

# Kinetics of the reaction between hydrogen peroxide and aqueous iodine: Implications for technical and natural aquatic systems



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## ABSTRACT

Oxidative treatment of iodide-containing waters can lead to a formation of potentially toxic iodinated disinfection byproducts (I-DBPs). Iodide ( $I^-$ ) is easily oxidized to HOI by various oxidation processes and its reaction with dissolved organic matter (DOM) can produce I-DBPs. Hydrogen peroxide ( $H_2O_2$ ) plays a key role in minimizing the formation of I-DBPs by reduction of HOI during  $H_2O_2$ -based advanced oxidation processes or water treatment based on peracetic acid or ferrate(VI). To assess the importance of these reactions, second order rate constants for the reaction of HOI with  $H_2O_2$  were determined in the pH range of 4.0–12.0.  $H_2O_2$  showed considerable reactivity with HOI near neutral pH ( $k_{app} = 9.8 \times 10^3$  and  $6.3 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$  at pH 7.1 and 8.0, respectively). The species-specific second order rate constants for the reactions of  $H_2O_2$  with HOI,  $HO_2^-$  with HOI, and  $HO_2^-$  with  $OI^-$  were determined as  $k_{H_2O_2+HOI} = 29 \pm 5.2 \text{ M}^{-1}\text{s}^{-1}$ ,  $k_{HO_2^-+HOI} = (3.1 \pm 0.3) \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ , and  $k_{HO_2^-+OI^-} = (6.4 \pm 1.4) \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ , respectively. The activation energy for the reaction between HOI and  $H_2O_2$  was determined to be  $E_a = 34 \text{ kJ mol}^{-1}$ . The effect of buffer types (phosphate, acetate, and borate) and their concentrations was also investigated. Phosphate and acetate buffers significantly increased the rate of the  $H_2O_2$ –HOI reaction at pH 7.3 and 4.7, respectively, whereas the effect of borate was moderate. It could be demonstrated, that the formation of iodophenols from phenol as a model for I-DBPs formation was significantly reduced by the addition of  $H_2O_2$  to HOI- and phenol-containing solutions. During water treatment with the  $O_3/H_2O_2$  process or peracetic acid in the presence of  $I^-$ ,  $O_3$  and peracetic acid will be consumed by a catalytic oxidation of  $I^-$  due to the fast reduction of HOI by  $H_2O_2$ . The  $O_3$  deposition on the ocean surface may also be influenced by the presence of  $H_2O_2$ , which leads to a catalytic consumption of  $O_3$  by  $I^-$ .

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## 1. Introduction

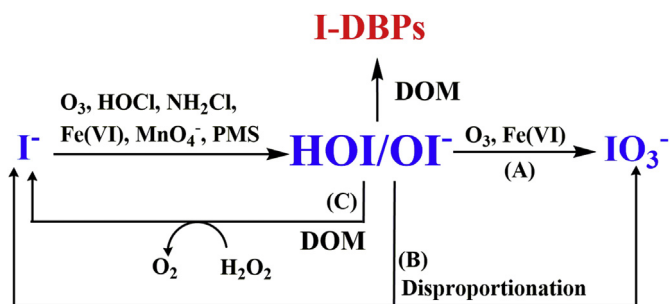
During oxidative water treatment at circumneutral pH, iodide ( $I^-$ ) is rapidly oxidized to aqueous iodine, mainly hypoiodous acid (HOI), which has a high potential to produce iodinated disinfection byproducts (I-DBPs) by its reactions with dissolved organic matter moieties (Bichsel and von Gunten, 1999; Bichsel and von Gunten, 2000a; Criquet et al., 2012; Allard et al., 2015). As a consequence, I-DBPs have been widely detected in oxidatively treated iodide-

containing waters (Krasner et al., 2006; Wei et al., 2013; Gong and Zhang, 2015; Pan et al., 2016). The formation of I-DBPs is of concern in drinking water because they are more cytotoxic, genotoxic, and mutagenic than their chlorinated and brominated analogues (Plewa et al., 2004; Richardson et al., 2008; Yang et al., 2014; Dong et al., 2019). Moreover, iodinated trihalomethanes (I-THMs), especially iodoform, can lead to an undesired medicinal taste and odor in finished drinking waters (Hansson et al., 1987).

To minimize the formation of I-DBPs, several studies have investigated the reactions of HOI with (in)organic constituents and various oxidants during drinking water treatment. HOI can be transformed by three competing pathways (Scheme 1): (A) oxidation to iodate ( $IO_3^-$ ), (B) disproportionation to  $I^-$  and  $IO_3^-$ , and (C) reduction to  $I^-$  by dissolved organic matter (DOM) or hydrogen peroxide ( $H_2O_2$ ) (Nagy

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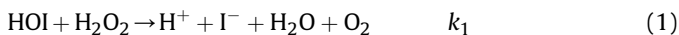
**Scheme 1.** Transformation pathways of  $I^-$  and  $HOI/OI^-$  during treatment of waters containing dissolved organic matter (DOM) with different oxidants.

et al., 1988; Bichsel and von Gunten, 1999; Bichsel and von Gunten, 2000a; Zhao et al., 2016; Li et al., 2017; Shin et al., 2018).

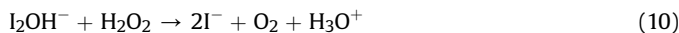
Iodate ( $IO_3^-$ ) is nontoxic and thus the desired sink for iodine during oxidative water treatment (Bürgi et al., 2001), however, many oxidants (i.e., chlorine, chlorine dioxide, chloramine, permanganate, manganese dioxide) have relatively low reactivity with HOI, wherefore,  $IO_3^-$  formation is slow or absent (Bichsel and von Gunten, 2000a; Zhao et al., 2016). During chlorination of bromide-containing water, the oxidation of HOI to  $IO_3^-$  is significantly enhanced by HOBr ( $k_{HOBr+OI^-} = 1.9 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ ), which is formed by the oxidation of bromide by chlorine (Criquet et al., 2012). However, at the same time, the formation of brominated I-DBPs is enhanced in the presence of bromide (Allard et al., 2015). Only ozone ( $O_3$ ) and ferrate ( $Fe(VI)$ ) show significant potential for a mitigation of I-DBPs by formation of  $IO_3^-$  through rapid oxidation of HOI (pH 7:  $k_{appO_3+HOI/OI^-} = 3.7 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$  and  $k_{appFe(VI)+HOI/OI^-} = 1.5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ ) (Bichsel and von Gunten, 1999; Shin et al., 2018). The formation of I-DBPs can also be minimized by reduction of HOI by reducing agents such as hydrogen peroxide ( $H_2O_2$ ) (Shah et al., 2015a; Shin et al., 2018).  $H_2O_2$  is widely used in oxidative water treatment, and intentionally added for some advanced oxidation processes (e.g.,  $O_3/H_2O_2$  or  $UV/H_2O_2$ ).  $H_2O_2$  is also present during various water treatment applications with peracids, such as peracetic acid (Shah et al., 2015a). Moreover, significant concentrations of  $H_2O_2$  (20–30% of the consumed  $Fe(VI)$ ) can be produced during treatment with  $Fe(VI)$  by self-decay of  $Fe(VI)$  (Lee et al., 2014).

During water treatment or in natural systems, HOI is the dominant species compared to molecular iodine ( $I_2$ ) because the  $I^-$  concentration is typically very low (maximum  $\sim 100 \mu\text{g/L}$  of  $I^-$  in surface water) and hence the equilibrium is on the side of HOI (Eq. (5) in Table 1) (Smedley, 2000; Moran et al., 2002; Richardson et al., 2008).

The reactions of iodine with  $H_2O_2$  have been studied previously. Eq. (1) was proposed as a dominant reaction pathway in the  $HOI-H_2O_2$  system (Bray and Liebhafsky, 1931). Eqs. (2)–(4) are based on the speciation of  $HOI/OI^-$  ( $pK_{a1} = 10.4$ ) and  $H_2O_2/HO_2^-$  ( $pK_{a2} = 11.8$ ).



The reported values of  $k_1$  ( $5-200 \text{ M}^{-1}\text{s}^{-1}$ ) (Bray and Liebhafsky, 1931; Furrow, 1987; Ishigure et al., 1986; Schmitz, 2010) and  $k_3$  ( $1.4 \times 10^7-6.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ) (Liebhafsky, 1932; Ishigure et al., 1986; Shiraishi et al., 1992) vary over several orders of magnitude in literature (Table 2). This might be related to experimental differences. Previously, to determine the second order rate constants for the reaction of HOI with  $H_2O_2$ , an indirect method was used, which measures the decrease of  $I_3^-$  in presence of excess  $I^-$  based on Eqs. (5) and (6) in Table 1. This approach can lead to different  $I_2$  concentrations depending on the experimental conditions (e.g., pH,  $[I_2]$ , or  $[I^-]_0$ ), wherefore, the reaction system may be ill-defined. Based on this approach, different pH-dependences of second order rate constants were found in several studies (e.g.,  $k \propto 1/[H^+]^2$ ) for the reaction of HOI with  $H_2O_2$ . As a consequence, reactions in Eqs. (9) and (10) were introduced as a dominant reaction pathway in some previous studies (Shiraishi et al., 1992; Ball and Hnativ, 2001).



Overall, a lot of conflicting information for the kinetics of the reaction of HOI with  $H_2O_2$  has been published, however, so far, no agreement has been reached, mainly due to the utilization of an indirect experimental approach.

In this study, second order rate constants for the reactions of HOI with  $H_2O_2$  were directly determined by measuring the HOI decrease or  $I^-$  formation over a wide pH range from 4.0 to 12.0 using stopped-flow and batch-type experiments, excluding the formation and reactions of  $I_2$ . This approach makes it possible to assess the importance of the reduction of HOI by  $H_2O_2$  compared to its other reactions in water treatment and  $H_2O_2$ -containing natural waters.

## 2. Materials and methods

### 2.1. Standards and reagents

All experiments were carried out with ultrapure water from a Milli-Q (Millipore) nanopure system. All chemicals and solvents were of the highest purity available and used as received without further purification (Supporting information, SI-Text 1). Hydrogen peroxide ( $H_2O_2$ ) stock solutions were prepared by diluting a commercial solution of  $H_2O_2$  (30 wt% in  $H_2O$ , Sigma) and standardized spectrophotometrically using the molar absorption coefficient of  $H_2O_2$  ( $\epsilon = 40 \text{ M}^{-1} \text{ cm}^{-1}$  at 240 nm (Bader et al., 1988)). Chlorine ( $HOCl/OCl^-$ ) stock solutions were prepared by diluting a commercial sodium hypochlorite solution (10–15%, Sigma) and standardized spectrophotometrically using the molar absorption coefficient

**Table 1**  
Reactions and equilibrium constants for iodine and hydrogen peroxide in aqueous solution.

Number	Reaction	$K_{eq}$ or $K_a$	$pK_a$	reference
5	$I_2 + H_2O \rightleftharpoons HOI + I^- + H^+$	$5.44 \times 10^{-13} \text{ M}^2$		Burger and Liebhafsky (1973)
6	$I_2 + I^- \rightleftharpoons I_3^-$	$725 \text{ M}^{-1}$		Burger and Liebhafsky (1973)
7	$HOI \rightleftharpoons H^+ + OI^-$	$4.0 \times 10^{-11} \text{ M}$	10.4	Bichsel and von Gunten (2000)
8	$H_2O_2 \rightleftharpoons H^+ + HO_2^-$	$2.5 \times 10^{-12} \text{ M}$	11.6	Staelin and Hoigné (1982)

**Table 2**Second order rate constants [ $M^{-1}s^{-1}$ ] for reactions of  $H_2O_2/HO_2^-$  with  $HOI/OI^-$ ,  $HOBr/OBr^-$ , and  $HOCl/OCl^-$ .

	$H_2O_2, M^{-1}s^{-1}$	Reference	$HO_2^-, M^{-1}s^{-1}$	Reference
HOI	<b><math>29 \pm 5.2</math></b> 37 200 5 23	<b>This study</b> Liebhafsky (1932) Ishigure et al. (1986) Furrow (1987) Schmitz (2010)	<b><math>(3.1 \pm 0.3) \times 10^8</math></b>	<b>This study</b>
$OI^-$	$6.0 \times 10^9$ $1.4 \times 10^7$ $6.6 \times 10^7$	Liebhafsky (1932) Ishigure et al. (1986) Shiraishi et al. (1992)	<b><math>(6.4 \pm 1.4) \times 10^7</math></b>	<b>This study</b>
HOBr	$1.5 \times 10^4$	von Gunten and Oliveras (1997)	$7.6 \times 10^8$	von Gunten and Oliveras (1997)
HOCl	–	–	$4.4 \times 10^7$	Held et al. (1978)

of  $OCl^-$  (pH > 11,  $\epsilon = 350 M^{-1} cm^{-1}$  at 292 nm (Kumar and Margerum, 1987)). Stock solutions of HOI (5–25  $\mu M$ ) were freshly prepared through oxidation of a slight excess of iodide (5.1–25.5  $\mu M$ ) by chlorine (5–25  $\mu M$ ) in pure water.

## 2.2. Kinetic experiments with stopped-flow

Kinetic studies for the reactions of HOI with  $H_2O_2$  were performed under pseudo-first order conditions with  $H_2O_2$  in molar excess over HOI with a Hi-Tech Scientific SF-61DX2 stopped-flow spectrometer (TgK Scientific, United Kingdom) in the pH range from 7.1 to 12 at  $22 \pm 2$  °C. Initial concentrations of  $H_2O_2$  were at least 4 times higher than HOI. A wide range (12 – 16'000  $\mu M$ ) of  $H_2O_2$  solutions were prepared in different buffer solutions (Table S1, SI). HOI solutions at concentrations of 6  $\mu M$  were in the same buffer solutions as the  $H_2O_2$  solutions to avoid mixing problems. Buffered  $H_2O_2$  and HOI solutions were then mixed in a 1:1 ratio to initiate the reaction and the formation of  $I^-$  was determined spectrophotometrically at 226 nm ( $\epsilon_{226nm} = 1.36 \times 10^4 M^{-1} cm^{-1}$ ; the UV spectrum of  $I^-$  is shown in Fig. S1 (SI)). The UV absorption of  $I^-$  was not affected by the other reactants (i.e.,  $H_2O_2$  and HOI), because their molar absorption coefficients at 226 nm are much lower ( $\epsilon < 80 M^{-1} cm^{-1}$ ) and their concentrations change proportionally with  $I^-$ . Therefore, the changes of the absorption at 226 nm are proportional to the relative changes of the  $I^-$  concentration, which can be used to calculate the apparent first order rate constant. The average  $I^-$  formation curves were calculated from at least eight replicate curves for each experimental condition. Pseudo-first order rate constants ( $k_{obs}$ ) were then calculated by an exponential regression (with the software *Kinetic studio 2.x*, TgK Scientific) from the average  $I^-$  formation curves.

## 2.3. Kinetic experiments with the ABTS method in batch reactors

Lower second order rate constants for the reactions of HOI with  $H_2O_2$  in the pH range 4–6.2 were determined by the ABTS method (Pinkernell et al., 2000; Shin et al., 2018). The kinetic experiments were conducted under pseudo-first order conditions with 1  $\mu M$  (or 2  $\mu M$ ) HOI with a molar excess of  $H_2O_2$  (20–200  $\mu M$ ) in the presence of 100  $\mu M$  of  $AgNO_3$ .  $Ag^+$  was added to quench  $I^-$  by forming  $AgI$  ( $K_{so} = 8.5 \times 10^{-17}$ ) (Lide, 2006) and hence suppress the formation and the reactions of  $I_2$ . This enabled us to determine the second order rate constants of the reaction of HOI with  $H_2O_2$  at low and neutral pHs. The reaction was initiated by adding a small volume ( $\leq 1$  mL) of a  $H_2O_2$  stock solution (20 mM) under vigorous mixing to a buffered solution (100 mL) containing HOI. The reaction solutions were then quenched with an ABTS solution after certain reaction times to measure the residual HOI concentrations (Pinkernell et al., 2000).

## 2.4. Formation of iodophenols in HOI-, $H_2O_2$ -, and phenol-containing waters

Solutions (20 mL) containing phenol (10  $\mu M$ ),  $H_2O_2$  (0–50  $\mu M$ ), and  $AgNO_3$  (100  $\mu M$ ) were prepared in glass bottles and then reactions were initiated by adding 1  $\mu M$  HOI at pH 7.0 (8 mM phosphate) and pH 9.0 (8 mM phosphate + 4 mM borate) under rapid mixing (10 s).

Iodo-phenols (2-iodo- and 4-iodo-phenols) were analyzed by HPLC (Dionex Ultimate 3000, USA) with UV detection at 231 nm. The separation was achieved by a Machery-Nagel C18 column using a mobile phase consisting of 70% 10 mM phosphoric acid and 30% methanol. The limit of quantification (LOQ) for both 2-iodophenol and 4-iodophenol was 0.05  $\mu M$ .

## 2.5. Data analysis

The species-specific second order rate constants were determined from the pH-dependent apparent second order rate constants by using the software GraphPad Prism ([www.graphpad.com](http://www.graphpad.com)). Model calculations to evaluate the influence of  $H_2O_2$  during various oxidative water treatment in the presence of  $I^-$  were performed using Kintecus (Ianni, 2017).

## 3. Results and discussion

### 3.1. Determination of reaction order and second order rate constants

At pH 7 or higher, the reaction kinetics for the reactions of HOI with  $H_2O_2$  followed a second-order rate law under our experimental conditions (Table S1, SI). During the reaction of HOI with excess  $H_2O_2$ , the evolution of  $I^-$  was exponential, indicating that the reaction is pseudo first-order with respect to the  $H_2O_2$  concentration (Fig. S2, SI).  $k_{obs}$  was calculated by an exponential regression (with the software *Kinetic studio 2.x*) from the  $I^-$  formation curves (Fig. S2, SI) and alternatively was also obtained from the slopes of the linear plots of the logarithmic relative residual concentration of HOI versus time (Fig. S3, SI). The relative residual concentration of HOI was calculated from the formation of  $I^-$  (Eq. (11)).

$$-\ln \frac{[HOI]_0 - [I^-]}{[HOI]_0} = k_{obs} \times time \quad (11)$$

The obtained  $k_{obs}$  values for the two methods were within 7.6% (Figures S2 and S3, SI). Fig. S4 (SI) shows the linearity of  $k_{obs}$  as a function of the  $H_2O_2$  concentration ( $R^2 \geq 0.999$ ) at pHs 8 and 9. The inset shows that the  $\log(k_{obs})$  versus  $\log([H_2O_2]_0)$  plot has a slope of 1 confirming a reaction order of one with respect to  $H_2O_2$ . Based on this, apparent second-order rate constants ( $k_{app}$ ) were determined by dividing  $k_{obs}$  by the corresponding initial  $H_2O_2$

concentrations (Eq. (12)). The calculated  $k_{app}$  values were  $6.3 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$  at pH 8.0 and  $3.7 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$  at pH 9.0 (Table S1 (SI) and Fig. 1 and Fig. S4 (SI)).

$$k_{app} = k_{obs}/[H_2O_2]_0 \quad (12)$$

For pH < 7.0, the kinetics for the reaction of HOI with  $H_2O_2$  did not follow pseudo-first order (1–3  $\mu\text{M}$  HOI in excess of  $H_2O_2$ ). This is illustrated as an example in Fig. S5 (SI), for pH 6 (HOI (3  $\mu\text{M}$ ) with excess  $H_2O_2$  (1, 2, and 4 mM)). This is due to the presence of  $I_2$  leading to several competitive reactions, which may have caused the wide range of reported second order rate constants for the reaction of HOI with  $H_2O_2$  in the literature (Table 2). Since  $I^-$  is produced during the reaction of HOI with  $H_2O_2$ , the  $I_2$  concentration increases with increasing formation of  $I^-$  in the course of the reaction, especially at low pH (Eq. (5), Table 1). Fig. S6 (SI) shows the speciation of  $I_2$ /HOI/OI $^-$  depending on  $I^-$  concentrations (0.1 and 2.0  $\mu\text{M}$ ) as a function of pH. HOI is the major species in the neutral pH (6–9) in the presence of low concentration of  $I^-$  (e.g., 0.1  $\mu\text{M}$ ). Meanwhile,  $I_2$  is the major species in presence of a high concentration of  $I^-$  (e.g., 2.0  $\mu\text{M}$ ) for a pH < 6.5.

To exclude the effect of  $I^-$ , 100  $\mu\text{M}$   $Ag^+$  was added before initiating the reactions at pH < 7.0, to avoid the formation of  $I_2$  (see above). Under these conditions, the decrease of HOI ( $[HOI]_0 = 1$  or 2  $\mu\text{M}$ ) in the presence of excess  $H_2O_2$  (20–200  $\mu\text{M}$ ) showed pseudo-first order kinetics (Fig. S7, SI). Second order rate constants ( $k_{app}$ ) were determined by Eq. (13), yielding  $34 \pm 1 \text{ M}^{-1}\text{s}^{-1}$ ,  $84 \pm 8 \text{ M}^{-1}\text{s}^{-1}$ , and  $940 \pm 60 \text{ M}^{-1}\text{s}^{-1}$  at pHs 4, 5, and 6, respectively.

$$-\ln \frac{[HOI]}{[HOI]_0} = k_{app} \times [H_2O_2]_0 \times \text{time} \quad (13)$$

### 3.2. pH dependence of the second order rate constant for the reaction between hypiodous acid and hydrogen peroxide

Table S1 (SI) compiles the observed pH-dependent first-order rate constants ( $k_{obs}$ ) and apparent second-order rate constants ( $k_{app}$ ) for the reactions of HOI with  $H_2O_2$ . The  $k_{app}$  are also plotted in Fig. 1 for the pH range 4–12. In general, the  $k_{app}$  values increase with increasing pH, which can be explained by the speciation of HOI and  $H_2O_2$  ( $pK_{a1}(\text{HOI/OI}^-) = 10.4$  and  $pK_{a2}(\text{H}_2\text{O}_2/\text{HO}_2^-) = 11.8$ ). Acid-base equilibria are considered to be faster than the redox reactions. From a kinetic point of view, the reactions in Eqs. (2) and (3) cannot be distinguished because they have the same pH dependence. Rather than considering the two reactions in parallel, it is assumed that only one of the two pathways is important. In the HOI– $H_2O_2$  systems, HOI is more electrophilic than  $OI^-$ , and  $HO_2^-$  is stronger nucleophile than  $H_2O_2$ . Therefore, the reaction of HOI with  $HO_2^-$  (Eq. (2)) is considered the major pathway for the reaction of HOI with  $H_2O_2$ . The same mechanistic interpretations for the HOCl– $H_2O_2$  and HOBr– $H_2O_2$  systems are discussed in the literature (Held et al., 1978; von Gunten and Oliveras, 1997). Meanwhile, at low or high pH, the reactions of HOI with  $H_2O_2$  or  $OI^-$  with  $HO_2^-$ , respectively, can also occur. Therefore, Eqs. (1), (2) and (4) should be considered to determine the species-specific second order rate constants.

The pH-dependent variation in  $k_{app}$  could be quantitatively modeled by Eq. (14), considering the species-specific reactions between HOI/OI $^-$  and  $H_2O_2$ /HO $_2^-$ .

$$k_{app} = k_1 \alpha_{HOI} \beta_{H_2O_2} + k_2 \alpha_{HOI} \beta_{HO_2^-} + k_4 \alpha_{OI^-} \beta_{HO_2^-} \quad (14)$$

where  $k_1$ ,  $k_2$ , and  $k_4$  are the species-specific second order rate constants in Eqs. (1), (2) and (4), respectively.  $\alpha_{HOI}$ ,  $\alpha_{OI^-}$ ,  $\beta_{H_2O_2}$ , and

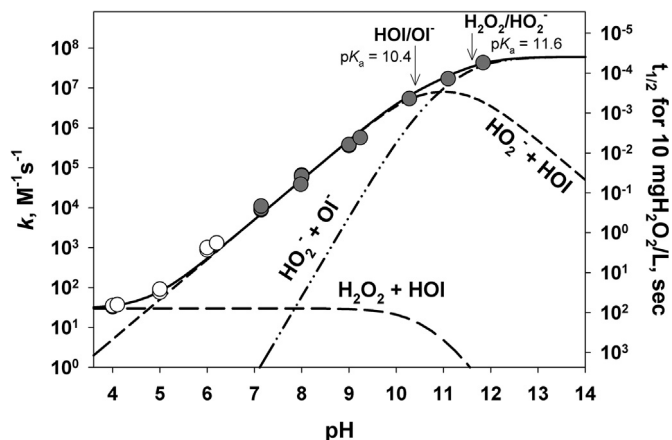


Fig. 1. Apparent second-order rate constants ( $k_{app}$ , left-axis) for the reaction of HOI with  $H_2O_2$  and half-lives for the HOI abatement in presence of  $10 \text{ mg L}^{-1} H_2O_2$  ( $t_{1/2}$ , right-axis) as a function of pH (4.0–11.8). The closed circles represent the  $k_{app}$  values determined with stopped-flow measurements and the open circles represent the  $k_{app}$  values determined by the ABTS method in a batch system in the presence of  $AgNO_3$ . The solid line represents the calculated  $k_{app}$  for the reaction of HOI with  $H_2O_2$  according to Eq. (14) in the text. The other lines represent the calculated contributions of the reactions of HOI with  $HO_2^-$  (dashed),  $OI^-$  with  $HO_2^-$  (dotted-dashed), and HOI with  $H_2O_2$  (long dashed) to the overall reaction as a function of the pH.

$\beta_{HO_2^-}$  represent the fractions of HOI,  $OI^-$ ,  $H_2O_2$ , and  $HO_2^-$ , respectively, which, at a given pH can be expressed as  $\alpha_{HOI} = [H^+]/([H^+] + K_{a,HOI})$ ,  $\alpha_{OI^-} = K_{a,HOI}/([H^+] + K_{a,HOI})$ ,  $\beta_{H_2O_2} = [H^+]/([H^+] + K_{a,H_2O_2})$ , and  $\beta_{HO_2^-} = K_{a,H_2O_2}/([H^+] + K_{a,H_2O_2})$ , with  $K_a$  being the corresponding acid-base equilibrium constants (see Table 1). The species-specific second order rate constants were calculated from least squares nonlinear regressions of the experimental  $k_{app}$  data (Table S1, SI) using the GraphPad Prism ([www.graphpad.com](http://www.graphpad.com)). The model could fit the experimental  $k_{app}$  well ( $R^2 > 0.92$ ). The species-specific second order rate constants were determined to be  $k_1(\text{HOI} + \text{H}_2\text{O}_2) = 29 \pm 5.2 \text{ M}^{-1}\text{s}^{-1}$ ,  $k_2(\text{HOI} + \text{HO}_2^-) = (3.1 \pm 0.3) \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ ,  $k_4(\text{OI}^- + \text{HO}_2^-) = (6.4 \pm 1.4) \times 10^7 \text{ M}^{-1}\text{s}^{-1}$  (Table 2). The error ranges for  $k_1$ ,  $k_2$ , and  $k_4$  are due to experimental variabilities and also due to the types and concentrations of the buffers.

The second order rate constants for the reactions of HOI with  $H_2O_2$  can be applied to calculate the half-life of HOI in  $H_2O_2$  containing water treatment. The calculations of the half-life of HOI are shown in Fig. 1 for  $10 \text{ mg L}^{-1} H_2O_2$ , which is an intermediate-high range dose applied to advanced oxidation processes (AOPs) (Stefan, 2017). Half-lives for the HOI abatement in the presence of  $10 \text{ mg/L}$  of  $H_2O_2$  are 4.4, 0.47, and 0.047 s at pH 6, 7, and 8, respectively.

### 3.3. Effect of the buffer type and concentrations on the kinetics of the reactions of HOI with $H_2O_2$

Previous studies have shown that buffer type and concentrations can influence the reactivity of HOI with oxidants (i.e., ferrate(VI) or permanganate(VII)) (Wang et al., 2018; Zhao et al., 2016) or phenols (Zhao et al., 2017) and the disproportionation of HOI (Bichsel and von Gunten, 2000b). The effects of different buffers (phosphate, borate, and acetate) at different pHs (pH 7.3, 9.0, and 4.7) on the reduction of HOI by  $H_2O_2$  were investigated (Table S2 and Figs. S8–S10 (SI)). During the reaction of HOI (3  $\mu\text{M}$ ) with  $H_2O_2$  (4 mM at pH 7.3, 40  $\mu\text{M}$  at pH 9.0), an exponential increase of  $I^-$  was monitored by stopped-flow in the presence of various concentrations of phosphate ( $pK_a = 7.2$  for  $H_2PO_4^-$  (Goldberg et al., 2002)) or borate buffer ( $pK_a = 9.2$  (Goldberg et al., 2002)) (Figs. S8 and S9 (SI)). At pH 4.7, the kinetics of the reactions of HOI with  $H_2O_2$

follow pseudo first order in the presence of 100  $\mu\text{M}$  of  $\text{Ag}^+$  with various concentrations of acetate ( $\text{p}K_a = 4.76$  (Goldberg et al., 2002)) (Fig. S10, SI). The rates of  $\text{I}^-$  formation and hence the HOI consumption increased with increasing phosphate, borate, and acetate concentrations. This indicates that the selected buffers enhance the reaction of HOI with  $\text{H}_2\text{O}_2$ . Among the selected buffers, phosphate shows the most significant enhancement of the reactivity, especially at pH 7.3 (Fig. S11, SI). At pH 7.3,  $k_{app}$  in presence of 1.25 mM phosphate buffer was  $7.6 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$ , which increased up to a factor of 4.3 for 25 mM phosphate ( $k_{app} = 3.3 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$ ). However, the effect of phosphate was less pronounced at pH 9.0. The reaction in presence of 50 mM phosphate was 1.6 times faster than without phosphate. Meanwhile, acetate enhanced the apparent second order rate constant from  $52 \text{ M}^{-1}\text{s}^{-1}$  (1 mM acetate) to  $140 \text{ M}^{-1}\text{s}^{-1}$  (25 mM acetate) at pH 4.7. Borate showed lower effects on the apparent second order rate constants, which ranged from  $2.5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$  (0.5 mM borate) to  $5.4 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$  (25 mM borate). The rate constants at zero buffer concentrations were also estimated by a linear regression based on Fig. S11 (SI). The y-axis intercept indicates each second order rate constant at zero buffer concentration ( $40.7 \text{ M}^{-1}\text{s}^{-1}$  at pH 4.7,  $5.6 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$  at pH 7.3, and  $2.4 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$  at pH 9.0). These second order rate constants are compared in Fig. S12 (SI) with the determined  $k_{app}$  (Fig. 1 and Table S1, SI) which were used for determining the species-specific rate constants. The measured  $k_{app}$  values at 3–6 mM acetate buffer (pH 4–5), at 5–10 mM phosphate buffer (pH 6–8), and at 5–10 mM borate buffer (pH  $\geq 9$ ) might be overestimated at most 2.4-, 3.2-, 1.7-fold, respectively, which is in the range of variations of experimental second order rate constants.

#### 3.4. Temperature effect on the kinetics of the reduction of HOI by $\text{H}_2\text{O}_2$

The effect of temperature on the kinetics of the reaction of HOI with  $\text{H}_2\text{O}_2$  was studied at 10.0–23.2  $^\circ\text{C}$  at pH 9.0 (5 mM phosphate + 5 mM borate buffer) (Fig. S13, SI). An Arrhenius plot shows good linearity ( $R^2 = 0.98$ ), between the logarithm of the apparent second order rate constants and the reciprocal of the absolute temperature (T) (Eq. (15)).

$$\ln k_{app} = \frac{-E_a}{R} \times \frac{1}{T} + \ln A \quad (15)$$

where A is a frequency factor,  $E_a$  is the apparent activation energy ( $\text{J mol}^{-1}$ ), R ( $8.314 \text{ J mol}^{-1}\text{K}^{-1}$ ) is the ideal gas constant, and T is absolute temperature (K). Based on Eq. (15) (Fig. S13, SI) an  $E_a$  of  $34 \text{ kJ mol}^{-1}$  can be obtained. This is significantly lower than the  $E_a$  value of  $125 \text{ kJ mol}^{-1}$  reported for the reaction of  $\text{I}_2$  with  $\text{H}_2\text{O}_2$  (Ball and Hnatiw, 2001).

#### 3.5. Formation of iodophenols in HOI-, $\text{H}_2\text{O}_2$ -, and phenol-containing waters

To evaluate the effect of  $\text{H}_2\text{O}_2$  on the formation of I-DBPs during oxidation processes, in which  $\text{H}_2\text{O}_2$  is present (e.g.,  $\text{O}_3/\text{H}_2\text{O}_2$ , UV/ $\text{H}_2\text{O}_2$ , ferrate(VI), peracetic acid treatment), phenol was added as a simplified surrogate for DOM and the formed iodophenols were quantified as a proxy for the extent of I-DBPs formation. The second order rate constant of the reaction of HOI with phenol is similar to the reaction of HOI with  $\text{H}_2\text{O}_2$  at pH 7 (i.e.,  $k_{\text{HOI}+\text{phenol}} = 2.6 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$  (Bichsel and von Gunten, 2000a) and  $k_{\text{HOI}+\text{H}_2\text{O}_2} = 4.9 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$  at pH 7.0 (this study)), 2-iodophenol and 4-iodophenol were detected during the reaction of HOI (1  $\mu\text{M}$ ) with phenol (10  $\mu\text{M}$ ) in the presence of varying concentrations of  $\text{H}_2\text{O}_2$  (0–50  $\mu\text{M}$ ) at pH 7.0 (8 mM

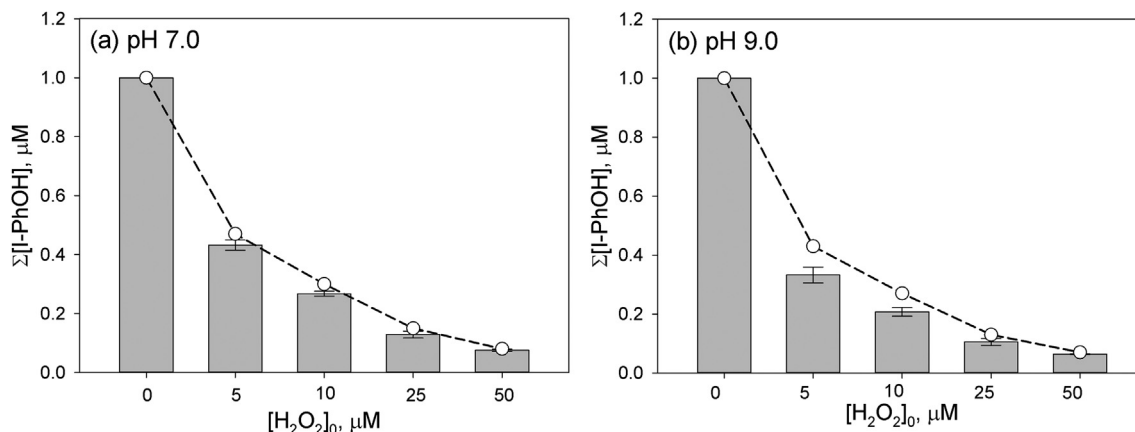
phosphate) and pH 9.0 (8 mM phosphate + 4 mM borate).  $\text{Ag}^+$  was added to exclude the formation and reactions of  $\text{I}_2$ . A HOI concentration of 1  $\mu\text{M}$  was chosen to simulate an elevated  $\text{I}^-$  level (130  $\mu\text{g/L}$ ) and the concentration of phenol was 10 times that of HOI. 10  $\mu\text{M}$  ( $\sim 0.94 \text{ mg/L}$ ) of phenol would correspond to a source water containing about 5 mgC/L DOC with a typical phenol content of around 20% (Önnby et al., 2018).

$\text{H}_2\text{O}_2$  is generally applied as 2–15 mg/L in advanced oxidation processes (Stefan, 2017). Nevertheless, relatively low concentrations of  $\text{H}_2\text{O}_2$  ( $\leq 2 \text{ mg/L}$ ) were applied here to evaluate the trend of iodophenol formation.

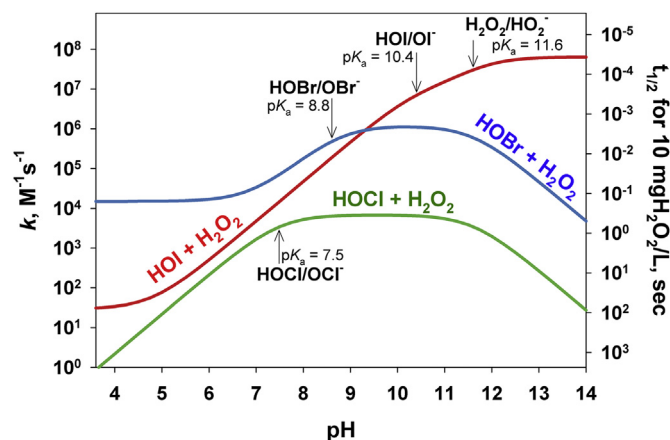
Fig. 2 shows that HOI was fully transformed to iodophenols during the reaction of HOI with phenol in the absence of  $\text{H}_2\text{O}_2$  at pHs 7.0 and 9.0. As expected, the formation of iodophenols decreased with increasing  $\text{H}_2\text{O}_2$  doses and at the maximum  $\text{H}_2\text{O}_2$  concentration of about 1.7 mg/L (50  $\mu\text{M}$ ) only low concentrations of iodophenols ( $< 0.1 \mu\text{M}$ ) were detected due to the reduction of HOI by  $\text{H}_2\text{O}_2$  to  $\text{I}^-$ . Even with these relatively low  $\text{H}_2\text{O}_2$  doses, a large effect on the minimization of the formation of iodophenols was observed. Similar levels of iodophenol formation were observed at both pH 7.0 and 9.0. This is because  $k_{app}$  of the reaction of HOI with phenol and the reaction of HOI with  $\text{H}_2\text{O}_2$  exhibit a similar pH dependency, with generally increasing apparent second order rate constants with increasing pH (Bichsel and von Gunten, 2000a; Zhao et al., 2017). The modeling results based on the reaction in Table S3 (SI) for the iodophenol formation were slightly higher than the experimental data by a factor of 1.05–1.15 at pH 7.0 and 1.1–1.3 at pH 9.0 (Fig. 2a and b, dashed lines with circles). This can be considered as a good agreement given the uncertainty in the values of the second order rate constants for the involved reactions.

#### 3.6. Comparison of the reactivities of $\text{H}_2\text{O}_2$ with HOI, HOCl, and HOBr

Fig. 3 and Table 2 show a comparison of the apparent and species-specific second order rate constants for the reactions of  $\text{H}_2\text{O}_2$  with HOI, HOBr, and HOCl, respectively. The species-specific second order rate constants for the reaction of  $\text{HO}_2^-$  with HOX, decrease in the order HOBr ( $7.6 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ ) > HOI ( $3.1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ ) > HOCl ( $4.4 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ ). This sequence has also been observed for electrophilic aromatic substitution reactions of HOX with phenols (Heeb et al., 2014). Based on the standard reduction potentials it would be expected that HOCl has the highest reactivity. However, since the reaction potentially involves a  $\text{X}^+$  transfer to  $\text{HO}_2^-$  (Heeb et al., 2014), the partial positive charge on X in HOX is also important. The electronegativity of the halogens decreases in the order  $\text{Cl} > \text{Br} > \text{I}$ , wherefore, the partial positive charge increases in the order  $\text{Cl} < \text{Br} < \text{I}$ . Based on this consideration, HOI should have the highest reactivity to form the H–O–O–X intermediate. This species decomposes under the formation of  $\text{X}^-$  and singlet oxygen. This reaction step is favored again by the more electrophilic halogen. Overall, the combination of these factors then leads to the observed sequence for the species-specific second order rate constants for the reactions of HOX with  $\text{H}_2\text{O}_2$ . The only exception was observed from the reaction of  $\text{HO}_2^-$  with  $\text{OI}^-$ . In the literature, the reaction of  $\text{HO}_2^-$  with hypohalite ions ( $\text{OBr}^-$  and  $\text{OCl}^-$ ) were not considered because of the strongly reduced partial positive charge on Br and Cl for the hypohalite ions. Meanwhile, the reaction of  $\text{HO}_2^-$  with  $\text{OI}^-$  was the major reaction at high pH ( $> 11.0$ ). This may be due to the lower electronegativity of I compared to Br or Cl, which means that there is still a significant partial positive charge on I in  $\text{OI}^-$ .



**Fig. 2.** Measured and modeled formation of iodo-phenols during the reaction of HOI with phenol as a function of increasing  $\text{H}_2\text{O}_2$  concentrations (0, 5, 10, 25, and 50  $\mu\text{M}$ ) for (a) pH 7.0 (8 mM phosphate) and (b) pH 9.0 (8 mM phosphate + 4 mM borate). Experimental conditions:  $[\text{phenol}]_0 = 10 \mu\text{M}$ ,  $[\text{HOI}]_0 = 1 \mu\text{M}$ , and  $[\text{AgNO}_3]_0 = 100 \mu\text{M}$ . Each bar represents the mean value, and the error bars represent the range of values from duplicate experiments. Dashed lines with circles represent the model calculation by Kintecus (Ianni, 2017). The model calculations are based on the reactions in Table S3 (SI).



**Fig. 3.** Comparison of the pH-dependent apparent second-order rate constants for the reactions of  $\text{H}_2\text{O}_2$  with HOI, HOBr, or HOCl. The rate constants for the reaction of  $\text{H}_2\text{O}_2$  with HOCl were obtained from Held et al. (1978), and with HOBr from von Gunten and Oliveras (1997).

### 3.7. Implications for water treatment and natural systems

#### 3.7.1. Water treatment

The formation of I-DBPs during drinking water disinfection has become an emerging concern. Their formation is initiated by the relatively easy oxidation of  $\text{I}^-$  to HOI by chemical oxidants during water treatment. However, most oxidants with the exception of  $\text{O}_3$  and Fe(VI) have low reactivity with HOI, which leads to the formation of I-DBPs by the reaction of HOI with DOM. In certain processes, in which  $\text{H}_2\text{O}_2$  is present together with a primary oxidant, the reduction of HOI to  $\text{I}^-$  by  $\text{H}_2\text{O}_2$  needs to be considered due to the significant reactivity of the two compounds.

A recent study showed a constant  $\text{I}^-$  concentration during UV/ $\text{H}_2\text{O}_2$  treatment in the presence of 130  $\mu\text{g/L}$  of  $\text{I}^-$ , 10  $\text{mg/L}$  of  $\text{H}_2\text{O}_2$ , and 3.5  $\text{mg/L}$  DOC at pH 7.0 (Zhang et al., 2018). In fact, in the UV/ $\text{H}_2\text{O}_2$  process,  $\text{I}^-$  is oxidized to HOI through the formation of radical species (i.e.,  $\text{I}^\bullet$ ,  $\text{I}_2^\bullet$ ) by the rapid reaction with OH radical ( $k \sim 10^{10} \text{ M}^{-1}\text{s}^{-1}$ ) (Elliot, 1992; Ellison et al., 1972; Nagarajan and Fessenden, 1985). However, the formed HOI will be quickly reduced to  $\text{I}^-$  by  $\text{H}_2\text{O}_2$ . As already mentioned above, half-lives for the HOI abatement in the presence of 10  $\text{mg/L}$  of  $\text{H}_2\text{O}_2$  at neutral pH were low, namely 0.5 and 0.05 s at pH 7 and 8, respectively. Thus,

UV/ $\text{H}_2\text{O}_2$  pre-oxidation followed by chlorination or chloramination still has a risk of I-DBP formation due to the remaining  $\text{I}^-$ .

In the  $\text{O}_3/\text{H}_2\text{O}_2$  process,  $\text{I}^-$  is quickly oxidized to HOI ( $k_{\text{O}_3+\text{I}^-} = 2.0 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ ). The resulting hypiodous acid (HOI/OI $^-$ ) has two competing reaction pathways: (1) reduction to  $\text{I}^-$  by  $\text{H}_2\text{O}_2$  ( $k_{\text{HO}_2+\text{HOI}} = 3.1 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$ ) and (2) oxidation to IO $_3^-$  through IO $_2^-$  by  $\text{O}_3$  ( $k_{\text{O}_3+\text{HOI}} = 3.6 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$  and  $k_{\text{O}_3+\text{OI}^-} = 1.6 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ ). Reduction of HOI by  $\text{H}_2\text{O}_2$  could lead to the loss of oxidation capacity of  $\text{O}_3$  by a catalytic cycle of oxidation of  $\text{I}^-$  by  $\text{O}_3$  and reduction of HOI by  $\text{H}_2\text{O}_2$  back to  $\text{I}^-$ . A kinetic simulation was used to calculate the relative contributions of various reactions to the  $\text{O}_3$  consumption, i.e., catalytic oxidation of  $\text{I}^-$ , reaction with  $\text{H}_2\text{O}_2$ , and further oxidation of HOI to IO $_3^-$ . For simplicity, the formation and reactions of  $\bullet\text{OH}$  were not considered in these model calculations. For the selected conditions of the  $\text{O}_3/\text{H}_2\text{O}_2$  process, 56–66% of  $\text{O}_3$  (i.e., 11.7–13.7  $\mu\text{M}$ ) was consumed by the catalytic oxidation of  $\text{I}^-$  (Fig. S14, SI), rather than for the formation of  $\bullet\text{OH}$  via its reaction with  $\text{H}_2\text{O}_2$  ( $k_{\text{O}_3+\text{HO}_2} = 9.6 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ ) for an elevated level of  $\text{I}^-$  (e.g., 1  $\mu\text{M}$  (~130  $\mu\text{g/L}$ ),  $[\text{O}_3] = 1 \text{ mg/L}$  (20.8  $\mu\text{M}$ ) and  $[\text{H}_2\text{O}_2] = (4\text{--}10 \text{ mg/L})$ ) at pH 8.0. IO $_3^-$  was the dominant iodine species only during ozonation with a low concentration of  $\text{H}_2\text{O}_2$  ( $[\text{H}_2\text{O}_2] \leq 2 \text{ mg/L}$ ) due to the fast reactions of  $\text{O}_3$  with  $\text{I}^-$  and with HOI forming IO $_3^-$ . However, significant concentrations of  $\text{I}^-$  could remain after complete consumption of  $\text{O}_3$  in the presence of relatively high  $\text{H}_2\text{O}_2$  ( $[\text{H}_2\text{O}_2] > 2 \text{ mg/L}$ ). Such conditions are typically applied for bromate control during the  $\text{O}_3/\text{H}_2\text{O}_2$  process (Pinkernell and von Gunten, 2001; Soltermann et al., 2017; von Gunten and Oliveras, 1997; von Gunten and Oliveras, 1998; von Sonntag and von Gunten, 2012). During post-disinfection with chlorine or chloramine, iodide can then be a precursor to I-DBPs. Therefore, if both  $\text{I}^-$  and  $\text{Br}^-$  are present in a source water, appropriate  $\text{H}_2\text{O}_2$  doses should be applied during ozonation to minimize the formation of both I-DBPs and  $\text{BrO}_3^-$ .

Peracetic acid (PAA) is a disinfectant considered for use in ballast water and wastewater treatment (Luukkonen and Pehkonen, 2017; Shah et al., 2015a,b; Werschkun et al., 2014).  $\text{H}_2\text{O}_2$  is always present in peracetic acid (PAA) solutions because PAA is synthesized by the reaction of acetic acid with  $\text{H}_2\text{O}_2$ . To evaluate the role of  $\text{H}_2\text{O}_2$  during the treatment of  $\text{I}^-$  and  $\text{Br}^-$  by PAA in an ocean-type water, a kinetic simulation was performed. Fig. S15 (SI) shows the evolutions of HOI, HOBr,  $\text{H}_2\text{O}_2$ , and PAA during treatment of 0.5  $\mu\text{M}$   $\text{I}^-$  and 460  $\mu\text{M}$   $\text{Br}^-$  by 2.15  $\text{mM}$  PAA in the presence of 0.65  $\text{mM}$   $\text{H}_2\text{O}_2$  at pH 8.0. In this system,  $\text{I}^-$  and  $\text{Br}^-$  are oxidized to HOI and HOBr by

PAA ( $k_{PAA+I^-} = 4.2 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$ ,  $k_{PAA+Br^-} = 0.24 \text{ M}^{-1}\text{s}^{-1}$ ) (Awad et al., 2003; Shah et al., 2015a), however, as soon as HOI or HOBr are produced, they are reduced by  $\text{H}_2\text{O}_2$  to  $\text{I}^-$  or  $\text{Br}^-$ . These reactions continued until most of the  $\text{H}_2\text{O}_2$  was consumed, and at the same time, PAA decreased to a similar extent as  $\text{H}_2\text{O}_2$ . For the selected conditions (Fig. S15, SI)  $\text{H}_2\text{O}_2$  was almost completely consumed at 20 min and  $\text{I}^-$  was rapidly oxidized to HOI whereas  $\text{Br}^-$  was slowly oxidized to HOBr by PAA. During PAA treatment,  $\text{H}_2\text{O}_2$  can be a barrier for the formation I-DBPs or Br-DBPs by minimizing the lifetime of the hypohalous acids HOI and HOBr. However, it can also lead to a rapid consumption of PAA by an iodide-catalyzed reaction. This catalyzed reaction was also reported in a previous study (Shah et al., 2015a).

$\text{H}_2\text{O}_2$  is one of the major products during the self-decay of Fe(VI) (Lee et al., 2014). The yield of  $\text{H}_2\text{O}_2$  ( $\Delta[\text{H}_2\text{O}_2]/\Delta[\text{Fe(VI)}]$ ) was  $\sim 0.2$  during the reaction of Fe(VI) with  $\text{I}^-$  or HOI (Shin et al., 2018). To assess the influence of  $\text{H}_2\text{O}_2$  formation on the fate of iodine, a kinetic simulation was performed for treatment of  $\text{I}^-$  by Fe(VI). To better understand the effect of  $\text{H}_2\text{O}_2$ , the following simplified boundary conditions were assumed:  $\text{H}_2\text{O}_2$  was not produced during the Fe(VI) reactions but was initially present as 30% of Fe(VI). Fig. S16 (SI) shows the modeling results for the evolution of HOI,  $\text{IO}_3^-$ ,  $\text{H}_2\text{O}_2$ , and Fe(VI) during the treatment of  $1 \mu\text{M}$  of  $\text{I}^-$  by  $17.9 \mu\text{M}$  Fe(VI) ( $1 \text{ mgFe/L}$ ) in the presence of  $5.4 \mu\text{M}$   $\text{H}_2\text{O}_2$  at pHs 7.0–9.0. At pH 7.0, 99% of  $\text{I}^-$  was oxidized to  $\text{IO}_3^-$  within 11 s by Fe(VI) without interference of  $\text{H}_2\text{O}_2$ . With increasing pH from 7.0 to 9.0, the oxidation rate of  $\text{I}^-$  to  $\text{IO}_3^-$  decreased. This is because the rate of Fe(VI) reaction with HOI and  $\text{I}^-$  decreases with increasing pH (i.e.,  $k_{\text{Fe(VI)+HOI}} = 1.8 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$  at pH 7.0 and  $4.7 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$  at pH 9.0) while the rate of HOI reduction by  $\text{H}_2\text{O}_2$  to  $\text{I}^-$  increases. Overall an increase in pH led to an increase in the consumption of  $\text{H}_2\text{O}_2$  and Fe(VI). At pH 7.0, only  $3 \mu\text{M}$  of Fe(VI) was consumed to completely oxidize  $1 \mu\text{M}$   $\text{I}^-$  to  $\text{IO}_3^-$  without consumption of  $\text{H}_2\text{O}_2$ , while, at pH 9.0,  $8.4 \mu\text{M}$  of Fe(VI) was consumed with a  $\text{H}_2\text{O}_2$  consumption of  $5.6 \mu\text{M}$  for a full oxidation of  $\text{I}^-$  to  $\text{IO}_3^-$ .

### 3.7.2. Natural systems

$\text{O}_3$  deposition to the seawater surface is a significant mechanism for the loss of atmospheric  $\text{O}_3$ , accounting for a loss of 600–1000 Tg  $\text{O}_3 \text{ yr}^{-1}$  (Ganzeveld et al., 2009). Aqueous inorganic iodine (i.e.,  $\text{I}^-$ , HOI) at the sea surface microlayer is one of the major contributors to the oceanic deposition of  $\text{O}_3$ . This is based on the fast reaction between  $\text{O}_3$  (gas) and  $\text{I}^-$ , which forms HOI in the aqueous phase and iodine oxide in the gaseous phase while  $\text{O}_3$  is reduced to  $\text{O}_2$  (Carpenter et al., 2013; Chang et al., 2004; Sarwar et al., 2015; Simpson et al., 2015). During this reaction,  $\text{O}_3$  deposition might be significantly enhanced by  $\text{H}_2\text{O}_2$  due to its high reactivity with HOI to form  $\text{I}^-$ . The concentration of  $\text{H}_2\text{O}_2$  at the sea surface varies from 10 to  $>500 \text{ nM}$  (Moore et al., 1993; Price et al., 1998; Zika et al., 1985). The gas-phase flux of  $\text{O}_3$  into the boundary layer can be determined by the product of the  $\text{O}_3$  deposition velocity ( $v_D$ ) and the  $\text{O}_3$  concentration ( $[\text{O}_3(\text{gas})]$ ). The  $\text{O}_3$  deposition velocity ( $v_D$ ) over seawater is highly variable ( $0.01$ – $0.27 \text{ cm s}^{-1}$ ) (Ganzeveld et al., 2009; Helmig et al., 2012), depending on several factors in the seawater (i.e., water quality) and the atmosphere (e.g., wind).

A simplified isolated kinetic modeling was performed to assess the impact of the seawater concentrations of  $\text{H}_2\text{O}_2$  on the  $\text{O}_3$  deposition to the sea surface microlayer in the presence of  $\text{I}^-$  and  $\text{Br}^-$  (Fig. S17, SI). Since the source of  $\text{O}_3$  is the atmosphere and the source of  $\text{I}^-$ ,  $\text{Br}^-$ , and  $\text{H}_2\text{O}_2$  is the ocean, it was assumed that the concentrations of each compound are in steady state. A steady-state concentration of HOI was applied instead of  $\text{I}^-$  since  $\text{I}^-$  is easily oxidized to HOI. Currently, HOI concentrations in the seawater are unknown due to the lack of analytical techniques with sufficient accuracy and sensitivity (Carpenter et al., 2013).

Considering the reported total inorganic iodine concentrations (e.g.,  $\text{I}^-$  and  $\text{IO}_3^-$ ) of 500 nM in seawater (Chance et al., 2014), the  $[\text{HOI}]_{\text{ss}}$  was varied between 25–500 nM. With increasing  $[\text{HOI}]_{\text{ss}}$ ,  $\text{O}_3$  deposition increases (SI-Text-3 and Fig. S17 (SI)). In a next step, the  $[\text{HOI}]_{\text{ss}}$  was fixed at an intermediate concentration of 100 nM and the steady-state concentrations of the other reactive species were assumed as follows:  $[\text{O}_3]_{\text{ss}} = 1 \text{ nM}$ ,  $[\text{Br}^-]_{\text{ss}} = 500 \mu\text{M}$ , and variable  $[\text{H}_2\text{O}_2]_{\text{ss}} = 0, 10, 25, 100, 250, 500 \text{ nM}$ . Virtual reaction products as tracers (i.e., P1, P2, ...P7 in Table S4, SI) were quantified by Kintecus modeling to obtain the relative contributions of the various reactions to  $\text{O}_3$  consumption (reactions 1 – 7 in Table S4, SI): (1) Oxidation of  $\text{I}^-$  was obtained from P3, (2) Oxidation of  $\text{Br}^-$  was obtained from P7, and (3) Oxidation of HOI to  $\text{IO}_3^-$  was determined by the summation of P4, P5, and P6. The reaction system reached steady-state within a few seconds, however, one year of modeling time was applied to obtain the total yearly  $\text{O}_3$  deposition.

As the  $\text{H}_2\text{O}_2$  concentration is increasing, the  $\text{O}_3$  consumption for the oxidation of  $\text{I}^-$  becomes increasingly important compared to the reaction with bromide, which dominates at low  $\text{H}_2\text{O}_2$  concentrations (Fig. S18a, SI). The contribution of the catalytic oxidation of  $\text{I}^-$  for the  $\text{O}_3$  consumptions increased from 36% to 97% for an increase of  $\text{H}_2\text{O}_2$  from 10 nM to 500 nM (Fig. S18a, SI). For all selected  $\text{H}_2\text{O}_2$  concentrations, the consumption of  $\text{O}_3$  by the oxidation of HOI to  $\text{IO}_3^-$  was insignificant ( $<10\%$ ) compared to the  $\text{O}_3$  consumption for the oxidation of  $\text{I}^-$  or  $\text{Br}^-$ .

In this kinetic modeling, the concentration of  $\text{I}^-$  reached steady-state within a few seconds. Fig. S18b (SI) shows that the resulting steady-state concentration of  $\text{I}^-$  ( $[\text{I}^-]_{\text{ss}}$ ) and the total  $\text{O}_3$  consumptions over 1 year depend on the initial  $[\text{H}_2\text{O}_2]_{\text{ss}}$ . According to kinetic modeling results, the  $[\text{I}^-]_{\text{ss}}$  increased linearly with increasing  $\text{H}_2\text{O}_2$  concentrations (0–500 nM). As a consequence, the total  $\text{O}_3$  deposition rate increased proportionally (2.8–82.1 mM per year). If these results are combined with variable  $[\text{HOI}]_{\text{ss}}$ , the total  $\text{O}_3$  deposition ranges from 3.6 mM (25 nM HOI/25 nM  $\text{H}_2\text{O}_2$ ) to 400 mM (500 nM HOI/500 nM  $\text{H}_2\text{O}_2$ ) per year.

Accounting for the area of the sea surface microlayer ( $3.5 \times 10^8 \text{ km}^2$ ) (Costello et al., 2010) and setting the depth of the boundary layer to 100  $\mu\text{m}$ , an  $\text{O}_3$  deposition rate of 6.2–400 Tg/year can be calculated depending on the HOI (25–500 nM) and the  $\text{H}_2\text{O}_2$  concentrations (0–500 nM). Depending on the boundary conditions, this deposition rate is about two orders of magnitude lower or in the same range as current estimates (see above). Therefore, our simplified estimate shows that  $\text{H}_2\text{O}_2$  may have a high potential to increase the  $\text{O}_3$  deposition by the catalytic oxidation of  $\text{I}^-$  at the sea surface, which might warrant an inclusion of these reactions to calculate  $\text{O}_3$  deposition in future modeling efforts. The reduction of HOI by  $\text{H}_2\text{O}_2$  can also occur in atmospheric waters, which may lead to a reduction of the  $\text{O}_3$  levels in the troposphere (Pillar et al., 2013).

## 4. Conclusions

Apparent and species-specific second order rate constants for the reactions of hydrogen peroxide with hypiodous acid were determined and the main conclusions are as follows:

- The reaction between HOI and  $\text{H}_2\text{O}_2$  is a second-order process. The species-specific second order rate constants for the reactions of  $\text{H}_2\text{O}_2$  with HOI,  $\text{HO}_2^-$  with HOI,  $\text{HO}_2^-$  with  $\text{OI}^-$  are  $k_{\text{H}_2\text{O}_2+\text{HOI}} = 29 \pm 5.2 \text{ M}^{-1}\text{s}^{-1}$ ,  $k_{\text{HO}_2^-+\text{HOI}} = (3.1 \pm 0.3) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , and  $k_{\text{HO}_2^-+\text{OI}^-} = (6.4 \pm 1.4) \times 10^7 \text{ M}^{-1}\text{s}^{-1}$ , respectively.
- Phosphate (1.25–25 mM) and acetate (1–25 mM) buffers lead to a significant enhancement of the  $\text{H}_2\text{O}_2$ –HOI reactivity at pH 7.3 by a factor of 4 and at pH 4.7 by a factor of 3, respectively.

Meanwhile, borate (0.5–25 mM) buffer showed a moderate effect (a factor of 2) on the  $\text{H}_2\text{O}_2$ –HOI reactivity at pH 9.0.

- The activation energy for the reaction between HOI and  $\text{H}_2\text{O}_2$  is  $E_a = 34 \text{ kJ mol}^{-1}$ .
- The formation of I-DBPs in a model system could be significantly reduced by addition of relatively low concentrations of  $\text{H}_2\text{O}_2$  to HOI- and phenol-containing solutions.
- The species-specific second order rate constants for the reactions of  $\text{HO}_2^-$  with HOX increased in the order of  $\text{HOCl} < \text{HOI} < \text{HOBr}$ .
- Oxidative water treatment of iodide-containing water in presence of  $\text{H}_2\text{O}_2$  can lead to a reduced formation of I-DBPs by minimizing the lifetime of HOI. However, due to the remaining  $\text{I}^-$ ,  $\text{H}_2\text{O}_2$  based pre-oxidation (e.g., UV/ $\text{H}_2\text{O}_2$ ), followed by chlorination or chloramination may still have a risk of I-DBP formation.
- $\text{O}_3$  deposition by the oxidation of  $\text{I}^-$  on the seawater surface can be significantly enhanced in presence of  $\text{H}_2\text{O}_2$ .

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.watres.2020.115852>.

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