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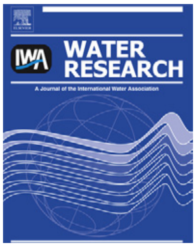

Effect of some parameters on the formation of chloroform during chloramination of aqueous solutions of resorcinol

Nicolas Cimetiere, Florence Dossier-Berne, 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

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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 ($[NH_4Cl]_0/[\text{Total free } Cl_2]_0$ ranging from 1.0 to 150 mol/mol). Kinetic experiments ($[\text{Resorcinol}]_0 = 5$ or 100 μM, $[NH_2Cl]_0/[\text{Resorcinol}]_0 = 20$ mol/mol, $pH = 8.5 \pm 0.1$) 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 mol of NH_2Cl/mole of resorcinol and were higher than the chlorine demands (≈7.3 mol/mol). Chloroform yields from monochloramination of resorcinol were lower than 8% (<80 mmol of $CHCl_3$/mole of resorcinol) and were less than the yields obtained by chlorination (0.9–0.95 mol/mol). Chloroform productions increased with increasing monochloramine dose and reaction time and decreased with increasing pH values within the pH range 6.5–10. 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 ($1.0 < N/Cl < 1.5$).

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 with 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

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[*] *Corresponding author*. Tel.: +33 5 49 45 39 21; fax: +33 5 49 45 37 68.
E-mail address: joseph.delaat@esip.univ-poitiers.fr (J. De Laat).

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distribution systems. Total concentrations of THMs, haloacetic acids or of other 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 of NOM depend on various parameters such as temperature, pH, bromide ion concentrations, nature of NOM, contact time, 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, 2008). The kinetics and the reaction pathways for the formation of DBPs by chloramination of NOM are not well documented. As demonstrated by Valentine's research group, the oxidation of NOM by monochloramine can be attributed to two distinct reaction pathways: direct reactions of monochloramine with NOM and indirect reactions involving free chlorine liberated from monochloramine hydrolysis (Jafvert and Valentine, 1992; Duirk et al., 2005; Duirk and Valentine, 2006):

$$NH_2Cl + H_2O \leftrightarrows HOCl + NH_3 \tag{1}$$

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 concentrations depend 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 depends 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 has been determined at various N/Cl ratios. Resorcinol, which is a meta-polyhydroxybenzene, has been used in this work as a model compound for the following reasons. Meta-polyhydroxybenzene moieties in NOM have been assumed to be responsible for the formation of THMs upon chlorination (Rook, 1977; Norwood et al., 1980). Resorcinol is one of the most efficient precursors of chloroform upon chlorination, with the formation of 0.9–0.95 mol of chloroform per mole of resorcinol (Norwood 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 ($[\text{Chlorine}]_0/[\text{Resorcinol}]_0 < 1$ mol/mol) 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–base forms ($Ar(OH)_2$, $Ar(OH)O^-$ and $Ar(O^-)_2$) 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 (0.1–4 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.

Iodometric titrations and spectrophotometric analyses of freshly prepared solutions of NH_2Cl showed that free chlorine introduced in the solution of ammonium chloride was quantitatively converted into NH_2Cl at pH ≈ 8.5.

Phosphate buffer was not used in the present work because phosphate ions are known to catalyze the autodecomposition of NH_2Cl (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 glasswares were cleaned with a solution of monochloramine (≈1 mM) and were 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 ($[NH_2Cl]_0/[\text{Resorcinol}]_0 = 20$ mol/mol). 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 solution of monochloramine (100 μM or