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Formation potential of nine nitrosamines from corresponding secondary amines by chloramination

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HIGHLIGHTS

- Corresponding secondary amines are the potential precursor of nitrosamine.
- Molar yield of nitrosamine depended on the structural properties of secondary amine.
- Nitrosamine formation was restrained considerably at lower pH (<7.0).

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ABSTRACT

Nitrosamines, a group of emerging disinfection by-products (DBPs) in drinking water, have recently caused significant concern because of their higher carcinogenic potential than that of currently regulated DBPs. In this study, the formation of nine representative nitrosamines by chloramination of their corresponding secondary amines was investigated under various conditions. All nine nitrosamines were detected in the corresponding reaction solutions, which confirmed that all the investigated secondary amines were the potential precursors of corresponding nitrosamines. The molar yields of nitrosamines from the corresponding secondary amines were quite different, depending on the structural characteristics of the secondary amines. The maximum molar yields for the formation of all nine nitrosamines occurred in the pH range of 7.0–9.0 and at the Cl/N molar ratio of 0.7 for chloramines, suggesting that monochloramine and unprotonated secondary amines may play a major role in the formation of nitrosamines. The molar yields of nitrosamines also exhibited a moderate upward tendency with rising temperature, but no consistent correlation was observed between the formation of nitrosamine and the initial concentrations of secondary amines and chloramines. The results of this study could be useful for devising strategies for controlling the formation of nitrosamines during the disinfection processes of drinking water.

1. Introduction

Since the identification of trihalomethanes (THMs) and haloacetic acids (HAAs) in 1970s (Bellar et al., 1974; Rook, 1974; Chu et al., 2011), disinfection by-products (DBPs) in drinking water have caused worldwide concern because of their potential carcinogenic effects (Richardson, 2003; Richardson et al., 2007; Hrudey, 2009). Nitrosamines, a group of emerging DBPs including nine major compounds of N-nitrosodimethylamine (NDMA), N-nitrosomethylethylamine (NMEA), N-nitrosodiethylamine (NDEA), N-nitrosodi-n-propylamine (NDPA), N-nitrosomorpholine (NMOR), N-nitrosopyrrolidine (NPYR), N-nitrosopiperidine (NPIP), N-nitrosodi-n-butylamine (NDBA) and N-nitrosodiphenylamine (NDPhA), have recently caused significant concern because of their higher carcinogenic potential than that of currently regulated DBPs (Choi and Valentine, 2002; Mitch et al., 2003a; Richardson et al., 2007). The US EPA has placed six nitrosamines on the third Unregulated Contaminant Monitoring Regulation (UCMR3) (US EPA, 2012) and five on the final version of the Drinking Water Contaminant Candidate List 3 (CCL 3) (US EPA, 2009). These compounds have frequently been detected in drinking water, and they have attracted great public attention (Zhao et al., 2006; Charrois et al., 2007; Asami et al., 2009; Bond et al., 2011a; Luo et al., 2012). Therefore, the US, Canada, and some other countries have established temporary regulations for several nitrosamines at regional and even at national levels (Nawrocki and Andrzejewski, 2011; Wang et al., 2011).

Because of the high carcinogenic risk of nitrosamines, a considerable amount of research has been conducted to investigate their potential precursors and formation processes with the aim of

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controlling or reducing nitrosamine formation, especially NDMA, in drinking water (Mitch and Sedlak, 2002; Mitch et al., 2003b; Schreiber and Mitch, 2006; Zhao et al., 2008; Bond et al., 2011b; Shah and Mitch, 2012; Sharma, 2012; Hatt et al., 2013; Krasner et al., 2013). Chloramination has been shown to produce higher amount of NDMA than other treatments of source water or wastewater, and a secondary amine of dimethylamine (DMA) has been identified as an important precursor of NDMA. Further studies have found that some tertiary and quaternary amines, polyelectrolytes, resins, fungicides, herbicides, pesticides, dyes, pharmaceuticals, and personal care products in environment water are also potential precursors of NDMA (Sharma, 2012; Krasner et al., 2013), and almost all of these identified precursors of NDMA contain one or more DMA groups (Chen and Young, 2008; Kemper et al., 2010; Chang et al., 2011; Le Roux et al., 2011; Shen and Andrews, 2011; Krasner et al., 2013), which revealed the importance of DMA functional groups in NDMA formation. Furthermore, diphenylamine (DPhA) also has been identified as an important precursor of NDPhA (Zhou et al., 2009). Therefore, it is assumed that secondary amines and the compounds containing secondary amine functional groups may be important or potential precursors of the corresponding nitrosamines.

In addition to DMA and DPhA, diethylamine (DEA), methylethylamine (MEA), di-n-propylamine (DPA), di-nbutylamine (DBA), pyrrolidine (PYR), piperidine (PIP), and morpholine (MOR) are the corresponding secondary amines for the nine representative nitrosamines. They are also important intermediates in chemical and pharmaceutical industries (Sacher et al., 1997; Wang et al., 2011), and some of them have been detected in source water or surface water (Akyüz and Ata, 2006; Kamarei et al., 2010; Wang et al., 2011; Zhang et al., 2012). Therefore, these secondary amines may also serve as precursors for the formation of corresponding nitrosamines in drinking water. Nine secondary amines have very different structures and properties, and thus the formation potential of the corresponding nitrosamines may be different. Therefore, it is necessary to investigate and compare the formation potential of different nitrosamines from the corresponding secondary amines, which is required for controlling or reducing nitrosamine formation during the disinfection process of drinking water.

In this study, nine secondary amines were utilized as model precursors to investigate the formation of corresponding nitrosamines from them by chloramination. The main objectives are to identify secondary amines as the precursors of corresponding nitrosamines and compare the formation potential of nine nitrosamines from corresponding secondary amines. In addition, further examinations were conducted to characterize the effects of solution pH, chloramine composition, reactant concentrations, and reaction temperature on nitrosamine formation. To the best of our knowledge, this is the first systematic research to investigate and compare the formation potential of these nine nitrosamines from their corresponding secondary amines.

2. Materials and methods

2.1. Materials

Nine secondary amines, DMA, MEA, DEA, DPA, DBA, PYR, PIP, MOR, and DPhA, were obtained from Sigma–Aldrich (USA) with purities higher than 98%. Their selected properties are listed in Table 1. A standard solution containing nine N-nitrosamines (NDMA, NMEA, NDEA, NDPA, NDBA, NPYR, NPIP, NMOR, and NDPhA in methylene chloride, 1000 $\mu g\ mL^{-1}$ of each) was purchased from Supelco (Sigma–Aldrich, USA). An isotope-labeled standard, NDMA-d_6 (98%), was obtained from Cambridge Isotope Laboratories (USA) and used as an internal standard for nitrosamine analyses. Sodium hypochlorite (13% active chlorine) was obtained from Acros Organics (USA). HPLC-grade methanol was purchased from Fisher Scientific (USA). All other chemicals such as L-ascorbic acid, ammonium chloride, sodium acetate, glacial acetic acid, potassium dihydrogen phosphate, sodium hydroxide, and sodium carbonate were obtained from Sinopharm Chemical Reagent Co., (China) with analytical grade. Chloramine solutions were freshly prepared daily by mixing ammonium chloride solution and sodium hypochlorite solution at a Cl:N molar ratio of 0.7, which is the chlorine-to-ammonia ratio used to form chloramines as described previously (Choi and Valentine, 2002; Zhou et al., 2009). All reaction solutions were prepared using ultrapure water produced by a Pall Cascada™-IX (Germany) water purifying system.

2.2. Nitrosamine formation experiments

Nitrosamine formation experiments were conducted in batches of 500-mL sealed amber glass bottles with Teflon-lined screw caps, and high doses of chloramines were applied to predict the ultimate formation potential. Unless otherwise specified, all reactions were conducted at room temperature (25 ± 1 °C), and the solutions were buffered with a mixture of potassium dihydrogen phosphate and sodium hydroxide (pH 7.0). DMA, MEA, DEA, DPA, DBA, PYR, PIP, MOR, and DPhA were respectively added and fully dissolved in 500 mL of aqueous 10.0 mM buffer water solution at predetermined concentrations. The solutions of the secondary amines were then reacted with chloramines for 24 h, after which the reactions were quenched by adding an excess of ascorbic acid powder. An appropriate aliquot of the reaction solution was then withdrawn and mixed with methanol and internal standard to directly measure the nitrosamine concentrations by LC/MS/MS. The dependence of nitrosamine formation on the reaction conditions was assessed by varying the initial concentrations of the secondary amines and chloramines, Cl:N molar ratio of chloramines, solution pH, and reaction temperature. An aliquot of 500 mL of ultrapure water without secondary amines was also processed using the same procedure to serve as a control sample. All experiments were performed at least in triplicate, and the mean values and standard deviations were reported. The formation potential of nitrosamines from the corresponding secondary amines was evaluated from percent molar yield on the basis of the following equation.

$$\text{Nitrosamine molar yield}(\%) = \frac{C_N}{C_{A0}} \times 100\% \qquad (1)$$

where C_N is the final molar concentration of nitrosamine (μM) in aqueous solution, and C_{A0} is the initial molar concentration of the corresponding secondary amine (μM).

2.3. LC/MS/MS analysis of nitrosamines

Nitrosamines were quantified by an QTrap 4000 mass spectrometer (Applied Biosystems, USA) coupled with an Agilent 1100 HPLC (USA) and Phenomenex C8 column (100 × 2.0 mm, i.d. 3 μm). The mobile phase was composed of solvent A (10 mM ammonium acetate in ultrapure water) and solvent B (100% methanol) with a flow rate of 0.15 $mL\ min^{-1}$. The following gradient program was used for the mobile phase: 0–2.0 min of 40% B; 2.0–5.0 min of 40–90% B; 5.0–15.0 min of 90% B; 15.0–16.0 min, of 90–40% B; and 16.0–25.0 min re-equilibration with 40.0% B. Sample injection volume was 10 μL. Positive electrospray ionization combined with multiple reactionmonitoring (MRM) mode was used for the quantitative analysis of nitrosamines. The method detection limits (MDLs) of LC/MS/MS for the nine nitrosamines ranged between 0.6 and 24 $\mu g\ L^{-1}$.