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Effect of some parameters on the formation of chloroform during chloramination of aqueous solutions of resorcinol

Nicolas Cimetiere, Florence Dossier-Berne and Joseph De Laat*

Université de Poitiers, Laboratoire de Chimie et Microbiologie de l'Eau, CNRS UMR 6008, Ecole Supérieure d'Ingénieurs de Poitiers,
40, Avenue du Recteur Pineau, 86022 Poitiers Cedex, France

*Corresponding author. phone: +33 5 49 45 39 21; fax: +33 5 49 45 37 68.

E-mail address: joseph.delaat@esip.univ-poitiers.fr

Abstract

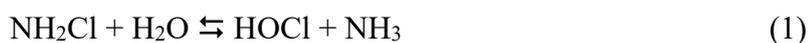
The effects of various factors (N/Cl ratio used to prepare monochloramine, monochloramine doses, pH and contact time) on the monochloramine demand and on the chloroform yield during chloramination of resorcinol have been investigated. Chloramination experiments were carried out at 24 ± 1 °C, at pH values ranging from 6.5 to 12 using a bicarbonate/carbonate buffer and preformed monochloramine solutions prepared at pH 8.5 with N/Cl ratios ($[\text{NH}_4\text{Cl}]_0/[\text{Total free Cl}_2]_0$) ranging from 1.0 to 150 mol mol⁻¹. Monochloramine determinations ($[\text{Resorcinol}]_0 = 5$ or 100 μM, $[\text{NH}_2\text{Cl}]_0/[\text{Resorcinol}]_0 = 20$ mol mol⁻¹, pH = 8.5 ± 0.1) showed a slow increase of the monochloramine consumption with reaction time. The monochloramine demands after reaction times of 7 days ($[\text{Resorcinol}]_0 = 100$ μM) and 14 days ($[\text{Resorcinol}]_0 = 5$ μM) were equal to 8.5 moles of NH₂Cl /mole of resorcinol and were higher than the chlorine demands (≈ 7.3 moles/mole). Chloroform yields from monochloramination of resorcinol were lower than 8 % (< 80 mmoles of CHCl₃/mole of resorcinol) and were less than the yields obtained by chlorination (0.9 - 0.95 mole/mole). Chloroform productions increased with increasing monochloramine dose and reaction time and decreased with increasing pH values within the pH range 6.5 to 10. Chloroform formation markedly decreased when the N/Cl ratio increased from 1 to 1.5 mol/mol and was suppressed at N/Cl > 100 mol/mol. The data obtained in the present work suggest that free chlorine released from monochloramine hydrolysis plays a significant role on the formation of chloroform during chloramination of resorcinol at N/Cl ratios close to unity ($1.0 < \text{N/Cl} < 1.5$).

Keywords: Monochloramine, Monochloramine demand, Trihalomethane, Free chlorine, Monochloramine hydrolysis.

1. Introduction

Chlorination is the most widely used process for drinking water disinfection. However, reactions between chlorine and naturally occurring organic matter, bromide and iodide produce numerous disinfection by-products (DBPs) of public health concern. Since the discovery of trihalomethanes (THMs) in chlorinated drinking waters in 1974 (Bellar et al., 1974; Rook, 1974), more than 600 DBPs have been reported in the literature (Richardson et al., 2007; Hrudey, 2009). Because of health risks associated to long term exposure to DBPs, most developed nations have set regulations or guidelines to minimize the concentrations of THMs and of other DBPs in finished drinking water.

Many utilities have adopted the use of monochloramine as a secondary disinfectant in order to meet the current or future regulations concerning the concentrations of DBPs in drinking water. Monochloramine is an efficient disinfectant. Monochloramine is less reactive with natural organic matter (NOM) and its use provides long lasting residuals in the water distribution systems. Total concentrations of THMs, haloacetic acids or of DBPs in chloraminated drinking waters or chloraminated solutions of natural organic matter (NOM) are lower than in chlorinated ones (Diehl et al., 2000; Hua and Reckhow, 2007; Yang et al., 2007; Goslan et al., 2009). The production and the speciation of DBPs formed by chloramination depend of NOM depend on various parameters such as temperature, pH, bromide ion concentrations, nature of NOM, contact time and the application modes of monochloramine (introduction of free chlorine into ammonia containing water or introduction of preformed monochloramine solution) and the N/Cl initial ratios used for the production of monochloramine (Qi et al., 2004; Yang et al., 2007 and 2008). The kinetics and the reaction pathways for the formation of DBPs by chloramination of MON are not well documented. As demonstrated by Valentine's research group, the oxidation of MON by monochloramine can be attributed to two distinct reaction pathways: direct reactions of monochloramine with MON and indirect reactions involving free chlorine liberated from monochloramine hydrolysis (Jafvert and Valentine, 1992; Duirk et al., 2005; Duirk and Valentine, 2006):



The value of the equilibrium constant for reaction (1) ($K = 5.1 \times 10^{-12}$ M; Morris and Isaac, 1983) indicates that free chlorine should be present at trace levels in organic-free solutions of monochloramine. Free chlorine concentration depends on the total concentration of oxidants, pH and the initial N/Cl ratios used to prepare monochloramine solutions. In the presence of organic compounds, free chlorine can be consumed by the organic solutes. This reaction shifts the equilibrium (1) to the right and thus increases the decay rate of monochloramine. The contribution of free chlorine to the degradation of organic solutes and to the formation of DBPs during

chloramination depend on various parameters such as the free chlorine concentration and the relative rate constants for the reactions of monochloramine and chlorine with the organic solutes.

In order to better understand the role played by free chlorine on the formation of DBPs during chloramination of organic compounds, solutions of resorcinol have been chloraminated in the present study and the production of chloroform have been determined at various N/Cl ratios. Resorcinol has been used in this work as a model compound for the following reasons. Metapolyhydroxybenzenic moieties in NOM have been assumed to be responsible for the formation of THM precursors upon chlorination (Rook, 1977; Nordwood et al., 1980). Resorcinol is one of the most efficient precursors of chloroform upon chlorination with the formation of 0.9-0.95 mole of chloroform per mole of resorcinol (Nordwood et al., 1980; De Laat et al., 1982; Boyce and Hornig, 1983; Gallard and von Gunten, 2002). The rate of formation of chloroform is very fast because chloroform production is possible at very low chlorination doses ($[\text{Chlorine}]_0/[\text{Resorcinol}]_0 < 1$ mole/mole) and can compete with the very fast reaction of formation of monochloramine when solutions of resorcinol are chlorinated in the presence of ammonia (De Laat et al., 1982). Furthermore, the absolute second-order rate constants for the reaction of hypochlorous acid (Rebenne et al. 1996) and monochloramine (Cimetiere et al., 2009) with the acid-forms ($\text{Ar}(\text{OH})_2$, $\text{Ar}(\text{OH})\text{O}^-$ and $\text{Ar}(\text{O}^-)_2$) of resorcinol, 4-chlororesorcinol and 4,6-dichlororesorcinol are now known. The apparent second-order rate constants for the reaction of free chlorine and monochloramine with resorcinol in the pH range 7- 11 indicate that free chlorine is ≈ 5 orders of magnitude more reactive than monochloramine (Cimetiere et al., 2009). These kinetic data suggest that free chlorine reactions may contribute to the formation of chloroform during chloramination of resorcinol. Therefore, this work was designed to examine the effect of some parameters (N/Cl ratio, pH, monochloramine dose, reaction time) on the production of chloroform during chloramination of resorcinol.

2. Experimental Section

2.1. Chemicals and Preparation of Solutions

All solutions were prepared from reagent-grade chemicals and purified water delivered by a Millipore system (Milli RX75/Synergy 185). Stock solutions of resorcinol (Sigma-Aldrich, ACS reagent, > 99 %), ammonium chloride (Fisher Scientific, > 99%) and free chlorine (NaOCl , 13 %, Acros Organics) were stored in the dark at 4 °C. Solutions of monochloramine (0.1 to 4 mM) were prepared daily by slowly adding free chlorine into an ammonium chloride solution in a well-stirred reactor. The pH of the sodium hypochlorite and ammonium chloride solutions were adjusted to 8.5

± 0.1 just before use. Solutions of monochloramine were prepared by using a nitrogen to chlorine molar ratio ($N/Cl = [\text{Ammonium chloride}]_0/[\text{Total chlorine}]_0$) ranging from 1.0 to 150 mol mol⁻¹. Iodometric titrations and spectrophotometric analyses of freshly prepared solutions of NH₂Cl showed that free chlorine introduced in the solution of ammonium chloride was quantitatively converted into NH₂Cl at pH ≈ 8.5 .

Phosphate buffer was not used in the present work because phosphate ions are known to catalyze the autodecomposition of NH₂Cl (Valentine and Jafvert, 1988) and are suspected to promote the resorcinol ring opening during chlorination (Heasley et al., 1989). Due to the low catalytic effect of carbonate ion toward monochloramine disproportionation (Jafvert and Valentine, 1992), a carbonate buffer (20 mM) was used in the present work. Initial pH was adjusted with hydrochloric acid or sodium hydroxide. All glassware was cleaned with a solution of monochloramine (≈ 1 mM) and was kept under monochloramine before the experiments.

2.2. Experimental Procedures

All chloramination experiments were conducted in batch reactors at 24 ± 1 °C.

The monochloramine demands of resorcinol were determined at pH 8.5 ± 0.2 (carbonate buffer: 20 mM), with two initial concentrations of resorcinol ($[\text{Resorcinol}]_0 = 5$ and 100 μM) and by using an excess of monochloramine ($[\text{NH}_2\text{Cl}]_0/[\text{Resorcinol}]_0 = 20$ mol mol⁻¹). Reactions were initiated by adding, under vigorous mixing, an appropriate volume of a stock solution of resorcinol (5 or 100 mM) into a freshly prepared carbonate buffered solutions of monochloramine (100 μM or 2 mM). Blank solutions ($[\text{Resorcinol}]_0 = 0$ mM) were systematically prepared under the same conditions in order to evaluate the monochloramine autodecomposition.

To determine the effects of pH ($6.5 < \text{pH} < 12$), N/Cl ratio ($1 \leq N/Cl \leq 150$ mol mol⁻¹) and monochloramine dose ($0 \leq [\text{NH}_2\text{Cl}]_0/[\text{Resorcinol}]_0 \leq 65$ mol mol⁻¹) on the chloroform yield from chloramination of resorcinol ($[\text{Resorcinol}]_0 = 10 - 100$ μM), the reaction was initiated by introducing under vigorous mixing an appropriate volume (typically 0.5 – 2 mL) of a stock solution a resorcinol into 1000 mL of a monochloramine solution. The pH of the monochloramine solution was set up to the desired pH before the addition of resorcinol. After the addition of resorcinol to the monochloramine solution, the pH of the solution was readjusted and 10 mL of solution were immediately transferred into a series of 20 mL head-space vials which were then hermetically sealed with PTFE-faced-silicone septa. At least 250 mL of the remaining chloraminated solution of resorcinol was kept in an amber bottle at 24 ± 1 °C and pH measurements performed at various reaction times indicate that pH did not vary by more than 0.2 pH unit. At timed intervals, the reaction of monochloramine with resorcinol in the vials was stopped by adding 100 μL of HCl (1

M) and 10 μL of sodium sulfite (2 M) through the septum. Each data point for chloroform yields represents the mean value of chloroform concentrations from two or three vials.

Aqueous solutions of resorcinol have also been chlorinated in the present work in order to validate our experimental methods and to compare oxidant demands and chloroform productions from chloramination and chlorination experiments. The data obtained from chlorination experiments of resorcinol have been presented in the Supplementary Content.

2.3. Analytical methods

Free chlorine and total chlorine concentrations in the stock solutions of sodium hypochlorite and monochloramine were determined iodometrically with sodium thiosulfate 0.01 M (Prolabo, > 99.9 %). Monochloramine concentrations were determined spectrophotometrically using a molar extinction coefficient of $446 \text{ M}^{-1} \text{ cm}^{-1}$ for NH_2Cl at 244 nm.

At various reaction times, total chlorine was determined spectrophotometrically by the I_3^- method. For an initial concentration of NH_2Cl of 2 mM, 0.1 mL sample of the solution was rapidly transferred into a 10 mL vial containing 4 mL of KI 0.2 M (Acros Organics, > 99 % for analysis) and 100 μL of acetic acid 1.7 M (Riedel-de Haën, 99 - 100 %). After a reaction time of 2 or 3 minutes, the mixture was then transferred into a 1 cm-spectrophotometer quartz cell and the concentration of triiodide ion was determined by measuring the absorbance at 351 nm (Shimadzu UVmini 1240 spectrophotometer). The concentration of monochloramine was calculated using a molar extinction coefficient of $2.69 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for I_3^- at 351 nm. This value which has been determined in the present work from calibration curves obtained from various standard solutions of chlorine or monochloramine was consistent with values reported in literature (Awtrey and Connick, 1951; Bichsel and von Gunten, 1999).

CHCl_3 was analyzed by GC/ECD using a gas chromatograph (Varian 3300 Star) equipped with an automatic headspace sampler (DANI HSS3950), a transfer line (heated at 250 $^\circ\text{C}$) between the sampler and the injector of the chromatograph, a capillary column (J&W/DB624 30 m x 0.53 mm) and an electron capture detector. Separation was carried out with nitrogen gas as carrier gas (1 $\text{mL}\cdot\text{min}^{-1}$). Operating temperatures are 250 $^\circ\text{C}$, 40 $^\circ\text{C}$ and 300 $^\circ\text{C}$ for the injector, the oven and the detector, respectively. Vials were introduced in the headspace sampler for at least 50 min at 50 $^\circ\text{C}$ in order to reach gas-liquid equilibrium. Calibration curves were performed with standard chloroform solutions (0.01 - 1.25 μM). Detection and quantification limits were 0.01 and 0.025 μM respectively.

In a few experiments ($[\text{Resorcinol}]_0 = 100 \mu\text{M}$), the total organic carbon (TOC) was determined at the beginning and at the end of the experiment by a Shimadzu TOC analyzer (TOC- V_{CSH}).

3. Results

3.1. Monochloramine demand of resorcinol

Fig.1 presents examples of concentration-time decays of monochloramine ($[\text{NH}_2\text{Cl}]_0 = 2 \text{ mM}$) obtained in the absence and in the presence of resorcinol ($[\text{Resorcinol}]_0 = 100 \mu\text{M}$). Under the conditions used (carbonate buffer = 20 mM, pH = 8.5 ± 0.1), a 18 % decay of monochloramine was observed in organic-free solutions after a reaction time of 7 days at pH 8.6. A much lower loss of monochloramine was obtained with an initial concentration of monochloramine of $100 \mu\text{M}$ ($\approx 4 \%$ decay after a reaction time of 14 days). The autodecomposition rates of monochloramine in organic-free solutions ($[\text{NH}_2\text{Cl}]_0 = 100 \mu\text{M}$ and 2 mM) could be well simulated by the kinetic model of Jafvert and Valentine (1992) which has been reported in Tables S1 and S2 in Supplementary Content. At a given pH, the overall rate of autodecomposition of monochloramine follows an apparent second-order kinetic law with respect to the concentration of monochloramine:

$$-\frac{d[\text{NH}_2\text{Cl}]}{dt} = k_{\text{app}} [\text{NH}_2\text{Cl}]^2 \quad (2)$$

As the contribution of the autodecomposition reactions of NH_2Cl to the overall consumption of monochloramine by resorcinol can not be always neglected, the monochloramine demand of resorcinol has been determined by subtracting the autodecomposition of monochloramine. The amount of monochloramine autodecomposed ($[\text{NH}_2\text{Cl}]_a - [\text{NH}_2\text{Cl}]_b$) between two consecutive sampling times t_a and t_b have been calculated from the integrated form of Eq(2):

$$\frac{1}{[\text{NH}_2\text{Cl}]_b} - \frac{1}{[\text{NH}_2\text{Cl}]_a} = k_{\text{app}} (t_b - t_a) \quad (3)$$

$$\text{or } [\text{NH}_2\text{Cl}]_b = \left(k_{\text{app}} (t_b - t_a) + \frac{1}{[\text{NH}_2\text{Cl}]_a} \right)^{-1} \quad (4)$$

where $[\text{NH}_2\text{Cl}]_a$ and $[\text{NH}_2\text{Cl}]_b$ represent the monochloramine concentrations in organic-free solution at reaction times t_a and t_b , respectively and k_{app} , the apparent second-order rate constant of decomposition of monochloramine in organic-free solution. Fig. 2 presents monochloramine demands of resorcinol at pH 8.5 ± 0.1 as a function of reaction time. The rates of monochloramine

consumption increased with increasing concentrations of reactants. For an initial concentration of resorcinol of 100 μM ($[\text{NH}_2\text{Cl}]_0 = 2 \text{ mM}$), the data showed that the N/Cl ratio ($\text{N/Cl} = 1.2$ and 5 mol mol^{-1}) did not significantly affect the rate of monochloramine consumption and the monochloramine demands. Monochloramine demands of 5.5, 7.7 and 8.6 moles of NH_2Cl /mole of resorcinol were measured at reaction times of 24, 72 and 168 h, respectively. For an initial concentration of resorcinol ($[\text{Resorcinol}]_0 = 5 \mu\text{M}$, $[\text{NH}_2\text{Cl}]_0 = 100 \mu\text{M}$; $\text{N/Cl} = 5 \text{ mol mol}^{-1}$), the monochloramine demands were equal to 4.0, 6.5 and 8.4 mol mol^{-1} after reaction times of 48, 168 and 480 h, respectively (Fig. 2).

Data obtained from chlorination experiments of resorcinol ($[\text{Resorcinol}]_0 = 20 \mu\text{M}$; $[\text{Free Chlorine}]_0 = 400 \mu\text{M}$; Fig. S1) exhibit a very fast consumption of chlorine because the chlorine demands obtained after a reaction time of 5 minutes were nearly equal to 5.5 and 6.4 moles of chlorine/mole of resorcinol in carbonate and in phosphate buffered solutions of resorcinol, respectively. For a reaction time higher than 15 hours, the measured chlorine demands ($7.2 \pm 0.1 \text{ mole/mole}$ in phosphate buffer) were in good agreement with previous works (Norwood et al., 1980; De Laat et al., 1982; Reckhow and Singer, 1986). A comparison between the shapes of the chlorine and monochloramine consumption curves also demonstrates that monochloramine is much less reactive than chlorine. Monochloramine demands did not reach a plateau within a reaction time of 168 h and were higher than the chlorine demand of resorcinol. The complete oxidation of one mole of resorcinol into CO_2 should require a theoretical amount of 12 moles of monochloramine. Since TOC removals in chloraminated solutions of resorcinol ($[\text{Resorcinol}]_0 = 100 \mu\text{M}$) were less than 30 % after a reaction time of 7 days, the unexpected high monochloramine demands obtained in this work ($\approx 8.5 \text{ moles/mole}$) suggest that oxidation by-products of resorcinol catalyze the decomposition of monochloramine. It is well known that proton donor inorganic species such as bicarbonate and phosphate ions catalyze the monochloramine disproportionation. Among the chloramination by products of resorcinol identified by Heasley et al. (1999), chloro-ketones and chlorocarboxylic acids may catalyze the decomposition of monochloramine.

3.2. Effect of N/Cl ratio upon chloroform formation

Preliminary experiments showed that chlorination of resorcinol ($[\text{Resorcinol}]_0 = 1 - 50 \mu\text{M}$; $[\text{Cl}_2]_0/[\text{Resorcinol}]_0 = 20 - 40 \text{ mol mol}^{-1}$, $7 < \text{pH} < 9$, reaction time $> 1 \text{ h}$) leads to a very fast production of $0.93 \pm 0.03 \text{ mol}$ of chloroform/mole of resorcinol (Fig. S2). In addition, significant productions of chloroform can also be formed at very low chlorine/resorcinol ratios ($< 1 \text{ mol/mol}$), indicating that the initial steps of chlorination of resorcinol represent rate limiting steps for the formation of chloroform (Fig. S3). All these data are in good agreement with literature (De Laat et al., 1982; Reckhow and Singer, 1986).

Figs 3 and 4 present chloroform yields obtained from solutions of resorcinol ($[\text{Resorcinol}]_0 = 50 \mu\text{M}$) which have been chloraminated at pH 8.5 with a $[\text{NH}_2\text{Cl}]_0/[\text{Resorcinol}]_0$ ratio of 20 mol mol^{-1} ($[\text{NH}_2\text{Cl}]_0 = 1 \text{ mM}$) and N/Cl ratios ranging from 1 to 150 mol mol^{-1} . The data show that chloroform productions slowly increased with reaction time (reaction time studied: 0 - 96 h) and markedly decreased when the N/Cl ratio increased from 1 to 150 mol mol^{-1} (Figs 3 and 4). For a reaction time of 48 h, chloroform yields decreased from $\approx 3.5 \%$ for $\text{N/Cl} = 1.02 \pm 0.02 \text{ mol mol}^{-1}$ to 0.4% for $\text{N/Cl} = 100 \text{ mol mol}^{-1}$ (a yield of 100 % is assumed to correspond to the formation of one mole of CHCl_3 /mole of resorcinol). As shown the curves in Fig. 4, the chloroform yield is very sensitive to the N/Cl ratio for N/Cl values between 1 and 1.5 mol mol^{-1} . It should also be noted that chloroform yield which is equal to 95 % for $\text{N/Cl} = 0 \text{ mol mol}^{-1}$ (chlorination experiments) decreases to 3.5 % when the N/Cl increases from 0 to 1.0 mol mol^{-1} .

3.3. Effect of monochloramine dose on chloroform formation

Solutions of resorcinol ($[\text{Resorcinol}]_0 = 100 \mu\text{M}$) have also been treated at monochloramine-to-resorcinol ratios ranging from 0 to 10 mol mol^{-1} at pH 8.5 and using various N/Cl ratios ($1 < \text{N/Cl} < 10 \text{ mol mol}^{-1}$). For a reaction time of 48 hours, GC/ECD analyses showed that chloroform was detected at concentrations close to the quantification limit in samples chloraminated at $[\text{NH}_2\text{Cl}]_0/[\text{Resorcinol}]_0$ doses lower than 2 mol mol^{-1} (Fig. 5). For $[\text{NH}_2\text{Cl}]_0/[\text{Resorcinol}]_0 > 2 \text{ mol mol}^{-1}$, the chloroform yields increased with monochloramine dose and did not exceed 0.5 % for the highest monochloramine dose used.

3.4. Effect of pH on chloroform formation.

To study the effect of pH on the formation of chloroform, solutions of resorcinol ($[\text{Resorcinol}]_0 = 10 \mu\text{M}$) were treated at a monochloramine dose of 0.65 mM ($[\text{NH}_2\text{Cl}]_0/[\text{Resorcinol}]_0 = 65$, $\text{N/Cl} = 10 \text{ mol mol}^{-1}$) and at pH values ranging from 6.5 to 12. Fig. 6 shows that the chloroform yield decreases from 7.7 % at pH 6.5 to $\approx 0.1 \%$ at pH 10. At pH higher than 10, the concentrations of chloroform were below the quantification limit of $0.025 \mu\text{M}$ (chloroform yield : $< 0.25 \%$). It should be noted that the decrease of the production of chloroform when the pH increases from pH 8 to 10 has also been previously observed for chlorination of resorcinol solutions (De Laat et al., 1982).

4. Discussion

4.1. Contribution of free chlorine to the initial steps of degradation of resorcinol

Free chlorine formed by the reversible hydrolysis reaction of monochloramine is always present in monochloramine solutions and can therefore contribute to the oxidation of organic solutes. In organic-free solutions, the concentration of free chlorine in equilibrium with monochloramine can be calculated from the equilibrium constant of the monochloramine hydrolysis reaction (reaction (1), $K_1 = 5 \cdot 10^{-12}$ M, Morris and Isaac, 1983), the acid dissociation constants of HOCl ($K_{a1} = 10^{-7.54}$, Morris, 1966) and NH_4^+ ($K_{a2} = 10^{-9.25}$, Morris, 1966) and the total concentration of nitrogen species ($[\text{Total Nitrogen}] = [\text{NH}_4^+] + [\text{NH}_3] + [\text{NH}_2\text{Cl}]$).

By neglecting the concentration of the aqueous chlorine ($[\text{Cl}_2]_{\text{aq}}$) at $\text{pH} > 5$, the equilibrium concentration of free chlorine is equal to:

$$[\text{Free Chlorine}]_{\text{eq}} = \frac{-\beta + \sqrt{\beta^2 - 4\alpha [\text{Total Chlorine}]}}{2\alpha} \quad (4)$$

$$\text{with } \alpha = \left(\frac{K_{a2}[\text{H}^+]}{K_1(K_{a1} + [\text{H}^+])(K_{a2} + [\text{H}^+])} \right) \quad (5)$$

$$\text{and } \beta = 1 + \alpha ([\text{Total Nitrogen}] - [\text{Total Chlorine}]) \quad (6)$$

In organic-free aqueous solutions of monochloramine, concentration of free chlorine should be at the minimum at $\text{pH} \approx 8.4$ ($\text{pH} = (\text{p}K_{a1} + \text{p}K_{a2})/2$) and would decrease when the concentration of free ammonia increases (or when the N/Cl ratio increases). As depicted calculated curves in Fig. S4, the theoretical concentrations of free chlorine in solutions containing 1 mM of monochloramine should be very low : $\approx 6 \times 10^{-7}$ M for N/Cl = 1.0 mol mol⁻¹, 7×10^{-10} M for N/Cl = 1.5 mol mol⁻¹ and 4×10^{-11} M for N/Cl = 10 mol mol⁻¹.

In the presence of organic compounds, free chlorine present in monochloramine solutions can react with organic solutes and these reactions accelerate the overall decay of monochloramine. As demonstrated in a previous paper (Cimetiere et al., 2009), the importance of these indirect reactions involving free chlorine in the overall rate of degradation of organic solutes by monochloramination depend on various parameters such as N/Cl ratio, pH and the reactivity of free chlorine and monochloramine with the organic solutes. In the case of resorcinol, the absolute rate constants for the reactions of chlorine (Rebenne et al., 1996) and monochloramine (Cimetiere et al, 2009) with resorcinol are known. Therefore, the contribution of free chlorine reactions to the degradation of resorcinol can be calculated by kinetic modelling (Table S2). Fig. 7 presents computed data calculated for the following conditions: $[\text{Resorcinol}]_0 = 50 \mu\text{M}$, $[\text{Monochloramine}]_0 = 4 \text{ mM}$, $6 <$

pH < 12, $1 < \text{N/Cl} < 2 \text{ mol mol}^{-1}$). Fig. 7 shows that the contribution of free chlorine to the degradation of resorcinol is highly sensitive to the N/Cl ratio in the range 1.0-1.5 mol mol⁻¹. For the conditions used in Fig. 7, the contributions of free chlorine reactions to the degradation of resorcinol at pH 8 are equal to 25 % for N/Cl = 1.05, 15 % for N/Cl = 1.1, 8.2 % for N/Cl = 1.2 and 1.8 % for N/Cl = 2. These data demonstrate that trace amounts of free chlorine in monochloramine solutions can play a significant role on the degradation of resorcinol at Cl/N ratio close to unity because apparent rate constants for the reaction of free chlorine are about 5 orders of magnitude higher than the rate constants of monochloramine.

4.2. Effect of N/Cl ratio and pH on the formation of chloroform

Kinetic modelling cannot be used to simulate chloroform formation during chlorination and chloramination of resorcinol because the reaction mechanisms and the rate constants of reactions leading to the formation of chloroform are not known. The reaction pathways for the formation of chloroform by chlorination of 1,3-dihydroxybenzenic model compounds such as resorcinol and orcinol have been investigated by several researchers (Christman et al., 1978; Norwood et al, 1980, Rook, 1980; Boyce and Hornig, 1983, Heasley et al., 1989, Tretyakova et al. 1994). These studies have shown that resorcinol degradation involves aromatic ring-substitution, oxidation, hydrolysis, decarboxylation, ring-contraction and ring-opening reactions. Chlorination of resorcinol leads to the formation of chlororesorcinols, non-cyclic and cyclic chloroketones and chloro-keto-carboxylic acids as intermediates, chloroform (≈ 0.9 - 0.95 mole/mole of resorcinol), CO₂ and short-chain chlorinated acids as end-products. The reaction of monochloramine with resorcinol in water and in ether has been investigated by Heasley et al (1999). These authors showed that chloramination of aqueous solutions of resorcinol (pH 7) also leads to the formation of chlororesorcinols and of a pentachloro intermediate which undergoes ring-opening with NH₂Cl/H₂O to produce CO₂ and non-cyclic chloroketones without significant productions of chloroform (≈ 0.04 mole of CHCl₃/mole of resorcinol).

The data obtained in the present work also confirmed that little chloroform is formed in the reaction of monochloramine with resorcinol. The highest chloroform yield measured in this work (0.077 mole CHCl₃/mole of resorcinol) was obtained at pH 6.5 (Fig. 6). Compared to chlorination, the rate of chloroform formation by chloramination is very slow. The large differences for chlorination and chloramination with respect to the formation of chloroform (rates of formation and chloroform yields) might be attributed to the fact that free chlorine is much more reactive than monochloramine with resorcinol, its chlorinated derivatives (chlororesorcinols) and with the ring-opening by-products (chloroketones, chloroketo-carboxylic acids), the latter represent the precursors of chloroform through the haloform reaction. As reported above, chlorine is about 5 orders of

magnitude more reactive than free chlorine with resorcinol, 4-chlororesorcinol and 4,6-dichlororesorcinol but the rate constants for the reaction of monochloramine with chloroketones and chloroketo-carboxylic acids are unknown.

5. Conclusions

Chloramination of resorcinol leads to the formation of chloroform at much lower yields (< 8 %) than by chlorination (\approx 90-95 %). Chloroform yields increased with increasing monochloramine dose and reaction time and with decreasing pH in the range 6.5 - 10. The data also showed a remarkable decrease of chloroform productions when the N/Cl ratio used to prepare monochloramine increased from 1 to 1.5 mol mol⁻¹ that is to say when the concentration of excess ammonia increases. Chloroform productions were nearly suppressed at very high N/Cl molar ratio (N/Cl > 100). The data obtained in the present work suggest that free chlorine formed by monochloramine hydrolysis might be largely responsible for the formation of chloroform during chloramination of resorcinol because conditions which favour the hydrolysis reaction of monochloramine into free chlorine (low N/Cl ratio, neutral pH) were found to enhance chloroform formation.

Free chlorine reactions may also contribute to the formation of chloroform and of other DBPs during monochloramination of other organic solutes or of drinking waters. The aim of research works which are currently conducted in our lab is to examine the effects of Cl/N on the production of chloroform and of other DBPs during chloramination of other phenolic compounds and of NOM extracts.

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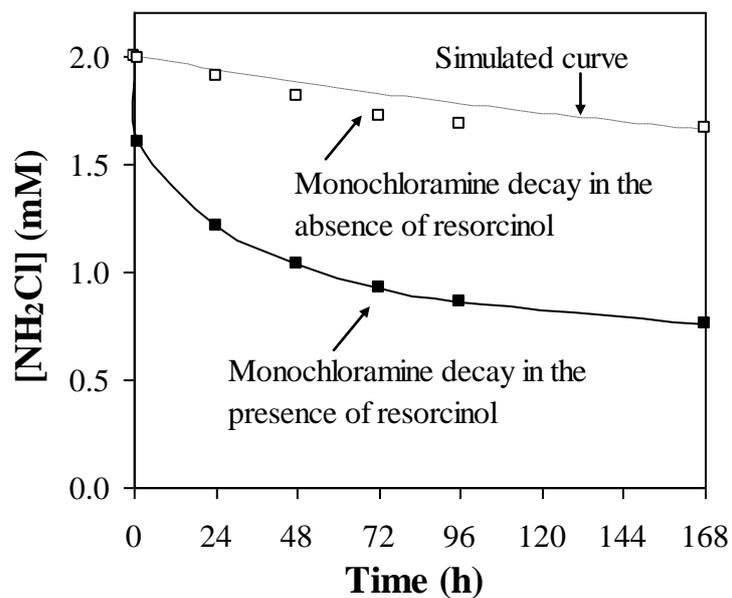


Fig. 1 - Concentration time profiles of monochloramine in the absence and in the presence of resorcinol. The dashed line represents the simulated autodecomposition curve of monochloramine in organic free solution calculated by the model of Jafvert and Valentine (1992). ($[\text{Resorcinol}]_0 = 0$ or $100 \mu\text{M}$, $\text{N/Cl} = 1.2 \text{ mol mol}^{-1}$, $[\text{NH}_2\text{Cl}]_0 = 2.0 \text{ mM}$, $\text{pH} = 8.5 \pm 0.1$).

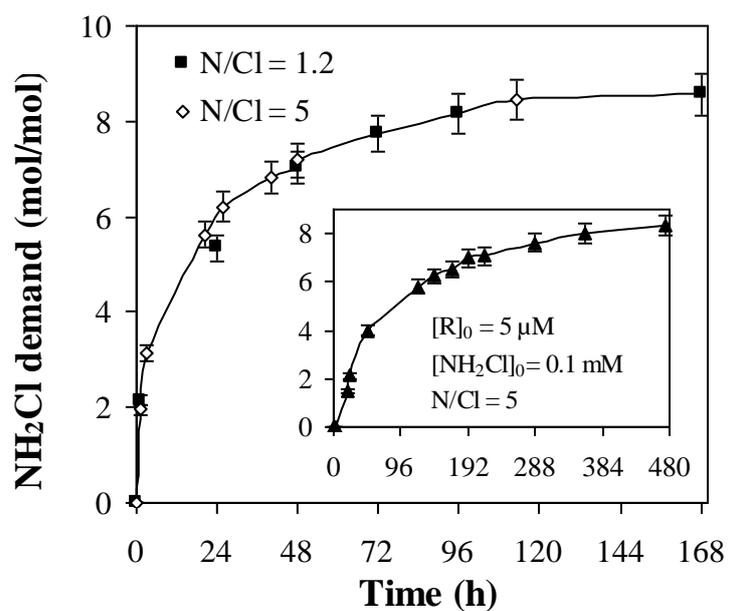


Fig. 2 - Monochloramine demand of resorcinol as a function of reaction time ($[\text{Resorcinol}]_0 = 200 \mu\text{M}$, $[\text{HOCl}]_0 = 2 \text{ mM}$, $\text{N/Cl} = 1.2$ and 5.0 mol mol^{-1} , $\text{pH} = 8.5 \pm 0.1$). Insert refers to monochloramine demand for $[\text{Resorcinol}]_0 = 5 \mu\text{M}$ and $[\text{NH}_2\text{Cl}]_0 = 0.1 \text{ mM}$, $\text{pH} = 8.5 \pm 0.1$).

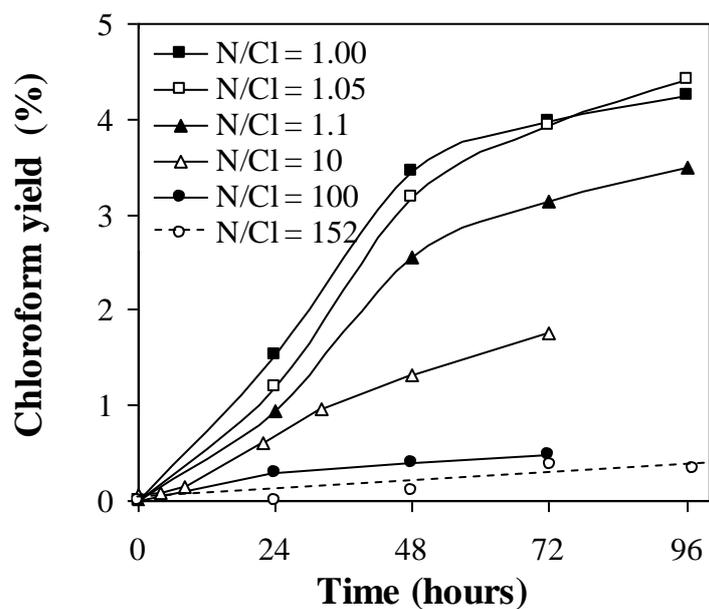


Fig. 3 - Effects of reaction time on the chloroform yield (%) obtained for the monochloramination of resorcinol at various N/Cl ratios ($[\text{Resorcinol}]_0 = 50 \mu\text{M}$, $[\text{NH}_2\text{Cl}]_0 = 1 \text{ mM}$, $1 \leq \text{N/Cl} \leq 152 \text{ mol mol}^{-1}$, $\text{pH} = 8.5 \pm 0.2$).

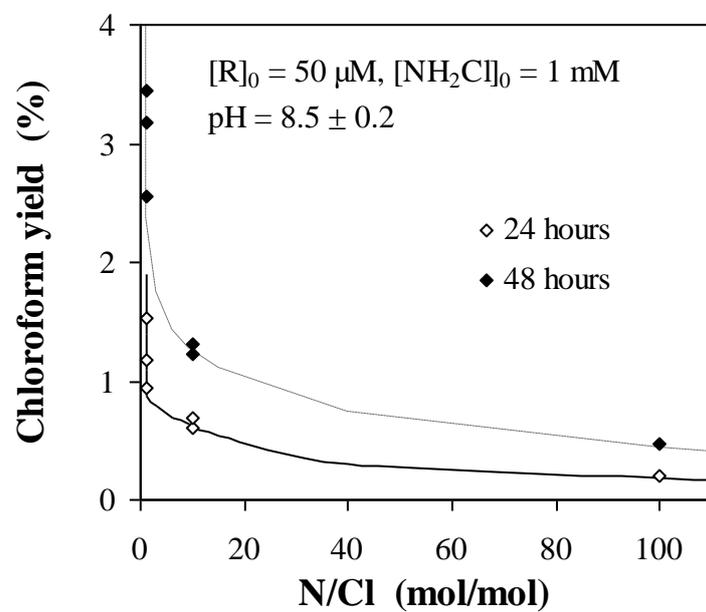


Fig. 4 - Effect of the N/Cl molar ratio on the production of chloroform by monochloramination of resorcinol ($[\text{Resorcinol}]_0 = 50 \mu\text{M}$, $[\text{NH}_2\text{Cl}]_0 = 1 \text{ mM}$, $1 \leq \text{N/Cl} \leq 152 \text{ mol mol}^{-1}$).

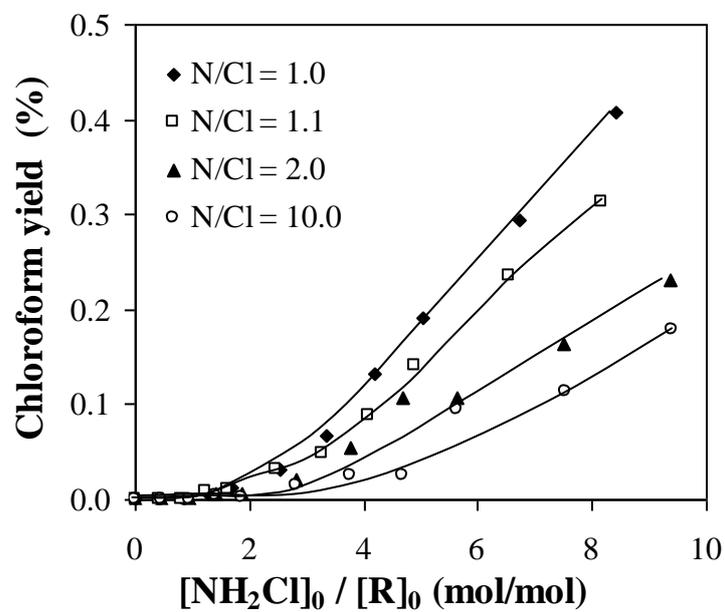


Fig. 5 - Effects of monochloramine dose on the production of chloroform by chloramination of resorcinol at various N/Cl ratios. ($[\text{Resorcinol}]_0 = 100 \mu\text{M}$, $\text{pH} = 8.5 \pm 0.2$, Contact time = 48 hours).

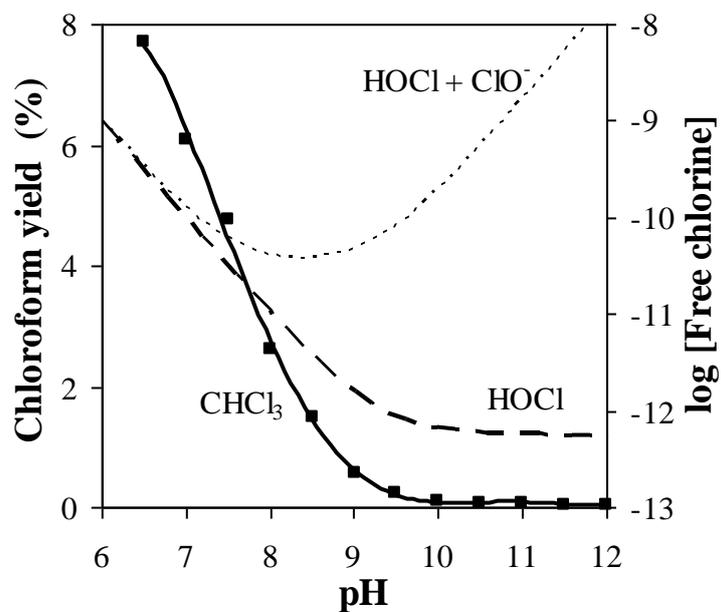


Fig. 6 - Effect of pH on the production of chloroform by monochloramination of resorcinol ($[\text{Resorcinol}]_0 = 10 \mu\text{M}$, $[\text{NH}_2\text{Cl}]_0 = 0,65\text{mM}$, $\text{N/Cl} = 10$, Reaction time : 48 h) and theoretical concentrations of free chlorine and hypochlorous acid in equilibrium with monochloramine for organic-free solutions of monochloramine

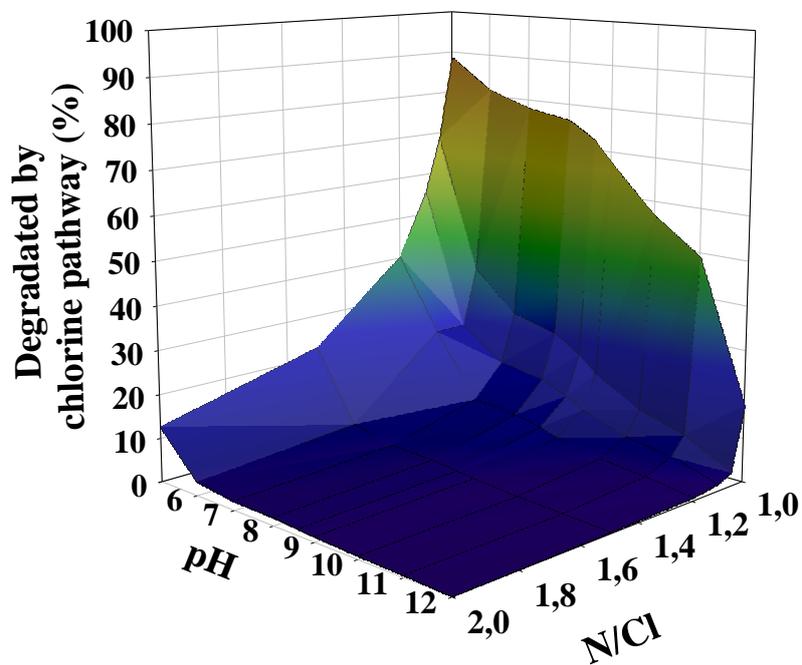


Fig. 7 – Contribution of free chlorine reactions to the degradation of resorcinol as a function of pH and N/Cl. Computed data obtained from kinetic modelling (Table S2).