



Halogenating reaction activity of aromatic organic compounds during disinfection of drinking water

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ABSTRACT

The halogenating reactions of five aromatic organic compounds (AOCs) with aqueous chlorine (HOCl/OCl^-) and aqueous bromine (HOBr/OBr^-) were studied with an aim to compare the formation properties of haloacetic acids (HAAs) for the corresponding chlorination or bromination reactions of AOCs, respectively. The experiment results indicated that the HAAs substitution efficiency for the bromination reactions of AOCs was greater than that for the chlorination reactions, and the formation of HAAs had a strong dependence on the chemical structure of AOCs. The chlorination or bromination reaction activities for the AOCs with electron donating functional groups were higher than that for them with electron withdrawing functional groups. The kinetic experiments indicated that the reactions of aqueous bromine with phenol were faster than those of aqueous chlorine with phenol and the halogen consumption exhibited rapid initial and slower consumption stages for the reactions of phenol with aqueous chlorine and bromine, respectively. In addition, the HAAs production for the chlorination reaction of phenol decreased with the increase of pH. These conclusions could provide the valuable information for the effective control of the disinfection by-products during drinking water treatment operation.

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1. Introduction

Drinking water safety is a widespread environmental problem. The disinfection has been widely used in drinking water treatment around the world to protect consumers against water-borne infectious diseases, and chlorination has been utilized as a kind of disinfection methods for nearly 100 years. Since the pioneering work of Rook [1], disinfection by-products (DBPs) have been a major concern during drinking water disinfection due to their potential harm to human health. Trihalomethanes (THMs) and haloacetic acids (HAAs) are the most prevalent DBPs. These DBPs in drinking water are suspected to be toxic, carcinogenic, and/or mutagenic to humans if ingested over extended years, or have acute reproductive and developmental effects [2–4].

HAAs consist of a total of nine chlorine- and/or bromine-containing species. The current maximum allowable running annual average (RAA) concentration of HAA5 (the sum of the monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, trichloroacetic acid, and dibromoacetic acid) is regulated at 60 $\mu\text{g}/\text{L}$ in the US Stage 1 Disinfectants/Disinfection By-products Rule (D/DBPR)[5]. Dihalooacetic acids (DXAAs) generally pose the great-

est health concerns, compared to monohalogenated HAAs (MXAAs) and trihaloacetic acids (TXAAs) [6].

In water treatment plants, hypobromous acid (HOBr) is more powerful than hydrochlorous acid (HOCl) and its role in the formation of DBPs is analogous to that of HOCl. Symons et al. [7] had indicated that the reaction of natural organic matter (NOM) with aqueous bromine (HOBr/OBr^-) was faster than that of NOM with aqueous chlorine (HOCl/OCl^-). The pK_a value of aqueous chlorine (7.5) is lower than that of aqueous bromine (8.8). Common disinfectants (HOCl, O_3) could rapidly oxidize Br^- to form HOBr/OBr⁻ [8,9]. The bromide ion can shift the distribution of HAAs to more brominated species [10], including bromodichloromethane, dibromochloromethane, bromoform and brominated acetic acids. The distribution of chlorinated DBPs and brominated DBPs depends on the ratios of HOCl/Br⁻ [11], Br⁻/NOM and Br⁻/free chlorine [12]. The disinfectant of ozone could oxidize Br⁻ in source water to form excessive bromate in the light of the recent D/DBP rule on the maximum permissible contaminant level of bromate (0.01 mg/L) [13]. Some brominated organic DBPs pose more significant health risks than chlorinated analogs [14]. Most of the experiments measured the formation of DBPs were conducted by adding HOCl to water in the presence of Br⁻ [15]. However, few studies were made to provide sufficiently direct comparison for the reaction activities of aromatic organic compounds (AOCs) with aqueous chlorine and aqueous bromine, respectively, and the

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knowledge of the comparison is needed for developing effective control technologies for DBPs in water treatment processes.

In recent years, some studies have indicated that AOCs in polluted source water have the similar chemical structures to humic substances. AOCs could react with aqueous chlorine to form DBPs during the disinfection procedure [9,16–21]. Hydroxy- and amino-functional groups on aromatic rings can increase their reaction activities with aqueous chlorine, and compounds with hydroxy-functional groups had high halogen consumption. Aqueous chlorine and bromine consumption by AOCs varied depending on their characteristics, but generally electron donating functional groups on AOCs result in an increase in the reaction rate for the reactions of AOCs with aqueous chlorine or aqueous bromine, and the reaction activities of methoxyl, hydroxy and ketonic functional groups on aromatic rings with aqueous chlorine are higher than that of alkyl or carboxyl functional groups. Few studies focused on the effects of functional groups on AOCs on the formation properties of DBPs for the reactions of AOCs with aqueous chlorine or aqueous bromine.

Considering all factors above, five AOCs with the representative functional groups were selected as potential DBP precursors to study the formation properties of HAAs from the reactions of AOCs with aqueous chlorine and bromine, respectively. The purpose of this study is to investigate (1) the HAAs production for the reactions of AOCs with aqueous chlorine or bromine, respectively, and the effects of functional groups on halogen consumption and HAAs formation; (2) the rate constants for the reactions of phenol with aqueous bromine and chlorine, respectively; (3) the effect of pH on HAAs production for the chlorination reaction of phenol. These results could provide more effective control of DBPs formation during drinking water treatment operation.

2. Materials and methods

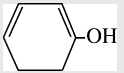
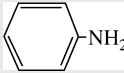
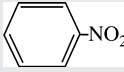
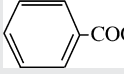
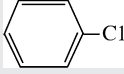
2.1. Materials

General functional groups have hydroxyl, amino, carboxyl, nitro, chlorine groups and so on. Previous studies have shown that aromatic structure of humic substances has higher halogenation activity. In recent years, organic compounds in polluted source water have mainly consisted of monocyclic aromatic hydrocarbon and polycyclic aromatic hydrocarbon. In order to examine effects of model functional groups on halogenation activity for reactions between AOCs with aqueous chlorine and aqueous bromine, respectively, Phenol, aniline, nitrobenzene, benzoic acid and chlorobenzene were selected as the representative AOCs and obtained from Acros Organics (USA). The five AOCs have similar chemical structure and model functional groups. Selected physico-chemical properties of the representative AOCs were presented in Table 1. Chloroacetic acid, dichloroacetic acid, trichloroacetic acid, bromoacetic acid, dibromoacetic acid and tribromoacetic acid were obtained from Acros Organics (USA) and the purities of them are greater than 99%. All reagents and chemicals were of analytical grade. The aqueous chlorine stock solution was prepared from commercial sodium hypochlorite (NaOCl, 5% active chlorine) and then diluted with super-pure water. The acute concentration of sodium hypochlorite solution was standardized by sodium thiosulfate titration, whereas aqueous bromine stock solution was prepared from pure liquid bromine. The pH of solution were adjusted by phosphoric acid solution and measured with a pH meter.

2.2. Reaction procedure

AOCs solutions were prepared and the pH of those was adjusted to be 7.5 with phosphoric acid solution. The excessive bromine or

Table 1
Summary of organic carbon sources

Molecular formula	Material	Molecular structure	MW (g/mol)
C ₆ H ₅ OH	Phenol		94.1
C ₆ H ₅ NH ₂	Aniline		93.1
C ₆ H ₅ NO ₂	Nitrobenzene		123.1
C ₆ H ₅ COOH	Benzoic acid		122.1
C ₆ H ₅ Cl	Chlorobenzene		112.5

chlorine was added, respectively, to AOCs samples in the reactors, which were placed in air bath with temperature maintained at 25 °C and reciprocating rate at 150 rpm. Samples were taken out at 24 h and residual halogen concentrations were measured at 24 h. The halogen residual in samples was decomposed by adding excess sodium thiosulfate. Within 24 h the samples were analyzed for HAAs.

Kinetic experiments were conducted to obtain second-order rate constants for the reactions of phenol with aqueous chlorine or bromine, respectively. Aqueous bromine and chlorine with a concentration of 2 μmol/L were respectively added to samples with initial phenol concentrations ranging from 0 to 100 μmol/L (assuming a carbon molecular weight of 12 g/mol). Pseudo-first-order rate constants were calculated for each phenol concentration and used to obtain second-order rate constants. Samples were taken out and the residual concentrations of aqueous bromine and chlorine were monitored over time respectively. The other kinetic experiment conditions were the same as above.

Aqueous chlorine with a concentration of 2 mg/L was added to samples with phenol concentration of 5 mg/L, of which the pH was adjusted to be 6, 7, 8, 9, respectively with phosphoric acid solution in the reactors, and placed in air bath with temperature maintained at 25 °C and reciprocating rate at 150 rpm. Samples were taken out at 24 h. The residual chlorine in samples was decomposed by adding excess sodium thiosulfate. The samples were analyzed for HAAs within 24 h.

2.3. Analytical methods

Aqueous chlorine and bromine concentrations were measured by the colorimetric *N,N*-diethyl-*p*-phenylenediamine (DPD) method [22], using a IPOA-2001 Spectrophotometer. DOC concentrations were determined using a catalytic-thermal combustion method with infrared gas analysis (Shimadzu TOC 5050A Analyzer). A micro-extraction procedure (extracting with methyl-*tert*-butyl ether and esterified with acidic methanol) was used for the HAAs analysis. The concentration of HAAs in the extraction was measured by gas chromatograph (Agilent 6890N) with an ECD and a fused silica capillary column (HP-5, 30 m × 0.32 mm i.d. × 0.25 μm film thickness), using a modified EPA method of 552.2 [23].

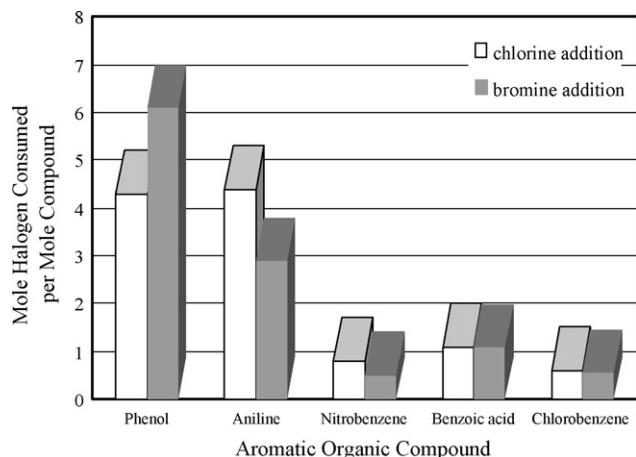


Fig. 1. Aqueous chlorine or bromine consumption in the reactions of AOCs with aqueous bromine and chlorine, respectively.

3. Results and discussion

3.1. Halogen consumption

Halogen consumption in the reactions of five AOCs with aqueous chlorine and bromine, respectively after the reaction period of 24 h was measured and the results were shown in Fig. 1. Aniline, had the largest aqueous chlorine consumption (mole aqueous chlorine consumed per mole compound), and chlorobenzene had the smallest one. Aqueous bromine consumption (mole aqueous bromine consumed per mole compound) of AOCs ranged from approximately 6.1 mol/mol for phenol, with one hydroxyl functional group ($-\text{OH}$), to 0.5 mol/mol for nitrobenzene, with one nitro functional group ($-\text{NO}_2$). Meanwhile, aniline and nitrobenzene consumed more aqueous chlorine than aqueous bromine, while phenol consumed more aqueous bromine than aqueous chlorine and the other substituted benzenes consumed similar amounts of aqueous bromine and aqueous chlorine. Overall, regarding halogen consumption (considering aqueous chlorine and aqueous bromine all together), the order was phenol > aniline > benzoic acid > nitrobenzene > chlorobenzene. That is to say, the effect of functional groups of compounds on the halogen consumption of AOCs followed the order of hydroxyl > amido > carboxyl > nitro > chlorine.

The results demonstrated that the distribution of model functional groups on benzene rings of AOCs influenced reaction activities of AOCs with halogen. Aqueous chlorine and bromine consumption by AOCs varied depending on their characteristics, but they were greatly affected by the presence of electron donating (hydroxyl, amido) or electron withdrawing (carboxyl, nitro, chlorine) functional groups. Norwood et al. [24] reported that resorcinol had higher chlorine consumption than vanillic acid and syringic acid. In a word, AOCs with electron donating functional groups easily and rapidly reacted with aqueous chlorine and aqueous bromine, respectively, which could be responsible for the high aqueous chlorine and bromine consumption.

3.2. HAAs formation

HAAs formation for five kinds of AOCs reaction with aqueous chlorine and bromine, respectively was shown in Table 2 and Table 3. HAAs production was measured in parallel with the halogen consumption experiments for the same reaction period of 24 h. In Table 2, HAAs production (HAAs produced per mole compound) ranged from about 0.62×10^{-3} mol/mol to

Table 2

HAAs formation per mole model compound with reaction chlorine (10^{-3} mol/mol) (reaction time = 24 h; pH 7.5)

Compound	Chloroacetic acid	Dichloroacetic acid	Trichloroacetic acid	HAAs
Phenol	0.84	16.45	31.78	49.07
Aniline	0.56	9.62	36.07	46.25
Nitrobenzene	0.00	0.29	0.49	0.78
Benzoic acid	0.00	0.34	0.71	1.05
Chlorobenzene	0.00	0.00	0.62	0.62

49×10^{-3} mol/mol. Meanwhile, in Table 3, HAAs production was the largest for the reaction of phenol with aqueous bromine and the smallest for the reaction of nitrobenzene with aqueous bromine among the reactions of five kinds of AOCs with aqueous bromine. Therefore, the order for the effect of functional groups on HAAs formation (aqueous chlorine and bromine synchronously) was phenol > aniline > benzoic acid > nitrobenzene > chlorobenzene.

The order for halogen consumption was the same as the one for HAAs formation for the reactions of AOCs with aqueous chlorine and bromine. But the reactions of AOCs with aqueous chlorine or bromine, respectively could produce a lot of DBPs (THMs, HANs, MX and so on) except HAAs, if halogen consumption for the reactions were high, HAAs production for the reactions were not always high. But the same as the former conclusion, HAAs production were higher for the reactions of compounds with electron donating functional groups towards aqueous chlorine or bromine than that for those of compounds with electron withdrawing functional groups. The literature lacks sufficiently direct evidence for the yield of HAAs for the reactions of AOCs with aqueous chlorine and bromine, respectively, and most of the literature was available on THMs production for the reactions of organic compounds with aqueous chlorine. Westerhoff et al. [25] had indicated that resorcinol, which contains two hydroxyl functional groups, had larger THMs yield than phenol, and compounds with hydroxyl functional groups had more THMs formation than them with carboxyl functional groups. Gallard and Von Gunten [9] and Rostad et al. [20] suggested that di-hydroxy-benzoic acids had high reaction activities towards aqueous chlorine. Together, the formation of HAAs had a strong dependence on the chemical structure of AOCs, and the electron donating functional groups resulted in an increase in HAAs production whereas the electron withdrawing functional groups had the opposite effects.

HAAs formation for the reactions of phenol, benzoic acid and chlorobenzene with aqueous bromine were larger than that for the reactions of them with aqueous chlorine, but aqueous bromine consumption was larger than aqueous chlorine consumption only for the corresponding bromination or chlorination reaction of phenol (Fig. 1), because the efficiency of HAAs substitution (R) was greater for aqueous bromine than for aqueous chlorine and it could be calculated by the following formula:

$$R = \frac{\text{HAAs}}{X_2} = \left(\frac{\text{HAAs}}{\text{compound}} \right) / \left(\frac{X_2}{\text{compound}} \right) \quad (1)$$

Table 3

HAAs formation per mole model compound with reaction bromine (10^{-3} mol/mol) (reaction time = 24 h; pH 7.5)

Compound	Bromoacetic acid	Dibromoacetic acid	Tribromoacetic acid	HAAs
Phenol	2.59	20.54	49.13	72.26
Aniline	1.35	13.89	20.07	35.31
Nitrobenzene	0.00	0.11	0.45	0.56
Benzoic acid	0.17	0.25	0.68	1.10
Chlorobenzene	0.00	0.15	0.43	0.58

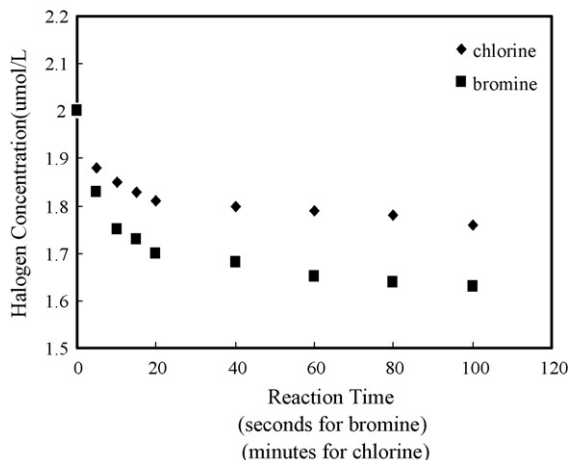


Fig. 2. Kinetic reactions of phenol with aqueous bromine and chlorine, respectively (initial halogen dose = 2 $\mu\text{mol/L}$; pH = 7.5; [DOC] = 40 $\mu\text{mol/L}$).

For phenol, aniline, nitrobenzene, benzoic acid and chlorobenzene, the efficiencies of HAAs substitution for chlorine were 1.14×10^{-2} , 1.05×10^{-2} , 9.75×10^{-4} , 9.55×10^{-4} , and 1.04×10^{-3} mol/mol, respectively, and the efficiencies of HAAs substitution for bromine were 1.18×10^{-2} , 1.21×10^{-2} , 1.12×10^{-3} , 1.02×10^{-3} and 1.04×10^{-3} mol/mol, respectively. Based on the HAAs substitution efficiency, aqueous bromine is a more effective substituting halogen than aqueous chlorine. Westerhoff et al. [25] suggested that bromoform production upon aqueous bromine consumed was higher than chloroform production upon aqueous chlorine consumed for phenol, aniline, and benzoic acid.

3.3. Rate constants

Kinetic experiments for the reactions of phenol with aqueous chlorine and aqueous bromine, respectively, were conducted and the results were shown in Fig. 2. Aqueous bromine reacted with phenol on the order of seconds, and aqueous chlorine reacted with phenol on the order of minutes. Halogen concentration decreased with the increase of reaction time for the reactions of phenol with aqueous chlorine and aqueous bromine, respectively, but the reaction of phenol with aqueous bromine was more rapid than that of phenol with aqueous chlorine and aqueous bromine consumption was larger than aqueous chlorine consumption. For the reactions of phenol with aqueous chlorine and aqueous bromine respectively, halogen consumption exhibited rapid initial and slower consumption stage. The reaction time of rapid initial consumption stage was from 0 to 20 s for the reaction of phenol with aqueous bromine and from 0 to 10 min for the reaction of phenol with aqueous chlorine. The reaction time of slower consumption stage was from 20 to 100 s for the reaction of phenol with aqueous bromine and from 10 to 120 min for the reaction of phenol with aqueous chlorine. That is to say, the cross-over between two reaction stages occurred over 10 min for the reaction of phenol with aqueous chlorine and 20 s for that of phenol with aqueous bromine.

Kinetic experiments for the slower consumption stage of the reaction of phenol with aqueous chlorine were shown in Fig. 3 (kinetic experiments for the slower consumption stage of the reaction of phenol with aqueous bromine were not shown). Pseudo-first-order rate constants (k ; min^{-1}) were calculated from the analysis of kinetic experiments for the reaction of phenol with aqueous chlorine at a range of DOC concentrations (from 0 to 100 $\mu\text{mol/L}$). Reaction time for the slower consumption stage of the reaction of phenol with aqueous chlorine was 10, 15, 20, 40,

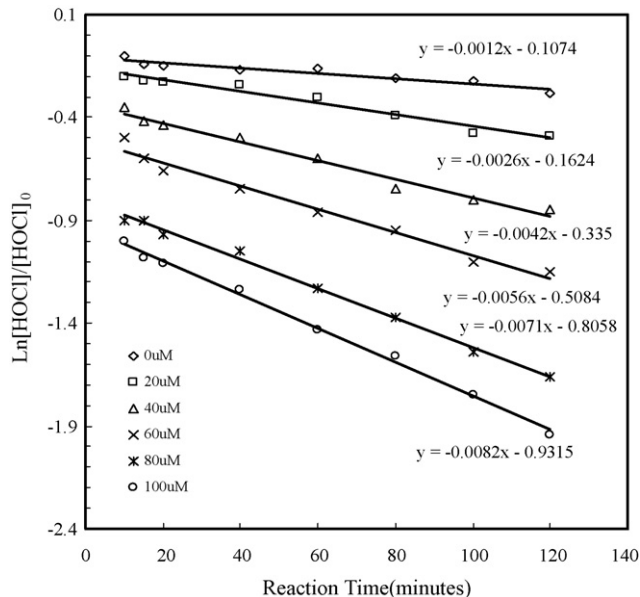


Fig. 3. Pseudo-first-order rate constants (k) for the reaction of phenol with aqueous chlorine.

60, 80, 100 and 120 min. As shown in Fig. 3, the rate of aqueous chlorine consumption increased with higher DOC concentrations and pseudo-first-order rate constants were indicated as the slope of the linear regression through data. The pseudo-first-order and second-order reaction rates were considered:

$$r = \frac{d[\text{HOCl}]t}{dt} = -k[\text{HOCl}]t = k'[\text{phenol}][\text{HOCl}]t \quad (2)$$

where $k = k'[\text{phenol}]$ and k' is a second-order rate constant. Fig. 4 indicated the analysis of k' for the reactions of phenol with aqueous chlorine and aqueous bromine respectively and illustrated a plot of k' values for different DOC concentrations. The slope from the linear analysis of data indicated a second-order rate constant (k'). The value of k' was $160 \text{ M}^{-1} \text{ s}^{-1}$ for the reaction of phenol with aqueous bromine and $70 \text{ M}^{-1} \text{ min}^{-1}$ for the reaction of phenol with aqueous chlorine, which indicated that the reaction of phenol with aqueous bromine was more easy and rapid than that with aqueous chlorine. Evidence from the model compounds work could suggest that the compounds bonded with electron donating functional groups resulted in greater k' values than those bonded with electron withdrawing functional groups in reactions with oxidants.

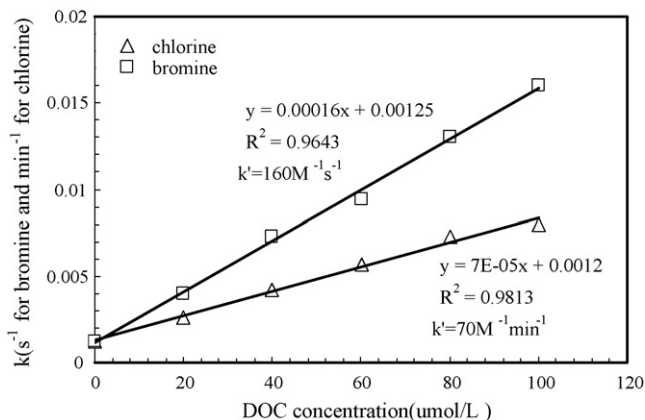


Fig. 4. Analysis of k' for the reactions of phenol with aqueous chlorine and bromine, respectively.

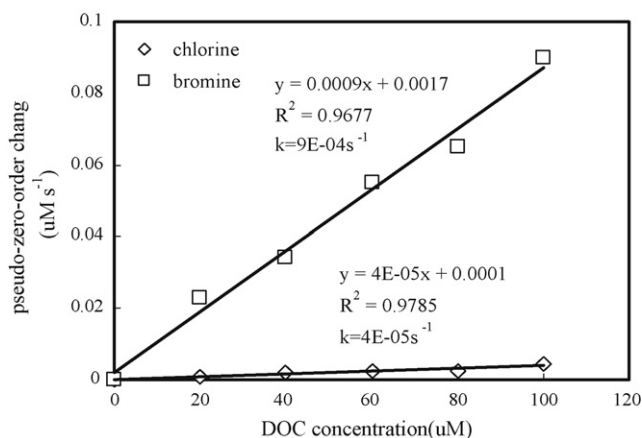


Fig. 5. Pseudo-first-order rate constants (k) for the reactions of phenol with aqueous chlorine and bromine, respectively, during the rapid initial consumption stage.

For the rapid initial consumption stage of the reactions of phenol with aqueous chlorine and aqueous bromine, respectively, halogen consumption was a function of DOC concentrations (Fig. 5). Due to fast reaction rate during the rapid initial stage, rate constants (k) could be estimated based upon the following series of the assumption: (1) observed change in aqueous chlorine or bromine concentration was pseudo-first-order; (2) the samples were completely mixed and rate constants could only be estimated from pseudo-zero-order calculations using the observed data, for example, pseudo-zero-order change ($\Delta\text{halogen}/\Delta t$, $\Delta t = 10$ min for phenol reaction with aqueous chlorine and $\Delta t = 40$ s for phenol reaction with aqueous bromine). Rate constants were indicated as the slope of the linear regression through data in Fig. 5, and the estimated k value for the reaction of phenol with aqueous chlorine could be about 1 order of magnitude lower than the one for the reaction of phenol with aqueous bromine during the rapid initial consumption stage.

3.4. The effect of pH

Four typical pH of natural water was tested and the effect of pH on HAAs formation for the reaction of aqueous chlorine with phenol was shown in Fig. 6. HAAs production decreased with the increase of the pH, but a pH in the range of 6–9 did not affect the decomposition of HAAs significantly and the change of HAAs production was only $31.2 \mu\text{g}/\text{L}$. As shown in Fig. 7, the increase of pH from 7 to 8 had large effect on and significantly decreased the for-

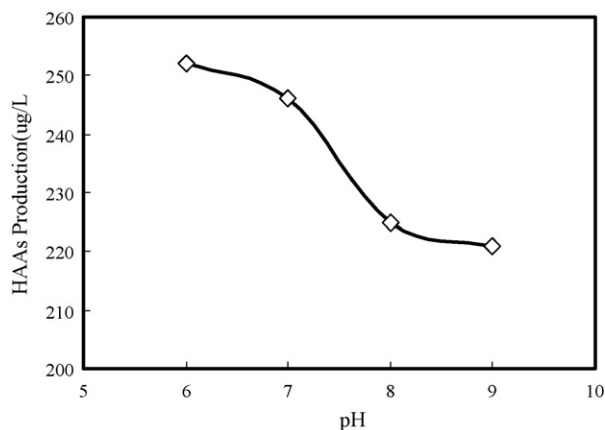


Fig. 6. The effect of pH on HAAs formation for the chlorination reaction of phenol.

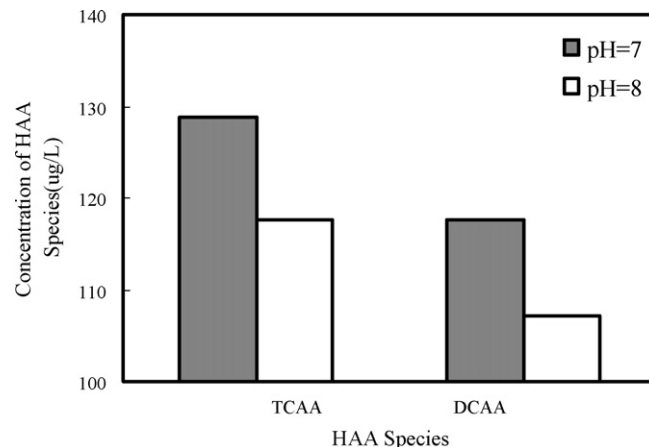


Fig. 7. The effect of pH on the speciation of HAAs for the chlorination reaction of phenol.

mation of the dichloroacetic acid (DCAA) and trichloroacetic acid (TCAA) species. Ge et al. [26] studied effects of pH on the chlorination process of phenol, and the results indicated that phenol was easy to be substituted by chlorine in neutral or alkaline media and the initial reaction rate of phenol increased with the increase of pH from 6 to 9. The kinetics of reaction of phenol with HOCl was studied in aqueous solutions between pH 2 and pH 12 [27]. Similar results were reported by Rebenne et al. [28], who studied aqueous chlorination kinetics and the mechanism of substituted dihydroxybenzenes and found that the apparent chlorination rate constants (k_{app}) were a minimum in the pH range of 3–6 and a maximum over the pH range of 8–11. For example, the $\log k_{\text{app}}$ of resorcinol was about $2.4 \text{ M}^{-1} \text{ s}^{-1}$ at pH 6, and then increased continuously to $4.3 \text{ M}^{-1} \text{ s}^{-1}$ till pH reached 11. Gallard and Von Gunten [9] also observed that the rate constants of chlorination of phenols varied from 0.02 to $2.71 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ using mono- and di-hydrobenzenes as model compounds in aqueous media over the pH range of 1–11. Brown [29] studied the thermal decarboxylation of carboxylic acids and pointed out that trichloro- and tribromo-acetic acids decompose as the anions:



Also since $\text{X}_3\text{CCO}_2\text{H}$ is a stronger weak acid ($\text{p}K_{\text{a}}$ is estimated to be <2.0) and X_3C^- is a strong base, the other two steps should be: $\text{X}_3\text{CCO}_2\text{H} \rightarrow \text{X}_3\text{CCO}_2^- + \text{H}^+$ and $\text{X}_3\text{C}^- + \text{H}^+ \rightarrow \text{X}_3\text{CH}$. Because acid dissociation or basic association reactions generally are very fast, Eq. (3) should be the rate-controlling step. For a weak acid, the ionic species are the predominant form when $\text{pH} > \text{p}K_{\text{a}} + 3$. Thus, almost all the $\text{X}_3\text{CCO}_2\text{H}$ is present in the ionic species at pH 6–9.

4. Conclusions

This study investigated the reactions of AOCs with aqueous chlorine or bromine, respectively. Five model AOCs with representative functional groups were selected to compare halogen consumption and HAAs formation in respective reactions with aqueous chlorine and bromine. Kinetic experiments were conducted to estimate rate constants for the reactions of phenol with aqueous chlorine and bromine, respectively. The effect of pH on HAAs production for the chlorination reaction of phenol could be provided. The following conclusions were obtained from the study:

- (1) From the reactions of AOCs with aqueous chlorine and bromine, respectively, the sequences of halogen consumption and HAAs formation were phenol > aniline > benzoic

acid > nitrobenzene > chlorobenzene, and it could be concluded that AOCs with electron donating functional groups (hydroxyl, amido) more easily and rapidly reacted with aqueous chlorine and bromine than them with electron withdrawing functional groups (carboxyl, nitro, chlorine).

- (2) For the reactions of AOCs with aqueous chlorine and bromine, respectively, the efficiency of HAAs substitution was greater for aqueous bromine than aqueous chlorine, and aqueous bromine is a more effective substituting halogen than aqueous chlorine.
- (3) Kinetic experiments indicated that halogen consumption exhibited rapid initial and slower consumption stages for the reactions of phenol with aqueous chlorine and bromine, respectively.
- (4) HAAs production decreased with the increase of pH for the chlorination reaction of phenol, and DCAA and TCAA formation significantly decreased with the increase of pH from 7–8.

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