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The stability of chlorinated, brominated, and iodinated haloacetamides in drinking water

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ABSTRACT

Haloacetamides (HAMs), a group of nitrogenous disinfection byproducts (N-DBPs), can decompose to form corresponding intermediate products and other DBPs. The stability of ten different HAMs, including two chlorinated, five brominated, and three iodinated species was investigated with and without the presence of chlorine, chloramines, and reactive solutes such as quenching agents. The HAM basic hydrolysis and chlorination kinetics were well described by a second-order kinetics model, including first-order in HAM and hydroxide and first-order in HAM and hypochlorite, respectively, whereas the HAM neutral hydrolysis kinetic was first-order in HAM. Furthermore, HAMs decompose instantaneously when exposed to hypochlorite, which was almost two and nine orders of magnitude faster than HAM basic and neutral hydrolysis, respectively. In general, HAM hydrolysis and chlorination rates both increased with increasing pH and the number of halogens substituted on the methyl group. Moreover, chlorinated HAMs are more unstable than their brominated analogs, followed by the iodinated ones, due to the decrease in the electron-withdrawing inductive effect from chlorine to iodine atom. During hydrolysis, HAMs mainly directly decompose into the corresponding haloacetic acids (HAAs) via a nucleophilic reaction between the carbonyl carbon and hydroxide. For HAM chlorination reactions, hypochlorite reacts with HAMs to form the *N*-chloro-HAMs (*N*-Cl-HAMs) via Cl^+ transfer from chlorine to the amide nitrogen. *N*-Cl-HAMs can further degrade to form HAAs via hypochlorous acid addition. In contrast, the reactions between chloramines and HAMs were found to be insignificant. Additionally, four common quenching agents, including sodium sulfite, sodium thiosulfate, ascorbic acid, and ammonium chloride, were demonstrated to expedite HAM degradation, whereas ammonium chloride was the least influential among the four. Taft linear free energy relationships were established for both HAM hydrolysis and chlorination reactions, based on which the hydrolysis and chlorination rate constants for three monohaloacetamides were estimated. The hydrolysis and chlorination rates of 13 HAMs decreased in the following order: TCAM > BDCAM > DBCAM > TBAM > DCAM > BCAM > DBAM > ClAM > BIAM > DIAM > MCAM > MBAM- > MIAM (where C = chloro, B = bromo, I = iodo, T = tri, D = di, M = mono). Lastly, using the HAM kinetic model established in this study, HAM half-lifes in drinking water distribution systems can be predicted on the basis of pH and residual chlorine concentration.

1. Introduction

Haloacetamides (HAMs) were first identified as a group of emerging nitrogenous disinfection byproducts (N-DBPs) during a US national survey in 2000–2002 (Krasner et al., 2006; Richardson et al., 2007). Since then, HAMs have received increasing interests due to their ubiquitous occurrence in municipal drinking waters

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(Bond et al., 2011, 2015; How et al., 2017; Kosaka et al., 2016; Krasner et al., 2006). Dihaloacetamides (DHAMs) and trichloroacetamide (TCAM) were the main HAMs detected, among which dichloroacetamide (DCAM) was the most predominant species with a maximum concentration of 5.6 μg/L from twelve drinking water treatment plants samples (Krasner et al., 2006; Richardson et al., 2007). Although HAM concentrations are typically much lower compared to those of regulated DBPs (i.e., trihalomethanes [THMs] and haloacetic acids [HAAs]), they were found to be up to two orders of magnitude more cytotoxic and genotoxic than THMs and HAAs using mammalian cell assays (Plewa et al., 2008; Richardson et al., 2007; Yang and Zhang, 2014). HAMs are 142, 2, and 1.4 times more cytotoxic than the 5 regulated HAAs, haloacetonitriles (HANs), and halonitromethanes (HNMs), respectively (Plewa et al., 2008). HAMs are slightly more genotoxic than HANs and HNMs, and substantially more genotoxic than THMs and haloacetaldehydes (HALs) (Jeong et al., 2015). Furthermore, iodinated HAMs are the most toxic, followed by the brominated and then the chlorinated analogs (Richardson et al., 2008; Wagner and Plewa, 2017). Work by Plewa and Wagner even indicated that diiodoacetamide (DIAM) and monoiodoacetamide (MIAM) are the first- and second-most cytotoxic of 87 DBPs, based on the fact that mammalian cell density is 50% compared to the control of the assay (Plewa and Wagner, 2015). Therefore, more attention should be paid to brominated and iodinated HAMs, which are deemed to be of high toxicity (and stability, as shown below).

Previous studies have found that many DBPs are intermediate products that can transform into other end products by hydrolysis (base- or acid-catalyzed) or chlorination (hypochlorite or hypochlorous acid). For example, Zhang and Minear demonstrated that trihaloacetic acids decompose to form corresponding THMs via a decarboxylation pathway (Zhang and Minear, 2002). HALs are another group of unstable intermediates, which can undergo hydrolysis under basic conditions (Xie and Reckhow, 1993). A subsequent study further demonstrated that trihalogenated HALs could partially degrade into their corresponding THMs (Koudjonou and LeBel, 2006). Previous research has shown that chloropicrin is unstable in the presence of Cl_2 or NH_2Cl at pH 9.0, with an approximate half-life of 3 days (Joo and Mitch, 2007). Perhaps most importantly, HAMs can be formed during HAN hydrolysis, which can undergo further decomposition to form the corresponding HAAs (Chu et al., 2015; Glezer et al., 1999). It has been shown that hypochlorite can react rapidly with HAMs to form *N*-chloro-haloacetamides (*N*-Cl-HAMs), with a second-order DCAM *N*-chlorination rate constant of $9.94 \times 10^4\ M^{-1}\ h^{-1}$ (Yu and Reckhow, 2017). However, the HAM chlorination reaction rates have not been reported for the other species, especially the brominated and iodinated ones. In disinfectant-free water, HAMs can undergo hydrolysis, with reaction rate constants being 0.012 and $0.048\ h^{-1}$ at pH 9.0 for DCAM and TCAM, respectively (Chu et al., 2009). However, the hydrolysis rates of brominated and iodinated HAMs have not yet been documented. It can take a few hours to several days for finished water to travel from the point of entry to consumers' taps and a few days between sample collection and analysis. Therefore, it is important to characterize HAM degradation kinetics and to understand its impact on the formation of HAM degradation products over increasing system residence time. In addition, samples should be preserved (adjusted to the appropriate pH, chlorine residual quenched) at the time of collection so that the analytes are stable until analysis in the laboratory. For example, some DBP samples are adjusted to a pH of 5.5 or 3–4 to prevent base-catalyzed hydrolysis (Krasner Stuart et al., 2012; Munch and Hautman, 1995). In general, residual Cl_2 or chloramines is quenched by an agent to prevent additional DBP formation and degradation during the holding time. However, common used quenching agents can react with DBPs, resulting in the decomposition of DBPs (Kristiana et al., 2014). One previous study even showed that the accidental reduction of *N*-Cl-HAMs by the quenching agent (i.e. ascorbic acid, sodium sulfite, and sodium thiosulfate) to HAMs during sample preservation may overestimate HAM occurrence, especially in chlorinated drinking waters (Kimura et al., 2013, 2015; Yu and Reckhow, 2017). Therefore it is important to investigate the decay of HAMs in the presence of quenching agents.

One of the objectives of this study was to investigate the stability of a more complete set of chlorinated, brominated, and iodinated HAMs, including DCAM, bromochloroacetamide (BCAM), dibromoacetamide (DBAM), chloroiodoacetamide (CIAM), bromoiodoacetamide (BIAM), DIAM, TCAM, dibromochloroacetamide (BDCAM), bromodichloroacetamide (DBCAM), and tribromoacetamide (TBAM). Another objective was to evaluate the impact of commonly used quenching agents on HAM stability. As the higher experimental error and lower coefficient (< 0.90) for kinetic rates resulted from low degradation rates and the higher limits of detection of monohalogenated HAMs (MHAMs) are higher than that of DHAMs and THAMs, it is difficult to directly test their hydrolysis and chlorination kinetics. Therefore, another goal of this study was to develop Taft linear free energy relationships (LFERs) for both HAM hydrolysis and chlorination reactions so that the reaction rate constants for MHAMs can be predicted.

2. Materials and methods

2.1. Materials

DCAM and TCAM were obtained from Alfa Aesar (Karlsruhe, Germany), while brominated and iodinated HAMs (i.e., BCAM, DBAM, CIAM, BIAM, DIAM, BDCAM, DBCAM, and TBAM) were purchased form CanSyn Chem Corp (Toronto, Canada). Detailed information regarding all 10 HAM standards is provided in Table SM1. HAM stock solutions (2 mg/mL) were individually prepared in methanol and were stored in 40-mL screw-cap amber glass vials at 4 °C. The stability of HAMs in methanol was investigated in a previous study (unpublished). It was found that the effect of small quantities of water contained in the methanol on the hydrolysis of HAMs can be neglected over 3 months. To control the manual error, the used HAM stock solutions were the same and less than 30 days. The EPA 552.2 HAA Calibration Mix was supplied by Supelco (St Louis, USA). Four quenching agents, ascorbic acid, sodium sulfite, sodium thiosulfate, and ammonium chloride, were obtained from Aladdin Industrial Inc. (Shanghai, China). All other chemical reagents were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China), which were of analytical grade unless otherwise noted. All solutions were prepared in ultrapure water produced by Millipore Milli-Q Gradient water purification system (Billerica, USA). Preformed monochloramine (NH_2Cl) solutions were prepared freshly by slowly adding sodium hypochlorite into chilled ammonium chloride solution at a hypochlorite to ammonia molar ratio of at least 1:1.3 (Mitch and Sedlak, 2002). The concentration of the NH_2Cl stock solution was ~4 g/L.

2.2. Experimental procedures

Batch experiments were conducted in 1 L glass bottles in the dark at 25.0 ± 0.5 °C. 100 μL of an individual HAM stock solution was introduced into 1 L phosphate- (for pH = 5.0, 6.0, 7.0, and 8.0) or carbonate- (for pH = 9.0) buffered solution (the total buffer concentrations used in the experiments were all 10 mM and the variation of pH after experiments can be neglected) to obtain an initial HAM concentration of 200 μg/L (1.56 μM for DCAM, 1.16 μM for BCAM, 0.92 μM for DBAM, 0.91 for CIAM, 0.75 μM for BIAM, 0.64 μM for DIAM, 1.23 μM for TCAM, 0.96 μM for BDCAM, 0.79 μM for