WATER RESEARCH 44 (2010) 2691–2702

Available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/watres

Nitrogenous disinfection byproducts formation and nitrogen origin exploration during chloramination of nitrogenous organic compounds

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ARTICLE INFO

Article history:
Received 23 October 2009
Received in revised form
25 January 2010
Accepted 26 January 2010
Available online 1 February 2010

Keywords:
N-DBPs
Disinfection byproducts
Monochloramine
Nitrogenous organic compound

ABSTRACT

Formation of nitrogenous disinfection by-products (N-DBPs) of cyanogen chloride (CNCl), dichloroacetonitrile (DCAN) and chloropicrin was evaluated during chloramination of several selected groups of nitrogenous organic (organic-N) compounds, including α-amino acids, amines, dipeptides, purines, and pyrimidines, The intermediates generated, reaction pathways, and nitrogen origin in N-DBPs were explored as well. CNCl was observed in chloramination of all tested organic-N compounds, with glycine giving the highest yields. DCAN was formed during chloramination of glutamic acid, cytosine, cysteine, and tryptophan. Chloramination of most organic-N compounds except for cysteine and glutamic acid generated chloropicrin. Aldehydes and nitriles were identified as the intermediates by negative mode electrospray ionization mass spectrometry during reactions of NH_2Cl and organic-N compounds. Labeled ^{15}N-monochloramine ($^{15}NH_2Cl$) techniques showed that nitrogen in N-DBPs may originate from both NH_2Cl and organic-N compounds and the nitrogen partition percentages vary as functions of reactants and pH.

1. Introduction

Nitrogenous organic compounds (organic-N) are prevalent in waters, especially in wastewater effluent-impacted waters and biofilm-rich distribution systems (Jang and Westerhoff, 2009). Organic-N compounds consume chlorine or chloramines to form organic chloramines, which are less effective disinfectants than inorganic chloramines (Donnermair and Blatchley, 2003). Organic chloramines interfere with total chlorine residual monitoring (Shang and Blatchley, 1999). Moreover, decomposition of organic chloramines leads to the formation of nitrogenous disinfection by-products (N-DBPs), such as haloacetonitriles, cyanogen halides, and halonitromethanes (Joo and Mitch, 2007; Shang et al., 2000; Ueno et al., 1996). Genotoxicity and cytotoxicity of some N-DBPs such as haloacetonitriles and halonitrimethanes are reported to be much higher than the regulated trihalomethanes (THMs) and haloacetic acids (HAAs) (Muellner et al., 2007; Plewa et al., 2004).

Formation of organic chloramines and their degradation during chlorination of α-amino acids has been investigated (Alouini and Seux, 1987; Hirose et al., 1988, 1989; Hureiki et al., 1994; Yang and Shang, 2004; Na and Olson, 2006). For example, aldehydes, nitriles, and chlorinated imines were formed

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doi:10.1016/j.watres.2010.01.029

during chlorination of α-amino acids and the generalized formation pathways are illustrated in Scheme 1. As shown, mono- or di- chlorinated organic-N compounds are formed firstly from chlorine transfer. Decarboxylation, elimination and hydrolysis lead to the formation of aldehydes and nitriles. In addition, chlorination of dipeptide glycylphenylalanine also results in the occurrence of nitriles (Keefe et al., 1997). Further chlorination of these products generates chlorinated DBPs, such as cyanogen chloride (CNCl) in the case of glycine.

Monochloramine (NH_2Cl) has gained its popularity as an alternative to chlorine due to its reduced formation of regulated THMs and HAAs. Studying reactions between NH_2Cl and organic-N compounds is not as extensive as that involving chlorine. Limited results showed that NH_2Cl can also transfer chlorine to organic-N compounds to form organic chloramines, but at a slower rate than chlorine does (Hureiki et al., 1994; Isaac and Morris, 1985; Margerum et al., 1978). Difference(s) should exist during chlorination and chloramination due to the direct incorporation of NH_2Cl in some steps of the latter. Meanwhile, both organic-N compounds and NH_2Cl contain nitrogen atoms in their molecular structures and may contribute to the formation of N-DBPs. Previous investigation showed that CNCl was formed from the chloramination of amino acids (Hirose et al., 1988), peptides (Hirose et al., 1989), and purines (Ohya and Kanno, 1989). Studies of chloramination of leucine and adenine using $^{15}N\text{-}NH_4^+$ demonstrated that the nitrogen in CNCl came from leucine and adenine. For peptide precursors, nitrogen in CNCl came from the chloramine. It should be noted that these studies were conducted by adding chlorine to the solutions containing organic-N compounds and ammonium ion instead of adding preformed monochloramine, which could give different results considering the competition reactions between organic-N compounds and ammonia with chlorine.

The objectives of this study are to evaluate formation of organic chloramines, N-DBPs, including CNCl, dichloroacetonitrile (DCAN), and chloropicrin, and intermediates during reactions between monochloramine and organic-N compounds and to investigate nitrogen sources of N-DBPs. A variety of organic-N compounds, including glycine, glutamic acid, cysteine, tryptophan, methylamine, glycylglycine, cytosine and adenine, are chosen to represent α-amino acids, amines, dipeptides, purines, and pyrimidines. Their structures and physical properties are shown in Table 1.

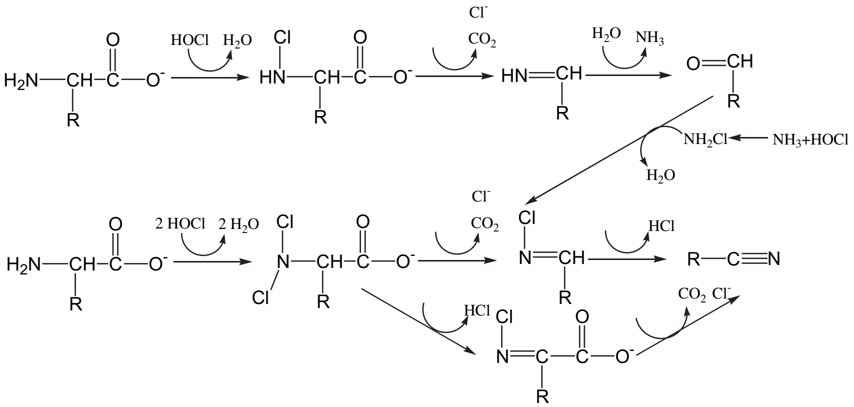
2. Materials and methods

2.1. Materials

Ultrapure water was produced by a Barnstead NANOpure Diamond system. Monochloramine (NH_2Cl) solutions were prepared daily by reacting equal volumes of ammonium chloride and sodium hypochlorite solutions at a weight ratio of 4 mg/L Cl_2 to 1 mg/L $N\text{-}NH_4^+$. The resulting solutions were standardized by DPD/FAS titration (Greenberg et al., 1998). Labeled $^{15}N\text{-}NH_2Cl$ was prepared by mixing $^{15}N\text{-}NH_4Cl$ (98% from Sigma) with chlorine in the same way as described above. Buffer solutions at pH 6.5, 7.0, 7.5, and 8.5 were prepared from phosphate salts. DCAN and chloropicrin standards, internal and surrogate standards were obtained from Supelco. A CNCl standard was purchased from Protocol.

2.2. Analytical methods

The total residual chlorine was measured by DPD colormetric titration (Greenberg et al., 1998). Inorganic chloramines and CNCl concentrations were measured using membrane introduction mass spectrometry (MIMS) and the detailed operation conditions can be found in previous studies (Shang and Blatchley, 1999; Yang and Shang, 2005). DCAN and chloropicrin analyses were carried out on a gas chromatograph (Finnigan TRACE GC) with an electron capture detector (ECD), according to USEPA method 551.1 (USEPA, 1995). The column used was a DB-5MS fused silica capillary column (30 m × 0.25 mm I.D. with 0.25 μm film thickness; J&W Scientific). The GC temperature program consisted of an initial temperature of 35 °C for 5 min, ramping to 70 °C at 10 °C/min and holding for 8 min, ramping to 110 °C at 10 °C/min and holding for 8 min. In nitrogen source study, DCAN analysis was performed on an HP 5892 bench-top gas chromatograph (Hewlett–Packard) containing an HP 5972A mass selective detector (MSD).



Scheme 1 – Chlorination of α-amino acid.