (1 mM) prior to the quantification of the probe compound and TOC. In general, the initial concentration ranges for iopromide (0.076–0.506 mM), KSP (0.4–20 mM) and the pH (2.6–11), were selected to monitor accurately the chemical reactions, ensure a reasonable reaction time (within 30–60 min), and examine a wide range of reaction kinetics for both academic and practical purposes.

Analysis of iopromide concentration was performed by HPLC (Waters 515 HPLC pump), connected to a Waters 2487 dual-wavelength absorbance detector. Chromatographic separation was carried out by a reverse phase column (5  $\mu$ m  $C_{18}$ , 250 mm long  $\times$  4.66 mm i.d., Alltech Econosphere) with a 5% (v/v) acetonitrile (99.9% purity) mobile phase, adjusted to pH 2.8 with formic acid. The flow of the mobile phase was adjusted by HPLC pump (model 426, Alltech, IL) to 1 mL  $min^{-1}$ , and the UV detector wavelength was set at 238 nm. The chromatographic conditions provided a relatively long compound retention time (12–14 min) to ensure a satisfactory resolution of the two iopromide isomers. Solution TOC was determined using a Shimadzu TOC-5000A analyzer with an ASI-5000A autosampler. All experiments were carried out in an air-conditioned room temperature of  $23 \pm 2$  °C.

## 3. Results and discussion

### 3.1. Effect of UV light intensity

The degradation kinetics of one of the two iopromide isomers (isomer 1) is shown in Fig. 2 with different light intensities (number of  $UV_{254}$  lamps) at an initial pH value of 3.5. As expected, the rate of compound degradation increased systematically with light intensity, and an overall degradation of 90% was achieved in 30 min for both isomers under a light intensity of 6 lamps ( $\approx 9 \times 10^{-6}$  Einstein  $L^{-1} s^{-1}$ ). The degradation kinetics were found to be approximately first-order (viz.  $\ln C - \ln C_0 = -kt$ ), and the first-order rate constant was linearly related to the light intensity (number of lamps), as shown in Fig. 3. It can be seen that there was a noticeable difference in reactivity between the two isomers, with the reaction rate of isomer 2 significantly greater than isomer 1. The linear relationship between the rate constant and the light intensity can be explained by the effects of both direct photolysis and  $SO_4^{\bullet-}$  radical reactions. For direct photolysis, the compound degradation rate,  $k_p$  ( $s^{-1}$ ), can be shown to be directly proportional to the light intensity as follows [19]:

$$k_p = 2.303\Phi I_\lambda \epsilon_\lambda l \quad (6)$$

where  $\Phi$  is the quantum yield (mol Einstein<sup>-1</sup>),  $I_\lambda$  is the intensity of the incident light at 253.7 nm (Einstein  $L^{-1} s^{-1}$ ),  $\epsilon_\lambda$  is the compound molar absorptivity at 253.7 nm ( $L mol^{-1} cm^{-1}$ ), and  $l$  is the light

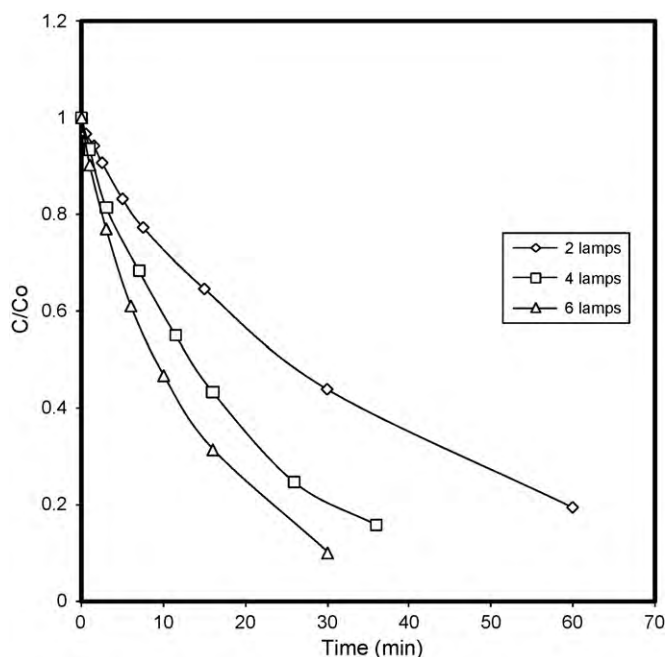


Fig. 2. The variation of iopromide (isomer 1) degradation with UV light intensity (0.126 mM iopromide, 2 mM KPS, pH 3.5).

path (cm). Based on this formula and using values of  $\Phi_{\text{Iop}}$  and  $\epsilon_{\lambda-\text{Iop}}$  recently reported for iopromide (viz.  $\Phi = 0.039 \text{ mol Einstein}^{-1}$ ,  $\epsilon_{\lambda} = 210.4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ; Canonica et al. [5]), the corresponding values for  $k_p$  are  $0.019 \text{ min}^{-1}$  (2 lamps),  $0.038 \text{ min}^{-1}$  (4 lamps) and  $0.057 \text{ min}^{-1}$  (6 lamps). By comparing these calculated values with those in Fig. 3 it can be seen that the measured values from UV/KPS are greater, particularly for isomer 2, and this increase may be attributed to simultaneous reactions with  $\text{SO}_4^{\bullet-}$  radicals, and KPS. The relationship between the rate constant and  $\text{SO}_4^{\bullet-}$  radical reactions is discussed in the next section.

### 3.2. Reaction kinetics

In theory, the kinetics of the iopromide degradation may be described as a combination of direct photolysis and chemical reactions between iopromide and KPS and  $\text{SO}_4^{\bullet-}$  radicals. The overall

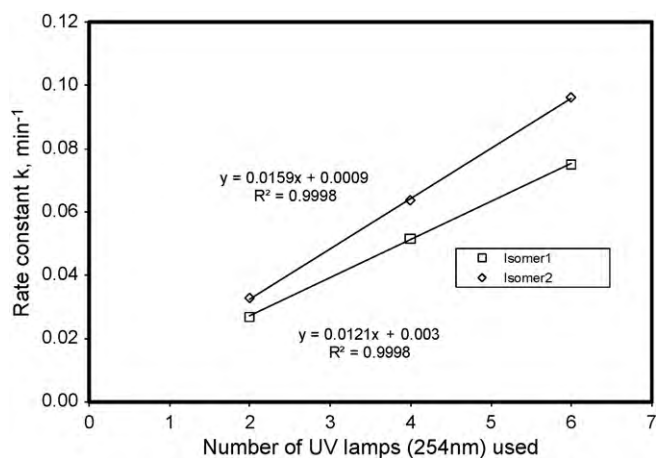


Fig. 3. Variation of first-order rate constants for the degradation of iopromide with UV light intensity.

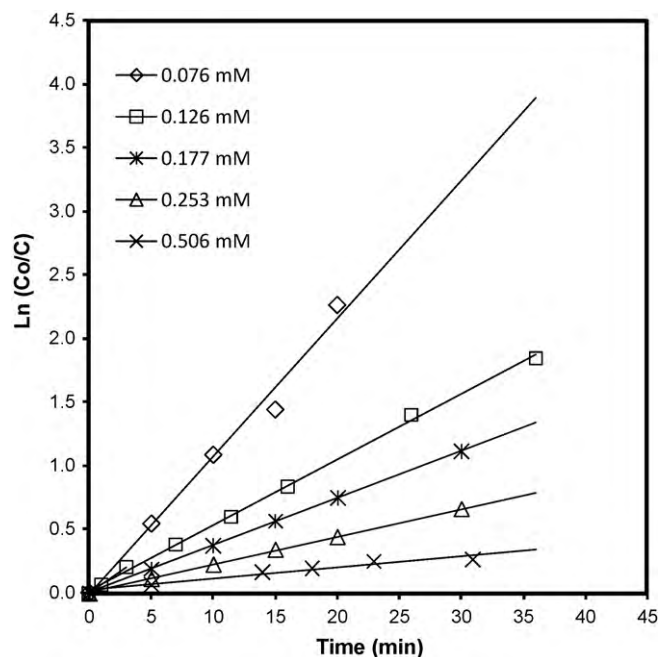


Fig. 4. First-order modelling of iopromide (isomer 1) degradation kinetics at different initial iopromide concentrations (2 mM KPS, 4x UV lamps, pH 4.2).

reaction rate may be expressed as follows:

$$-\frac{d[\text{C}_{\text{Iop}}]}{dt} = k_p[\text{C}_{\text{Iop}}]^q + k_{\text{SO}_4}[\text{SO}_4^{\bullet-}]^r[\text{C}_{\text{Iop}}]^q + k_{\text{KPS}}[\text{KPS}]^p[\text{C}_{\text{Iop}}]^q \quad (7)$$

where  $[\text{C}_{\text{Iop}}]$ ,  $[\text{SO}_4^{\bullet-}]$  and  $[\text{KPS}]$  are the iopromide, radical and KPS concentrations, respectively, and  $k_p$ ,  $k_{\text{SO}_4}$  and  $k_{\text{KPS}}$  are the corresponding reaction rate constants. The exponent for iopromide concentration, 'q', was assumed for simplicity to be the same for all the  $[\text{C}_{\text{Iop}}]$  terms and this was justified subsequently. To evaluate the reaction exponents, 'p', 'q' and 'r', iopromide degradation experiments were carried out with varying concentrations of iopromide and KPS; varying the KPS concentration also varied the  $\text{SO}_4^{\bullet-}$  concentration. In the first set of experiments the reaction conditions were kept constant (i.e. KPS concentration, UV intensity, pH), except for the initial iopromide concentration ( $\text{C}_{\text{Iop}}$ ) which was varied in the range, 0.0758–0.506 mM. From Eq. (7) it can be seen that if the value of the exponent 'q' can be assumed to be unity, then the equation describes a first-order reaction for the temporal change of  $\text{C}_{\text{Iop}}$  (assuming all other reaction conditions are constant); whereupon after integration, the variation of  $\text{C}_{\text{Iop}}$  is given by the linear relationship:  $\ln(\text{C}_0/\text{C}) = kt$ . The results of the tests for isomer 1 for each initial iopromide concentration ( $\text{C}_0$ ) can be seen in Fig. 4, where the value of  $\ln(\text{C}_0/\text{C})$  is plotted versus time. It can be seen that in each case the first-order model fitted the results closely, within experimental error, and thus the value of the exponent 'q' can be assumed to be one. Therefore, Eq. (7) can be simplified as:

$$-\frac{d[\text{C}_{\text{Iop}}]}{dt} = \{k_p + k_{\text{SO}_4}[\text{SO}_4^{\bullet-}]^r + k_{\text{KPS}}[\text{KPS}]^p\} [\text{C}_{\text{Iop}}] \quad (8)$$

The  $\text{SO}_4^{\bullet-}$  radical concentration is the result of  $\text{SO}_4^{\bullet-}$  generation by the photolysis of KPS (Eq. (1)) and consumption by reactions and scavenging within the water matrix. The photolytic generation of  $\text{SO}_4^{\bullet-}$  radicals can be expressed as follows, where 2 radical molecules are produced from one  $\text{S}_2\text{O}_8^{2-}$  molecule:

$$-\frac{d[\text{SO}_4^{\bullet-}]}{dt} = 2(2.303)\Phi_{\text{S}_2\text{O}_8}(I_{\lambda})_{\text{S}_2\text{O}_8}(\epsilon_{\lambda})_{\text{S}_2\text{O}_8}[\text{KPS}] \quad (9)$$

The value of  $\Phi_{\text{S}_2\text{O}_8}$  has been determined to be 0.52 [20], and  $(\epsilon_{\lambda})_{\text{S}_2\text{O}_8}$  has been reported as  $24.1 \text{ L mol}^{-1} \text{ cm}^{-1}$  [21]. The consump-

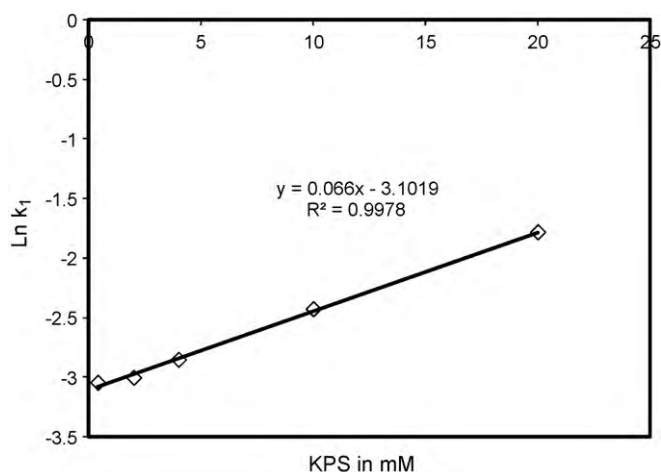
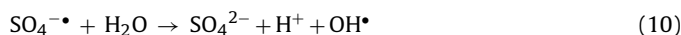


Fig. 5. Variation of rate constant ( $k_1$ ) with KPS concentration (iopromide isomer 1).

tion of  $\text{SO}_4^{\bullet-}$  radicals is assumed to be predominantly through reaction with water molecules leading to a reduction in solution pH (as observed in this study), as follows:



The rate constant for this reaction (Eq. (10)),  $k_W$ , has been reported to lie in the range of  $360\text{--}1000\text{ s}^{-1}$  [20]. It is assumed that parallel reactions with iopromide, KPS, and  $\text{SO}_4^{\bullet-}$  chain reactions are minor relative to the reaction with water and can be incorporated approximately into the rate constant,  $k_W$ . For example, the rate constant for  $\text{SO}_4^{\bullet-}$  scavenging by KPS has been reported to be  $\sim 10^4\text{ M}^{-1}\text{ s}^{-1}$  [20], so for  $[\text{KPS}]_0 = 2\text{ mM}$ , the scavenging rate is approximately  $20\text{ s}^{-1}$  ( $\ll k_W$ ). By assuming a steady state, whereby the rate of  $\text{SO}_4^{\bullet-}$  radical generation is equal to the radical consumption rate, the net rate will be zero. Thus:

$$\begin{aligned} -\frac{d[\text{SO}_4^{\bullet-}]}{dt} &= \{2(2.303)\Phi_{\text{S}_2\text{O}_8}(I_\lambda)_{\text{S}_2\text{O}_8}(\epsilon_\lambda)_{\text{S}_2\text{O}_8} I[\text{KPS}]\} \\ &\quad - k_W[\text{SO}_4^{\bullet-}] = 0 \end{aligned} \quad (11)$$

Rearranging Eq. (11) gives the steady state  $\text{SO}_4^{\bullet-}$  radical concentration:

$$[\text{SO}_4^{\bullet-}] = \{2(2.303)\Phi_{\text{S}_2\text{O}_8}(I_\lambda)_{\text{S}_2\text{O}_8}(\epsilon_\lambda)_{\text{S}_2\text{O}_8} I[\text{KPS}]\} / k_W \quad (12)$$

Simplifying Eq. (12) by substituting  $k'$  for  $[2(2.303)\Phi_{\text{S}_2\text{O}_8}(I_\lambda)_{\text{S}_2\text{O}_8}(\epsilon_\lambda)_{\text{S}_2\text{O}_8} I]$ , then  $[\text{SO}_4^{\bullet-}] = (k'/k_W)[\text{KPS}]$ , and substituting for  $[\text{SO}_4^{\bullet-}]$  in Eq. (8) gives:

$$-\frac{d[\text{C}_{\text{Iop}}]}{dt} = \left\{ k_p + k_{\text{SO}_4} \left( \frac{k'}{k_W} \right)^r [\text{KPS}]^r + k_{\text{KPS}}[\text{KPS}]^p \right\} [\text{C}_{\text{Iop}}] \quad (13)$$

A second series of tests were undertaken in which the initial concentration of iopromide was kept constant ( $0.126\text{ mM}$ ), and the initial KPS concentration varied in the range,  $0.4\text{--}20\text{ mM}$ , whilst under a constant UV irradiation intensity (4 lamps). The results of the tests indicated that the iopromide degradation rate increased with KPS concentration. The form of the relationship was found to be semi-logarithmic, as shown in Fig. 5, with the following general form:  $\ln(k_1) = h[\text{KPS}] + f$ , where  $h$  and  $f$  are constants. Thus, it can be shown that  $k_1 = (g)\exp(h[\text{KPS}])$ , where  $g$  is a new constant ( $f = \ln(g)$ ). The exponential term,  $\exp(h[\text{KPS}])$  can be represented approximately by the first three terms of the exponential series expansion,  $1 + h[\text{KPS}] + (h/2)[\text{KPS}]^2$ . Thus, the iopromide degradation rate equation can be expressed as:

$$-\frac{d[\text{C}_{\text{Iop}}]}{dt} = \left\{ g + gh[\text{KPS}] + \left( \frac{gh}{2} \right) [\text{KPS}]^2 \right\} [\text{C}_{\text{Iop}}] \quad (14)$$

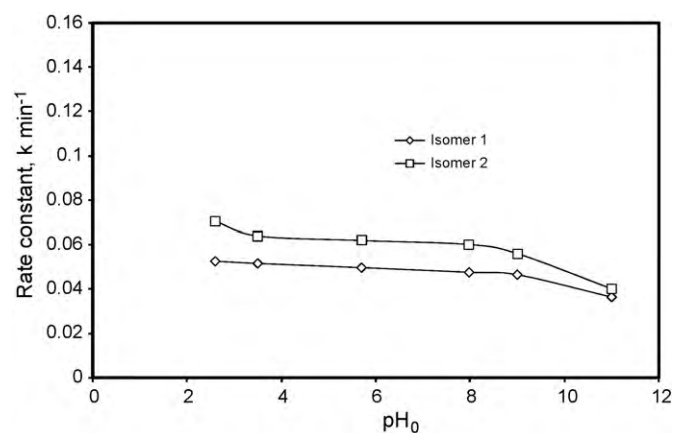


Fig. 6. Variation of iopromide degradation rate constants with initial pH value ( $0.126\text{ mM}$  iopromide,  $2\text{ mM}$  KPS,  $4\times$  UV lamps).

By comparing Eqs. (13) and (14), it can be deduced that the value of the exponents  $r$  and  $p$ , are 1 and 2, respectively. Thus, the overall degradation rate equation can be written as:

$$-\frac{d[\text{C}_{\text{Iop}}]}{dt} = \left\{ k_p + k_{\text{SO}_4} \left( \frac{k'}{k_W} \right) [\text{KPS}] + k_{\text{KPS}}[\text{KPS}]^2 \right\} [\text{C}_{\text{Iop}}] \quad (15)$$

By using the values of  $g$ , ( $gh$ ) and ( $gh/2$ ) obtained from the experiments (shown in Fig. 5) and assuming  $k_W = 600 \pm 200\text{ s}^{-1}$ , the corresponding values for  $k_{\text{SO}_4}$  and  $k_{\text{KPS}}$  were determined as follows:

$$\text{Isomer 1: } k_{\text{SO}_4} = 1.53 (\pm 0.51) \times 10^4\text{ M}^{-1}\text{ s}^{-1}, \text{ and } k_{\text{KPS}} = 1.64\text{ M}^{-2}\text{ s}^{-1}.$$

$$\text{Isomer 2: } k_{\text{SO}_4} = 1.60 (\pm 0.53) \times 10^4\text{ M}^{-1}\text{ s}^{-1}, \text{ and } k_{\text{KPS}} = 1.48\text{ M}^{-2}\text{ s}^{-1}.$$

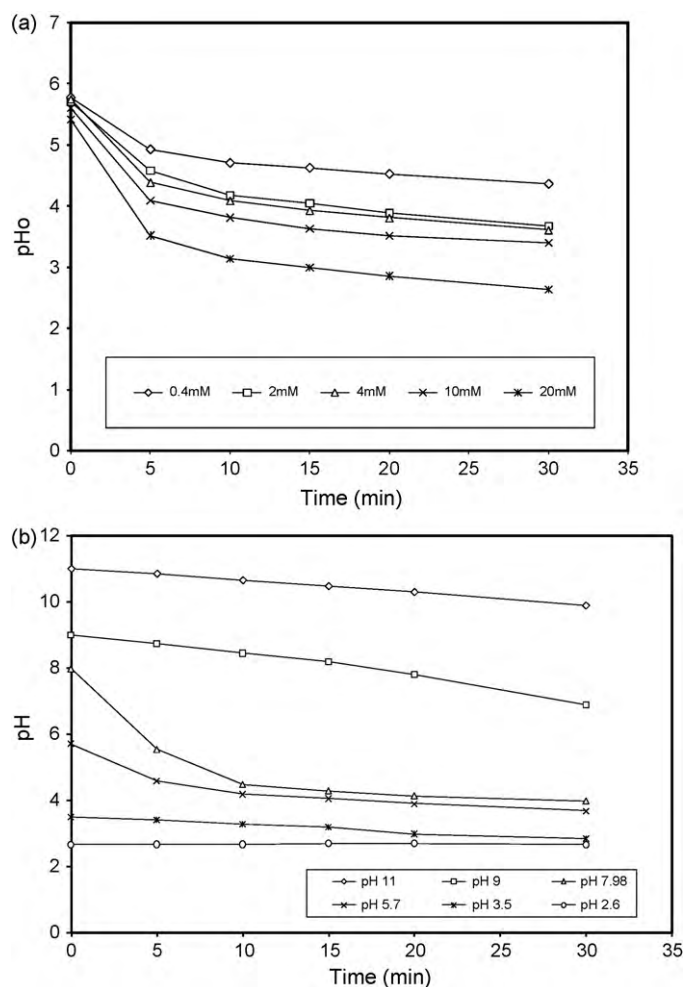
It can be deduced from these calculated values of  $k_{\text{SO}_4}$  that the consumption rate of  $\text{SO}_4^{\bullet-}$  by reactions with iopromide,  $k_{\text{SO}_4}[\text{C}_{\text{Iop}}]$ , is  $\sim 2\text{ s}^{-1}$ , assuming a 1:1 molar stoichiometry, which is consistent with the assumption made in this analysis that these reactions are negligible compared to those with water (cf.  $k_W = 600 \pm 200\text{ s}^{-1}$ ).

The values of  $k_{\text{SO}_4}$  are relatively low which may reflect the recalcitrance of the iopromide molecular structure and the discriminating nature of  $\text{SO}_4^{\bullet-}$  radical reactions, involving electron transfer, addition or hydrogen abstraction [20]. Similar values have been reported for  $\text{SO}_4^{\bullet-}$  reaction with acetic acid ( $1.4\text{--}20 \times 10^4\text{ M}^{-1}\text{ s}^{-1}$ ; [20]), which is another compound generally resistant to oxidation.

Previously, it was observed that under otherwise constant conditions the iopromide degradation rate was linearly related to the UV irradiation intensity (Fig. 3). By reference to Eq. (15), it can be seen that both  $k_p$  and  $k'$  terms incorporate the UV intensity,  $I_\lambda$ , and thus the overall first-order degradation rate of iopromide is directly proportional to the UV intensity, which is consistent with the test results (Fig. 3).

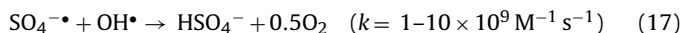
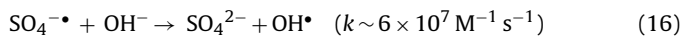
### 3.3. Effect of initial pH

The influence of initial solution pH on the reaction was investigated with a UV intensity of  $6 \times 10^{-6}\text{ Einstein L}^{-1}\text{ s}^{-1}$  (4 lamps) and pH values of 2.6, 3.5, 5.7, 8.0, 9.0 and 11.0. At each pH the reaction kinetics were observed and the pseudo first-order reaction rate constant was determined. The relationship between the rate constants and pH is shown in Fig. 6 for the two iopromide isomers. It can be seen that the rate constant was not substantially affected by pH, but generally decreased with increasing pH. The decrease was  $<8\%$  with increasing pH for the initial pH range of 3–8, but was greater



**Fig. 7.** Temporal change in pH during iopromide reaction (0.126 mM iopromide, 4× UV lamps): (a) with initial KPS concentrations (pH<sub>0</sub> 5.7); (b) with initial pH value (2 mM KPS).

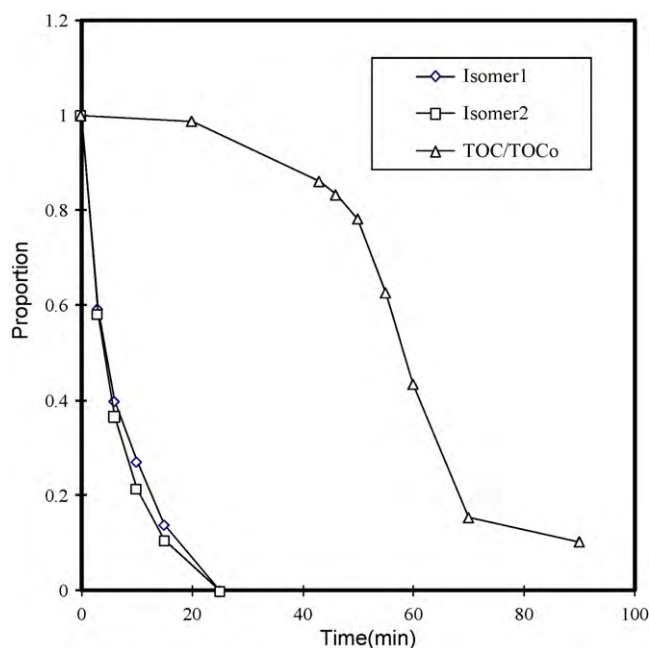
between pH 9 and 11 (22–29%). At pH 11, the iopromide degradation rate was close to the theoretical rate for direct photolysis alone (0.038 min<sup>-1</sup>), indicating a high degree of SO<sub>4</sub><sup>-•</sup> radical scavenging under such conditions. The following are possible scavenging reactions responsible for this [20]:



Criquet and Karpel Vel Leitner [20] also reported a decrease in reaction rate with pH for acetic acid degradation by UV/KPS between pH 5 and 11, citing the reaction between the sulphate radical and OH as the principal cause. At very low pH (~<4) the slightly greater iopromide degradation rate may be due to significant complementary, indirect reactions with OH<sup>•</sup> radicals arising from the scavenging of SO<sub>4</sub><sup>-•</sup> (Eq. (10)). Such indirect reactions could be very rapid since Ning and Graham [6] have reported an iopromide/OH<sup>•</sup> radical rate constant of 2 × 10<sup>-9</sup> M<sup>-1</sup> s<sup>-1</sup>.

### 3.4. Overall reaction

It was observed that with each degradation reaction there was a decrease in solution pH with time. These changes are illustrated in Fig. 7a and b. In Fig. 7a, the influence of KPS concentration is shown whereby the decrease in solution pH increased systematically with KPS concentration for the initial period (0–5 min). This is



**Fig. 8.** Comparative degradation kinetics of iopromide and solution TOC (6× UV lamps, 0.126 mM iopromide, 2 mM KPS, pH 3.4).

consistent with the direct relationship between sulfate radical generation and KPS concentration, as represented by Eq. (9), thereby leading to increasing H<sup>+</sup> ions being generated as a consequence of aqueous SO<sub>4</sub><sup>-•</sup> scavenging (Eq. (10)). After the initial period, the further decrease in pH with time was relatively gradual and similar for all the KPS concentrations. It seems reasonable to speculate that in the initial reaction period (0–5 min), substantial degradation of iopromide occurs leading to intermediate products, some of which may behave as weak organic acids leading to the buffering of solution pH, both during the initial period and subsequently. Similarly, the results shown in Fig. 7b, for the same specific oxidation conditions (4 lamps, 0.126 mM iopromide, 2 mM KPS) but different initial pH values, show a reduction in solution pH with time corresponding to approximately equivalent H<sup>+</sup> production as a result of the scavenging of sulfate radicals.

Although no investigation of reaction products was carried out in this study, there were clear indications that substantial quantities of reaction intermediates were formed. Changes in iopromide concentration and solution TOC (total organic carbon) can be seen in Fig. 8, which demonstrated that there was very little loss of TOC (conversion to CO<sub>2</sub>-mineralisation) in the early stages of the reactions (<10 min) where the corresponding degradation of iopromide was substantial. Continuation of the oxidation conditions beyond the point of full iopromide degradation leads to near-complete mineralisation of the reaction products (i.e. loss of solution TOC) after approximately 70–80 min. In general, little work has been reported on the degradation mechanisms of ICM compounds, but one recent study has indicated that oxidation by OH<sup>•</sup> radicals of iomeprol lead to the conversion of hydroxyl moieties on the compound side chains by hydrogen abstraction to aldehyde or ketone groups [22]; similar products have been reported for iopromide undergoing biodegradation [23]. In contrast, Ning and Graham [6] observed in ozone reactions with ICM compounds the release of iodine during the period of compound degradation, suggesting cleavage of the iodine–carbon bond on the aromatic ring. Further work is required to investigate the degradation mechanisms for iopromide in the UV/KPS system, and the pathways arising from direct photolysis and sulphate radical reaction.

#### 4. Conclusions

The aqueous degradation behaviour of iopromide, as a representative non-ionic ICM compound, in the presence of photo-activated potassium peroxydisulfate (KPS) has been studied under various conditions of UV<sub>254</sub> light intensity, reactant concentrations, and solution pH. As iopromide has been found to be a recalcitrant environmental contaminant, the application of advanced oxidation processes to wastewaters containing ICM compounds represents the most viable method of treatment. The results of laboratory experiments with photo-activated KPS have shown that under specific conditions complete removal of iopromide was achieved within 30 min, and near-complete mineralisation within 80 min. The mechanisms of degradation are believed to involve a combination of direct photolysis, sulphate radical attack, and, to a minor degree, direct oxidation by peroxydisulfate. Approximate values for the reaction rate constants have been determined and found to be equal to  $1\text{--}2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  for sulfate radicals, and  $1\text{--}2 \text{ M}^{-2} \text{ s}^{-1}$  for direct reactions with KPS ( $\text{S}_2\text{O}_8^{2-}$ ). The rate constants appear to be relatively low compared to published values for sulphate radical reactions with other organic substrates, but this is believed to be due to the discriminating nature of  $\text{SO}_4^{\cdot-}$  radical reactions, involving electron transfer, addition or hydrogen abstraction, and the recalcitrant nature of the iopromide molecule. Overall compound degradation was observed to follow first-order kinetics where the rate constant decreased with initial solution pH. During the reaction the pH of the solution was observed to decrease with time, which was believed to be the consequence of sulfate radical scavenging.

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