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Formation of haloacetamides during chlorination of dissolved organic nitrogen aspartic acid

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ABSTRACT

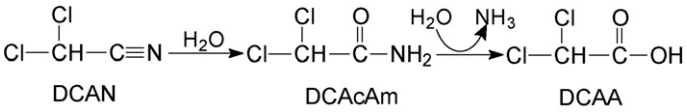
The stability of haloacetamides (HAcAms) such as dichloroacetamide (DCAcAm) and trichloroacetamide (TCAcAm) was studied under different experimental conditions. The yield of HAcAms during aspartic acid (Asp) chlorination was measured at different molar ratio of chlorine atom to nitrogen atom (Cl/N), pH and dissolved organic carbon (DOC) mainly consisted of humic acid (HA) mixture. Ascorbic acid showed a better capacity to prevent the decay of DCAcAm and TCAcAm than the other two dechlorinating agents, thiosulfate and sodium sulfite. Lower Cl/N favored the DCAcAm formation, implying that breakpoint chlorination might minimize its generation. The pH decrease could lower the concentration of DCAcAm but favored dichloroacetonitrile (DCAN) formation. DCAcAm yield was sensitive to the DOC due to higher chlorine consumption caused by HA mixture. Two possible pathways of DCAcAm formation during Asp chlorination were proposed. Asp was an important precursor of DCAN, DCAcAm and dichloroacetic acid (DCAA), and thus removal of Asp before disinfection may be a method to prevent the formation of DCAcAm, DCAN and DCAA.

1. Introduction

As one of the most important public health advances in the last century, chlorination adequately inactivates pathogenic microbes in drinking water [1]. Owing to its low cost and high disinfection capacity, chlorine is the most frequently used disinfecting agent in drinking water treatment in the world [2,3]. However, undesirable chemical disinfection byproducts (DBPs) with harmful health effects, especially trihalomethanes (THMs) and haloacetic acids (HAAs), may be produced during the chlorination process [4,5]. To meet more stringent effluent limitations on THMs and HAAs, many utilities are switching from chlorine to chloramine disinfection. However, nitrogenous disinfection byproducts (N-DBPs) can also be formed, such as nitrosamines [6–9], halonitroalkane [9–11] and nitriles [9,12]. Generally, N-DBPs are composed of nonhalogenated N-DBPs such as nitrosamines (e.g. N-nitrosodimethylamine (NDMA)), and halogenated N-DBPs. The latter, featured with nitro (–NO_2; e.g., halonitromethanes) and nitrile (–CN; e.g., cyanogen chloride and haloacetonitriles) functional groups, are of particular concern due to their high toxicity [10,13]. For example, the mammalian cell genotoxicity of halonitromethanes (HNMs) exceeds that of the halofuranone, MX [10]; and haloacetonitriles (HANs) accounts for 10% of the 50 DBPs predicted to be the most carcinogenic [10,11].

Recently, haloacetamides (HAcAms), a type of new halogenated N-DBPs, have been identified and quantified as part of the U.S. nationwide DBP occurrence study [11]. A toxicologic study indicated that the HAcAms were 99×, 142×, 2×, and 1.4× more cytotoxic than 13 HAAs, 5 regulated HAAs, HANs, and HNMs, respectively. Moreover, they were 19×, 12×, 2.2× more genotoxic than the 13 HAAs, 5 regulated HAAs and HNMs, respectively [14]. Although many efforts have been made to understand the formation mechanisms of THMs, HAAs, NDMA, HNMs, HANs and cyanogen halides (CNCl), and the impacts of operational factors (e.g. reaction time, pH, temperature, and disinfectant doses) on their production [9,15–18], little information is available on the formation of HAcAms during chlorination.

It is essential to investigate the stability of N-DBPs before examining their formation mechanism [19]. Stability of HANs depends greatly on their chemical structures and the solution pH [20]. A faster hydrolysis pathway of DCAN in basic media was reported by Glezer and co-workers as shown in Eq. (1) [19].



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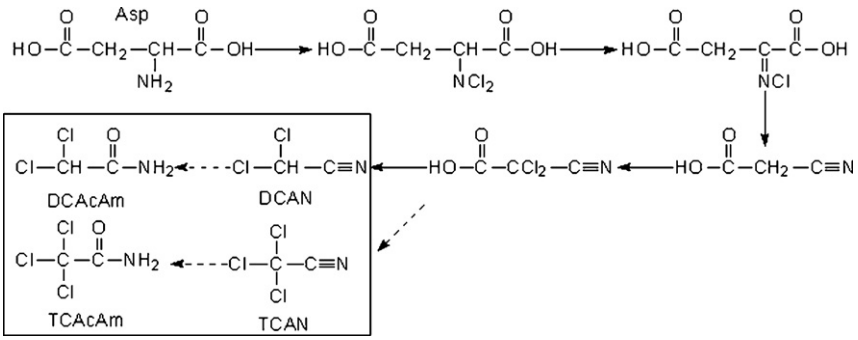


Fig. 1. Proposed formation pathway of DCAN during Asp chlorination.

In our recent study, it was found that stability of HAcAms was similar with that of HANs [21]. In weakly acidic and neutral solution, the DCAcAm decay was greatly slow. DCAcAm and TCAcAm were the most stable at pH 5 than at pH 4, 6 and 7. Once the solution pH was greater than 9.0, the decay was significantly increased. The hydrolysis of DCAcAm under alkaline condition followed a pseudo-first-order kinetic behavior. The hydrolysis rate constant of DCAcAm were 4.85×10^{-2}, 2.80×10^{-1} and 6.47×10^{-1} d^{-1} at pH 8, 9 and 10, respectively. Although TCAcAm was stable at weak acidic and neutral condition similar to DCAcAm, its decay more dramatically decreased under alkaline condition.

In this study, DCAcAm and TCAcAm were selected as the two representatives of HAcAms since they are typically present at higher levels in finished water than other HAcAms. Aspartic acid (Asp) was used as the model dissolved organic nitrogen (DON) constituent, because it is a major amino acid (a significant portion of DON) in natural water [22,23]. Asp can be chlorinated to HANs and may be an important precursor of HAcAms [14,19]. This study is to investigate the influence of dechlorinating agents on HAcAms and evaluate the role of DON on the HAcAms formation during chlorination of Asp under different experimental conditions. In addition, the plausible pathways of DCAcAm formation during this process are proposed.

2. Materials and methods

2.1. Materials

All chemicals were at least analytical grade except as noted. DCAcAm (98.5%) and TCAcAm (99%) were purchased from Alfa Aesar (Karlsruhe, Germany). EPA 551B mixture standard solution containing dichloroacetonitrile (DCAN, 99.9%) and trichloroacetonitrile (TCAN, 99.9%) were obtained from Supelco (Bellefonte, United States). HAAs mixture standard solution and 1,2-dibromopropane internal standard solutions were purchased from Sigma–Aldrich (St. Louis, United States). Asp (97%) and humic acids (HA) mixture were obtained from Wako (Osaka, Japan). Extractant normal hexane (n-hexane), ethyl acetate (ETAC) and methyl-tert-butyl-ether (MTBE) were supplied from Fisher Scientific (Waltham, United States). Ultrapure water (18 MΩ cm) was produced by a water purification system (Milli-Q Synthesis). Buffer solutions at pH 4–5, pH 6–8, and pH 9–10 were prepared from acetate, phosphate, and carbonate salts, respectively. All bottles used were prewashed with phosphate-free detergent, rinsed with deionized water and ultrapure water, and dried in an oven at 105 °C for 24 h.

2.2. Experimental procedures

All experiments were conducted in a 40-mL zero head space glass screw-cap vials with PTFE-lined septa at room temperature. In a typical run, the designated amounts of chlorine and HA were added to 10 mM Asp solution in the vials. The molar ratio of chlorine atom to nitrogen atom in Asp (Cl/N), one of the influencing factors, was adjusted by varying the chlorine dose. The yield of DBP is defined as molar ratio of DBP to Asp, that is, DBP yield = [DBP]/[Asp] × 100%.

2.3. Analytical methods

Dissolved organic carbon (DOC) was measured by TOC analyzer (Shimadzu, TOC-V CPN) after the solution was filtered by 0.45 μm microfiltration membrane. Residual disinfectants were measured by the total and free DPD (N,N-diethyl-p-phenylenediamine) colorimetric method 4500-Cl [24]. Prior to analysis of DBPs, the

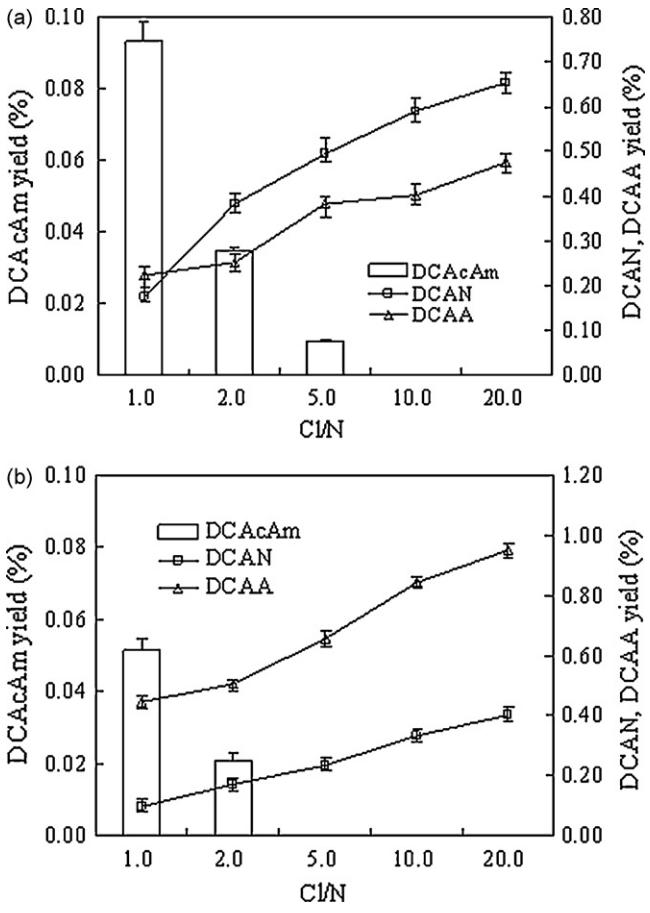


Fig. 2. DCAcAm, DCAN, and DCAA formation during Asp chlorination at different Cl/N. Reaction conditions: initial Asp concentration = 50 μM, pH 7.0, DBP yield is calculated based on 50 μM Asp. (a) Reaction time = 3 h; (b) reaction time = 3 d.

disinfectant residuals were quenched with ascorbic acid with normality twice as the initial normality of chlorine added. Glacial acetic acid was used to lower the pH at 4.8–5.5 for the THM and HAN analysis [9], and at 5.0 ± 0.2 for the HAcAm analysis [21]. THMs, HANs and HAAs were analyzed by a gas chromatograph (Shimadzu-QP2010) with an electron capture detector (ECD), based on the USEPA method 551.1 and 552.2. HAcAms were analyzed using liquid–liquid extraction (LLE) and GC/MS (Shimadzu-QP2010S). The details of the HAcAms analysis are available elsewhere [25].

3. Results and discussion

3.1. Effect of various dechlorinating agents on HAcAms stability

Once added, dechlorinating agents can eliminate chlorine residual and terminate the reactions between chlorine and N-containing organics. Due to the high reducibility of dechlorinating agents, they may react with HAcAm compound to reduce the yield of HAcAm during chlorination. The effect of various dechlorinating agents on stability of the DCAcAm and TCAcAm was examined (no data shown). When no dechlorinating agent was added, DCAcAm and TCAcAm concentration remained stable, which implied the effect of hydrolysis on HAcAm stability is negligible under neutral condition within 1 d. The rank of reactivity of the DCAcAm and TCAcAm in the presence of various dechlorinating agents at pH 7.0 is sodium thiosulfate > sodium sulfite > ascorbic acid. It can be deduced that DCAcAm and TCAcAm was easily dechlorinated by sodium thiosulfate and sodium sulfite due to their higher reducing capacity. Unlike sodium thiosulfate and sodium sulfite, ascorbic acid did not significantly reduce the HAcAm compounds concentration. Therefore, ascorbic acid was a very effective agent to eliminate chlorine residual and prevent the decay of DCAcAm and TCAcAm.

3.2. Influence of Cl/N

As shown in Fig. 1, Asp, when chlorinated, can first form DCAN through a series of reactions [20,26], and then partial portion of DCAN can be transformed to DCAcAm and DCAA through hydrolysis [19]. Fig. 2(a) and (b) shows the yields of DCAcAm, DCAN, and DCAA at different Cl/N (1.0, 2.0, 5.0, 10.0 and 20.0) during Asp chlorination at 3 h and 3 d, respectively.

At the first 10 min, only DCAN was detectable at Cl/N = 10.0, and then DCAcAm became detectable after 30 min (no data shown). At 3 h, DCAN, DCAcAm and DCAA were all detected as shown in Fig. 2(a). DCAN and DCAA yields increased with the increasing Cl/N, and peaked at 0.653% and 0.475% at Cl/N = 20.0, respectively. Nevertheless, the DCAcAm yield had a maximum value of 0.093% at Cl/N = 1.0 and decreased with the increasing Cl/N. At the initial Cl/N ≥ 10.0, DCAcAm was undetectable within 3 h. The yields of DCAcAm, DCAN, and DCAA within 3 d had similar trends as those at 3 h, as seen in Fig. 2(b). The DCAN and DCAA yields peaked at 0.405% and 0.917% when Cl/N = 20.0, while DCAcAm maximized at 0.053% when Cl/N = 1.0. Once the Cl/N was above 5.0, DCAcAm became undetectable within 3 d. Of note, the residual chlorine increased with the increasing initial Cl/N. Therefore, the decrease of DCAcAm at higher Cl/N was probably due to rapid hydrolysis of DCAcAm catalyzed by the residual free chlorine, based on these reactions of chlorination study of DCAN as shown in Eq. (2) [27]. Moreover, DCAcAm yield at 3 d were lower than that at 3 h probably because

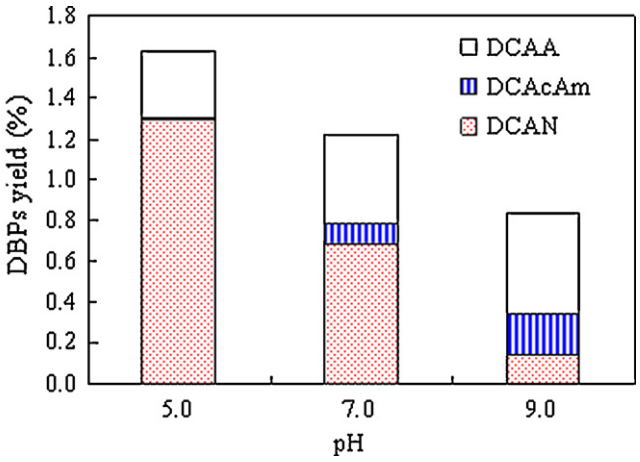
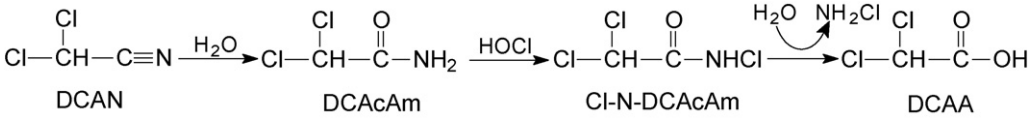


Fig. 3. DCAcAm, DCAN and DCAA formation from Asp during chlorination at different pH. Reaction conditions: initial Asp concentration = 50 μM, Cl/N = 1.0, and reaction time = 3 h; DBP yield is calculated based on 50 μM Asp.

DCAcAm was further transformed to DCAA through hydrolysis and chlorination (Eqs. (1) and (2)). In addition, the chlorination at pH 7.0 did not produce detectable TCAcAm and TCAN within 3 d.



(2)

3.3. Influence of pH

The effects of pH on the formation of DCAN, DCAcAm, and DCAA were shown in Fig. 3. The DCAN yield decreased with the increasing pH from 5.0 to 9.0 with a peak at 1.29% at pH 5. The DCAN yield at pH 9 was approximately one-ninth at pH 5, indicating that acidic conditions favored the DCAN formation, similar to the report of Peters et al. study [26]. DCAcAm and DCAA yields after 3 h increased with the increasing the pH, maximized 0.20% and 0.49% at pH 9, respectively. The DCAcAm yield at pH 9 was greater than the twofold yield at pH 7. Since alkaline condition favored formation of DCAcAm and DCAA, some DCAN hydrolyzed to form DCAcAm and DCAA, in agreement with the above-mentioned hydrolysis pathway of DCAN (Eq. (1)).

Of note, DCAN is very stable and difficultly hydrolyzed to form DCAcAm and DCAA in acidic conditions [20]. However, as shown

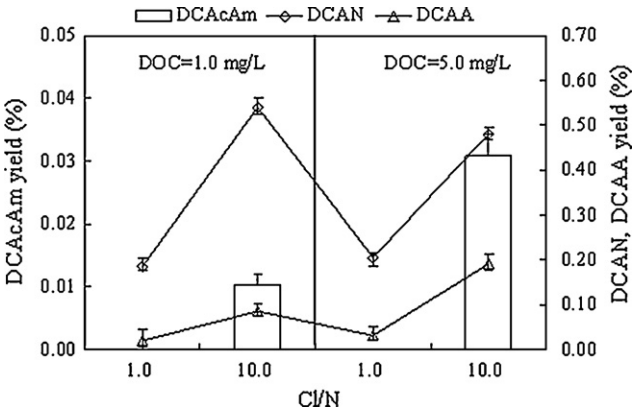


Fig. 4. DCAcAm, DCAN and DCAA formation from Asp during chlorination at different DOC. Reaction conditions: initial Asp condition = 50 μM, Cl/N = 1.0 and 10.0, DOC = 1.0 or 10.0 mg/L, reaction time = 3 h; DBP yield is calculated based on 50 μM Asp.

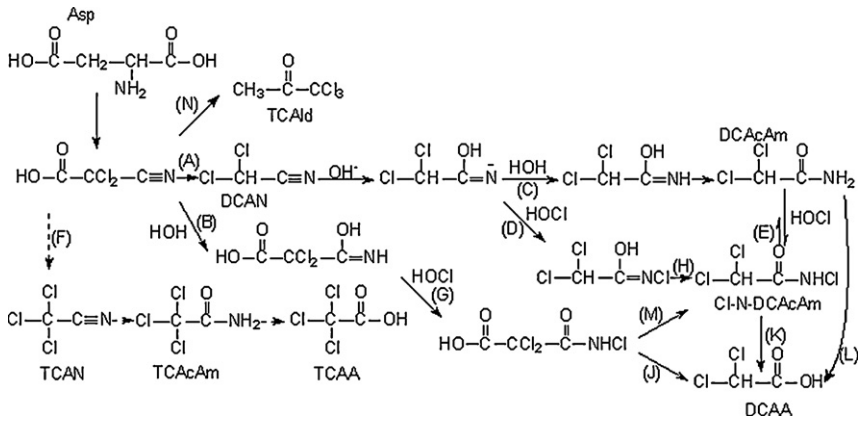


Fig. 5. Proposed formation pathway of DCAcAm during Asp chlorination.

in Fig. 3, the DCAcAm yield in acidic conditions was higher than in neutral conditions. This observation is probably because DCAN hydrolysis is not the only pathway to form DCAcAm.

3.4. Influence of DOC

DOC is an important factor influencing the formation of DBPs [7]. HA mixture was served as DOC to assess the formation of DCAcAm, DCAN and DCAA. As shown in Fig. 4, DCAcAm was undetectable at Cl/N = 1.0 in the presence of HA mixture. However, DCAcAm was detected at Cl/N = 10.0, and its yield increased from 0.01% to 0.03% with the increasing DOC from 1.0 to 5.0 mg/L. We also assessed the formation potential of DCAcAm from HA mixture in the absence of Asp and found that DCAcAm was rarely formed during HA mixture chlorination only (no data shown).

At Cl/N = 1.0, the chlorine was first rapidly quenched by HA mixture, and thus the DCAcAm could not be formed due to limited available chlorine in the solution. In our tests, at Cl/N = 1.0, the residual chlorines at 3 h were both undetectable. However, the residual chlorine was greatly increased when Cl/N increased to 10.0.and the residual chlorines were 2.2 and 0.3 mg/L, respectively, corresponding to 1.0 and 5.0 mg/L initial DOC. According to the results of Section 3.2, DCAcAm trended to produce at lower chlorine concentration. Therefore, at Cl/N = 10.0, the DCAcAm yield of 0.03% corresponding to 5.0 mg/L initial DOC was higher than 0.01% DCAcAm yield with 1.0 mg/L initial DOC. As shown in Fig. 4, DOC appeared not to significantly influence DCAN production. At 1.0 or 5.0 mg/L DOC, the DCAN yield increased roughly from 0.012% approximately to 0.035% with the increasing Cl/N from 1.0 to 10.0. Fig. 4 also showed that DCAA yield trended to slightly increase with the increase of Cl/N at the same DOC level. It is well known that DCAN and DCAA can be transformed from HA. Therefore, in the tests, DCAN and DCAA derived from degradation of HA and Asp, but all of the DCAcAm came from the transformation of Asp.

3.5. Preliminary analysis of DCAcAm formation pathway

The possible pathways of DCAcAm formation during Asp chlorination are proposed, as shown in Fig. 5. DCAN, DCAA and trichloroacetic aldehyde (TCAld) were reported as the primary products in previous studies [20,26]. Under typical disinfection conditions, Asp reacted with chlorine to form DCAN and TCAld via reactions (A) and (N) in Fig. 5. In our study, DCAN was observed to be produced within 10 min prior to the formation of DCAcAm formed after 30 min. The DCAcAm was probably generated through hydrolysis and chlorination of DCAN via reactions (C) and (D), respectively, as proposed by Reckhow et al. [27]. Peters et al. [26] suggested that HAN chlorination followed either direct hypochlorite catalyzed hydrolysis of the cyano group producing an amide to give DCAcAm (reaction (C)) or an indirect route through chlorination by HOCl to generate Cl-N-DCAcAm (reactions (D) and (H)) that reacted with HOCl to give DCAcAm. On the other side, Glezer et al. [19] reported that TCAN readily hydrolyzed to TCAcAm and then transformed to TCAA in alkaline conditions. Similarly, DCAA could be produced by further hydrolysis of DCAcAm via reaction (L). And other DCAA might also be produced from direct chlorination of DCAcAm via Cl-N-DCAcAm (reactions (E) and (K)). In addition, according to the presumption of Section 3.3, besides through hydrolysis and chlorination of DCAN, some DCAcAm might be formed via hydrolysis and subsequent chlorination of cyanoacetic acid (CEA) as shown in reactions (B), (G) and (J).

4. Conclusion

Because Asp is an important precursor of DCAcAm, DCAN and DCAA, removal of Asp before chlorination is very necessary to prevent the formation of DCAcAm, DCAN and DCAA. Too high dose of chlorine inhibits the formation of DCAcAm, implying breakpoint chlorination may be effective to reduce the DCAcAm yield. In addition, increasing detention time of drinking water after disinfection may also favor the control of DCAcAm and TCAcAm, but increase the DCAA concentration. The decrease of pH could reduce the concentrations of DCAcAm and DCAA but favored DCAN formation. DCAcAm, DCAN and DCAA yields vary significantly with DOC due to higher chlorine consumption caused by DOC. The formation pathway of DCAcAm is similar with the DCAA generation. Besides hydrolysis and chlorination of DCAN, another pathway contributing to the formation of DCAcAm is direct hydrolysis and chlorination of CEA by HOCl, forming Cl-N-DCAcAm that reacts with HOCl to produce DCAcAm.

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