# Formation of Iodo-Trihalomethanes during Disinfection and Oxidation of Iodide-Containing Waters

YVES BICHSEL AND URS VON GUNTEN\* Swiss Federal Institute for Environmental Science and Technology EAWAG, CH-8600 Dübendorf, Switzerland

The formation of iodo-trihalomethanes (I-THMs) such as iodoform (CHI<sub>3</sub>) during oxidative treatment of iodide-containing drinking waters can be responsible for taste and odor problems. I-THMs are formed by reactions of hypoiodous acid (HOI) with natural organic matter. HOI is quickly formed from naturally occurring iodide (I-) by oxidation with ozone, chlorine, or chloramine. The kinetics of reactions of HOI with organic model compounds as well as the resulting CHI<sub>3</sub> formation were measured. Substituted phenols, phenol, and, to a smaller extent,  $\alpha$ -methyl carbonyl compounds were found to be reactive toward HOI and also to yield CHI<sub>3</sub>. Resorcinol (*m*-hydroxyphenol) had the highest yield of CHI<sub>3</sub>. The kinetics of I-THM formation were also measured in natural waters which were oxidatively treated with ozone, chlorine, or chloramine. When ozone was used, no I-THMs were detected and  $\geq$ 90% of I<sup>-</sup> was transformed to IO<sub>3</sub><sup>-</sup>. Chlorine led to the formation of both  $IO_3^-$  and I-THMs. With increasing chlorine doses, the CHI<sub>3</sub> formation decreased, whereas IO<sub>3</sub><sup>-</sup> formation, as well as the formation of classical THMs such as chloroform, increased. In chloramination processes, I-THMs (especially CHI<sub>3</sub>) were the main products. The CHI3 formation in the oxidation of natural waters increased in the order  $O_3 < CI_2 < NH_2CI$ .

### Introduction

About 25 years ago, the formation of chlorine- and brominecontaining trihalomethanes (THMs: chloroform (CHCl<sub>3</sub>), bromodichloromethane (CHBrCl<sub>2</sub>), dibromochloromethane (CHBr<sub>2</sub>Cl), and bromoform (CHBr<sub>3</sub>)) during drinking water chlorination was discovered (1-3). Their toxicity led to stringent regulations, e.g., in the European Union (4) and in the United States (5). In this study, these compounds will be referred to as "classical THMs".

In iodide-containing waters, the formation of six additional THMs, the iodo-trihalomethanes (I-THMs), is possible through incorporation of one or more iodine atoms into a THM. The resulting compounds are iodoform (CHI<sub>3</sub>), chlorodiiodomethane (CHCII<sub>2</sub>), bromodiiodomethane (CH-BrI<sub>2</sub>), dichloroiodomethane (CHCl<sub>2</sub>I), dibromoiodomethane (CHBr<sub>2</sub>I), and bromochloroiodomethane (CHBrCII). In the late 1980s I-THMs (especially CHI<sub>3</sub>) were found to be responsible for the occurrence of bad taste and odor in drinking waters ( $\beta$ – $\vartheta$ ). The organoleptic threshold concentration of CHI<sub>3</sub> lies between 0.03 and 1  $\mu$ g/L, which is the lowest value of all of the I-THMs ( $\vartheta$ , 10). Total iodine concentrations in water resources are usually in the range of 0.5–20  $\mu$ g/L but can exceed 50  $\mu$ g/L in certain groundwaters near the sea coast or under special geological circumstances (11). Therefore, the formation of CHI<sub>3</sub> above its organoleptic threshold concentration from naturally occurring iodide ( $I^-$ ) is possible during oxidative drinking water treatment.

I-THMs were detected in several drinking waters. In one case, a change from chlorination to chloramination led to the formation of 5  $\mu$ g/L CHI<sub>3</sub> from an I<sup>-</sup> concentration of 50  $\mu$ g/L (8). In another water, up to 30  $\mu$ g/L CHI<sub>3</sub> and only low concentrations of the classical THMs were formed from 200  $\mu$ g/L I<sup>-</sup> when chloramine was utilized (12). When chlorine was used to treat the same water, only classical THMs were observed; no CHI<sub>3</sub> was detected. Another study reports the appearance of CHI<sub>3</sub> after the chlorination of a water with a high I<sup>-</sup> concentration (150–200  $\mu$ g/L) (6). The same study describes the formation of I-THMs in an ozonation process during failure of the ozonation step (90  $\mu$ g/L I<sup>-</sup>). Another study showed that I-THMs were formed in several waters during chlorination although the iodide concentration in the raw water was orders of magnitude lower than the bromide concentration (13).

I<sup>-</sup> is quickly oxidized to hypoiodous acid (HOI) in the presence of ozone, chlorine, or chloramine (*14*). The further reaction of HOI with natural organic matter (NOM) can result in the formation of I-THMs. In the present study, we investigated the kinetics of the reaction of HOI with organic compounds and the formation kinetics of I-THMs in both natural and model waters. The relative reaction rates of the oxidation of HOI to  $IO_3^-$  (*14*), the disproportionation of HOI (*15*), and its addition to organic compounds determine the product distribution between  $IO_3^-$  and iodoorganic compounds such as I-THMs. The formation of  $IO_3^-$  is probably not a toxicological problem because ingested  $IO_3^-$  is quickly reduced to I<sup>-</sup> in vivo by glutathione (*16*).

To describe the reactivity of HOI toward organic compounds and oxidants, its pH-dependent speciation has to be considered. HOI (p $K_a = 10.4$ ) can be deprotonated to hypoiodite (OI<sup>-</sup>) (*14*, *15*). At a low pH, H<sub>2</sub>OI<sup>+</sup> (p $K_a = 1.4 \pm$ 0.3 (*17*, *18*)) can be formed by protonation of HOI.

### Materials and Methods

With the exception of pinacolone, which was redistilled, all chemicals were used without further purification and were of the highest purity grade. HOI was freshly produced through oxidation of I<sup>-</sup> by HOCl from a NaOCl stock solution (Aldrich) of approximately 0.68 M prior to experiments because it is not stable in water (disproportionation). The exact [OCl<sup>-</sup>] could be determined in excess of I<sup>-</sup> as I<sub>3</sub><sup>-</sup> ( $\epsilon_{288}$  nm = 38 200 M<sup>-1</sup> cm<sup>-1</sup>) (*19*). The pH measurements were carried out with a Ross electrode (ATI Orion, Boston, MA) and a Metrohm 632 pH-meter (Metrohm, Herisau, Switzerland) which was calibrated with standard buffer solutions (Merck). Spectrophotometric measurements were performed on an Uvikon 940 spectrophotometer (Kontron Instruments, Eching, Germany).

**Consumption of HOI by Organic Model Compounds.** The kinetics of the consumption of HOI by organic model compounds were measured in double-distilled water in 250-mL batch reactors (for slow kinetics) and in a continuous-flow apparatus (for fast kinetics) under pseudo-first-order conditions ([model compound]  $\gg$  [HOI]) at 25 ± 2 °C. HOI was prepared by mixing I<sup>-</sup> and OCI<sup>-</sup> in a volumetric flask and diluting it to a concentration of 1–4  $\mu$ M. Between pH 3 and 11, pH was controlled by 0.5–5 mM of phosphate buffer. For pH < 3, only sulfuric acid was used, whereas for pH > 11, only NaOH was used. More experimental details are presented later in Tables1–3.

<sup>\*</sup> Corresponding author phone: +41 1 823 52 70; fax: +41 1 823 52 10; e-mail: vongunten@eawag.ch.

			phosphate	phenol	[HOI](t = 0)		observed rate constants (M <sup>-1</sup> s <sup>-1</sup> )		
compound	р <i>К</i> а	pH range	(mM)	(μM)	(μM)	nc	<i>k</i> <sub>2</sub>	<i>k</i> <sub>3</sub>	$k_4$
<i>p</i> -methoxyphenol <i>p</i> -cresol phenol <i>p</i> -chlorophenol <i>p</i> -iodophenol <i>p</i> -cyanophenol	10.20 <sup>a</sup> 10.26 <sup>a</sup> 9.99 <sup>a</sup> 9.43 <sup>a</sup> 9.20 <sup>a</sup> 7.86 <sup>b</sup>	3.1-4.7 2.5-4.9 3.1-8.6 1.0-7.7 0.5-8.2 1.9-8.4	1 0-1 2.5-5 0-1 0-1 0-1	10-20 10 10-500 10-200 10-200 10-1000	$\begin{array}{c} 1.1 - 3.5 \\ 0.8 - 2.6 \\ 1.7 - 5.0 \\ 1.2 - 2.3 \\ 0.8 - 5.0 \\ 1.1 - 2.3 \end{array}$	11 8 27 14 16 18	$\begin{array}{c} (5\pm1)\times10^4\\ (4.0\pm1.5)\times10^4\\ (5\pm2)\times10^4\\ (3\pm1)\times10^3\\ (4\pm1)\times10^3\\ (2\pm1)\times10^2 \end{array}$		$\begin{array}{c} (7\pm2)\times10^8\\ (7\pm3)\times10^8\\ (2\pm1)\times10^6\\ (1.6\pm0.5)\times10^5\\ (1.5\pm0.8)\times10^5\\ (4\pm2)\times10^2 \end{array}$
<sup>a</sup> Reference 33. <sup>b</sup>	This wor	rk. <sup>c</sup> n = nu	mber of kin	etic experim	ents ([HOI] v	's <i>t</i> ).			

The continuous-flow apparatus consisted of three mechanically driven glass syringes (Dosimat 665, Metrohm, Herisau, Switzerland) which pumped a solution of HOI and phosphate, a solution of the model compound, and an iodide solution (0.45 M KI), respectively. All three solutions were pumped with the same flux of 5 mL/min. The HOI solution and the model compound solution were mixed in a mixing tee. Thereafter, they passed a capillary tube of well-defined volume. The I<sup>-</sup> solution was added through a second mixing tee at the end of the capillary tube (observation point). This experimental setup was similar to the one applied in ref 20. I- stopped the reaction and allowed at the same time detection of the residual HOI in a 5-cm flow-through photometric cell by formation of  $I_{3^-}$  ( $\epsilon_{351 \text{ nm}} = 25\ 700\ \text{M}^{-1}$ cm<sup>-1</sup> (19)) as shown in eq 1 ( $k_{\text{HOI+I}} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  (21),  $k_{I_2+I} = 6.2 \times 10^9 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1} (\hat{22})$ ). The second absorption maximum at 351 nm was chosen in these experiments because of interferences of organic model compounds at 288 nm.

$$HOI + 2 I^{-} + H^{+} = I_{3}^{-} + H_{2}O$$
 (1)

The reaction time of the model compound with HOI was defined by the volume of the capillary tube and the flux of the mixed solution. It varied from 0.8 to 2.7 s. The pH was measured at the observation point.

The decrease of HOI in batch experiments was measured by placing 25-mL aliquots of the reaction solution into a 10-cm photometric cell together with 5 mL of 1 M KI. I<sup>-</sup> stopped the reaction immediately according to eq 1. Detection at 351 nm resulted in a detection limit for HOI of 0.4  $\mu$ M.

**Formation of CHI**<sup>3</sup> **in Model Solutions.** The kinetics of the formation of CHI<sub>3</sub> in model solutions were investigated in Nanopure water (Barnstead B-pure system) in batch reactors at 25  $\pm$  2 °C. The pH was controlled by 1 mM phosphate buffer (pH = 7.0) and 1 mM borate buffer (pH = 9.0). The initial concentrations were 1  $\mu$ M for the model compound and 6  $\mu$ M for HOI. This excess of HOI allowed iodine addition over several steps which eventually led to CHI<sub>3</sub>. In addition, a residual HOI concentration could be guaranteed for the duration of the experiment (32 h). HOI, CHI<sub>3</sub>, and IO<sub>3</sub><sup>-</sup> were analyzed in these experiments (HOI by photometry).

Analysis of the I-THMs was performed with liquid-liquid extraction into methyl tert-butyl ether (Fluka, "for residue analysis", ≥99.8%, Buchs, Switzerland) and by gas chromotography/electron-capture detection (GC/ECD) according to ref 23. Chromatographic separation was performed on a DB-5 column (30 m  $\times$  0.25 mm i.d., 0.25  $\mu$ m film thickness, J&W Scientific, Folsom, CA). The temperature program was as follows: 35 °C (5 min), heating rate 2 °C/min to 45 °C (0 min), heating rate 15 °C/min to 220 °C (3 min). The following compounds were detected by this method: CHCl<sub>2</sub>I (limit of detection (LOD) 1.3  $\mu$ g/L (S/N = 3)), CHBrClI (LOD 0.9  $\mu$ g/ L), CHBr<sub>2</sub>I (LOD 0.6 µg/L), CHClI<sub>2</sub> (LOD 0.3 µg/L), CHBrI<sub>2</sub> (LOD 0.07  $\mu$ g/L), and CHI<sub>3</sub> (LOD 0.1  $\mu$ g/L). With the exception of CHI<sub>3</sub>, I-THM standards are not commercially available. For this study, standards were supplied by F. Ventura, Societat General d'Aigües de Barcelona (AGBAR), and stored as methanolic solutions at -18 °C. Standard aqueous solutions of 10  $\mu$ g/L I-THMs in ambered flasks were stable for at least two weeks at room temperature (stable peak areas) in the pH range 6–9.

 $IO_3^-$  was analyzed with ion chromatography and postcolumn reaction with UV–vis detection with a detection limit of 0.1  $\mu$ g/L (0.6 nM) in natural waters (*19*).

**Formation of I-THMs and IO**<sub>3</sub><sup>-</sup> **in Natural Waters.** Two natural waters (from the Seine River, Paris, France, and Lake Zurich, Zurich, Switzerland) were spiked with varying amounts of I<sup>-</sup> and oxidatively treated with chloramine, chlorine, or ozone at  $25 \pm 2$  °C. The dissolved organic carbon (DOC) concentration was 1.3 mg/L in the lake water and 3.5 mg/L in the river water, [Br<sup>-</sup>] was 30  $\mu$ g/L in the river water and 15  $\mu$ g/L in the lake water, and [ammonia] was below 6  $\mu$ g N/L in both waters. The pH was controlled by addition of 10 mM B(OH)<sub>3</sub> and adjusted to 8.0 by NaOH (1 M, 10.8 M). The solutions were transferred to headspace free bottles immediately after the addition of the oxidant. The following parameters were analyzed during the reaction time (24–35 h): HOI, I-THMs, IO<sub>3</sub><sup>-</sup>, classical THMs, oxidant, and pH.

Because of the interference of oxidants (NH<sub>2</sub>Cl, Cl<sub>2</sub>, and  $O_3$ ), it was not possible to analyze HOI by the photometric method as described above. HOI was quenched with phenols and analyzed as iodophenol by HPLC. An aliquot of 20  $\mu$ M phenol was added to an aliquot of the reaction solution to transform HOI to iodophenol. Phenol reacts quickly and quantitatively with HOI (see below). Both p-iodophenol and o-iodophenol were formed in this reaction. Because iodophenols react about 10 times slower with HOI than phenols do (see Table 1) and because phenol was present in high excess, it can be assumed that no di- or triiodophenols were formed. The two iodophenols were quantified relative to a *p*-iodophenol standard solution by assuming that both iodophenols had the same sensitivity. The [HOI] was calculated from their sum. The HPLC separation was done on a Nucleosil 103-5 C<sub>18</sub> column (Macherey-Nagel, Düren, Germany) with an eluent consisting of 65% methanol, 34.9% water, and 0.1% acetic acid (retention times 5.5 min for o-iodophenol and 6.5 min for p-iodophenol). UV detection at 231 nm yielded a detection limit of 0.3  $\mu$ g I/L.

The four classical THMs (CHCl<sub>3</sub>, CHBrCl<sub>2</sub>, CHBr<sub>2</sub>Cl, and CHBr<sub>3</sub>) were analyzed by headspace GC/ECD. Detection limits (S/N = 3) were 0.06  $\mu$ g/L for CHBrCl<sub>2</sub>, 0.1  $\mu$ g/L for CHBr<sub>2</sub>Cl, 0.3  $\mu$ g/L for CHCl<sub>3</sub>, and 0.5  $\mu$ g/L for CHBr<sub>3</sub>.

Oxidant concentrations were determined by the indigo method (for ozone) (24) or the ABTS method (for chlorine and chloramine) (25).

### **Results and Discussion**

Model Compounds: Consumption of HOI and Formation of CHI<sub>3</sub>. Several organic model compounds have been tested for their reactivity toward HOI and formation of CHI<sub>3</sub> in these reactions. The two main classes which have been investigated are phenols and  $\alpha$ -methyl carbonyl compounds. These compounds are present in substructures of NOM and are known to react with halogens (*26*).



FIGURE 1. pH dependence of the observed second-order rate constants of the reaction of HOI with some phenols. Symbols, experimental results; lines, results calculated according to eqs 2–4. Conditions: [phenol] =  $10-1000 \ \mu$ M, [HOI] =  $0.8-5.0 \ \mu$ M.

Consumption of HOI by Phenols. The kinetics of the reactions of HOI with six para-substituted phenols were investigated under pseudo-first-order conditions ([phenol]  $\gg$  [HOI]) in a batch and in a continuous-flow system. Experimental details (pH, buffer concentrations, concentrations of phenols, initial HOI concentrations, and numbers of experiments) and the calculated rate constants are shown in Table 1. The kinetics were always first-order in phenol and first-order in HOI. The rate constants were determined by a least-squares fit for eqs 2–4.

$$H_2OI^+ +$$
(substituted)phenol  $\xrightarrow{k_2}$  products (2)

HOI + (substituted)phenol 
$$\xrightarrow{\Lambda_3}$$
 products (3)

HOI + (substituted)phenolate 
$$\xrightarrow{\kappa_4}$$
 products (4)

Figure 1 depicts the pH-dependence of the observed second-order rate constants for a highly reactive phenol (pmethoxyphenol), a moderately reactive phenol (p-iodophenol), and a less reactive phenol (p-cyanophenol). At low pH values, the reaction  $H_2OI^+$  + phenol is dominant (eq 2). The results for *p*-iodophenol confirm the pK<sub>a</sub> value of  $1.4 \pm 0.3$ for  $H_2OI^+$  (see Figure 1) (17, 18). At pH < 3.5, the observed second-order rate constant increases with decreasing pH due to the shift of HOI to H<sub>2</sub>OI<sup>+</sup>. The H<sub>2</sub>OI<sup>+</sup> is expected to have a higher reactivity as a result of its higher electrophilic character. This increase stops at pH < 1, where  $[H_2OI^+]$  does not further increase. However, the rate constant continues to increase at pH < 1 for *p*-cyanophenol. Other unknown reactions might be responsible for this behavior. At higher pH values (3.5-5), the observed second-order rate constants go through a minimum. In this pH range, reaction 3 involving HOI and the phenol becomes important for p-cresol, phenol, p-iodophenol, and p-cyanophenol. For p-chlorophenol and p-methoxyphenol, only reactions 2 and 4 contributed to the overall reaction. Reaction 3 was much slower than reactions 2 and 4. It is therefore only possible to indicate a maximum value for  $k_3$ . At high pH values (pH > 5), the overall reaction is dominated by the phenolate (reaction 4). Although phenol is the major species at pH = 5, the reaction HOI + phenolate dominates the system because of the much higher reaction rate constant. This behavior results in a 10-fold increase of the overall rate constant with every pH unit until the pK<sub>a</sub> of the phenol is reached. All determined rate constants  $k_2$ ,  $k_3$ , and  $k_4$  are shown in Table 1. They cover a range of almost 9 orders of magnitude (from 1.5 to  $7 \times 10^8$  M<sup>-1</sup> s<sup>-1</sup>). A representation of the measured rate constants with respect to the Hammett coefficients,  $\sigma_p$ , of the substituents shows good linearity (*27*). This indicates that the electron density on the aromatic system, which is strongly influenced by the substituent, is a key factor for the reaction rate of the phenols with HOI. This subject is discussed in further detail elsewhere (*28*).

The reactions of HOI with substituted phenols are significantly faster than the corresponding reactions of HOCl. *p*-Cresol reacts 2000–20 000 times faster with HOI than with HOCl ( $k_3^{HOCl} = 0.14 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_4^{HOCl} = 30 000 \text{ M}^{-1} \text{ s}^{-1}$ ) (*29*). The difference between HOCl and HOI is smaller for the more electrophilic phenols such as *p*-cyanophenol (factor 4–60:  $k_3^{HOCl} = 0.025 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_4^{HOCl} = 90 \text{ M}^{-1} \text{ s}^{-1}$ ) (*29*). HOI can therefore compete with HOCl for the reaction with phenols even if HOCl is present in high excess relative to HOI.

Formation of CHI<sub>3</sub> from Phenols. The formation of CHI<sub>3</sub> was measured at pH values of 7 and 9 with an initial concentration of 6  $\mu$ M HOI and 1  $\mu$ M phenol or resorcinol. Both compounds resulted in CHI<sub>3</sub> formation but resorcinol yielded much more CHI<sub>3</sub> (normalized to HOI exposure) than phenol did. For resorcinol, 4–7% of the C atoms were incorporated into CHI<sub>3</sub> after 6 h. This corresponds to 0.25–0.4 mol of CHI<sub>3</sub> per mol of resorcinol. The HOI consumption of both compounds occurred mainly in the first 2 h and amounted to 2 mol of HOI per mol of phenol and 5 mol of HOI per mol of resorcinol.

To be able to compare the results of the model solutions with natural waters (see below), the CHI<sub>3</sub> yield (q) with respect to the exposure to HOI (f[HOI] dt) and the initial [DOC] (in mol/L C) was calculated according to eq 5. This yield is a measure for [CHI<sub>3</sub>] which was formed as a result of a certain HOI exposure on a certain [DOC].

$$q = \frac{[\text{CHI}_3]}{\int [\text{HOI}] dt[\text{DOC}]} \qquad \text{or}$$
$$\frac{[\text{CHI}_3]}{[\text{DOC}]} = q \int [\text{HOI}] dt \quad (5)$$

Figure 2 shows a representation of the experimental data expressed in terms of eq 5. CHI<sub>3</sub> yield, *q*, can be read as the slope of a linear fit of the data. For phenol (triangles) this value is lower than 0.002 M<sup>-1</sup> s<sup>-1</sup> at pH = 7. At pH = 9, no CHI<sub>3</sub> formation could be detected from phenol. For resorcinol (circles) *q* reaches a maximum value of 1.1 M<sup>-1</sup> s<sup>-1</sup> during the first 6 h (*f*[HOI] dt < 0.05 Ms). This steep increase corresponds to a CHI<sub>3</sub> formation of, e.g., 15 nM h<sup>-1</sup>or 6  $\mu$ g L<sup>-1</sup> h<sup>-1</sup> in a solution of 10  $\mu$ g L<sup>-1</sup> of HOI and 1 mg L<sup>-1</sup> of resorcinol.

Consumption of HOI by  $\alpha$ -Methyl Carbonyl Compounds. The consumption of HOI by  $\alpha$ -methyl carbonyl compounds was investigated in batch reactors under pseudo-first-order conditions. Since 1822, the reaction of iodine with these compounds has been known as the "iodoform reaction" (*30*). A reaction scheme is presented in eq 6.



According to eq 6, HOI does not react directly with the carbonyl compound but only with the enol. The formation of the enol (enolization) can be catalyzed by several species:  $H^+$ ,  $H_2O$ , and  $OH^-$ . The halogenation of an  $\alpha$ -methyl carbonyl compound proceeds three times until the methyl group has been transformed into a triiodomethyl group. The triiodocarbonyl compound then hydrolyzes with the formation of CHI<sub>3</sub> and the corresponding acid (RCOOH).

For the first halogenation step, either the enolization or the addition of HOI to the enol is rate-determining. If the enolization is rate-determining, the overall reaction rate depends only on the carbonyl concentration and the pH, but not on [HOI], and the rate law becomes zero-order in HOI (eq 7). It was demonstrated previously that under certain conditions this was the case because the rate constants of iodination and bromination reactions were equal (*31*). This shows that the halogen does not participate in the ratedetermining step under the corresponding conditions.

At the pH values investigated in this study,  $OH^-$  and  $H_2O$  were the main catalysts for the enolization. The rate of HOI consumption can be formulated as

$$-\frac{\mathrm{d[HOI]}}{\mathrm{d}t} = k_{\mathrm{H}_{2}\mathrm{O}}[\mathrm{ketone}] + k_{\mathrm{OH}}[\mathrm{OH}^{-}][\mathrm{ketone}] \quad (7)$$

Experimental results for the reaction of HOI with acetone (at pH < 8.3), pinacolone, and acetaldehyde could be modeled with eq 7. Acetate was also investigated but no reaction could be detected. The calculated rate constants are presented in Table 2. In the literature, a value of  $0.52 \text{ M}^{-1} \text{ s}^{-1} (k_{\text{OH}})$  is given for the hydroxide-catalyzed enolization of acetone (*32*). This compares quite well with our findings ( $k_{\text{OH}} = 0.25 \text{ M}^{-1} \text{ s}^{-1}$ ). In Figure 3, the experimental data (symbols) are shown

together with the fitted pH dependence of the observed firstorder rate constant (lines). Acetaldehyde is the most reactive of these compounds, whereas pinacolone is the least reactive.

The iodination rate increases with increasing pH because of enhanced OH<sup>-</sup> catalysis. For a high enough pH, the enolization becomes faster than the addition of HOI to the enol. In this case, the HOI addition to the enol becomes the rate-determining step. This results in a first-order behavior in HOI. For acetone, this was observed at pH > 9.1. From the dependence of the observed second-order rate constant of HOI plus acetone on the pH (9.1 < pH < 11.6), it can be concluded that two reactions significantly contribute to the overall decrease of HOI, HOI plus enol and OI<sup>-</sup> plus enolate (eq 8).

$$\frac{\mathrm{d}[\mathrm{HOI}]}{\mathrm{d}t} = k_5[\mathrm{HOI}][\mathrm{acetone}] + k_6[\mathrm{OI}^-][\mathrm{OH}^-][\mathrm{acetone}]$$
(8)

Formation of CHI<sub>3</sub> from α-Methyl Carbonyl Compounds. The formation of  $CHI_3$  was measured at pH = 7 and 9 with initial concentrations of 6  $\mu$ M HOI and 1  $\mu$ M acetone or methylglyoxal (CH<sub>3</sub>COCHO). At pH = 7, acetone yielded no CHI<sub>3</sub> and methylglyoxal resulted in a small CHI<sub>3</sub> formation. At pH = 9, higher CHI<sub>3</sub> concentrations were found. In Figure 2, the experimental data are plotted according to eq 5. At pH = 9, the CHI<sub>3</sub> formation yield, q, is in the range of 0.05–0.1  $M^{-1}\ s^{-1}$  for both acetone (squares) and methylglyoxal (diamonds). At pH = 7, *q* is below 0.001  $M^{-1} s^{-1}$  for acetone and about 0.005 M<sup>-1</sup> s<sup>-1</sup> for methylglyoxal. For acetone, CHI<sub>3</sub> formation is about 25% of the value which was expected if HOI consumption was rate-determining. The observed difference could be due to a retardation of the overall reaction by the final hydrolysis of triiodoacetone. This gives an indication that the hydrolysis is the rate-determining step in CHI<sub>3</sub> formation from acetone and HOI. Another experiment which was performed in excess of acetone over HOI showed that the second iodination step of acetone is about 30 times faster than the first iodination step at pH = 9. The third iodination step is at least 30 times faster than the second step (28).

Consumption of HOI by Other Organic Compounds. Besides phenols and carbonyl compounds, other organic model compounds (allyl alcohol, glucosamine, glycine, toluene, and oxalate) were tested for their reactivity toward HOI. Table 3 shows that all of these compounds are unreactive. Rate constants were below 1  $M^{-1} s^{-1}$  or even below 0.1  $M^{-1} s^{-1}$ .

**Consumption of HOI and Formation of THMs and IO\_3^during Disinfection/Oxidation of Natural Waters.** The kinetics of HOI consumption and the formation of  $IO_3^-$ , I-THMs, and classical THMs were measured during the first 24 h of the oxidation of two natural waters (Lake Zurich, Switzerland, and Seine River, France) spiked with I<sup>-</sup>.

Figure 4 shows the formation of  $IO_3^-$ , CHI<sub>3</sub>, and total I in I-THMs together with the decrease of HOI and chlorine during chlorination of the lake water (pH = 8.0, 0.5 mg/L Cl<sub>2</sub>, 400 nM/50  $\mu$ g/L I<sup>-</sup>). For the calculation of the parameter I in I-THMs, the concentrations of the individual I-THMs were multiplied by the number of iodine atoms they contain. With this value the percentage of iodine which was incorporated into the I-THMs can be compared to the percentage of iodine incorporated into IO<sub>3</sub><sup>-</sup>.

More than 90% of HOI had disappeared after 30 min. However, the I-THMs, especially CHI<sub>3</sub>, were not released immediately. Half of their final concentration was reached only after 2 h. As speculated above, the hydrolysis of the trihalomethyl group could be the rate-determining process in I-THM formation. Fifty percent of the final  $IO_3^-$  concen-



FIGURE 2. Formation of CHI<sub>3</sub> from model compounds and in natural waters (data transformed according to eq 5). Model compounds: resorcinol (circles), acetone (open squares), methylglyoxal (open diamonds), and phenol (open triangles). Conditions: pH = 7 (dashed lines) and pH = 9 (solid lines). Inset: Natural waters from Lake Zurich, 1 mg/L NH<sub>2</sub>CI (full triangles) and 0.5 mg/L NH<sub>2</sub>CI (full diamonds); Seine river, 0.5 mg/L NH<sub>2</sub>CI (full squares). Conditions: pH = 8.

TABLE 2. Rate Co	onstants for th	ne Reaction o	of $\alpha$ -Methyl C	arbonyl Compounds	with HOI		
compound CH₃COR	R	pH range	phosphate (mM)	α-methyl carbonyl (mM)	[HOI]( <i>t</i> = 0) (µM)	nª	observed rate constants
acetaldehyde	Н	6.8-8.6	1-2	0.1-10	2.2-2.9	10	$k_{\rm H_{2}O} = (9 \pm 1) \times 10^{-8}  {\rm s}^{-1};$
pinacolone	tert-butyl	4.8-8.9	1-2	1-100	2.0-4.0	14	$k_{OH} = (0.90 \pm 0.04) \text{ M}^{-1} \text{ S}^{-1}$ $k_{H_{2}O} = (4 \pm 2) \times 10^{-9} \text{ S}^{-1}$ ; $k_{H_{2}O} = (0.027 \pm 0.002) \text{ M}^{-1} \text{ S}^{-1}$
acetate	O <sup></sup>	8.3-9.9	1	100-1000	2.0-2.3	5	$k_{H_{20}} < 2 \times 10^{-10} \text{ s}^{-1};$ $k_{H_{20}} < 2 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$
acetone	$CH_3$	6.0-8.3	1	31-64	1.7-5.5	9	$k_{\text{H}_2\text{O}} = (1.3 \pm 0.4) \times 10^{-8} \text{ s}^{-1};$ $k_{\text{H}_2\text{O}} = (0.25 \pm 0.02) \text{ M}^{-1} \text{ s}^{-1}$
acetone	$CH_3$	9.1-11.6	0-1	2.0-8.4	1.3-3.8	9	$k_{\text{OH}^-} = (0.25 \pm 0.05) \text{ M}^{-1} \text{ s}^{-1};$ $k_5 = (2.5 \pm 1.0) \text{ M}^{-1} \text{ s}^{-1};$ $k_6 = (3 \pm 1) \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$
<sup>a</sup> $n =$ number	of kinetic exper	iments ([HOI]	vs <i>t</i> ).				

tration was reached after 1 h. The formation of all iodinecontaining disinfection byproducts was finished after 10 h.

In additional experiments in lake and river water, some of the reaction parameters (oxidant, oxidant dose, and [I-]) were changed. Figure 5 shows the final concentrations (24 h after the oxidant addition) of IO<sub>3</sub><sup>-</sup>, CHI<sub>3</sub>, the total I in I-THMs, and the total concentrations of the six I-THMs and the four classical THMs. The highest CHI<sub>3</sub> formation (16 nM CHI<sub>3</sub>) was observed in the lake water when using chloramine (Figure 5, experiments C and D) where 47 nM I, or 12% of the initial  $I^-$  (400 nM), was incorporated into CHI<sub>3</sub>. The compounds CHI<sub>3</sub>, CHClI<sub>2</sub>, CHCl<sub>2</sub>I, and CHBrClI were found in several experiments, but neither CHBr<sub>2</sub>I nor CHBrI<sub>2</sub> was ever detected. The concentration of Br- in the investigated waters was too low to lead to a significant incorporation of bromine into the THMs. CHBrClI was the only brominecontaining I-THM which was detected, with a maximum concentration of 24 nM in the chlorinated river water (experiment G).

Byproduct Formation during Chloramination, Chlorination, and Ozonation. The smaller chemical reactivity of chloramine compared to that of chlorine leads to two general differences in the formation of iodine-containing disinfection byproducts when comparing these two oxidants. First, chloramine is not capable of oxidizing HOI to IO3- but chlorine is capable of this (14). This explains the higher  $IO_3^$ formation in chlorination processes compared to chloramination processes (Figure 5; experiments B, D). As a consequence, HOI has a longer lifetime in chloramination processes which leads to an increased reaction time with NOM. Second, the competition between chlorine and iodine for incorporation into the THMs is much higher in the presence of chlorine than in the presence of chloramine. This shifts the product distribution from CHI<sub>3</sub> in chloramination processes to the mixed I-THMs (e.g., CHCl<sub>2</sub>I) in chlorination processes. In the investigated lake water, chloramination resulted in 16 nM CHI3 and 34 nM mixed I-THMs (experiment C). Under the same conditions, chlorine induced the formation of 3 nM CHI3 and 120 nM mixed I-THMs (experiment A). When ozone was applied (experiment E), IO<sub>3</sub><sup>-</sup> was the only iodinecontaining byproduct detected. However, I<sup>-</sup> was not quantitatively transformed to IO3<sup>-</sup> despite the fast oxidation of HOI by O<sub>3</sub> ( $t_{1/2} < 1$  s) (14). Organic compounds which are highly reactive toward HOI successfully competed with O<sub>3</sub>.



FIGURE 3. Observed first-order rate constants for the iodination of three  $\alpha$ -methyl carbonyl compounds. Symbols, experimental data; lines, fits according to eq 7.

compound	р <i>К</i> а	pH range	phosphate (mM)	model compounds (mM)	[HOI]( <i>t</i> = 0) (µM)	nc	observed rate constants
allyl alcohol		7.2-8.2	0.5-1	0.5-10	1.5-2.0	6	$k_{\rm obs} \le 1 \ { m M}^{-1} \ { m s}^{-1}$
glucosamine	7.58 <sup>a</sup>	5.5-9.2	1	3-50	1.8-2.5	11	$k_{\rm obs} < 1 \ {\rm M}^{-1} \ {\rm s}^{-1}$
glycine	9.78 <sup>b</sup>	6.1-9.0	0-1	2-1000	0.6-2.5	10	$k_{\rm obs} < 0.1 \ {\rm M}^{-1} \ {\rm s}^{-1}$
oxalate	1.25, 4.27 <sup>b</sup>	6.0-8.1	1	10-200	1.7-2.2	7	$k_{\rm obs} < 0.1 \ {\rm M}^{-1} \ {\rm s}^{-1}$
toluene		4.1-7.3	1	2-4	1.0-2.9	5	$k_{\rm obs}^{\rm obs} < 1 \ {\rm M}^{-1} \ {\rm s}^{-1}$

TABLE 3. Rate Constants for the Reaction of Model Compounds with HOI

Such competitors could be phenolic compounds which have a higher apparent rate constant with HOI than  $O_3$  has.

Chlorine Dose. For a chlorine dose of 0.5 mg/L, 4% (experiment F) and 26% (experiment A) of the iodine was transformed to IO<sub>3</sub><sup>-</sup> in the river water and the lake water, respectively. With an increased chlorine dose of 1 mg/L, 43% (experiment G) and 75% (experiment B) of the total iodine was found as  $IO_3^{-}$ . In the river water (higher [DOC]), the  $IO_3^{-}$ yield was lower than that in the lake water. Due to the higher [DOC], the reaction of HOI with the NOM was more important and chlorine was less stable in the river water. As a result of this, less HOI was oxidized to IO<sub>3</sub><sup>-</sup>. The distribution among the I-THMs was also affected by the chlorine dose. In the river water, 8 nM CHI<sub>3</sub> and 54 nM mixed I-THMs were detected for 0.5 mg/L Cl<sub>2</sub> (experiment F). At a higher chlorine dose of 1 mg/L, [CHI<sub>3</sub>] decreased to 1 nM and the mixed I-THMs increased to 110 nM (experiment G). In the lake water, 0.5 mg/L Cl<sub>2</sub> resulted in 3 nM CHI<sub>3</sub> and 120 nM mixed I-THMs (experiment A), whereas for 1 mg/L chlorine (experiment B), no CHI<sub>3</sub> but 46 nM mixed I-THMs were formed. The lower yield of mixed I-THMs at the higher chlorine dose in the lake water is a result of the high IO3formation (75% of total I). For the prevention of medicinal taste and odor caused by CHI<sub>3</sub>, an increased chlorine dose can be a reasonable solution. A drawback of that is the enhanced formation of the classical THMs. The increase of the chlorine dose from 0.5 to 1 mg/L led to an increase in the sum of the classical THMs from 45 nM (5.8  $\mu$ g/L) to 210 nM ( $29 \mu g/L$ ) in the river water (experiments F, G). However, the overall result is still positive because CHI3 is below the threshold value and the sum of the classical THMs is below the current drinking water standards (4, 5).

*I*<sup>-</sup> *Concentration.* At  $[I^-] = 10 \ \mu g/L$ , formation of mixed I-THMs but no CHI<sub>3</sub> formation was observed. The competition between HOI and HOCl was shifted in favor of HOCl under these conditions. Therefore, a potential problem with CHI<sub>3</sub> must be expected only for  $[I^-] \gg 10 \ \mu g/L$ .

Incorporation of Iodine and Chlorine into THMs. Because of the high excess of HOCl (7  $\mu$ M/0.5 mg/L Cl<sub>2</sub>) over HOI (0.4  $\mu$ M) in experiment F (f[HOCl] dt : f[HOI] dt = 15), iodine has to react much faster with THM precursors than chlorine does in order to produce I-THMs. This was obviously the case because approximately the same amounts of iodine and chlorine were incorporated into THMs (both classical and I-THMs) in this experiment. If HOI reacted 15 times faster than HOCl did with the THM precursor groups, the HOCl excess would be compensated and a chlorine and iodine incorporation in equal amounts (as observed) would be expected. As shown above, the reaction of HOI with phenols can be 4–20 000 times faster than the corresponding reaction of HOCl. Therefore, such functionalities might be responsible for our observations.

Apparent Rate Constant HOI + NOM. In the experiments with chloramine as the oxidant, HOI only reacted with the NOM but was not further oxidized by NH<sub>2</sub>Cl. In both the lake and the river waters, the half-life of HOI was about 5 h. A rate constant for the reaction of HOI with NOM was fitted for both first-order and zero-order behaviors in HOI. On a C-atom base for the NOM, the rate constants amount to 0.4  $M^{-1}$  s<sup>-1</sup> or 6  $\times$  10<sup>-6</sup> s<sup>-1</sup> in the lake water and 0.1  $M^{-1}$  s<sup>-1</sup> or



FIGURE 4. Consumption of HOI and chlorine together with the formation of  $IO_3^-$ ,  $CHI_3$ , and the sum of I in I-THMs. Conditions: initially 400 nM I<sup>-</sup> (50  $\mu$ g/L), 15  $\mu$ g/L Br<sup>-</sup>, 1.3 mg/L DOC, 0.5 mg/L CI<sub>2</sub>, pH = 8.0.



FIGURE 5. Formation of disinfection byproducts in the oxidation of natural waters (24 h after addition of the oxidant). Conditions: pH = 8.0,  $I^- = 400$  nM (50  $\mu$ g/L). I in THMs (column 3) is the concentration of iodine in THMs (concentration of I-THMs multiplied by the number of iodine atoms they contain). Column 4 is the total concentration of I-THMs. The concentrations of the classical THMs were not measured in experiments B–E.

 $9 \times 10^{-6} \text{ s}^{-1}$  in the river water. These values describe the reaction of HOI with NOM<sub>1</sub> which leads to iodoorganic compounds such as I-THMs (eq 9).

 $HOI + NOM_1 = I - NOM$ (9)

$$HOI + NOM_2 = I^- + NOM_{2.ox}$$
(10)

According to eq 10, HOI can also be reduced to  $I^-$  by NOM<sub>2</sub>.

2790 ■ ENVIRONMENTAL SCIENCE & TECHNOLOGY / VOL. 34, NO. 13, 2000

However, this reaction has no influence on the kinetics of the HOI decrease because the formed I<sup>-</sup> is quickly reoxidized to HOI by chloramine. The above-mentioned rate constants can be compared with the rate constants of HOI with model compounds at pH = 8 (on a C-atom base: phenols  $3 \times 10^{1-6} \times 10^{5} \text{ M}^{-1} \text{ s}^{-1}$ , carbonyl compounds  $6 \times 10^{-9} - 5 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$ ). A comparison of rate constants from natural waters and model compounds shows that phenolic entities (but not

# TABLE 4. Semiquantitative Assessment of the Sinks of Iodine during Disinfection: Influence of Disinfectant

	products					
disinfectant	iodoform	other I-THMs	iodate			
ozone chlorine chloramine	_ + +++	_ ++ ++	+++ ++ _			

carbonyl entities) as part of the NOM could account for the experimental results.

Yield of CHI<sub>3</sub>. CHI<sub>3</sub> formation yield, q, according to eq 5, was also calculated for the chlorination of the natural waters (see Figure 2, inset). During chloramination processes, CHI<sub>3</sub> formation faced less competition from the formation of mixed I-THMs. In the lake water, q reached a value of 0.12 M<sup>-1</sup> s<sup>-1</sup> for 0.5 mg/L NH<sub>2</sub>Cl (diamonds in Figure 2, inset) and 0.24  $M^{-1}$  s<sup>-1</sup> for 1.0 mg/L NH<sub>2</sub>Cl (triangles in Figure 2, inset). From the investigated model compounds, only resorcinol yielded enough CHI<sub>3</sub> to account for the results from the lake water. For the river water (squares in inset Figure 2), q was 0.002-0.035 M<sup>-1</sup> s<sup>-1</sup>. The highest values were found at the beginning of the experiment. The observed q values could be explained principally by methylglyoxal or acetone, but only if they accounted for more than 35% of the NOM. Because this percentage is too high for NOM, it is more likely that phenolic groups in the NOM account for the observed CHI3 formation in the river water. Here again, phenolic groups as part of the NOM could explain the experimental results whereas carbonyl compounds could not.

Operational Considerations for Drinking Water Treatment. The formation of CHI<sub>3</sub> during oxidative drinking water treatment is influenced by parameters such as the stability of the oxidant, I<sup>-</sup> concentration, type and concentration of NOM, ammonia concentration, temperature, pH, and others. Cases of taste and odor problems related to CHI3 formation in drinking water treatment practice occurred commonly in chloramination processes and rarely in chlorination processes, but never in well-operated ozonation processes (6-8). Even though we only performed experiments in two natural waters with a few variable parameters, the observations from the literature compare well with the results we obtained in these oxidation experiments. The main results are summarized semiguantitatively in Table 4. Chloramine is the oxidant which most likely results in CHI<sub>3</sub> formation. During chloramination, reactions competitive with the formation of CHI<sub>3</sub>, such as those for the formation of IO<sub>3</sub><sup>-</sup> or mixed I-THMs, are not important. When free chlorine (ammonia-free water) is used, part of HOI can be oxidized to IO<sub>3</sub><sup>-</sup>. This reaction which prevents CHI<sub>3</sub> formation is especially important for high chlorine doses and stabilities. When taste and odor problems are faced in chlorination processes, an increase of the chlorine dose is a possible solution. However, this may also lead to an increased formation of undesired classical THMs such as chloroform. Another competition reaction which prevents CHI<sub>3</sub> formation in the presence of chlorine is the formation of mixed I-THMs such as CHCl<sub>2</sub>I. One factor in this context is the concentration and reactivity of the NOM. If HOI is consumed quickly by NOM which is connected to a low chlorine stability, only minor quantities of IO3- are formed. For less reactive NOM, HOI and chlorine persist longer and, in turn, high amounts of IO<sub>3</sub><sup>-</sup> can be expected. In general, the amount of IO<sub>3</sub><sup>-</sup> formation is the most important factor for the final fate of iodine. When ozone was used, CHI<sub>3</sub> formation was not observed in the drinking water treatment practice or in our experiments. Overall, the risk of production of CHI3-related taste and odor problems increases in the order ozone < chlorine < chloramine.

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