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# Chlorination and Formation of Organoiodinated Compounds: The Important Role of Ammonia

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This study has been undertaken to determine the conditions of formation of organoiodinated compounds responsible for medicinal tastes and odors frequently observed after chlorination of waters containing iodides. It has been shown that iodoform was formed in the presence of chloramines, in a region where the formation of the most classical chlorinated and brominated THMs is usually unfavored. Reactions would take place between monochloramine, organic matter, and iodides to yield iodoform. These interactions are favored when iodide ions are replaced by iodine. Oxidation by iodine alone in the presence of ammonia and without monochloramine does not explain the yield of the iodinated THMs observed. However, nitrogenated molecules such as amines and amino acids would take part during chlorination in the production of organoiodinated compounds to a small extent.

## A. Introduction

The characteristic medicinal odors which appear quite frequently in chlorinated finished drinking waters have been shown to be associated with the formation of iodinated trihalomethanes (THMs) (*1, 2*). Hansson et al. (*3*) mentioned that an iodoform concentration of 5 $\mu$g/L is sufficient to yield a medicinal taste. This compound, associated with other iodinated THMs, could explain the problems encountered in a number of waters containing iodides. Iodide ions concentration in groundwaters usually ranges from 0.01 to 20 $\mu$g/L (*4*). Although much information is available on the formation and occurrence of chlorine and bromine containing trihalomethanes (*5, 6*), very little research has been performed on iodinated THMs. The example of bromide ions shows that, in natural waters, competitive reactions of chlorine take place with the organic matter, ammonium ions, and bromide ions (*7*). Among the various alternatives for minimizing the formation of THMs, the practice of chloramination is found to be an efficient one. However, the literature reports that the production of iodoform, which seems to be related to the iodide content, is dependent upon the order of addition of the chlorine and ammonia (*3*). Moreover, the chloramination would favor not only medicinal odors but also organoiodinated compounds formation (*1, 3, 8*).

This work is part of a larger examination of the reactions promoted by various oxidants in waters containing halides and, in particular, of the induced organohalogenated byproducts formation. The aim of the present laboratory study was to determine factors governing the formation of iodoform during chlorination of drinking waters containing iodides. To reach this objective, there was a need to spike the studied natural waters with potassium iodide in order to increase the very small natural iodide content.

## B. Materials and Methods

**1. Studied Raw Waters.** Experiments were carried out on a groundwater from the west region of France (see Table 1). This area, influenced by the sea level, contained 20−30 $\mu$g/L of iodide ions during the period of this study (January 1995−June 1996).

For experiments, this water was aerated for ferrous ions oxidation. Then the solutions were filtrated either on a 1.2 $\mu$m porosity membrane for experiments in the presence of ammonium ions ($N{-}NH_4^+ \approx 0.7 \pm 0.2$ mg/L) or on a biologically coated sand filter for nitrification. In both cases, for analytical reason, the water was spiked with 200 $\mu$g/L (1.6 $\mu$M) of iodide ions. This value, although high, can be encountered in several groundwaters (*9*).

**2. Oxidation Operating Conditions.** Whatever oxidant used, the applied oxidant dose was 1.5 mg $Cl_2$/L. For chlorination, commercial hypochlorous acid (Labosi, France) was used. For chloramination experiments, a concentrated monochloramine solution (400 mg/L) was prepared from phosphate buffered ultrapure water (pH 8.5) added with ammonium ions and hypochlorous acid (chlorine/ammonium ions = 0.8 mol/mol). Under such conditions, residual chlorine was lowered (<3%). Commercial iodine stock solutions (Labosi, $[I_2] = 0.1$ N; 1.55 mg of $I^-$/mg of $I_2$ at pH 6) were used for experiments with iodine.

The reactions were run for 6 h in the dark and at an ambient temperature of 20 ± 2 °C. This time was chosen on the basis of preliminary experiments which indicated that tastes and odors reached significant values.

Then the samples were quenched with sodium metaarsenite for chlorine and iodine removal and with sulfite ions for chloramination experiments.

**3. Analytical Procedures.** Chlorine and chloramines were analyzed with the *N,N*-diethyl phenylene−1,4-diamine (DPD) colorimetric method. At pH 6.2−6.5, the oxidation of DPD by chlorine residual leads to the formation of a stable product with absorption bands at 510 and 550 nm (*10*). The procedure used was established for small sample volumes (*11*). A total of 250 $\mu$L of buffer (24 g/L $Na_2HPO_4$; 46 g/L $KH_2PO_4$; 0.8 g/L disodium EDTA; 0.02 g/L $HgCl_2$) are mixed with 250 $\mu$L of DPD solution (2 mL/L concentrated $H_2SO_4$; 0.2 g/L disodium EDTA; 1.1 g of anhydrous *N,N*-diethyl phenylene−1,4-diamine) and with a 5 mL sample. This procedure allows the determination of free chlorine in the range 0.05−2 mg/L and of total chlorine after iodide addition (∼50 mg/sample).

Iodide ions were determined by an electrochemical method with an iodide ion selective electrode (Radiometer XS 230). The detection limit was 10 $\mu$g of $I^-$/L.

Chlorinated and brominated THMs were quantified by gas chromatography equipped with a headspace (DANI HSS 3950) injection system (bath temperature: 40 °C). The analysis was performed with a capillary column (J&W DB 624; 30 m × 0.53 mm i.d.) on a Varian 3300 apparatus programmed from 50 to 120 °C with a 5 °C/min temperature rise. With an electron capture detector, the detection limit was 0.5 $\mu$g/L $CHCl_3$ for an injection volume of 100 $\mu$L.

Iodoform was determined by gas chromatography after extraction with pentane, using 1,1,1,2-tetrachloroethane as

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**TABLE 1. Characteristics of the Groundwater Studied**

| | RWa | RWb |
|---|---|---|
| pH (20 °C) | 7.9 ± 0.3 | 8.1 |
| $NH_4^+$ (mg/L) | 0.7 ± 0.2 | 0.6 |
| $Fe^{2+}$ (mg/L) | 1.8 | ND[a] |
| $Mn^{2+}$ (mg/L) | 0.7 | ND |
| $I^-$ (μg/L) | 20 ± 10 | 13.0 |
| $Br^-$ (μg/L) | 90 | ND |
| TOC (mg/L) | 2.5 ± 0.2 | 2.7 |

[a] ND, not determined.

**TABLE 2. Chlorination of the Raw Water Spiked with Iodide Ions; Influence of Ammonia and of the Contact time on THMs Formation[a]**

| contact time | $t = 0$ raw water RWa | $t = 6$ h | | t = 24 h | |
|---|---|---|---|---|---|
| | | $NH_4^+ =$ 0.47 (mg/L) | $NH_4^+ = 0$ | $NH_4^+ =$ 0.47 (mg/L) | $NH_4^+ = 0$ |
| residual total $Cl_2$ (mg/L) | | 0.67 | 0.45 | 0.58 | 0.19 |
| $CHCl_3$ (μg/L) | <DL[b] | 1.5 | 10.8 | 1.1 | 16.2 |
| $CHCl_2Br$ (μg/L) | <DL | 5.8 | 9.1 | 0.4 | 12.7 |
| $CHBr_2Cl$ (μg/L) | <DL | <DL | 7.2 | <DL | 9.2 |
| $CHBr_3$ (μg/L) | <DL | <DL | <DL | <DL | <DL |
| $CHI_3$ (μg/L) | <DL | 19.0 | 0.42 | 31.3 | 0.46 |

[a] $[N\text{-}NH_4^+]_o = 0.47$ mg/L; $[I^-] = 215$ μg/L; pH 7.7. [b] DL, detection limit.

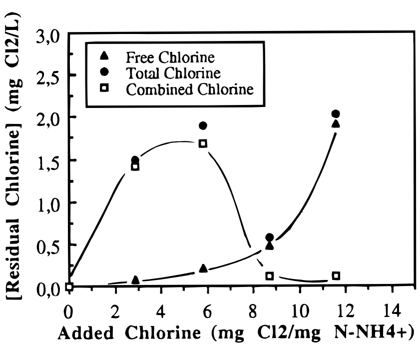

**FIGURE 1. Chlorination of the raw water RWa: evolution of chlorine species. $[N\text{-}NH_4^+]_o = 0.7$ mg/L; $[I^-]_o = 260$ μg/L; $pH_o = 7.7$.**

**TABLE 3. Influence of the Chlorine Dose on the Formation of THMs[a]**

| $Cl_2$ added (mg of $Cl_2$/-mg of $N\text{-}NH_4^+$) | $CHI_3$ (μg $L^{-1}$) | $CHCl_3$ (μg $L^{-1}$) | $CHCl_2Br$ (μg $L^{-1}$) | $CHBr_2Cl$ (μg $L^{-1}$) | $CHBr_3$ (μg $L^{-1}$) |
|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | <DL |
| 2.15 | 14.0 | 1.2 | 0.1 | <DL | <DL |
| 2.9 | 11.2 | 0.8 | 0.1 | <DL | <DL |
| 4.3 | 12.9 | 4.0 | 1.0 | <DL | <DL |
| 5.8 | 9.0 | 4.1 | 1.6 | <DL | <DL |
| 6.4 | 12.0 | 6.3 | 2.1 | 0.2 | <DL |
| 8.6 | 13.3 | 9.2 | 4.6 | 1.3 | <DL |
| 8.7 | <DL | 13.3 | 9.4 | 6.2 | <DL |
| 11.6 | <DL | 18.2 | 11.5 | 6.3 | <DL |
| 12.9 | <DL | 20.6 | 13.6 | 10.0 | 0.5 |

[a] $[N\text{-}NH_4^+]_o = 0.7$ mg/L; $[I^-]_o = 260$ μg/L; $pH_o = 7.7$.

internal standard. A 2 μL extract was injected in the on-column injection mode into a DB1701, 30 m × 0.25 mm i.d. fused-silica column (J&W) using a Fisons Instruments GC 8000 Series gas chromatograph equipped with an electron capture detector. The temperature was programmed from 50 °C (with a 2-min hold) to 100 °C at 10 °C/min and then to 180 °C at 5 °C/min. These conditions allowed a 0.3 μg/L $CHI_3$ detection limit.

## C. Results

**1. Chlorination of Iodide-Containing Water in the presence of $NH_4^+$: Influence of the Ammonia Presence.** The chlorination of the raw water was first realized with 1.5 mg of $Cl_2$/L in the presence or in the absence of $NH_4^+$. Analyses of THMs presented in Table 2 were performed after 6 and 24 h contact time.

For both contact times (6 and 24 h), total chlorine residual is higher in the presence of ammonia (Table 2), indicating that the chloramine formed is less reactive than free chlorine toward inorganics and organics present in iodide-spiked water.

In the absence of ammonia, among the THMs encountered, chlorinated ones are the most frequent ($CHCl_3$ > $CHCl_2Br$ > $CHBr_2Cl$), with concentrations increasing with time. As now well established, the formation of brominated and chlorinated THMs is inhibited in the presence of ammonia due to chloramine formation (*7, 12–14*). Concerning the iodinated halomethanes quantified, among the three standards available ($CHI_3$, $CH_2ICl$, and $CH_2I_2$), iodoform was the only product observed during chlorination. Opposite to the classical chlorinated and brominated THMs, the concentration of iodoform, close to the detection limit (0.3 μg/L) in the absence of ammonium ions, reaches 19–31 μg/L (0.048–0.079 μM) between 6 and 24 h contact time in the presence of ammonia. Ammonia seems to play an important role in the iodoform-related pathways. Other iodinated THMs were identified by mass spectrometry detection. $CHClI_2$ and $CHBrI_2$ were found in the presence and in the absence of $NH_4^+$, whereas $CHBr_2I$ and $CHCl_2I$ seemed to be observed only in $NH_4^+$ free solutions. The tastes of the water containing ammonia after chlorination was qualified as medicinal. Since a correlation between the formation of iodoform and the medicinal flavor of these chlorinated waters can be established, iodoform has been chosen as an indicator of tastes and odors for the following experiments.

**Effect of Chlorine Dose.** The raw water RWa (Table 1) in the presence of ammonium ions ($[N{-}NH_4^+] = 0.69$ mg/L) and spiked with iodide ions ($[I^-] = 260$ μg/L) was oxidized with different chlorine doses (2 to 13 mg/L). The Figure 1 which presents the evolution of free, combined and total residual chlorine indicates a breakpoint value corresponding to 8.5–9.0 mg of $Cl_2$/mg of $N{-}NH_4^+$ after 6 h of contact time. Note that the shift of breakpoint (above 7.6 g of $Cl_2$/g of $N{-}NH_4^+$) is probably due to organics and halides in water.

The concentration of chlorinated, brominated, and iodinated trihalomethanes (THMs) was also determined as a function of the applied chlorine dose. Results in Table 3 show that the production of chlorinated and brominated THMs (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) increases when the chlorination yield increases. The formation of dibromochloromethane only appears above the breakpoint whereas bromoform is only observed for the highest chlorine dose ($Cl_2/N{-}NH_4^+ =$ 12.9 mg/mg). By contrast, iodoform is formed only below the breakpoint. In this range, the concentration of this iodinated THM does not evolve to a great extent (9–14 μg/L).

**Effect of Ammonia Concentration.** Similar experiments were performed by introducing a given chlorine dose (10 mg/L) in the raw water RWa with iodides and different ammonium ions concentrations (0.4–4.5 mg of $NH_4^+$/L) added after biological nitrification. Results obtained are presented in Figure 2 and Table 4. In agreement with the literature (*7, 12, 14*), below the breakpoint, the competitive reactions between chlorine and organic and inorganic species

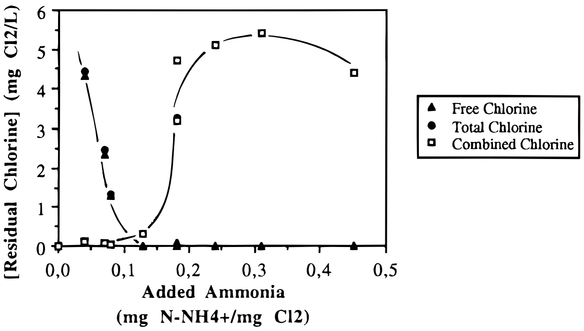

**FIGURE 2. Chlorination of the raw water RWa: evolution of chlorine species. $[Cl_2]_o = 10$ mg/L; $[NH_4^+]_o = 0.4-4.5$ mg $NH_4^+$/L; $[I^-]_o = 200$ $\mu$g/L; $pH_o = 7.9$.**

**TABLE 4. Influence of Ammonia Concentration on the Formation of THMs**[a]

| $NH_4^+$ added (mg of N-$NH_4^+$/mg of $Cl_2$) | $CHI_3$ ($\mu$g $L^{-1}$) | $CHCl_3$ ($\mu$g $L^{-1}$) | $CHCl_2Br$ ($\mu$g $L^{-1}$) | $CHBr_2Cl$ ($\mu$g $L^{-1}$) |
|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 |
| 0.04 | <DL | 18.0 | 11.2 | 6.5 |
| 0.07 | <DL | 16.8 | 10.3 | 6.3 |
| 0.08 | <DL | 15.4 | 9.9 | 6.6 |
| 0.13 | 1.2 | 8.4 | 4.2 | 2.0 |
| 0.18 | 12.7 | 3.7 | 0.9 | <DL |
| 0.24 | 12.4 | 3.4 | 0.5 | 0.5 |
| 0.31 | 15.3 | 3.1 | 0.4 | 0.4 |
| 0.45 | 14.0 | 3.0 | 0.3 | <DL |

[a] $[Cl_2]_o = 10$ mg/L; $[NH_4^+]_o = 0.4$ to 4.5 mg of $NH_4^+$/L; $[I^-]_o = 200\,\mu$g/L; $pH_o = 7.9$; $[CHBr_3] <$ DL.

($NH_3$, $I^-$, $Br^-$) favor the formation of chloramines, thus lowering the production of chlorinated and brominated THMs. As observed previously, these conditions promote the formation of iodoform. Furthermore, this production seems to only depend on the presence of chloramine ($Cl_2$/N$-NH_4^+$ value with respect to the breakpoint) and not on the amount of chloramine formed (compare Figures 1 and 2 and Tables 3 and 4).

**2. Chlorination of Iodide-Containing Water in the Presence of Organic Amines.** To better understand the role of nitrogen in the formation of iodoform during chlorination, the impact of organic nitrogen molecules was investigated. Therefore, after nitrification for ammonium ions removal, the raw water RWa was spiked with the amino acid glycine frequently encountered in natural waters (*15*). The concentration added was 50 $\mu$mol/L (i.e., equivalent to the yield of ammonia found in the raw water used in this study). Another experiment was carried out by replacing glycine by methylamine. In both cases, after addition of iodide ions (200 $\mu$g/L), increasing chlorine doses were applied. Using the DPD method, the analysis of free and total chlorine was performed after a 6 h contact time (Figures 3 and 4). The curves of chlorine residual obtained from the chlorination of glycine are similar to those obtained with ammonia with a breakpoint value corresponding to 2 mol of $Cl_2$/mol of glycine. This stoichiometry is consistent with the decomposition of the chloroamino acids formed (*16*). In the case of methylamine, free and combined chlorine are present simultaneously in solutions for chlorine doses above 2 mol of $Cl_2$/mol of methylamine as observed by Poncin et al. (*17*), meaning that organic dichloramines are only weakly removed in this case.

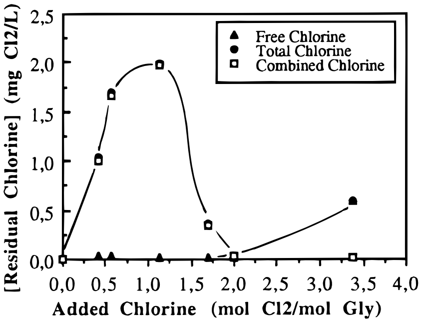

**FIGURE 3. Chlorination of the raw water spiked with glycine HOOC-$CH_2$-$NH_2$ ($[Gly]_o = 50\,\mu$mol/L). Influence of the applied chlorine dose on the different chlorine species.**

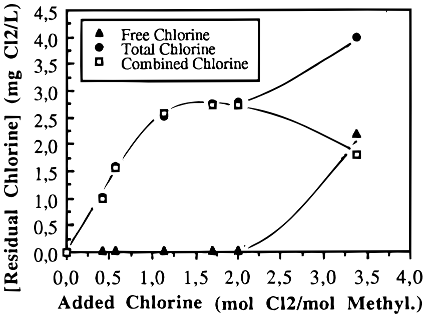

**FIGURE 4. Chlorination of the raw water spiked with methylamine $CH_3NH_2$ ($[Meth]_o = 50\,\mu$mol/L). Influence of the applied chlorine dose on the different chlorine species.**

**TABLE 5. Influence of the Applied Chlorine Dose on the Formation of THMs in the Raw Water Spiked with Glycine ($[Gly]_o = 50\,\mu$mol/L); $[I^-]_o = 200\,\mu$g/L**

| $Cl_2$/glycine (mol/mol) | $CHI_3$ ($\mu$g $L^{-1}$) | $CHCl_3$ ($\mu$g $L^{-1}$) | $CHCl_2Br$ ($\mu$g $L^{-1}$) | $CHBr_2Cl$ ($\mu$g $L^{-1}$) | $CHBr_3$ ($\mu$g $L^{-1}$) |
|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | <DL |
| 0.4 | 12.5 | 0.2 | <DL | <DL | <DL |
| 0.6 | 12.1 | <DL | <DL | <DL | <DL |
| 1.1 | 1.8 | 0.3 | 0.8 | 0.4 | <DL |
| 1.7 | <DL | 2.2 | 1.9 | 0.6 | <DL |
| 2.0 | <DL | 3.7 | 2.5 | 0.8 | <DL |
| 3.4 | <DL | 8.8 | 7.2 | 4.6 | 0.2 |

**TABLE 6. Influence of the Applied Chlorine Dose on the Formation of THMs in the Raw Water Spiked with Methylamine ($[Meth]_o = 50\,\mu$mol/L); $[I^-]_o = 200\,\mu$g/L**

| $Cl_2$/methyl (mol/mol) | $CHI_3$ ($\mu$g $L^{-1}$) | $CHCl_3$ ($\mu$g $L^{-1}$) | $CHCl_2Br$ ($\mu$g $L^{-1}$) | $CHBr_2Cl$ ($\mu$g $L^{-1}$) | $CHBr_3$ ($\mu$g $L^{-1}$) |
|---|---|---|---|---|---|
| 0 | 0 | 0 | 0 | 0 | <DL |
| 0.4 | 13.6 | 0.2 | <DL | <DL | <DL |
| 0.6 | 27.1 | 0.2 | <DL | <DL | <DL |
| 1.1 | 29.9 | 1.3 | 0.7 | 0.5 | <DL |
| 1.7 | 20.2 | 4.4 | 1.3 | 3.2 | <DL |
| 2.0 | 10.4 | 5.9 | 2.0 | 3.7 | <DL |
| 3.4 | <DL | 19.3 | 7.9 | 4.9 | 0.2 |

The formation of THMs corresponding to this set of experiments is summarized in Tables 5 and 6. In both cases, the concentrations of chlorinated and brominated THMs increase from the applied dose of about 1 mol of $Cl_2$/mol of amine or amino acid. Considering the production of iodoform, significant yield only appears below 1 mol of $Cl_2$/mol of glycine, corresponding to the presence of α-*N*-chloroamino acid (*16*). Iodoform production from methylamine chlorination is higher. The concentration reaches 30 $\mu$g/L (0.076 $\mu$M) for the ratio $Cl_2$/methylamine $\approx$ 1 mol/mol and then decreases before total organic chloramines decrease.

**3. Chloramination of Iodide-Containing Water.** Investigations of iodoform production were also conducted

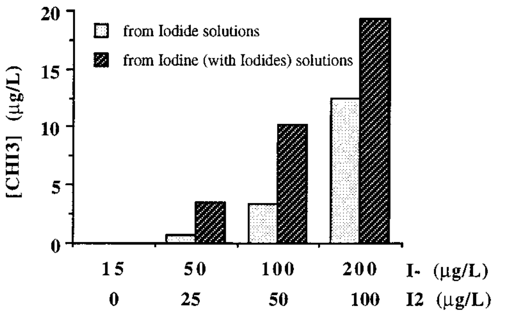

**FIGURE 5. Chloramination of the raw water: influence of iodides and iodine concentration on the production of iodoform. $[NH_2Cl] = 1.5$ mg of $Cl_2$/L; $pH_o = 8.0$.**

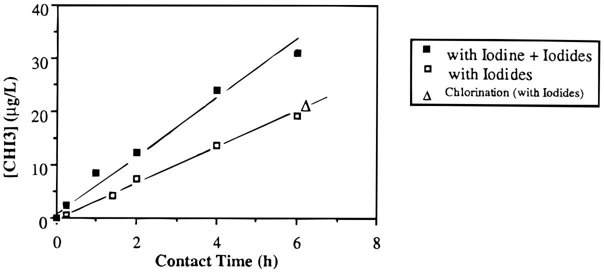

**FIGURE 6. Chloramination of the raw water RWb containing iodine and/or iodide ions: influence of the contact time on the production of iodoform. $[NH_2Cl]_o = 1.5$ mg of $Cl_2$ /L; $[I^-]_o = 200$ µg/L or $[I_2 + I^-]_o = 200$ µg/L; $[N\text{-}NH_4^+]_o = 0.6$ mg/L. ΔChlorination (with iodides): chlorination of the raw water RWb ($[Cl_2]_o = 1.5$ mg/L) in the presence of ammonium and iodide ions; $[I^-]_o = 200$ µg/L.**

from chloramination of the raw water RWa containing various concentrations of iodine and/or iodide ions. The Figure 5 shows the production of iodoform for a monochloramine dose of 1.5 mg of $Cl_2$/L in the presence of 50−200 µg of $I^-$/L or 25−100 µg of $I_2$/L with 1.9 mg of $I^-$/mg of $I_2$ at pH 8. Results indicate that the yield of iodoform increases as the concentration of the inorganic iodine species increases. Data obtained in the presence of iodides alone and when both iodine and iodides are present indicate that iodine in solution induces a greater $CHI_3$ formation during chloramination than equal content of iodide ions. As an example, 100 µg/L $I^-$ alone led to 3.4 µg/L $CHI_3$, whereas 10.2 µg/L $CHI_3$ was produced with 50 µg/L additional $I_2$.

The production of iodoform with time was examined during the chloramination of the raw water RWb with a chloramine dose of 1.5 mg of $Cl_2$/L. This water, taken on the same site but in a period different from the previous experiments, was spiked with iodine and/or iodide ions [$([I_2]_o + [I^-]_o) = 200$ µg/L or $[I^-]_o = 200$ µg/L respectively]. Iodoform analysis indicates a linearity up to 6 h contact time (Figure 6). The slopes calculated in the presence of iodide alone and associated with iodine [3.3 and 5.5 µg $L^{-1}$ $h^{-1}$ (i.e., 8.4 × $10^{-3}$ and 14.0 × $10^{-3}$ µM $h^{-1}$), respectively] confirm that the reaction yielding iodoform is enhanced by the presence of iodine. The chlorination of the same water containing ammonium ions and spiked with iodides gave similar results as chloramination (Figure 6, 6 h contact time) since the reaction leading to monochloramine is rapid (*18*) and does not represent the limiting step in the mechanism.

**4. Oxidation of Water with Iodine.** The relative impact of reactive species induced by reactions with chloramines versus the direct reaction between iodine, ammonia, and organic matter is of primarily interest for the determination of the mechanism of iodoform formation. Thereby, the raw water RWa containing ammonia was oxidized by iodine. As shown in Table 7, iodoform was not detected for 100 and 200 µg/L initial concentration of iodine. Indeed iodine, in an amount that could be produced in water by the oxidation of iodides, is not the active species responsible for the observed iodoform during chlorination. The reaction between iodine and the organic matter to produce iodoform at pH 8.0 is possible only from high concentrations of iodine (*7, 19−21*). Iodoform was found only for the two highest $I_2$ applied doses (1 and 2 mg/L). It was also observed that doubling the concentration of $I_2$ has weak influence on the amount of $CHI_3$ formed since the iodine consumed under both conditions was around 1 mg $I_2$/L. Furthermore, under these conditions, $CHI_3$ production does not appear to be dependent on the presence of ammonia. Ammonium ions are not consumed during oxidation by iodine as indicated by Doré (*7, 19*). Thus, the interaction iodine/ammonia does not constitute a pathway for the production of iodoform.

**TABLE 7. Oxidation of the Raw Water RWa by Iodine: Influence of the Iodine Dose on the Formation of Iodoform[a]**

| iodine applied $[I_2]$ (µg $I_2$/L) (µmol/L) | iodoform produced after 6 h $CHI_3$ (µg/L) (µmol/L) |
|---|---|
| 0 | <DL[b] |
| 100 (0.4) | <DL |
| 200 (0.8) | <DL |
| 1000 (3.9) | 21.5 (0.054) |
| 2000 (7.9) | 26.6 (0.067) |
| no $NH_4^+$: 1000 (3.9) | 21.3 (0.054) |

[a] $[N\text{-}NH_4^+]_{RWa} \approx 0.8$ mg/L; iodide ions content of solutions: 1.9 mg of $I^-$/mg of $I_2$; $pH_o$ ~8.0. [b] DL: detection limit (0.3 µg/L).

## D. Discussion

This study was undertaken to determine the conditions of formation of iodoform responsible for medicinal tastes and odors frequently observed after chlorination of waters containing iodides. As already shown in the literature (*7*), competitive reactions with chlorine occur between halides, ammonia, and organic matter in natural waters. Owing to the concentrations of these solutes in most water sources [0.01−20 µg of $I^-$ $L^{-1}$; 10−2500 µg of $Br^-$ $L^{-1}$; 0.05−1.0 mg of $NH_4^+$ $L^{-1}$; total organic carbon = 1−10 mg of C $L^{-1}$ (*4, 9, 22−24*)], and considering the rate constants of chlorine toward iodides, bromides, and ammonia [respectively, 1−2 × $10^3$ $M^{-1}$ $s^{-1}$, 3 × $10^3$ $M^{-1}$ $s^{-1}$, and 4.2 × $10^6$ $M^{-1}$ $s^{-1}$ at pH ~7 (*18, 25, 26*)], the reaction-producing chloramine and even bromine then bromamine [$k_{HOBr/NH_4^+} = 7.5 \times 10^7$ $M^{-1}$ $s^{-1}$ (*27*)] are favored and rapid when low chlorine doses are applied. For chlorine doses below the “breakpoint”, this presence of haloamines (quantified as combined chlorine) allows to explain the weak yield of chlorinated and brominated THMs observed in this work. On the opposite, it was shown that iodoform was formed in the presence of chloramines, in a region where the formation of the most classical chlorinated and brominated THMs is usually unfavored.

Thus, the new result of this work is that nitrogen (as ammonia or organic amines) was found to enhance iodoform formation during chlorination of iodides containing waters at chlorine/ammonia or amines ratios corresponding to the presence of inorganic or organic chloramines. With inorganic chloramines in large exces, iodoform production was only weakly influenced by the concentration of combined chlorine. On the contrary, iodoform concentration was found to increase with increasing $I^-$ or $I_2$. Since the production of $CHI_3$ in the presence of chloramines is increased with $I_2$, this latter could be involved in the reaction pathway even if its formation from the oxidation of $I^-$ by chlorine is not favored. However, in the pH range 7.7−8.0, the direct reaction of $I_2$ with THM precursors is slow, independent of the presence of ammonium ion, and cannot explain the amount of $CHI_3$ observed in this study.

Some nitrogen functional groups of organic molecules can also take part in a mechanism leading to iodoform. Thus, intermediates resulting from the reaction of hypochlorous acid on glycine or methylamine, for chlorine doses up to 1 or 2 mol/mol, respectively, can be involved in the reactions of halogenation. In the case of methylamine, *N*-chloromethylamine is produced from the rapid reaction of one molecule of chlorine. *N*,*N*-Dichloromethylamine appears for chlorine doses above 1 mol/mol of methylamine simultaneously to the *N*-chloromethylamine concentration decrease (*17*).

$$CH_3{-}NH_2 + HOCl \rightarrow CH_3{-}NHCl + H_2O \qquad k = 3.6 \times 10^8\ M^{-1}\ s^{-1}$$

$$CH_3{-}NHCl + HOCl \rightarrow CH_3{-}NCl_2 + H_2O \qquad k = 1.1 \times 10^3\ M^{-1}\ s^{-1}$$

The production of $CHI_3$ was shown to follow the concentration of *N*-chloromethylamine. Iodoform was not produced above the breakpoint value of 2 mol/mol despite the presence of stable dichloromethylamine residual thus indicating that only monochloromethylamine was effective in producing $CHI_3$. With their amino group, free amino acids behave like aliphatic amines, i.e., have a high reactivity toward chlorine. In the case of glycine, the rate constant is $8.5 \times 10^7\ M^{-1}\ s^{-1}$ at neutral pH for the production of the N-chlorinated derivative. This reaction is generally followed by the formation of carbonyl byproducts and ammonia via an imine structure (*16*), but a parallel reaction leads also to dichloroamino acids then nitriles. Maximum $CHI_3$ production was observed for chlorine doses below 1 mol/mol, a region where the concentration of the *N*-chloro amino acid could also be optimum. Above this, only traces of the monochloroamino acid would be present due to its decomposition and to the competitive formation of the dichloroamino acid. Like monochloromethylamine, the *N*-chloroamino acid appears as a more effective $CHI_3$ precursor than dichloroamino derivatives. Furthermore, in this case, the release of ammonia resulting from the decomposition of the *N*-chloroamino acids represents a minor route and can only weakly explain the formation of iodoform. It must be noted that the chlorinated byproduct of methylamine, which is more stable than the derivatives of glycine, also leads to a higher concentration of iodoform.

Under water-treatment conditions, taking into account the amine and amino acids content of natural waters [less than 10 $\mu$mol/L for total amino acids (*15*)], this class of compounds will only take a small part in the mechanism of formation of iodoform during chlorination of drinking waters.

Concerning the mechanism approach, two possible routes could account for the observations made in this work: (1) the chloramines formed could react with organic matter to produce some chlorinated compounds followed by reaction with iodide or iodine to form $CHI_3$, and (2) the formation of iodamines or chloroiodamines could occur first from reactions between chloramines and iodides, and then the production of $CHI_3$ would result from the action of these intermediates on dissolved organic matter.

Further experiments will have to be performed to determine which one occurs. Moreover, the additional iodinated halomethanes ($CHClI_2$, $CHBrI_2$, $CHCl_2I$, and $CHBr_2I$) identified during this work and by other authors (*28*, *29*) also merit attention.

In practical view, the removal of ammonia from water by a biological process (nitrification step) would allow to inhibit the iodoform formation potential and to apply the final chlorination step. Another alternative consists of replacement of chlorination by oxidation with chlorine dioxide as it will be shown in another article.

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## Literature Cited

(1) Bruchet, A.; N'guyen, K.; Mallevialle, J.; Anselme, C. *Proceedings of AWWA Annual Conference*, Los Angeles, California, June 18, 1989; pp 125−141.

(2) Gittelman, T. S.; Yohe, T. L.; Staudte, P. B. *Proc. Water Qual. Technol. Conf.* **1989**, *17*, 101−115.

(3) Hansson, R. C.; Henderson, M. J.; Jack, P.; Taylor, R. D. *Water Res.* **1987**, *21*, 1265−1271.

(4) Ali-Mohamed, A. Y.; Jamali, S. G. A. *Water Res.* **1989**, *23*, 659−662.

(5) Rook, J. J. *J. Water Treat. Exam.* **1974**, *23*, 234−243.

(6) Minear, R. A.; Bird, J. C. In *Water Chlorination: Environ. Impact and Health Effects*; *Vol. 3*; Jolley, R. L., et al., Ed.; Ann Arbor Science Publishers: Ann Arbor, MI, 1980; pp 151−160.

(7) Dore, M.; Merlet, N.; De Laat, J.; Goichon, J. *J. Am. Water Works. Assoc.* **1982**, *74*, 103−107.

(8) Gittelman, T. S.; Yohe, T. L. *Proceedings of AWWA Annual Conference*, Los Angeles, California, June 18, 1989; pp 105−123.

(9) Gould, J. P.; Giabbai, M.; Kim, J.-S. In *Water Chlorination: Chemistry, Environ. Impact and Health Effects*; *Vol. 5*; Jolley, R. L., et al., Ed.; Ann Arbor Science Publishers: Ann Arbor, MI, 1985; pp 923−936.

(10) APHA AWWA WEF, *Standard Methods for the Examination of Water and Wastewater*, 19th ed.; American Public Health Association: Washington, DC, 1995.

(11) Ventresque, C.; Bablon, G.; Legube, B.; Jadas-Hecart, A.; Dore, M. In *Water Chlorination: Chemistry, Environ. Impact and Health Effects*; Vol. 6; Jolley, R. L., et al., Eds.; Lewis Publishers: Chelsea, MI, 1990; pp 715−728.

(12) Hubbs, S. A.; Amundsen, D.; Olthius, P. *J. Am. Water Works. Assoc.* **1981**, *73*, 97−102.

(13) Reynolds, G.; Mekras, C.; Perry, R.; Graham, N. *Environ. Technol. Lett.* **1989**, *10*, 591−600.

(14) Norman, T. S.; Harms, L. L.; Looyenga, R. W. *J. Am. Water Works Assoc.* **1980**, *72*, 176−180.

(15) Dossier-Berne, F.; Panais, B.; Merlet, N.; Cauchi, B.; Legube, B. *Environ. Technol.* **1994**, *15*, 901−916.

(16) Stanbro, W. D.; Smith, W. D. *Environ. Sci. Technol.* **1979**, *13*, 446−451.

(17) Poncin, J.; Le Cloirec, C.; Martin, G. *Environ. Technol. Lett.* **1984**, *5*, 263−274.

(18) Weil, I.; Morris, J. C. *J. Am. Chem. Soc.* **1949**, *71*, 1664−1671.

(19) Doré, M.; Goichon, J. *Water Res.* **1979**, *14*, 657−663.

(20) Batchelor, B.; Fusilier, D.; Murray, E. H. *J. Am. Water Works. Assoc.* **1987**, *1*, 50−55.

(21) Reckhow, D. A.; Edzwald, J. K. *J. Am. Water Works. Assoc.* **1991**, *83*, 67−73.

(22) Martin, G. *Point sur l'épuration et le traitement des effluents*, Vol. 2.1; Technique et Documentation Lavoisier, 1985; pp 15−30.

(23) Masschelein, W. J.; Denis, M. *Rev. Fr. Sci. Eau* **1982**, *1*, 63.

(24) Thurman, E. M. *Developments in Biochemistry: Organic geochemistry of natural waters*; Nijhoff, M.; Junk, W., Pub.; Dordrecht, 1985.

(25) Farkas, L.; Lewin, M.; Bloch, R. *J. Am. Chem. Soc.* **1949**, *71*, 1988−1991.

(26) Morris, J. C.; Isaac, R. A. In *Water Chlorination: Environ. Impact and Health Effects*, Vol. 4; Jolley, R. L., et al., Ed.; Ann Arbor Science Publishers: Ann Arbor, MI, 1983; pp 49−62.

(27) Wajon, J. E.; Morris, J. C. In *Water Chlorination: Environ. Impact and Health Effects*, Vol. 3; Jolley, R. L., et al., Ed.; Ann Arbor Science Publishers: Ann Arbor, MI, 1980; pp 171−181.

(28) Bunn, W. W.; Haas, B. B.; Deane, E. R.; Kleopfer, R. D. *Environ. Lett.* **1975**, *10*, 205−213.

(29) Thomas, R. F.; Weisner, M. J., Brass, H. J. In *Water Chlorination: Environ. Impact and Health Effects*, Vol. 3; Jolley, R. L., et al., Ed.; Ann Arbor Science Publishers: Ann Arbor, MI, 1980; pp 161−168.

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