



# Reactions of hypiodous acid with model compounds and the formation of iodoform in absence/presence of permanganate



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## ABSTRACT

The kinetics for the reactions of hypiodous acid (HOI) with various phenols (phenol, 4-nitrophenol, 4-hydroxybenzoic acid), 3-oxopentanedioic acid (3-OPA) and flavone were investigated in the pH range of 6.0–11.0. The apparent second order rate constants for the reactions of HOI with phenolic compounds, 3-OPA, flavone and citric acid at pH 8.0 are  $10\text{--}10^7 \text{ M}^{-1}\text{s}^{-1}$ ,  $(4.0 \pm 0.3) \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ ,  $(2.5 \pm 0.2) \times 10^3 \text{ M}^{-1}\text{s}^{-1}$  and  $<1 \text{ M}^{-1}\text{s}^{-1}$ , respectively. The effect of buffer type and concentration was investigated with acetate, phosphate and borate. All tested buffers promote the HOI reactions with phenols. The percentage of iodine incorporation for various (hydroxyl)phenolic compounds and two NOM extracts ranges from 5% to 98%, indicating that electrophilic aromatic substitution and/or electron transfer can occur. The extent of these reactions depends on the number and relative position of the hydroxyl moieties on the phenolic compounds. Iodoform formation rates increase with increasing pH and iodoform yields increase from 9% to 67% for pH 6.0–10.0 for the HOI/3-OPA reactions. In the permanganate/HOI/3-OPA and permanganate/iodide/3-OPA system at pH < 8.0, iodoform formation is elevated compared to the HOI/3-OPA system in absence of permanganate. For pH > 8.0, in presence of permanganate, iodoform formation is significantly inhibited and iodate formation enhanced, which is due to a faster permanganate-mediated HOI disproportionation to iodate compared to the iodination process. The production of reactive iodine in real waters containing iodide in contact with permanganate may lead to the formation of iodinated organic compounds.

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## 1. Introduction

### 1.1. Formation and fate of hypohalous acids: reactivity with organic compounds and formation of disinfection by-products

When bromide and/or iodide-containing water is treated with chlorine (HOCl), bromide or iodide can be oxidized to hypobromous acid/hypobromite (HOBr/OBr<sup>-</sup>) or hypiodous acid/hypiodite (HOI/OI<sup>-</sup>), respectively (Kumar and Margerum, 1987; Nagy et al., 1988). There is no further oxidation of HOBr/OBr<sup>-</sup> by HOCl/OCl<sup>-</sup> (Margerum and Huff Hartz, 2002), however, HOI/OI<sup>-</sup> can be further oxidized to iodate by HOCl/OCl<sup>-</sup> in a pH-dependent

reaction ( $k_{\text{HOCl}+\text{HOI}} = 8.2 \text{ M}^{-1}\text{s}^{-1}$ , and  $k_{\text{OCl}+\text{HOI}} = 52 \text{ M}^{-1}\text{s}^{-1}$ ) (Bichsel and von Gunten, 1999). Iodate formation during chlorination is accelerated in presence of bromide by a relatively fast bromine reactions with HOI/OI<sup>-</sup> ( $k_{\text{HOBr}+\text{IO}^-} = 1.9 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ ,  $k_{\text{BrO}^-+\text{IO}^-} = 1.8 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ ) (Criquet et al., 2012).

Depending on the lifetime of hypohalous acids, it can further react with natural organic matter (NOM) to produce halogenated disinfection by-products (DBPs) (Allard et al., 2013, 2015).  $\beta$ -Dicarbonyl moieties and phenolic moieties within the NOM are reported to be precursors for the formation of such DBPs (Bond et al., 2009; Criquet et al., 2015; Dickenson et al., 2008). The apparent second order rate constants for the reactions of HOBr with phenolates at pH 7.0 are about three orders of magnitude higher than for HOCl due to the higher electrophilicity of HOBr, whereas HOI has an intermediate reactivity (Criquet et al., 2015). The apparent second order rate constants for the reactions of HOBr and HOI with phenols at pH 7.0 are in the range of  $10^4\text{--}10^7$  and  $10^2\text{--}10^5 \text{ M}^{-1}\text{s}^{-1}$ , respectively (Criquet et al., 2015; Bichsel and von

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Gunten, 2000). The reactivity of HOI with phenolic moieties varies significantly depending on the nature and location of the substituents on the aromatic ring (Bichsel and von Gunten, 2000; Lee et al., 2005). Compared to HOBr or HOCl, HOI is more sensitive to the substitution effects on the aromatic ring of phenols, because the Hammett slope for HOI ( $\rho = -7.1$ ) for quantitative structure activity relationships for phenolic compounds is higher than for HOBr ( $\rho = -3.3$ ) or HOCl ( $\rho = -3.0$ ), respectively (Lee et al., 2005).

In chlorinated waters containing iodide and phenols, significant concentrations of chlorinated and iodinated by-products were found due to electrophilic aromatic substitution reactions by the hypohalous acids (Vikesland et al., 2013). During the chlorination of bromide/iodide-containing waters with high DOM concentrations, mixed Cl-Br-I-DBPs were formed (Allard et al., 2015; Hua and Reckhow, 2007a, 2007b, 2012; Jones et al., 2012a,b). I-DBPs are reported to be more cytotoxic, mutagenic and genotoxic to mammalian cells than their chlorinated and brominated analogues (Liu and Zhang, 2014; Richardson et al., 2008; Plewa et al., 2008). It was demonstrated that the addition of bromide and iodide increases the cytotoxicity and genotoxicity during chlorination of drinking water (Yang et al., 2014).

### 1.2. Stability of iodine in presence of permanganate and formation of iodinated DBPs

In a previous study, it was shown that iodide can be oxidized by permanganate to reactive iodine species ( $I_2$  and/or  $HOI/OI^-$ ), which are further oxidized by permanganate or undergo a permanganate-mediated disproportionation (Zhao et al., 2016). Based on the obtained apparent second order rate constants for HOI depletion in presence of permanganate, the half-life of HOI for a  $MnO_4^-$  concentration of  $10 \mu M$  ( $1.6 \text{ mg/L}$ ) can be calculated to be 2.8 or 5.2 h for pH 7.0 or 8.0, respectively. Lower half lives of HOI for pH < 7.0 and pH > 8.0 can be expected due to higher apparent second order rate constants for HOI transformation in these pH ranges (Zhao et al., 2016). Therefore, I-DBPs formation in iodide-containing waters treated with permanganate will be more pronounced under typical water treatment conditions in the pH range of 7.0–8.0.

It was found that iodoform is the major I-DBPs during treatment of iodide-containing water with permanganate and iodoform formation is most favorable at near neutral pH (Ye et al., 2012; Zhang et al., 2015). In another study, an increase of I-DBPs was observed from monochloramination after permanganate pre-oxidation, which cannot be accounted for by pre-oxidation alone. This indicates that the reaction of permanganate with natural organic matter is equally important in I-DBPs formation as the oxidation of iodide by permanganate to HOI (Jones et al., 2012a). It was also reported that Br/I-DBPs formation is generally more favorable for NOM components with lower  $SUVA_{254}$  (Hua and Reckhow, 2007b). Despite these previous studies, there is only limited information on the reactivity of HOI with organic moieties and the I-DBPs formation during treatment with permanganate.

The objectives of this study were (i) to determine the pH dependence of the apparent second order rate constants for the reactions of HOI with selected organic compounds including phenolic compounds, 3-oxopentanedioic acid (3-OPA) and flavone, (ii) to investigate the type of the reactions of HOI with phenols, (iii) to evaluate the formation of iodoform in presence and absence of permanganate using 3-OPA as a model compound, (iv) to assess the effects of various parameters including permanganate, iodide and 3-OPA concentrations on the iodate and iodoform formation and (v) to elucidate the dominant mechanisms in the HOI/3-OPA and permanganate ( $Mn(VII)$ )/iodide/3-OPA reaction systems. Based on the information from model compound reactions, mechanisms for iodoform formation are proposed.

## 2. Materials and methods

### 2.1. Reagents

A sodium hypochlorite solution with 10% active chlorine was obtained from Sigma-Aldrich. Potassium iodide with a purity of 99% was obtained from Fluka. HOI was prepared by reaction of  $I^-$  with  $HOCl/OCl^-$  by the following procedure: HOI was obtained by adding 1 mL of a 10 mM KI solution to 100 mL of a pH-buffered (2.5 mM tetraborate buffer, pH 8.0) solution containing 0.1 mM NaOCl. The oxidation of iodide to iodine occurred within < 1 s (Nagy et al., 1988). Because HOI is not stable in aqueous solution, it was freshly prepared prior to each experiment. Phenol (purity 99%), 2,6-dibromophenol (2,6-DBP, purity 99%), 2,6-dichlorophenol (2,6-DCP, purity 99%), 4-nitrophenol (4-NP, purity 99%), 4-hydroxybenzoic acid (4-HBA, purity 99%) and flavone (purity 95%), phloroglucinol (purity 99%), resorcinol (purity 99%) citric acid (purity 99%), ferulic acid (purity 99%), catechol (purity 99%) and hydroquinone (purity 99%) were obtained from Sigma-Aldrich and used as received. 3-OPA was obtained from Sigma-Aldrich and used after recrystallisation in ethanol. Nordic Lake fulvic acid (NLFA) and Pony Lake fulvic acid (PLFA) were obtained from the International Humic Substances Society (IHSS) and used as received. All solutions were prepared with  $18.2 \text{ M}\Omega \text{ cm}$  Milli-Q water. The concentrations of permanganate solutions were measured spectrophotometrically at 525 nm ( $\epsilon = 2500 \text{ M}^{-1}\text{cm}^{-1}$ ) (Jiang et al., 2012).

### 2.2. Experimental procedures

Apparent second order rate constants for the reactions of HOI with the selected model compounds were determined as a function of pH under first order conditions in excess of the model compounds (at least 10-fold). For relatively slow kinetics ( $k_{app} < 5000 \text{ M}^{-1}\text{s}^{-1}$ ), reactions were initiated by adding the model compounds to 100 mL of a buffered solutions containing HOI at  $23 \pm 1 \text{ }^\circ\text{C}$ . At certain time intervals, 4 mL samples were withdrawn and a solution containing diethyl-p-phenylene diamine (DPD) (0.1 mL) and 0.1 mL phosphate buffer (1 M, pH 6.0) was then added to measure the residual HOI. For fast kinetics ( $k_{app} > 10^4 \text{ M}^{-1}\text{s}^{-1}$ ), a quench-flow apparatus (Biologic SFM-400/Q) was used as follows: HOI was prepared by mixing HOCl and iodide at pH 8.0 with a contact time of 100 ms in the quench-flow system. The contact time of 100 ms for completion of the reaction was based on kinetic modeling, which showed that HOI formation is completed within 10 ms (Fig. S1). After its formation, HOI was mixed with the model compounds in excess and at predetermined time intervals (0–1028 ms), the residual HOI was quenched by the DPD/phosphate buffer. The DPD/phosphate buffer mixture was purged by nitrogen prior to use, to avoid oxygen interferences due to oxidation of DPD in the solution. For the determination of the second order rate constants for the reactions of HOI with resorcinol or phloroglucinol, a competition kinetics method (Text S1) was used, because these reactions were too fast for quench-flow. The experimental conditions are shown in Table S1.

3-OPA was chosen as the model compound for investigating the formation of iodoform from its reaction with HOI or iodide in absence/presence of permanganate. Reactions were initiated by adding HOI or iodide to 250 mL of buffered solutions containing 3-OPA and/or permanganate. Samples were taken and quenched by  $10 \mu\text{L}$  0.2 M hydroxylamine hydrochloride, whereby both reactants, iodine and permanganate, were reduced to iodide and Mn(II), respectively. These samples were then used for iodoform and iodate/iodide measurements. Acetate (10 mM) or tetraborate (2.5 mM) were used as buffers for the pH ranges of 4.0–6.0, or 7.0–11.0, respectively. pH changes were <0.2 pH units during all

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