1. Introduction

During oxidative water treatment at circumneutral pH, 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 (H₂O₂) plays a key role in minimizing the formation of I-DBPs by reduction of HOI during H₂O₂-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 H₂O₂ were determined in the pH range of 4.0–12.0. H₂O₂ showed considerable reactivity with HOI near neutral pH (k app = 9.8 × 10⁷ and 6.3 × 10⁷ M⁻¹s⁻¹ at pH 7.1 and 8.0, respectively). The species-specific second order rate constants for the reactions of H₂O₂ with HOI, HO₂⁻ with HOI, and HO₂⁻ with I⁻ were determined as k H₂O₂-HOI = 29 ± 5.2 M⁻¹s⁻¹, k HO₂⁻-HOI = (3.1 ± 0.3) × 10⁸ M⁻¹s⁻¹, and k HO₂⁻-I⁻ = (6.4 ± 1.4) × 10⁷ M⁻¹s⁻¹, respectively. The activation energy for the reaction between HOI and H₂O₂ was determined to be E_a = 34 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 H₂O₂–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 H₂O₂ to HOI- and phenol-containing solutions. During water treatment with the O₃/H₂O₂ process or peracetic acid in the presence of I⁻, O₃ and peracetic acid will be consumed by a catalytic oxidation of I⁻ due to the fast reduction of HOI by H₂O₂. The O₃ deposition on the ocean surface may also be influenced by the presence of H₂O₂, which leads to a catalytic consumption of O₃ by I⁻.

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HOI is formed by the oxidation of bromide by chlorine (Criquet 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 (IO₃⁻) 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, peracids, such as peracetic acid (Shah et al., 2015a)). Moreover, during chlorination of bromide-containing water, the oxidation of HOI to IO₃⁻ is significantly enhanced by HOBr (k_HOBr/OI⁻ = 1.9 × 10⁶ M⁻¹s⁻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 (O₃) and ferrate (Fe(VI)) show significant potential for a mitigation of I-DBPs by formation of IO₃⁻ through rapid oxidation of HOI (pH 7: k_DryReac HOI/OI⁻ = 3.7 × 10⁸ M⁻¹s⁻¹ and k_DryReac HOI/OI⁻ = 1.5 × 10⁹ M⁻¹s⁻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 (H₂O₂) (Shah et al., 2015a; Shin et al., 2018). H₂O₂ is widely used in oxidative water treatment, and intentionally added for some of Fe(VI) (Lee et al., 2014).

During water treatment or in natural systems, HOI is the dominant species compared to molecular iodine (I₂) because the I⁻ concentration is typically very low (maximum ~ 100 μg/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 H₂O₂ have been studied previously. Eq. (1) was proposed as a dominant reaction pathway in the HOI/OI⁻ system (Bray and Liebhafsky, 1931). Eqs. (2)-(4) are based on the specification of HOI/OI⁻ (pK_a1 = 10.4) and H₂O₂/H₂O₂ (pK_a2 = 11.8).

\[
\text{HOI} + \text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{I}^- + \text{H}_2\text{O} + \text{O}_2 \quad k_1 \quad (1)
\]

The reported values of k₁ (5–200 M⁻¹s⁻¹) (Bray and Liebhafsky, 1931; Furrow, 1987; Ishigure et al., 1986; Schmitz, 2010) and k₂ (1.4 × 10⁻⁶–6.0 × 10⁹ M⁻¹s⁻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 H₂O₂, an indirect method was used, which measures the decrease of I₂ in presence of excess I⁻ based on Eqs. (5) and (6) in Table 1. This approach can lead to different I₂ concentrations depending on the experimental conditions (e.g., pH, [I₂], or [I⁻]), 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 ≈ 1/[H⁺]²) for the reaction of HOI with H₂O₂. 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 Hnatiw, 2001).

\[
\text{I}_2 + \text{OH}^- \Rightarrow \text{I}_2\text{OH}^- \Rightarrow \text{HOI} + \text{I}^- \quad (9)
\]

\[
\text{I}_2\text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{I}^- + \text{H}_2\text{O} + \text{O}_2^+ \quad (10)
\]

Overall, a lot of conflicting information for the kinetics of the reaction of HOI with H₂O₂ 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 H₂O₂ 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 I₂. This approach makes it possible to assess the importance of the reduction of HOI by H₂O₂ compared to its other reactions in water treatment and H₂O₂-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, SL-Text 1). Hydrogen peroxide (H₂O₂) stock solutions were prepared by diluting a commercial solution of H₂O₂ (30 wt% in H₂O, Sigma) and standardized spectrophotometrically using the molar absorption coefficient of H₂O₂ (ε = 40 M⁻¹cm⁻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
of OCl\(^{-}\) (pH > 11, \(\varepsilon = 350 \text{ M}^{-1} \text{ cm}^{-1}\) 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 \(\text{H}_2\text{O}_2\) were performed under pseudo-first order conditions with \(\text{H}_2\text{O}_2\) 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 \(\text{H}_2\text{O}_2\) were at least 4 times higher than HOI. A wide range (12 – 16'000 \(\mu\)M) of \(\text{H}_2\text{O}_2\) 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 \(\text{H}_2\text{O}_2\) solutions to avoid mixing problems. Buffered \(\text{H}_2\text{O}_2\) 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 \(\varepsilon_{226\text{nm}} = 1.36 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}\); 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., \(\text{H}_2\text{O}_2\) and HOI), because their molar absorption coefficients at 226 nm are much lower (\(\varepsilon < 80 \text{ M}^{-1} \text{ cm}^{-1}\)) 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 \(k_{\text{obs}}\) 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 \(\text{H}_2\text{O}_2\) 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 \(\text{H}_2\text{O}_2\) (20–200 \(\mu\)M) in the presence of 100 \(\mu\)M of AgNO\(_3\). Ag\(^{+}\) was added to quench I\(^{-}\) by forming AgI \(\left(K_{\text{sp}} = 8.5 \times 10^{-17}\right)\) (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 \(\text{H}_2\text{O}_2\) at low and neutral pHs. The reaction was initiated by adding a small volume (\(\leq 1\) mL) of a \(\text{H}_2\text{O}_2\) stock solution (20 \(\mu\)M) under vigorous mixing to a buffered solution (100 \(\mu\)L) 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-, \(\text{H}_2\text{O}_2\)-, and phenol-containing waters

Solutions (20 mL) containing phenol (10 \(\mu\)M), \(\text{H}_2\text{O}_2\) (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). Model calculations to evaluate the influence of \(\text{H}_2\text{O}_2\) 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 \(\text{H}_2\text{O}_2\) followed a second-order rate law under our experimental conditions (Table S1, SI). During the reaction of HOI with excess \(\text{H}_2\text{O}_2\), the evolution of I\(^{-}\) was exponential, indicating that the reaction is pseudo first-order with respect to the \(\text{H}_2\text{O}_2\) concentration (Fig. S2, SI). \(k_{\text{app}}\) 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)).

\[
\ln \left( \frac{[\text{HOI}]_0}{[\text{HOI}]} - [I^-] \right) = k_{\text{obs}} \times \text{time}
\]

The obtained \(k_{\text{obs}}\) values for the two methods were within 7.6% (Figures S2 and S3, SI). Fig. S4 (SI) shows the linearity of \(k_{\text{obs}}\) as a function of the \(\text{H}_2\text{O}_2\) concentration \((R^2 \geq 0.999)\) at pHs 8 and 9. The inset shows that the log(\(k_{\text{obs}}\)) versus log([\text{HOI}]_0) plot has as slope of 1 confirming a reaction order of one with respect to \(\text{H}_2\text{O}_2\). Based on this, apparent second-order rate constants \((k_{\text{app}})\) were determined by dividing \(k_{\text{obs}}\) by the corresponding initial \(\text{H}_2\text{O}_2\)...
concentrations (Eq. (12)). The calculated $k_{app}$ values were $6.3 \times 10^{4} M^{-1} s^{-1}$ at pH 8.0 and $3.7 \times 10^{5} M^{-1} s^{-1}$ at pH 9.0 (Table S1 (SI) and Fig. 1 and Fig. S4 (SI)).

$$k_{app} = k_{obs}/[H_{2}O_{2}]_{0}$$

(12)

For pH < 7.0, the kinetics for the reaction of HOI with H$_{2}$O$_{2}$ did not follow pseudo-first order (1–3 μM HOI in excess of H$_{2}$O$_{2}$). This is illustrated as an example in Fig. S5 (SI), for pH 6 (HOI (3 μM) with excess H$_{2}$O$_{2}$ (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$_{2}$O$_{2}$ in the literature (Table 2). Since I$^{-}$ is produced during the reaction of HOI with H$_{2}$O$_{2}$, the I$^{-}$ 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 μM) 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 μM). Meanwhile, I$_{2}$ is the major species in presence of a high concentration of I$^{-}$ (e.g., 2.0 μM) for a pH < 6.5.

To exclude the effect of I$^{-}$, 100 μM 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 μM) in the presence of excess H$_{2}$O$_{2}$ (20–200 μM) showed pseudo-first order kinetics (Fig. S7, SI). Second order rate constants ($k_{app}$) were determined by Eq. (13), yielding $34 \pm 1 M^{-1} s^{-1}$, $84 \pm 8 M^{-1} s^{-1}$, and $940 \pm 60 M^{-1} s^{-1}$ at pHs 4, 5, and 6, respectively.

$$-ln[H_{2}O_{2}]/[HOI]_{0} = k_{app} \times [H_{2}O_{2}]_{0} \times time$$

(13)

3.2. pH dependence of the second order rate constant for the reaction between hypochlorous 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$_{2}$O$_{2}$. 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$_{2}$O$_{2}$ (pK$_{a1}$[HOI/OI$^{-}$] = 10.4 and pK$_{a2}$[H$_{2}$O$_{2}$/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$_{2}$O$_{2}$ systems, HOI is more electrophilic than OI$^{-}$, and HO$_{2}^{-}$ is stronger nucleophile than H$_{2}$O$_{2}$. Therefore, the reaction of HOI with HO$_{2}^{-}$ (Eq. (2)) is considered the major pathway for the reaction of HOI with H$_{2}$O$_{2}$. The same mechanistic interpretations for the HOCl–H$_{2}$O$_{2}$ and HOBr–H$_{2}$O$_{2}$ 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$_{2}$O$_{2}$ 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$_{2}$O$_{2}$/HO$_{2}^{-}$.

$$k_{app} = k_{1}[HOI] \beta_{HO2} + k_{2}[HOI] \beta_{HO2} - k_{4}[OI^{−}] \beta_{HO2}$$

(14)

where $k_1$, $k_2$, and $k_4$ are the species-specific second order rate constants in Eqs. (1), (2) and (4), respectively. $\alpha_{HOI}$, $\alpha_{OI^{-}}$, $\beta_{HO2}$, and $\beta_{HO2}$ are the fractions of HOI, OI$^{-}$, H$_{2}$O$_{2}$, and HO$_{2}^{-}$, respectively, which, at a given pH can be expressed as $\alpha_{HOI} = [HI^{+}] / [HI^{+}] + k_{2}[HOI][[HI^{+}] + k_{4}[HOI]$, $\beta_{HO2} = [HI^{+}] / [HI^{+}] + k_{3}$$[HO2^{-}]$, and $\beta_{HO2} = k_{3}[HO2^{-}] / k_{4}[OI^{-}] + k_{2}$$[HO2^{-}]$, with $K_{a1}$ 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). The model could fit the experimental $k_{app}$ well ($R^2 > 0.92$). The species-specific second order rate constants were determined to be $k_{1}$ (HOI + H$_{2}$O$_{2}$) = 29 ± 5.2 M$^{-1}$ s$^{-1}$, $k_{2}$ (HOI + HO$_{2}^{-}$) = (3.1 ± 0.3) $\times 10^{8}$ M$^{-1}$ s$^{-1}$, $k_{4}$ (OI$^{-}$ + HO$_{2}^{-}$) = (6.4 ± 1.4) $\times 10^{7}$ M$^{-1}$ 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$_{2}$O$_{2}$ can be applied to calculate the half-life of HOI in H$_{2}$O$_{2}$ containing water treatment. The calculations of the half-life of HOI are shown in Fig. 1 for 10 mg L$^{-1}$ H$_{2}$O$_{2}$, 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 mg/L of H$_{2}$O$_{2}$ 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$_{2}$O$_{2}$

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, 2006b). 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$_{2}$O$_{2}$ were investigated (Table S2 and Figs. S8–S10 (SI)). During the reaction of HOI (3 μM) with H$_{2}$O$_{2}$ (4 mM at pH 7.3, 40 μM 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$_{2}$PO$_{4}^{-}$ (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$_{2}$O$_{2}$
follow pseudo first order in the presence of 100 μM of Ag⁺ with various concentrations of acetate (pKₐ = 4.76 (Goldberg et al., 2002)) (Fig. S10, SI). The rates of 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 H₂O₂. 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, kₐp in presence of 1.25 mM phosphate buffer was 7.6 × 10⁵ M⁻¹ s⁻¹, which increased up to a factor of 4.3 for 25 mM phosphate (kₐp = 3.3 × 10⁶ M⁻¹ 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 M⁻¹ s⁻¹ (1 mM acetate) to 140 M⁻¹ 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 × 10⁵ M⁻¹ s⁻¹ (0.5 mM borate) to 5.4 × 10⁵ M⁻¹ 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 M⁻¹ s⁻¹ at pH 4.7, 5.6 × 10³ M⁻¹ s⁻¹ at pH 7.3, and 2.4 × 10³ M⁻¹ s⁻¹ at pH 9.0). These second order rate constants are compared in Fig. S12 (SI) with the determined kₐp (Table S1, SI) which were used for determining the species-specific rate constants. The measured kₐp 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 ≥ 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 H₂O₂

The effect of temperature on the kinetics of the reaction of HOI with H₂O₂ was studied at 10.0–23.2 °C at pH 9.0 (5 mM phosphate + 5 mM borate buffer) (Fig. S13, SI). An Arrhenius plot shows good linearity (R² = 0.98), between the logarithm of the apparent second order rate constants and the reciprocal of the absolute temperature (T) (Eq. (15)).

\[
\ln k_{\text{app}} = -\frac{E_a}{R} \times \frac{1}{T} + \ln A
\]  

where A is a frequency factor, E_a is the apparent activation energy (J mol⁻¹ K⁻¹), R (8.314 J mol⁻¹ 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 kJ mol⁻¹ can be obtained. This is significantly lower than the E_a value of 125 kJ mol⁻¹ reported for the reaction of I₂ with H₂O₂ (Ball and Hnatiw, 2001).

3.5. Formation of iodophenols in HOI-, H₂O₂-, and phenol-containing waters

To evaluate the effect of H₂O₂ on the formation of I-DBPs during oxidation processes, in which H₂O₂ is present (e.g., O₃, H₂O₂, UV/H₂O₂, ferrate(VI), peracetic acid treatment), H₂O₂ 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 H₂O₂ at pH 7 (i.e., k_{HOI-phenol} = 2.6 × 10⁷ M⁻¹ s⁻¹ (Bichsel and von Gunten, 2000a), and k_{HOI-H₂O₂} = 4.9 × 10⁵ M⁻¹ s⁻¹ at pH 7.0 (this study)). 2-iodophenol and 4-iodophenol were detected during the reaction of HOI (1 μM) with phenol (10 μM) in the presence of varying concentrations of H₂O₂ (0–50 μM) at pH 7.0 (8 mM phosphate) and pH 9.0 (8 mM phosphate + 4 mM borate). Ag⁺ was added to exclude the formation and reactions of I⁻. A HOI concentration of 1 μM was chosen to simulate an elevated I⁻ level (130 μg/L) and the concentration of phenol was 10 times that of HOI. 10 μM (-0.94 mg/L) of phenol would correspond to a source water containing about 5 mg/L DOC with a typical phenol content of around 20% (Onnby et al., 2018).

H₂O₂ is generally applied as 2–15 mg/L in advanced oxidation processes (Stefan, 2017). Nevertheless, relatively low concentrations of H₂O₂ (<2 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 H₂O₂ at pHs 7.0 and 9.0. As expected, the formation of iodophenols decreased with increasing H₂O₂ doses and at the maximum H₂O₂ concentration of about 1.7 mg/L (50 μM) only low concentrations of iodophenols (<0.1 μM) were detected due to the reduction of HOI by H₂O₂ to I⁻. Even with these relatively low H₂O₂ 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 kₐp of the reaction of HOI with phenol and the reaction of HOI with H₂O₂ 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 H₂O₂ with HOI, HOCl, and HOBBr

Fig. 3 and Table 2 show a comparison of the apparent and species-specific second order rate constants for the reactions of H₂O₂ with HOI, HOBr, and HOCl, respectively. The species-specific second order rate constants for the reaction of HOCl with HOX, decrease in the order HOBr (7.6 × 10⁷ M⁻¹ s⁻¹) > HOI (3.1 × 10⁸ M⁻¹ s⁻¹) > HOCl (4.4 × 10⁷ M⁻¹ 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 X⁻ transfer to HO₂ (Heeb et al., 2014), the partial positive charge on X, wherefore, the partial positive charge increases in the order Cl⁻ > Br⁻ > I⁻. Based on this consideration, HOI should have the highest reactivity. This may be due to the lower electronegativity of I compared to Br and Cl, which means that there is still a significant partial positive charge on I in I⁻.
7.0 (8 mM phosphate) and (b) pH 9.0 (8 mM phosphate + 4 mM borate). Experimental conditions: [phenol]_0 = 10 μM, [HOI]_0 = 1 μM, and [AgNO3]_0 = 100 μM. 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. 2. Measured and modeled formation of iodo-phenols during the reaction of HOI with phenol as a function of increasing H2O2 concentrations (0, 5, 10, 25, and 50 μM) for (a) pH 7.0 (8 mM phosphate) and (b) pH 9.0 (8 mM phosphate + 4 mM borate). Experimental conditions: [phenol]_0 = 10 μM, [HOI]_0 = 1 μM, and [AgNO3]_0 = 100 μM. 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 H2O2 with HOI, HOBr, or HOCl. The rate constants for the reaction of H2O2 with HOCI were obtained from Held et al. (1978), and with HBBr 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 I− to HOI by chemical oxidants during water treatment. However, most oxidants with the exception of O3 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 H2O2 is present together with a primary oxidant, the reduction of HOI to I− by H2O2 needs to be considered due to the significant reactivity of the two compounds.

A recent study showed a constant I− concentration during UV/H2O2 treatment in the presence of 130 μg/L of I−, 10 mg/L of H2O2, and 3.5 mg/L DOC at pH 7.0 (Zhang et al., 2018). In fact, in the UV/H2O2 process, I− is oxidized to HOI through the formation of radical species (i.e., HO•, HO2•−) by the rapid reaction with OH radical (k = 1010 M−1 s−1) (Elliott, 1992; Ellison et al., 1972; Nagarajan and Fessenden, 1985). However, the formed HOI will be quickly reduced to I− by H2O2. As already mentioned above, half-lives for the HOI abatement in the presence of 10 mg/L of H2O2 at neutral pH were low, namely 0.5 and 0.05 s at pH 7 and 8, respectively. Thus, UV/H2O2 pre-oxidation followed by chlorination or chloramination still has a risk of I-DBP formation due to the remaining I−.

In the O3/H2O2 process, I− is quickly oxidized to HOI (kO3/1 = 2.0 × 105 M−1s−1). The resulting hypoiodous acid (HOI/OI−) has two competing reaction pathways: (1) reduction to I− by H2O2 (kH2O2/HOI = 3.1 × 108 M−1s−1) and (2) oxidation to IO3− through IO2− by O3 (kO3/H2O2 = 3.6 × 104 M−1s−1 and kO3/HI = 1.6 × 106 M−1s−1). Reduction of HOI by H2O2 could lead to the loss of oxidation capacity of O3 by a catalytic cycle of oxidation of I− by O3 and reduction of HOI by H2O2 back to I−. A kinetic simulation was used to calculate the relative contributions of various reactions to the O3 consumption, i.e., catalytic oxidation of I−, reaction with H2O2, and further oxidation of HOI to IO3−. For simplicity, the formation and reactions of "OH were not considered in these model calculations. For the selected conditions of the O3/H2O2 process, 56–66% of O3 (i.e., 11.7–13.7 μM) was consumed by the catalytic oxidation of I− (Fig. S14, SI), rather than for the formation of "OH via its reaction with H2O2 (kO3/1 = 9.6 × 105 M−1s−1) for an elevated level of I− (e.g., 1 μM (−130 μg/L), [O3] = 1 mg/L (20.8 μM) and [H2O2] = (4–10 mg/L)) at pH 8.0. IO3− was the dominant iodine species only during ozonation with a low concentration of H2O2 (56 μg/L) due to the fast reactions of O3 with I− and with HOI forming IO3−. However, significant concentrations of I− could remain after complete consumption of O3 in the presence of relatively high H2O2 (56 μg/L) and IO3−. Such conditions are typically applied for bromate control during the O3/H2O2 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 I− and Br− are present in a source water, appropriate H2O2 doses should be applied during ozonation to minimize the formation of both I-DBPs and BrO3−. 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). H2O2 is always present in peracetic acid (PAA) solutions because PAA is synthesized by the reaction of acetic acid with H2O2. To evaluate the role of H2O2 during the treatment of I− and Br− by PAA in an ocean-type water, a kinetic simulation was performed. Fig. S15 (SI) shows the evolution of HOI, HOBr, H2O2, and PAA during treatment of 0.5 μM I− and 460 μM Br− by 2.15 mM PAA in the presence of 0.65 mM H2O2 at pH 8.0. In this system, I− and Br− are oxidized to HOI and HOBr by...
H₂O₂ is one of the major products during the self-decay of Fe(VI) (Lee et al., 2014). The yield of H₂O₂ (Δ[H₂O₂]/Δ[Fe(VI)]) was ~0.2 during the reaction of Fe(VI) with I⁻ or HOI (Shin et al., 2018). To assess the influence of H₂O₂ formation on the fate of iodine, a kinetic simulation was performed for treatment of I⁻ by Fe(VI). To better understand the effect of H₂O₂, the following simplified boundary conditions were assumed: H₂O₂ 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, IO₃⁻, H₂O₂, and Fe(VI) during the treatment of 1 μM of I⁻ by 17.5 μM Fe(VI) (1 mgFe/L) in the presence of 5.4 μM H₂O₂ at pH 7.0–9.0. At pH 7.0, 99% of I⁻ was oxidized to IO₃⁻ within 11 s by Fe(VI) without interference of H₂O₂. With increasing pH from 7.0 to 9.0, the oxidation rate of I⁻ to IO₃⁻ decreased. This is because the rate of Fe(VI) reaction with HOI and I⁻ decreases with increasing pH (i.e., kFe(VI) /HOI = 1.8 × 10⁻³ M⁻¹ s⁻¹ at pH 7.0 and 4.7 × 10⁻³ M⁻¹ s⁻¹ at pH 9.0) while the rate of HOI reduction by H₂O₂ to I⁻ increases. Overall, an increase in pH led to an increase in the consumption of H₂O₂ and Fe(VI). At pH 7.0, only 3 μM of Fe(VI) was consumed to completely oxidize 1 μM I⁻ to IO₃⁻ without consumption of H₂O₂, while at pH 9.0, 8.4 μM of Fe(VI) was consumed with a H₂O₂ consumption of 5.6 μM for a full oxidation of I⁻ to IO₃⁻.

3.7.2. Natural systems

O₃ deposition to the seawater surface is a significant mechanism for the loss of atmospheric O₃, accounting for a loss of 600–1000 Tg O₃ yr⁻¹ (Ganzeweld et al., 2009). Aqueous inorganic iodine (i.e., I⁻, HOI) at the oceanic deposition of O₃. This is based on the fast reaction between O₃ (gas) and I⁻, which forms HOI in the aqueous phase and iodine oxide in the gaseous phase while O₃ is reduced to O₂ (Carpenter et al., 2013; Chang et al., 2004; Sarwar et al., 2015; Simpson et al., 2015). During this reaction, O₃ deposition might be significantly enhanced by H₂O₂ due to its high reactivity with HOI to form I⁻. The concentration of H₂O₂ at the sea surface varies from 10 to >500 nM (Moore et al., 1993; Price et al., 1998; Zika et al., 1985). The gas-phase flux of O₃ into the boundary layer can be determined by the product of the O₃ deposition velocity (vD) and the O₃ concentration ([O₃(gas)])). The O₂ deposition velocity (vD) over seawater is highly variable (0.01–0.27 cm s⁻¹) (Ganzeweld et al., 2009; Helming 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 H₂O₂ on the O₃ deposition to the sea surface microlayer in the presence of I⁻ and Br⁻ (Fig. S17, SI). Since the source of O₃ is the atmosphere and the source of I⁻ and Br⁻, and H₂O₂ 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 I⁻ since 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., I⁻ and IO₃⁻) of 500 nM in seawater (Chance et al., 2014), the [HOI]ss was varied between 25–500 nM. With increasing [HOI]ss, O₃ deposition increases (SI-Text 3 and Fig. S17 (SI)). In a next step, the [HOI]ss was fixed at an intermediate concentration of 100 nM and the steady-state concentrations of the other reactive species were assumed as follows: [O₂]ss = 1 nM, [Br⁻]ss = 500 μM, and variable [H₂O₂]ss = 0, 10, 25, 100, 250, 500 nM. Virtual reaction products as tracers (i.e., P₁, P₂, P₅, P₆ in Table S4, SI) were quantified by Kintecus modeling to obtain the relative contributions of the various reactions to O₃ consumption (reactions 1–7 in Table S4, SI): (1) Oxidation of I⁻ was obtained from P₃, (2) Oxidation of Br⁻ was obtained from P₇, and (3) Oxidation of HOI to IO₃⁻ 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 O₃ deposition. As the H₂O₂ concentration is increasing, the O₃ consumption for the oxidation of I⁻ becomes increasingly important compared to the reaction with bromide, which dominates at low H₂O₂ concentrations (Fig. S18a, SI). The contribution of the catalytic oxidation of I⁻ for the O₃ consumption increases from 36% to 97% for an increase of H₂O₂ from 10 nM to 500 nM (Fig. S18a, SI). For all selected H₂O₂ concentrations, the consumption of O₃ by the oxidation of HOI to IO₃⁻ was insignificant (<10%) compared to the O₃ consumption for the oxidation of I⁻ or Br⁻.

In this kinetic modeling, the concentration of I⁻ reached steady-state within a few seconds. Fig. S18b (SI) shows that the resulting steady-state concentration of I⁻ ([I⁻]ss) and the total O₃ consumptions over 1 year depend on the initial [H₂O₂]ss. According to kinetic modeling results, the [I⁻]ss increased linearly with increasing H₂O₂ concentrations (0–500 nM). As a consequence, the total O₃ deposition rate increased proportionally (2.8–82.1 mM per year). If these results are combined with variable [HOI]ss, the total O₃ deposition ranges from 3.6 mM (25 nM HOI/25 nM H₂O₂) to 400 mM (500 nM HOI/500 nM H₂O₂) per year.

Accounting for the area of the sea surface microlayer (3.5 × 10⁶ km²) (Costello et al., 2010) and setting the depth of the boundary layer to 100 μm, an O₃ deposition rate of 6.2–400 Tg/year can be calculated depending on the HOI (25–500 nM) and the H₂O₂ 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 H₂O₂ may have a high potential to increase the O₃ deposition by the catalytic oxidation of I⁻ at the sea surface, which might warrant an inclusion of these reactions to calculate O₃ deposition in future modeling efforts. The reduction of HOI by H₂O₂ can also occur in atmospheric waters, which may lead to a reduction of the O₃ 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 hypoiiodous acid were determined and the main conclusions are as follows:

- The reaction between HOI and H₂O₂ is a second-order process. The species-specific second order rate constants for the reactions of H₂O₂ with HOI, HO₂ with HOI, HO₂ with OI⁻ are k₁H₂O₂+HOI = 29 ± 5.2 M⁻₁ s⁻¹, k₃HO₂+HOI = (3.1 ± 0.3) × 10³ M⁻¹ s⁻¹, and k₅HO₂+OI⁻ = (6.4 ± 1.4) × 10⁷ M⁻¹ s⁻¹, respectively.
- Phosphate (1.25–25 mM) and acetate (1–25 mM) buffers lead to a significant enhancement of the H₂O₂–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 HOCl–HOI reactivity at pH 9.0.

- The activation energy for the reaction between HOI and HO2 is $E_a = 34$ kJ mol$^{-1}$.
- The formation of I-DBPs in a model system could be significantly reduced by addition of relatively low concentrations of HO2 to HOI- and phenol-containing solutions.
- The species-specific second order rate constants for the reactions of HO2 with HOX increased in the order of HOCI < HOI < HOBr.

Oxidative treatment of iodide-containing water in presence of HO2 can lead to a reduced formation of I-DBPs by minimizing the lifetime of HOI. However, due to the remaining I$, HO2 based pre-oxidation (e.g., UV/HO2), followed by chlorination or chloramination may still have a risk of I-DBP formation.

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