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Characterization of the reactivity and chlorinated products of carbazole during aqueous chlorination☆

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ABSTRACT

Carbazole in source water is a potential precursor for toxic chlorocarbazoles in drinking water when chlorine is used as a disinfection agent in drinking water treatment plants. However, the reactivity of carbazole and the specific structures and predominant analogues of chlorocarbazoles produced during aqueous chlorination remain unknown. In this study, the aqueous chlorination of carbazole was performed to characterize its reactivity and the chlorinated products. Chlorocarbazoles generated from carbazole were identified by a comprehensive two-dimensional gas chromatography-mass spectrometry method, and their molecular structures were predicted by the Fukui index of electrophilic attack, $f^{-1}(r)$. As a result, the comprehensive chlorination pathway of carbazole was extrapolated with a total of nine chlorocarbazoles identified, including two monochlorocarbazoles (3-chlorocarbazole and 1-chlorocarbazole), four dichlorocarbazoles (3,6-dichlorocarbazole, 1,6-dichlorocarbazole, 1,3-dichlorocarbazole and 1,8-dichlorocarbazole), two trichlorocarbazoles (1,3,6-trichlorocarbazole and 1,3,8-trichlorocarbazole) and one tetrachlorocarbazole (1,3,6,8-tetrachlorocarbazole). The $f^{-1}(r)$ value indicates that the C1, C3, C6 and C8 atoms of carbazole were the favored positions for electrophilic attack, with the C3 and C6 atoms being the predominant sites for chlorine substitution. 3-Chlorocarbazole, 3,6-dichlorocarbazole, 1,3,6-trichlorocarbazole and 1,3,6,8-tetrachlorocarbazole were the major analogues of each chlorocarbazole group; however, the production of minor analogues such as 1-chlorocarbazole and 1,6-dichlorocarbazole should not be overlooked. The chlorination of carbazole was a pseudo first order reaction with a reaction rate of 0.1836 nmol/(L· h) and half-life of 3.77 h (pH = 6.4, Cl_2 = 4.7 mg/L), and the chlorination rate of carbazole was approximately 5 times faster than that of an known chlorination precursor pyrene. These results showed that Fukui index was efficacious to predict the chlorination sites of aromatic compounds, and that carbazole is readily transformed into toxic chlorocarbazoles in drinking water treatment plants that use chlorine as a disinfection agent.

1. Introduction

Carbazole is an environmental carcinogenic and mutagenic compound that structurally resembles polycyclic aromatic hydrocarbons (PAHs). Carbazole has been detected in various environments such as atmospheric particles, soil, sediment and water (Esen et al., 2010; Grosser et al., 1995; Carlsson and. Östman, 1997; Stackelberg et al., 2007; Kochany and Maguire, 1994). Carbazole originates in the environment from anthropological sources such as the petroleum industry and the manufacturing of carbazole-based industrial materials such as dyes, medicines and insecticides (Benedik et al., 1998). Additionally, carbazole may form from N-fertilizers in an analogy to the formation of PCDFs from pesticides due to the structural similarity between carbazole and PCDFs (Altarawneh et al., 2009a). Also, catalytic-assisted coupling of direct precursors such as aniline may produce carbazole

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(Altarawneh et al., 2008). However, the fate of carbazole in the environment is still unclear (Esen et al., 2010; Benedik et al., 1998). Recently, the presence of carbazole's chlorinated derivatives in the environment has drawn increased attention due to their toxicity and wide spread occurrence (Trobs et al., 2011; Reischl et al., 2005; Kronimus et al., 2004; Grigoriadou and Schwarzbauer, 2011; Guo et al., 2014).

As the chlorinated derivatives of carbazole, chlorocarbazoles are considered to be a class of emerging organic contaminates, which are structurally similar to chlorinated dibenzofurans (Riddell et al., 2015). Several chlorocarbazole analogues, including 3-chlorocarbazole and 3,6-dichlorocarbazole, have been shown to induce dioxin-like activity using ethoxyresorufin-*O*-deethylase (EROD) induction in rat hepatoma cells and CYP1A1 and CYP1B1 gene expression in Ah-responsive breast cancer cells (Trobs et al., 2011; Riddell et al., 2015; Mumbo et al., 2015). Although it has been found that halogenated indigo dyes are possible sources of bromocarbazoles in the environment, the origin of chlorocarbazoles is still under debate (Parette et al., 2015), as they may come from both natural and anthropologic sources (Luk et al., 1983). Recently, Altarawneh et al (Altarawneh and Dlugogorski, 2015). found agreement between computational predictions and environmental profiles of chlorocarbazoles and suggested the formation of chlorocarbazoles by electrophilic substitution. To date, the occurrence of chlorocarbazoles has only been reported in soil (Trobs et al., 2011; Reischl et al., 2005) and sediment (Kronimus et al., 2004; Grigoriadou and Schwarzbauer, 2011), and the possible presence of chlorocarbazoles in aqueous environments has not been discussed. Considering the formation mechanism of chlorocarbazoles proposed by Altarawneh et al. (Altarawneh and Dlugogorski, 2015), we believe that the chlorination disinfection of raw water containing carbazole in drinking water treatment plants is a possible source of chlorocarbazoles in drinking water.

Chlorination is a globally used method for the effective removal of hazardous microorganisms in drinking water. Apart from well-known disinfection by-products such as trihalomethanes (THMs) and haloacetic acids (HAAs), active chlorine residues can also transform toxic micro-organic pollutants in source water into their chlorinated derivatives, which may be more toxic and resistant to being metabolized (Deborde and von Gunten, 2008; Lane et al., 2015; Hu et al., 2006). Previous studies have confirmed that PAHs type compounds can be transformed into chlorinated polycyclic aromatic hydrocarbons (Cl-PAHs) during the chlorination disinfection of drinking water due to the electrophilic substitution reaction between the PAHs and active chlorine species, especially hypochlorous acid (HClO) (Hu et al., 2006; Mori et al., 1991; Georgi et al., 2007; Nakamura et al., 2007). Similar to PAHs, carbazole has an aromatic structure, which could easily participate in the electrophilic substitution reaction. Since the presence of carbazole has been reported in source water (Stackelberg et al., 2007), we believe carbazole is a potential precursor of chlorocarbazoles in drinking water when chlorine is used as a disinfection agent in drinking water treatment plants. To our knowledge, only Lin et al (Lin and Carlson, 1984). in 1984 and Onodera et al. (1989). in 1989 subjected carbazole to aqueous chlorination using sodium hypochlorite and found that carbazole produced chlorocarbazoles with 1–4 chlorine atom substitutions, but both studies were unable to elucidate the specific structures of the chlorocarbazoles formed during aqueous chlorination. Furthermore, the reactivity of carbazole, which determines the formation potential of chlorocarbazoles, has not been studied. This lack of information may result from the complexity of chlorocarbazole isomers and the lack of proper analytical methods and reference materials. However, with the recent increasing attention to chlorocarbazole's toxicity and environmental presence (Riddell et al., 2015; Mumbo et al., 2015; Parette et al., 2015), it is crucial to characterize the reactivity and chlorinated products of carbazole during aqueous chlorination.

Therefore, in this study, the aqueous chlorination of carbazole was carried out to determine its reactivity with active chlorine and to characterize the chlorocarbazole analogues using a comprehensive two-dimensional gas chromatography-mass spectrometry (GC × GC-MS) method, and the molecular structures of chlorocarbazole analogues were predicted by the Fukui index of electrophilic attack.

2. Materials and methods

2.1. Aqueous chlorination

For each treatment, sodium hypochlorite solution (8%–12% free chlorine) and 1 L of ultrapure water generated by a Milli-Q system (Millipore, USA) were mixed in amber glass. The free chlorine concentration was measured by a pocket colorimeter for free chlorine (HACH, USA). Sulfuric acid (0.5 M) was used to adjust the solution to the desired pH level, which was measured by a pH meter (HACH, USA). Immediately, a mixed solution (200 nmol/L) containing carbazole and pyrene (Accustandard, USA) was added to start the chlorination reaction with an initial concentration of 5 nmol/L at room temperature (20 °C). Two pH levels were examined (3.8 and 6.4). For pH = 6.4, eight reaction times (0.5 h, 1 h, 2 h, 4 h, 8 h, 12 h, 24 h and 48 h) were studied; for pH = 3.8, ten reaction times (2 min, 5 min, 10 min, 20 min, 40 min, 80 min, 160 min, 320 min, 12 h and 24 h) were studied. After each reaction time, excess sodium thiosulfate ($Na_2S_2O_4$) was added to terminate the reaction. Each sample had three replicates. Before solid phase extraction (SPE), all samples were spiked with a surrogate standard (Phenanthrene-d10) to monitor the overall recovery efficiency. To properly enrich the unknown compounds formed after chlorination, a C18 cartridge (500 mg, Supelco, USA) coupled with a HLB cartridge (500 mg, Waters, USA) was used for SPE to ensure the proper extraction of possible polar and non-polar products. After extraction, the cartridges were eluted with 10 mL of dichloromethane (HPLC grade), and the extracts were evaporated under a gentle stream of nitrogen to 0.5 mL and then stored at −20 °C for further instrumental analysis.

2.2. Instrumental analysis

GC × GC-MS was used for the identification of chlorinated derivatives. The apparatus consisted of an Agilent 7890 gas chromatography and an Agilent 5975C quadrupole MSD. Modulation was accomplished by a loop-type cryogenic modulator (Zoex, USA). The column used for separation was a standard non-polar/polar set. The first column was a DB-5 MS column (30 m × 0.25 mm × 0.25 μm, Agilent, USA), and the second column was a BPX-50 column (2 m × 0.1 mm × 0.1 μm, SGE, USA). The modulation period was 6 s, and the flow of cooling nitrogen was 5 L/min. The hot jet was programmed to increase from 150 °C to 350 °C at a rate of 3.0 °C/min and with a hot pulse of 400 ms. The oven temperature was programmed with an initial temperature of 60 °C, then ramped at 3.0 °C/min to 300 °C, and held for 10 min. Helium was used as the carrier gas with a 1.0 mL/min flow rate in constant flow mode, and 1 μL of sample was injected in splitless mode. Quadrupole MSD was used in scan mode over a mass range from 100 amu to 500 amu, the mass acquisition rate was 12 500 amu/sec, and the scan rate was 19.8 spectra/sec. Data were processed by the GC Image V 2.2 software.

GC-MS was used for the quantification of carbazole and pyrene. The apparatus consisted of an Agilent 6890 gas chromatography