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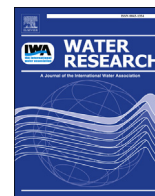
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Rapid degradation of brominated and iodinated haloacetamides with sulfite in drinking water: Degradation kinetics and mechanisms

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ABSTRACT

The effective removal of haloacetamides (HAMs) as a group of emerging disinfection by-products is essential for drinking water safety. This study investigated the degradation of 10 HAMs, including chlorinated, brominated, and iodinated analogues, by sodium sulfite (S(IV)) and the mechanism behind it. The results indicated that all HAMs, excluding chlorinated HAMs, decomposed immediately when exposed to S(IV). The reductive dehalogenation kinetics were well described by a second-order kinetics model, first-order in S(IV) and first-order in HAMs. The degradation rates of HAMs increased with the increase of pH and they were positively correlated with sulfite concentration, indicating that the reaction of S(IV) with HAMs mainly depends on sulfite. The rank order and relative activity of the reaction of sulfite with HAMs depends on bimolecular nucleophilic substitution reaction reactivity. The order of the reductive dehalogenation rates of HAMs versus the substitution of halogen atoms was iodo- > bromo- >> chloro-. During reductive dehalogenation of HAMs by sulfite, the α -carbon bound to the amide group underwent nucleophilic attack at 180° to the leaving group (halide). As a consequence, the halide was pushed off the opposite side, generating a transition state pentacoordinate. The breaking of the C-X bond and the formation of the new C-S bond occurred simultaneously and HAM sulfonate formed as the immediate product. Results suggest that S(IV) can be used to degrade brominated and iodinated HAMs in drinking water and therefore should not be added as a quenching agent before HAM analysis to accurately determine the HAM concentrations produced during water disinfection.

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1. Introduction

Haloacetamides (HAMs), which were identified as a group of emerging disinfection by-products (DBPs) in finished water for the first time in a 2000–2002 US survey, have received considerable attention (Krasner et al., 2006). Subsequent studies indicated that HAMs were widely detected at low $\mu\text{g/L}$ levels in disinfected samples, final waters, and distribution samples (Bond et al., 2011, 2015; Richardson et al., 2007). Although the concentrations of HAMs

were lower than those of regulated carbonaceous DBPs (C-DBPs), including trihalomethanes (THMs) and haloacetic acids (HAAs), they were nearly two orders of magnitude more cytotoxic and genotoxic in mammalian cell assays (Plewa et al., 2008). The cytotoxicity and genotoxicity of the HAMs by halogen substituent types decrease in the following order: iodo- > bromo- >> chloro- (Plewa et al., 2008). The study of Plewa and Wagner even indicated that diiodoacetamide (DIAM) and monoiodoacetamide (MIAM) are the first- and second-most cytotoxic of 87 aliphatic DBPs, based on the fact that mammalian cell density is 50% compared to the control of the assay (Plewa and Wagner, 2015). Therefore, it is important to remove HAMs, particularly brominated and iodinated ones, according to their high toxicity (Richardson et al., 2008).

Although the pre-treatments to remove DBP precursors and the

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modification of disinfection methods can mitigate the formation of DBPs (Chu et al., 2015; Chuang and Mitch, 2017; Jiang et al., 2017; Li et al., 2017; Zhang et al., 2017), DBPs still presents ubiquitously in municipal drinking waters. Therefore, the third category, i.e. the removal of DBPs after their formation is significantly important for drinking water safety. Especially, relatively nontoxic, low cost, and effective methods for the mitigation of HAMs (esp., brominated and iodinated HAMs) and other DBPs are urgently needed.

A recent study investigated the effects of four commonly used quenching agents, i.e. sodium sulfite (S(IV)), sodium thiosulfate, ascorbic acid, and ammonium chloride, on the stability of HAMs. Results showed that S(IV) at a low dosage (20 μM) and pH of 7.0 led to a quick loss of HAMs, compared to the three other quenching agents (Ding et al., 2018). A previous study also indicated that several aliphatic DBPs were all adversely affected by S(IV) between sample collection at the sampling sites and analysis in the laboratory (Kristiana et al., 2014). It was also reported that trichloroacetonitrile (TCAN), chloropicrin, and cyanogen chloride all reacted with S(IV) to form dehalogenated species (i.e. dichloroacetonitrile, dichloronitromethane, and cyanogen, respectively) via dehalogenation reactions (Croue and Reckhow, 1989; Shang et al., 2005). Yiin et al. (1987) comprehensively explored the degradation of chloramines, including monochloramine, dichloroamine, and trichloroamine, in the presence of S(IV), and results indicated that reduction was proceeded through the transition state formed by nucleophilic attack of sulfite on Cl, coupled with proton donation to the non-bonding electron pair of N by H_3O^+ or by a buffer acid (Batterman et al., 2000). Also, some studies indicated that carbon bound to the halide was subjected to nucleophile attack by sulfite during the reduction of 3-bromopropene, 2-bromopropene, and 1-bromocyclohexane (Fam and Stenstrom, 1988; Haag and Mill, 1988). A common oxidation product of S(IV) is sulfate, which is relatively nontoxic. Xie (2003) summarized the degradation kinetics of a range of chlorinated and brominated DBPs. However, the degradation kinetics and reaction mechanisms of DBPs (especially for the highly-toxic iodinated HAMs) in the presence of S(IV) are still unknown and require to be further investigated.

The objectives of this study were to investigate the degradation kinetics of 10 HAMs, including dichloroacetamide (DCAM), bromochloroacetamide (BCAM), dibromoacetamide (DBAM), chloroiodoacetamide (CIAM), bromoiodoacetamide (BIAM), DIAM, trichloroacetamide (TCAM), bromodichloroacetamide (BDCAM), dibromochloroacetamide (DBCAM), and tribromoacetamide (TBAM), by S(IV) and to obtain a fundamental understanding of HAM decomposition mechanisms as well as the nature of consequent reaction products in the presence of S(IV). This study will provide new insight about the selective mitigation of brominated and iodinated DBPs in drinking water by a easy-operation and low-costs method.

2. Materials and methods

2.1. Materials

Monochloroacetamide (MCAM), DCAM, and TCAM were obtained from Alfa Aesar (Karlsruhe, Germany). Monobromoacetamide (MBAM) and MIAM were obtained from Sigma-Aldrich (St. Louis, USA). BCAM, DBAM, CIAM, BIAM, DIAM, BDCAM, DBCAM, and TBAM were all purchased from CanSyn Chem. Corp. (Toronto, Canada). The HAMs were dissolved separately in methanol (2 mg/mL) to prepare HAM stock solutions and then stored at 4 °C. The HAA mixed standard containing 9 HAAs was supplied by Supelco (St. Louis, USA). S(IV) (99%) and methyl *tert*-butyl ether (MTBE) were obtained from Aladdin Industrial Inc.

(Shanghai, China). S(IV) solution was freshly prepared by dissolving S(IV) in ultrapure water before use. All other chemical reagents were at least analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) unless otherwise noted. All solutions were prepared using ultrapure water produced by a Millipore Milli-Q Gradient water purification system (18 M Ω ·cm; Billerica, USA).

2.2. Experimental procedures

Batch experiments were performed in 1 L transparent glass volumetric bottles in the dark at 25.0 ± 0.5 °C. Into 1 L of 10 mM phosphate buffer (pH 6.0), 50 μL of individual trihalogenated HAM (THAM) stocking solution (2 mg/mL in methanol) was introduced to obtain the desired initial HAM concentration (i.e. 100 $\mu\text{g/L}$) at the start of each experiment, and then the predetermined volumes of S(IV) was injected into the aqueous samples to obtain the desired initial concentrations (0, 2.5, 5, 7.5, and 10 μM). The degradation of 4 THAMs with 5 μM S(IV) under pH 5.5, 6.0, 6.5, and 7.0 (10 mM phosphate buffer) were performed to investigate the effect of pH on the degradation of THAMs. In addition, to compare the effect of halogen substituent types of HAMs on the degradation rates, the degradation of 6 dihalogenated HAMs (DHAMs) (i.e. DCAM, BCAM, DBAM, CIAM, BIAM, and DIAM) with 5 μM S(IV) at pH 6 was conducted. For each experiment, a reference group with only HAMs, without S(IV) was added to distinguish the HAM hydrolysis from the reduction by S(IV). After predetermined time intervals, desired portions of the aqueous solution were withdrawn for DBP concentration analysis. A previous study demonstrated that the TCAN and chloropicrin underwent decomposition to form corresponding dehalogenated species in the presence of sulfite (Croue and Reckhow, 1989). To verify and elucidate the degradation pathway of the reaction of HAMs with sulfite, three DHAMs and two monohalogenated HAMs (MHAMs) were also targeted during the degradation of HAMs at pH 6.0. The volatilization of HAMs and HAAs is negligible owing to their high boiling points. The error bars in all figures represent the relative standard deviation of three analyses.

2.3. Analytical methods

HAMs were immediately extracted at the end of the predetermined reaction time by adding 2 mL MTBE to a 10 mL aqueous sample, which was then shaken for 3 min using a multi-tube vortex mixer (DMT-2500, Shanghai, China) at 2300 rpm. The HAMs were analysed immediately using a gas chromatograph equipped with an electron capture detector (GC/ECD; Shimadzu Corporation, QP2010plus, Japan). HAAs were derivatized to their corresponding esters using 10% sulfuric acid in methanol (v/v) and were analysed by the Shimadzu QP2010plus GC coupled with a QP2020 mass spectrometer (GC/MS) (Korshin et al., 2007). Injections of 1.0 μL of MTBE extract were separated via a splitless injector onto a GC column (RTX-5MS, 30 m \times 0.25 mm ID, 0.25 μm film thickness). Detailed information about the DBP analysis methods is available in the supplementary materials (Table S1) and described in a previous study (Chu et al., 2016a). Chloride and bromide were measured using an ion chromatography (Dionex ICS-1000, USA) (Chu et al., 2011).

3. Results and discussion

3.1. Kinetics of HAM degradation under different doses of S(IV)

The degradation of 4 THAMs were conducted individually under pH 6.0 condition with five different S(IV) doses (0, 2.5, 5,

7.5, and 10 μM). The pH of aqueous solutions were buffed at pH 6.0, because the degradation of three brominated THAMs by S(IV) at alkali conditions is too fast to determine the degradation kinetic constants during initial experiments. As is evident in Fig. 1, the relationship between HAM molar concentration and time was consistent with pseudo-first-order reaction kinetics for the degradation of HAMs by S(IV). The overall reaction can be expressed by Eq. (1) using K_{obs} as the pseudo-first-order observed rate constant. Rearranging and integrating Eq. (1) produces Eq. (2). The K_{obs} values for the degradation of HAMs in the presence of S(IV) can be calculated from the slope of the fitted line in Fig. 1 and are shown in Table S2. It should be noted that neutral water and hydroxide also result in the hydrolysis of HAMs (Chu et al., 2009; Yu and Reckhow, 2015). As shown in Fig. 1a, slight TCAM degradation was observed in the absence of S(IV), while the presence of S(IV) resulted in a rapid loss of the THAMs. Therefore, HAMs was predominantly degraded through the reaction of the HAMs with S(IV) and the hydrolysis of HAMs is minor fate mechanism. For HAMs degradation, K_{obs} can be expressed by Eq. (3). In Eq. (3), K_H and K_S represent the hydrolysis and S(IV) reaction rate constants, respectively.

$$\frac{d[\text{HAM}]}{dt} = -K_{obs} \times [\text{HAM}] \quad (1)$$

$$\ln[\text{HAM}] - \ln[\text{HAM}]_0 = -K_{obs} \times t \quad (2)$$

$$K_{obs} = K_H + K_S \quad (3)$$

$$K_{obs} = K_H + K_{app} \times [S(\text{IV})] \quad (4)$$

Fig. 1 and Table S2 show that the degradation rate of HAMs increased with the increase of S(IV) concentration, demonstrating that S(IV) concentration drove HAM degradation. Based on the previous study (Shang et al., 2005), K_{obs} can be expressed via a hierarchical structure, which is proposed in Eq. (4), in which K_{app} represents the apparent-second-reaction rate constant of S(IV). K_{obs} was fitted for the degradation of HAMs at different S(IV) concentrations through the application of linear least squares regression and by fixing the intercept at the K_{obs} value in the absence of S(IV) (Fig. SM1). The hydrolysis rate constants of the HAMs were determined and were shown in Table S3. Strong linear

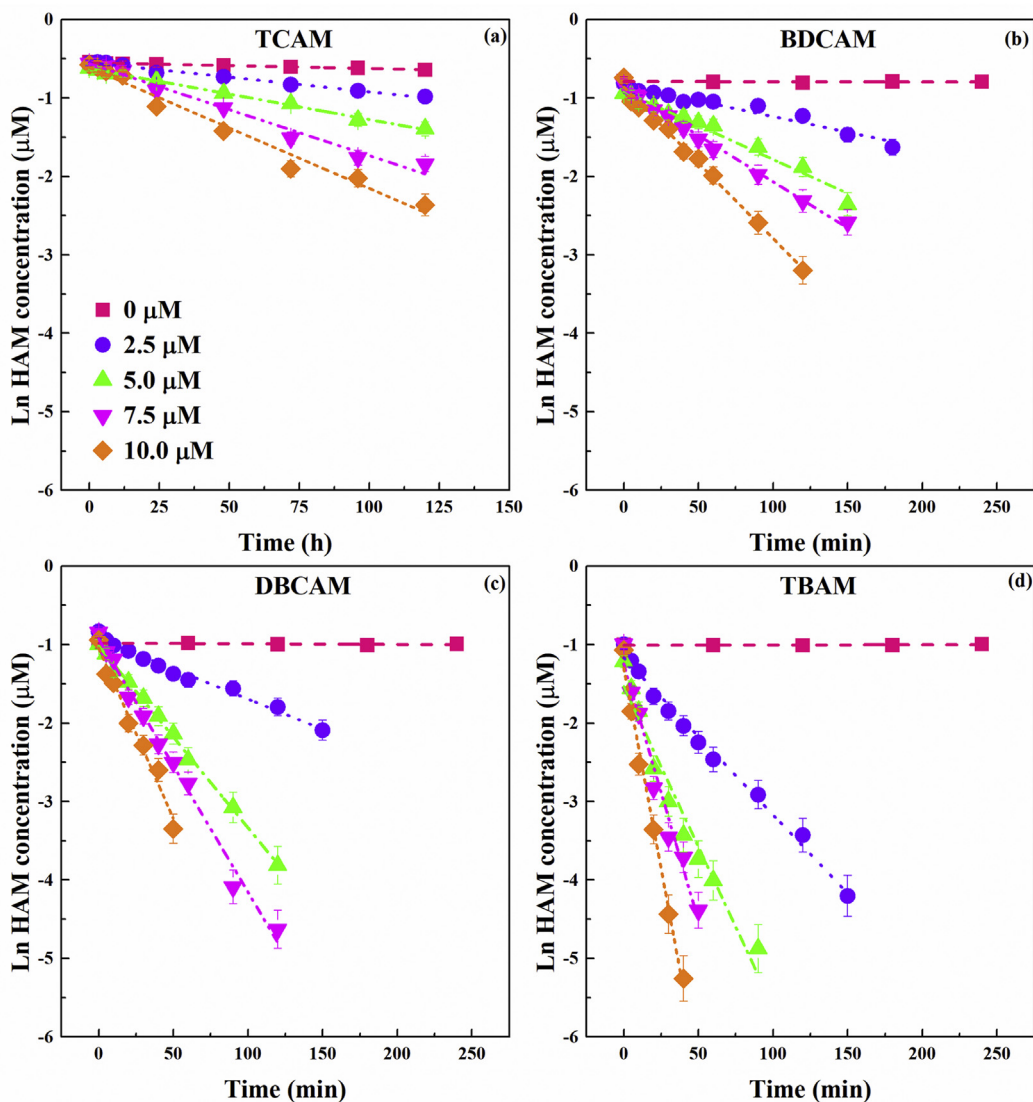
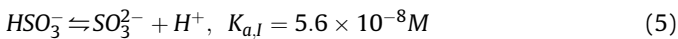


Fig. 1. Semilogarithmic plots of residual HAM concentrations versus reaction time for five S(IV) doses (i.e. 0, 2.5, 5, 7.5, and 10 μM) at pH 6.0. The symbols represent the experimental data, and the lines represent the linear least squares regression of the experimental data. The unit on the x axis is hour for Fig. 1a and min for the others.

regressions between S(IV) concentration and K_{obs} ($R^2 > 0.98$) indicated that the reaction between the HAMs and S(IV) followed second-order kinetics. It should be noted that the degradation of other DBPs by activated carbon or other treatment methods follow the two-stage degradation kinetic (Tung et al., 2006; Xie, 2003). The difference of the degradation kinetics for HAMs and other DBPs was attributed to the different degradation mechanisms. Fig. 1 illustrates that S(IV) reacted immediately with three brominated HAMs (i.e. BDCAM, DBCAM, and TBAM), resulting in the quick loss of brominated HAMs within 2 h under a S(IV) concentration of 10 μ M. However, the decomposition of TCAM was far slower than the brominated analogues and TCAM was not eliminated after 120 h of contact under the same conditions. The degradation rates for these four THAMs increased in the following order: TCAM \ll BDCAM $<$ DBCAM $<$ TBAM, which was consistent with a previous study indicating that compared with chlorinated HAMs, brominated HAMs were more easily reduced by zero-valent iron (ZVI) (Chu et al., 2016b). In general, the degradation of HAMs by the substitution of halogen atoms in the presence of S(IV) decreased in the following order: bromo- \gg chloro-, which was attributed to the different bond lengths and decreasing dissociation energies of the halogens (Croue and Reckhow, 1989). These phenomena will be discussed in detail in section 3.3.

3.2. Kinetics of HAM degradation at different pH levels

The reactivity of S(IV) depends on its speciation, which is pH-dependent (Eqs. (5) and (6)) (Croue and Reckhow, 1989). The α_0 and α_1 of Eq. (6) represent the distribution fractions of bisulfite and sulfite at a specific pH. To determine the effects of different S(IV) species (i.e. sulfite and bisulfite) on the decomposition of HAMs, the degradation of four THAMs (i.e. TCAM, BDCAM, DBCAM, and TBAM) with an initial S(IV) concentration of 5 μ M at pH 5.5, 6.0, 6.5, and 7.0 conditions was investigated in Fig. 2 (It is too fast to examine the degradation kinetics of three brominated THAMs at the alkali conditions). The degradation of TCAM was relatively slow compared to the brominated THAMs at all pH levels, which was consistent with last section. At pH 5.5, the three brominated THAMs were incompletely degraded up to 7 h, whereas they were completely degraded at pH 7.0 within 1 h as the same S(IV) concentration. As for the TCAM, less than half of it was decomposed at pH 5.5 after 120 h. Similar to that in the last section, the relationship between HAM molar concentration and time was consistent with pseudo-first-order reaction kinetics for the degradation of HAMs at different pH levels, and the K_{obs} can be calculated from the slope of the linear least squares regression fitted line in Fig. 2 (Eq. (2)).



$$\alpha_0 = \frac{[H^+]}{[H^+] + [K_{a,I}]}; \quad \alpha_1 = \frac{[K_{a,I}]}{[H^+] + [K_{a,I}]} \quad (6)$$

$$\frac{d[HAM]}{dt} = -\left(K_H + K_{HSO_3^-} \times [HSO_3^-]_t + K_{SO_3^{2-}} \times [SO_3^{2-}]_t\right) \times [HAM] \quad (7)$$

$$\frac{d[HAM]}{dt} = -\left(K_H + K_{HSO_3^-} \times \alpha_0 \times [S(IV)] + K_{SO_3^{2-}} \times \alpha_1 \times [S(IV)]\right) \times [HAM] \quad (8)$$

$$\ln[HAM] - \ln[HAM]_0 = -K_H \times t - \left(K_{HSO_3^-} \times \alpha_0 + K_{SO_3^{2-}} \times \alpha_1\right) \times [S(IV)] \times t \quad (9)$$

$$K_{obs} = K_H + \left(K_{HSO_3^-} \times \alpha_0 + K_{SO_3^{2-}} \times \alpha_1\right) \times [S(IV)] \quad (10)$$

$$K_{app} = \frac{(K_{obs} - K_H)}{[S(IV)]} = K_{HSO_3^-} \times \alpha_0 + K_{SO_3^{2-}} \times \alpha_1 \quad (11)$$

$$K_{app} = \frac{(K_{obs} - K_H)}{[S(IV)]} = K_{SO_3^{2-}} \times \alpha_1 \quad (12)$$

To clearly see the relationship between HAMs decomposition and the sulfite, the calculated apparent second-order rate constants K_{app} for HAMs decomposition and the distribution of sulfite and bisulfite under different pHs are presented in Fig. 3. With the increase of pH, the distribution ratio of sulfite and bisulfite increased, that is sulfite percentage increased, and the calculated K_{app} for HAMs decomposition increased. The positive relationship of K_{app} and sulfite levels indicates that the reaction of HAMs with S(IV) might depend on sulfite. The pH dependence of the full second-order rate constants can be formulated by Eqs. (7) and (8) to determine the specific reaction rate constants of sulfite and bisulfite. Rearranging and integrating Eq. (8) results in Eq. (9). Substituting Eq. (10) into Eq. (4) results in Eq. (11). Thereby, the apparent-second-order rate constants K_{app} for the degradation of HAMs by considering HAM reactivity with each of these two forms of S(IV) can be expressed as Eq. (11). Then, the $K_{HSO_3^-}$ and $K_{SO_3^{2-}}$ values for the degradation of HAMs can be calculated via the non-linear least squares regression and the reaction rate constants are shown in Table S5. Results showed that the values for $K_{SO_3^{2-}}$ were nearly two orders of magnitude higher than the $K_{HSO_3^-}$ values for the degradation of individual HAMs. A previous study also indicated that the role of bisulfite can be neglected during the degradation of chloropicrin and HANs (Croue and Reckhow, 1989). This is expected, as sulfite is a much stronger nucleophile than bisulfite (Croue and Reckhow, 1989). Therefore, the second-order degradation kinetics for HAMs can be expressed using Eq. (12) by dropping the bisulfite term, resulting in the higher degrees of freedom for kinetic functions. The $K_{SO_3^{2-}}$ values can be calculated from the slope of the fitted line in Fig. SM2 and are shown in Table 1. Good linear fit ($R^2 > 0.98$) in Fig. SM2 further confirmed that sulfite is the only reactive S(IV) ion for HAMs degradation.

3.3. Effect of halogen substituent types of HAMs on the degradation rates

Fig. 4 presents the reaction of S(IV) with six DHAMs, including DCAM, BCAM, DBAM, CIAM, BIAM, and DIAM, at pH 6.0 to investigate the effect of halogen substituent types on the degradation of HAMs. Similar to previous sections, the pseudo-first-order observed rate constant K_{obs} values for the degradation of DHAMs in the presence of S(IV) can be calculated from the slope of the fitted line in Fig. 4 and are shown in Table S6. The hydrolysis constants for 6 DHAMs at pH 6.0 were also shown in Table S6. The $K_{SO_3^{2-}}$ values for the degradation of DHAMs can be calculated using Eq. (12) and are shown in Table 1. Fig. 4 and Table 1 showed that the degradation rates for the 6 DHAMs increased in the following order: DCAM $<$ BCAM $<$ DBAM $<$ CIAM $<$ BIAM $<$ DIAM. The decomposition of DHAMs by S(IV) for the substitution of halogen atoms in water increased in the following order: chloro- \ll bromo- $<$ iodo-. For the three iodine-containing DHAMs, more than 50%

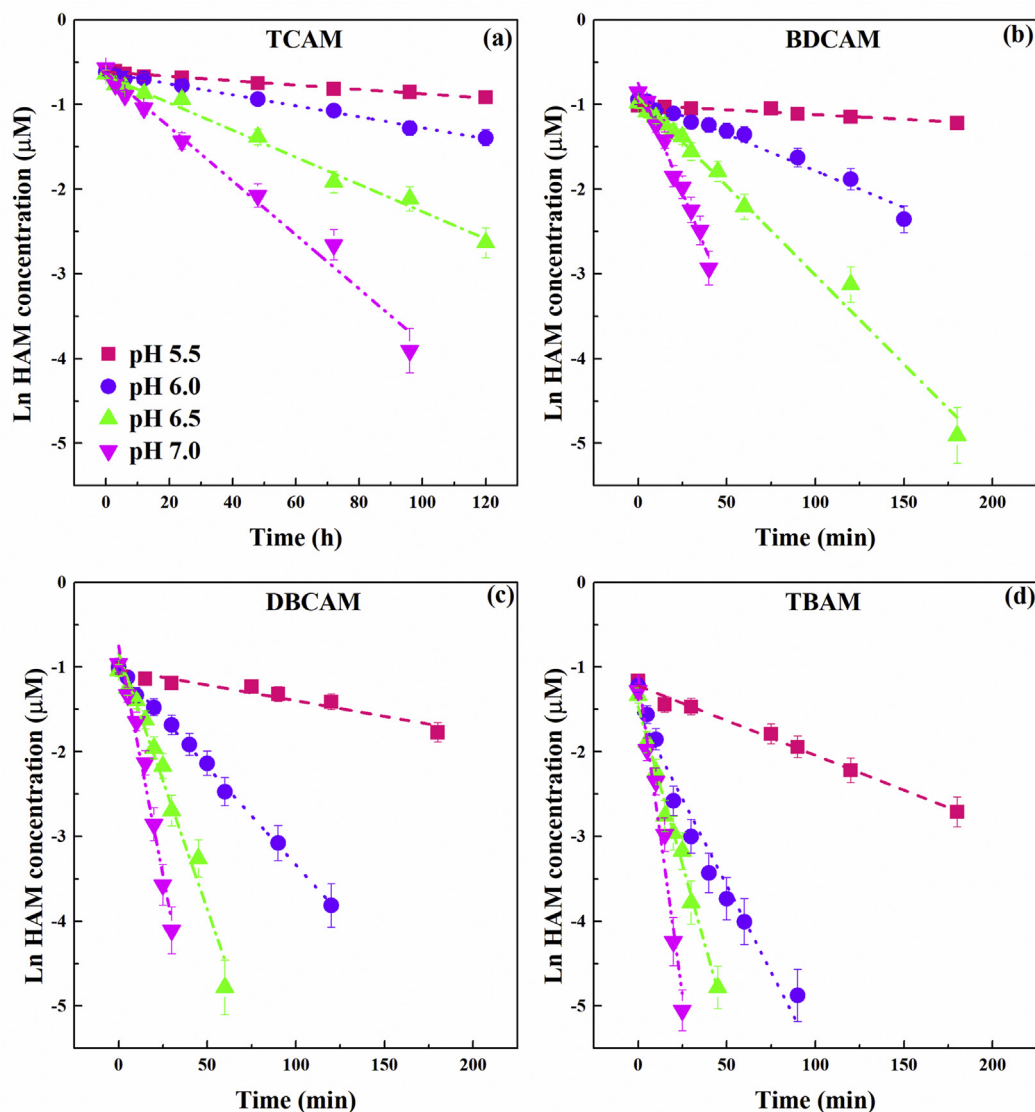


Fig. 2. Semilogarithmic plots of residual HAM concentrations versus reaction time for four pH levels (i.e. pH 5.5, 6.0, 6.5, and 7.0) with 5 μM S(IV). The symbols represent the experimental data, and the lines represent the linear least squares regression of the experimental data. The unit on the x axis is hour for Fig. 1a and min for the others.

disappeared after 48 h of reaction, whereas the loss of DCAM can be ignored until 96 h. Results showed that no significant difference existed for the decomposition of DCAM in the presence of S(IV) (Fig. SM3), whereas there was a substantial discrepancy in the other DHAM degradation rates between the absence of S(IV) and the presence of S(IV) (Table S6). The rank order and relative activity of the reaction of HAMs with S(IV) are related to their bimolecular nucleophilic substitution reaction ($\text{S}_{\text{N}}2$) reactivity (Croue and Reckhow, 1989). Owing to increasing bond length and decreasing dissociation energy, the leaving tendency of the halogen in alkyl halides followed the order $\text{I} > \text{Br} \gg \text{Cl}$. The $\text{S}_{\text{N}}2$ reactivity of alkyl iodide was 3-fold to 5-fold greater than that of alkyl bromide, which was 50-fold greater than that of alkyl chloride (Plewa et al., 2004). The degradation rate of DIAM by S(IV) in this study was 2.4-fold greater than that of DBAM, which was several orders greater than that of DCAM.

Because of a more rapid reaction at a higher pH, applying S(IV) under neutral or alkali conditions may be an efficient and promising method for the decomposition of brominated and iodinated HAMs, which have significantly higher toxicity than chlorinated

HAMs. Assuming that the hydrolysis and the competition from the other oxidants can be ignored, Eq. (13) derived by Eq. (12) can be used to predict the HAM concentration with time under specific pH and S(IV) concentration.

$$\frac{[\text{HAM}]}{[\text{HAM}_0]} = e^{-K_{\text{S}02^-} \times \alpha_1 \times [\text{S(IV)}] \times t} \quad (13)$$

As the real pH value in natural waters is around 7.5, Fig. SM4 presents the modelled degradation kinetics of HAM in the presence of 50 μM S(IV) at pH 7.5 based on Eq. (13). A rapid HAM degradation was estimated at pH 7.5 (Fig. SM4). It can be seen that the time for a half of HAMs decomposition were 13–19 mins for iodinated DHAMs (CIAM, BIAM, and DIAM), 30–42 mins for brominated DHAMs (BCAM and DBAM) and even 0.2–0.8 min for the brominated THAMs (BDCAM, DBCAM, and TBAM). Based on the rapid degradation of HAM in a few mins, a suggestion for HAM analysis may be that the addition of S(IV) as a quenching agent resulted in substantial loss of HAMs during the holding time and

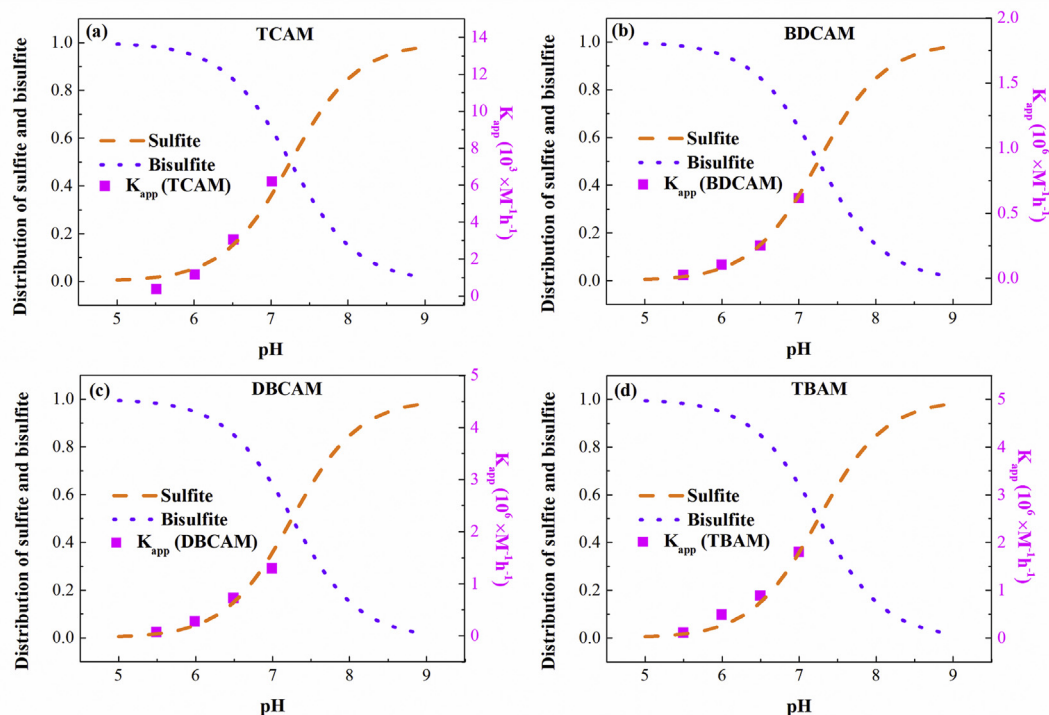


Fig. 3. pH-dependence of the apparent-second-order rate constants of THAMs degradation by S(IV). The square symbols represent apparent-second-order rate constants K_{app} calculated based on Eq. (11) and the dotted lines represent the distribution ratio of sulfite and bisulfite at specific pH calculated based on Eqs. (5) and (6).

Table 1
DBP degradation rate constants by sulfite.

DBP	TCAM	BDCAM	DBCAM	TBAM	DCAM	BCAM	DBAM	CIAM	BIAM	DIAM	TCAN ^a	Chloropicrin ^a
K_{SO_3} ($M^{-1} h^{-1}$)	1.71×10^4	1.72×10^6	3.82×10^6	5.24×10^6	NS	3.13×10^4	4.33×10^4	6.82×10^4	8.50×10^4	1.03×10^5	1.48×10^5	3.06×10^5

NS = Not significant, ^a adapted from [Croue and Reckhow \(1989\)](#).

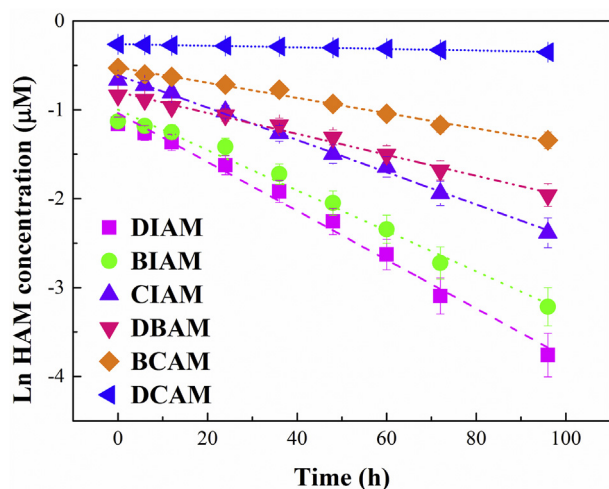


Fig. 4. Semilogarithmic plot of residual HAM concentrations versus reaction time for different halogen substituent types under pH 6.0 conditions with $5 \mu M$ S(IV). The symbols represent the experimental data, and the lines represent the linear least squares regression of the experimental data.

should be avoided. Additionally, considering that residual disinfectant is needed to prevent bio-growth in drinking water distribution systems, it was unsuitable to directly add sulfite into drinking water treatment plant effluents. As shown in [Fig. SM4](#), the

half degradation times for brominated and iodinated HAMs at pH 7 with $50 \mu M$ sulfite were less than 1 h. Therefore, it is better to apply sulfite nearby consumer point-of-use to remove HAMs and other potential DBPs.

3.4. Products and mechanisms of HAMs degradation by S(IV)

As shown in [Fig. 5a](#), the concentration of TCAM continuously decreased and the concentration of DCAM as a product of TCAM increased with time. [Fig. 5a](#) demonstrates that trichloroacetic acid (TCAA) as another product of TCAM formed after 24 h of contact and then gradually increased with time. [Fig. 5b, c, and 5d](#) show that reactions of BDCAM, DBCAM, and TBAM with S(IV) produced DCAM, BCAM, and DBAM, respectively. The hydrolysis products (i.e. HAAs) for three brominated THAMs were unidentified for the short reaction time and lower hydrolysis reaction rates ([Yu and Reckhow, 2015](#)). The rank order of the instability of HAMs by substitution of halogen atoms in water was chloro- > bromo- > iodo-, which can be explained by the different electronegativity of the halogens ([Ding et al., 2018](#); [Glezer et al., 1999](#)). The difference about the effects of halogen substitute type on the hydrolysis and reductive degradation by S(IV) was attributed to the different degradation mechanisms. The higher electron-withdrawing effect from the halogen activates amide carbon, the more easily renders electrophilic attack ([Yu and Reckhow, 2015](#)). However, there was a substantial discrepancy between the molar sum of the residual THAMs, formed DHAMs (i.e. dehalogenated species), and corresponding HAAs and

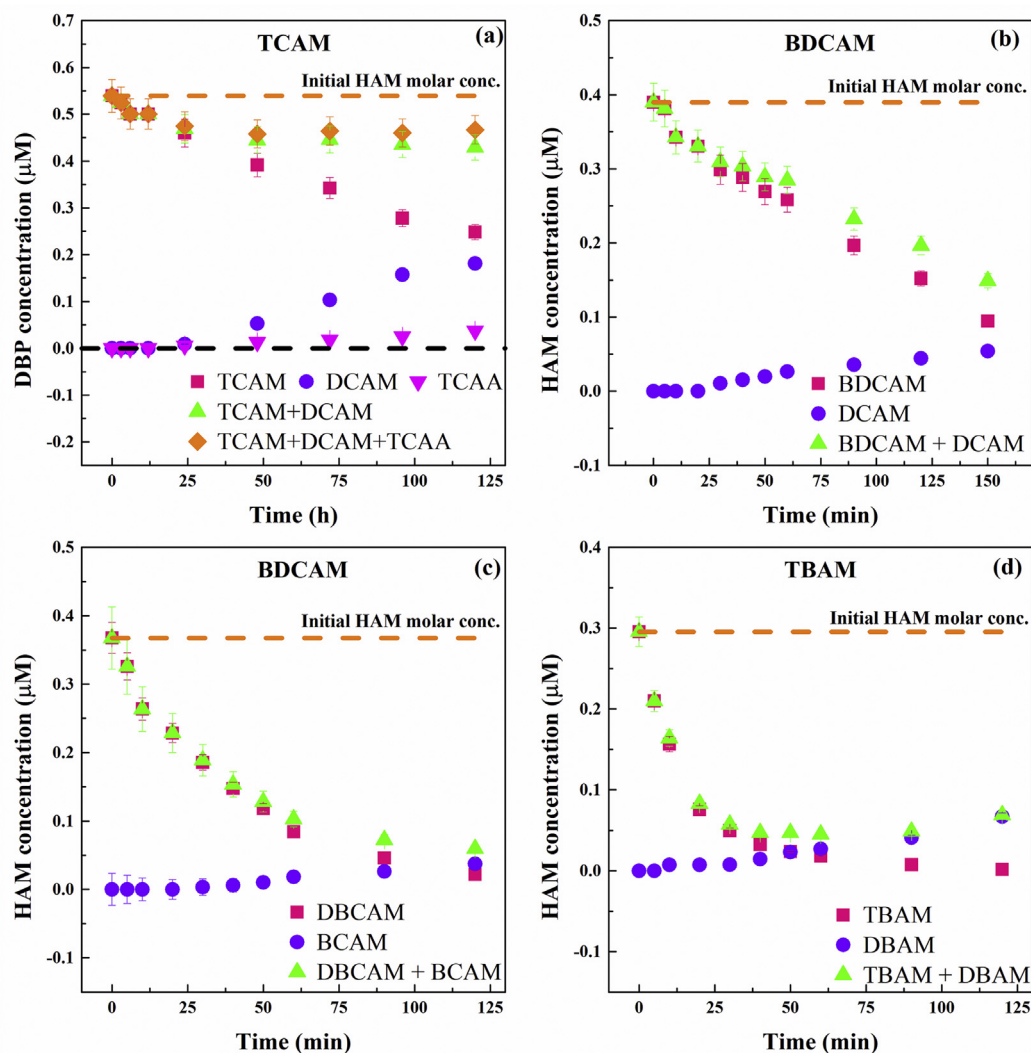


Fig. 5. Degradation of THAMs and formation of products for the reaction of HAMS with 5 μM S(IV) at pH 6.0. The symbols and orange dashed lines represent the experimental data and initial HAM molar concentration, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

the initial THAM doses (Fig. 5). Besides, the mass balance was not attributed to the formation of MHAMs, as MCAMs and MBAMs were not identified. The molar concentration of TCAM + TCAA + DCAM (Fig. 5a), BDCAM + DCAM (Fig. 5b), and DBCAM + BCAM (Fig. 5c) decreased with time, whereas the sum molar concentration of DBAM and TBAM (Fig. 5d) decreased initially and then increased. The notable mass loss indicates that there must be some other unknown intermediate products, which was reported as the first time. Previous studies indicated dichloronitromethane and dichloroacetonitrile were the main products of the reaction of sulfite with chloropicrin and TCAN (Croue and Reckhow, 1989; Shang et al., 2005).

It was also reported that the reaction of haloalkanes with sulfite generated alkyl sulfonate, which was not observable via the solvent extraction procedure used for analysis of haloalkanes, and alkyl sulfonate did not hydrolyse rapidly within the time frame of the experiments (Fam and Stenstrom, 1988; Haag and Mill, 1988). During reductive dehalogenation, HAMS decomposition occurred via nucleophilic attack by sulfite, which is consistent with the $\text{S}_{\text{N}}2$ mechanism (Rossi et al., 2003). The α -carbon bound to the amide group undergoes nucleophilic attack at 180° to the leaving group (halide), as this provides the best overlap between the

nucleophile's lone pair and the C-X σ^* antibonding orbital, generating a transition state pentacoordinate (Kuder et al., 2012). Then, the halide is pushed off the opposite side (Kuder et al., 2012). Breaking of the C-X bond and formation of the new C-S bond occur simultaneously to form dehalogenated products. Therefore, this unknown immediate product was proposed to be HAM sulfonate (Fig. 6). HAM sulfonate quite slowly hydrolyses to form corresponding HAMS (Haag and Mill, 1988; Yiin et al., 1987), which explained that the molar sum concentration of TBAM and DBAM first decreased and then increased (Fig. 5d). In addition, experiments applying TCAM (1 mg/L) and TBAM (1 mg/L) reacted with 50 μM S(IV) at pH 7.0 were also conducted to quantify the halide concentrations. Fig. SM5 shows that the halide concentrations are nearly equal to the initial HAM concentrations when the TCAM or TBAM completely disappeared and neither MCAM nor MBAM were detected. Therefore, the α -carbon bound to the amide group undergoes nucleophilic attack by sulfite, resulting in the degradation of HAMS (Fig. 6). Besides, the nature of the substituents (bound to carbon atom of the CX_3 -group) influences the reaction rate due to its electron-donor or withdrawing effect. Electron-withdrawing groups make the carbon atom of the CX_3 -group more electrophilic, so that the reaction rates of HAMS with S(IV) should be faster.

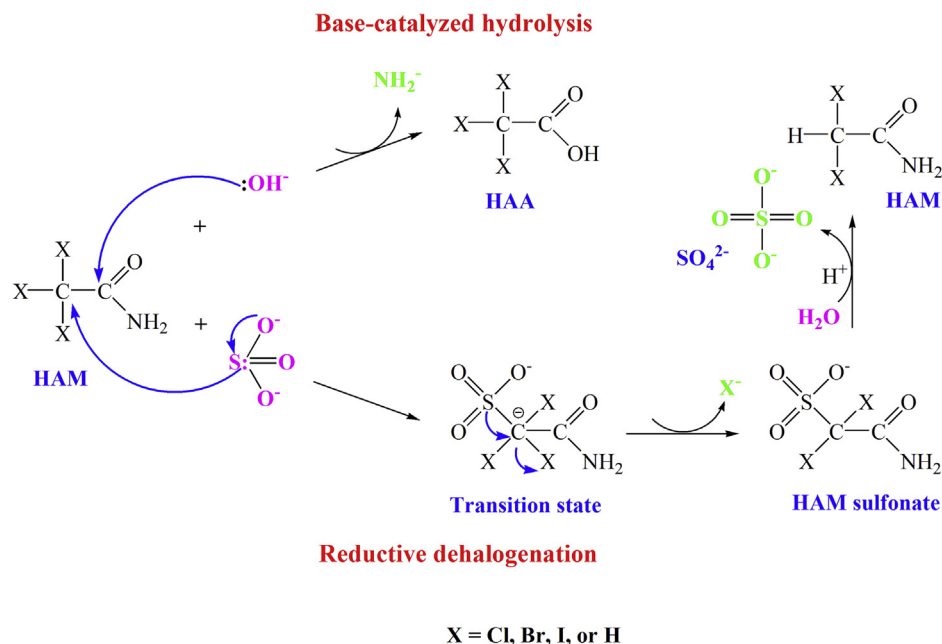


Fig. 6. Proposed mechanisms of HAM hydrolysis and reductive dehalogenation by sulfite.

Comparing the rates of chloropicrin, TCAN, and TCAM (Table 1), results show that the reaction rates increased with the increasing electron-withdrawal of substituents ($-\text{NO}_2 > -\text{CN} > -\text{CONH}_2$).

In an alternate mechanism (Fig. SM6), the nucleophilic attack by sulfite occurs at halides rather than at α -carbon bound to amide group, resulting in the formation of a transition state via a proton transfer to HAM as halide (+1) transfers to the sulfur of sulfite. Previous studies showed that this proposed transition state was very unstable (Yiin et al., 1987; Yiin and Margerum, 1990). The first product of this reaction would be the halosulfate (XSO_3^-) and corresponding dehalogenated HAM (Yiin et al., 1987). Accordingly, this reaction may also account for the formation of dehalogenated HAM. Hence, the nucleophilic attack by sulfite may also occur at the halide.

4. Conclusions

Under a pH range of 5.5–7.0, brominated and iodinated HAMs decompose immediately when exposed to S(IV), whereas the reactions of S(IV) with chlorinated HAMs (i.e. DCAM and TCAM) were much slower. The results indicated that the degradation of HAMs exhibited pseudo-first-order reaction kinetics and the degradation rates of the 10 HAMs decreased in the following order: TBAM > DBCAM > BDCAM > DIAM > BIAM > CIAM > DBAM > BCAM > TCAM > DCAM. The destruction of HAMs was primarily attributable to the chemical reduction pathway, whereas the hydrolysis of HAMs, excluding TCAM, can be ignored under pH 5.5–7.0. The degradation kinetics were well described by a second-order kinetics model, first-order in S(IV) and first-order in HAMs, and the second-order kinetics constants ranged from negligible quantity (DCAM) to $5.24 \times 10^6 \text{ M}^{-1} \text{ h}^{-1}$ (TBAM). The reaction of S(IV) with HAMs is mainly with respect to sulfite rather than to bisulfite. The degradation rates increased with increasing concentration of S(IV) and pH, which can be explained by the increase of sulfite with the increase of pH. The HAM sulfonate, was formed as the main intermediate product during HAMs decomposition, via a nucleophilic substitution reaction on the α -carbon bound to the amide group. It should be noted that HAM sulfonate was not

directly identified by instruments. Based on the HAM kinetic model established in this study, the calculated brominated and iodinated HAM half-times in drinking water were less than 1 h in the condition of $50 \mu\text{M S(IV)}$ and pH 7.5. Therefore, the simple addition of S(IV) in drinking water may be a promising method to remove the brominated and iodinated HAMs which have significantly higher toxicity than chlorinated HAMs and many other aliphatic DBPs. And, it is important to note for HAM analysis that the addition of S(IV) as a quenching agent results in substantial loss of HAMs during the holding time between sample collection and analysis, and thus it should be avoided during the collection of the HAM sample.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.watres.2018.06.049>.

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