The bromination kinetics of phenolic compounds in aqueous solution

Gaimei Guo [a,b,*], Fengkai Lin [a]

[a] School of Resource and Environmental Engineering, East China University of Science and Technology, Shanghai 200237, China
[b] Department of Water Conservancy Engineering, Zhejiang Water Conservancy & Hydropower College, Hangzhou, Zhejiang 310018, China

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ABSTRACT

The purpose of this study was to investigate the bromination kinetics of selected phenolic compounds in aqueous solutions over the pH range of 5–11. The experiment results indicated that the reaction of hypobromous acid with the phenoxide ions controlled the overall reaction rate, whereas the reaction between hypobromite ion and the phenoxide ions and the reaction between hypobromous acid and the undissociated phenolic species were considered to be negligible respectively in the pH range of 7–9. The apparent second-order rate constants of the reaction of hypobromous acid with the phenoxide ions ranged from $7.9 \times 10^6\,M^{-1}\,s^{-1}$ for 3-chlorophenol to $6.5 \times 10^8\,M^{-1}\,s^{-1}$ for 3-methoxyphenol, respectively. The Hammett correlation could be successfully used to estimate the reactivity of bromine with substituted phenols and the linear regression was $\log(k_2) = -2.856 + 8.00$. The rate constants of the reaction of bromine with phenol-like organic compounds were about three orders of magnitude higher than with chlorine and two to three orders of magnitude lower than with ozone.

1. Introduction

Disinfection by-products (DBPs) have caused great public health concerns due to their potential harm to human health. In the presence of bromide in natural waters, hypobromous acid (HOBr) is formed when chlorine or ozone used a disinfectant [1]. Hypobromous acid reacts with natural organic matter (NOM) in source water and its role in DBPs formation is analogous to that of hypochlorous acid (HOCl). HOBr can shift the distribution of DBPs to much brominated and mixed chlorobromo by-products [2], such as bromoform (TBM), dichlorobromomethane (BDCM) and dibromochloromethane (DBCM) [3,4]. The distribution of chlorinated, brominated and mixed chlorobromo by-products depends on the ratios of $HOCl/Br^-$, Br^-/NOM and Br^-/free chlorine [5,6]. DBPs are suspected to be toxic, carcinogenic, and/or mutagenic to humans if ingested over extended years, or have acute reproductive and developmental effects [7–9]. It has been reported that 5000 cases of bladder cancer per year and 8000 cases of rectal cancer per year may be associated with the consumption of chlorinated drinking water in the US. Bull and Kopfler [10] and Boorman et al. [11] have reported some brominated DBPs pose much significant health risks than chlorinated analogs, and brominated DBPs are associated with colon cancer by toxicological studies. The United States Environmental Protection Agency (USEPA) has regulated in Stage I of the disinfection/disinfection by-products rule (D/DBPs Rule) the maximum contaminant level (MCL) of trihalomethanes (THMs) and haloacetic acids (HAAs) at 0.080 and 0.060 mg/L, respectively [12].

During ozonation, hypobromous acid is the key intermediate in the formation mechanism of bromate (BrO_3^-), an inorganic DBP. Bromate is a potential carcinogenic by-product of ozonation in waterworks [13,14]. The formation of bromate in the presence of ozone presents a problem in the light of the recent D/DBPs rule on the maximum permissible contaminant level of bromate (0.01 mg/L) [15]. The formation mechanism of bromate has been extensively studied in purified water [14]. However, because hypobromous acid reacts also with NOM in complex reactions, study on the formation mechanism of bromate becomes difficult in natural waters. Accordingly, further research on the kinetics of reaction of NOM with hypobromous acid is necessary in bromide-containing natural waters.

NOM consists of a heterogeneous mixture of humic substances, hydrophilic acids, protein, lipids, carbohydrates, carboxylic acid, amino acid and hydrocarbon [16]. However, reactions between NOM and chlorine have shown that general aromatic compounds (e.g. phenols) have more commonly been suggestive and predictive of DBP formation [17]. Some studies are available on the reaction of chlorine and bromine with model organic compounds of NOM, such as phenolic compounds, in order to better understand the reactivity of chlorine and bromine with NOM. The reaction rates are second order with respect to the organic compounds and chlorine [18–21]. It is generally accepted that bromine reacts faster than chlorine with NOM. For example, hypobromite was a more effective oxidant and

* Corresponding author. Tel.: +86 571 86929059; fax: +86 571 86929061.
 E-mail addresses: jiaokaifang@126.com, gmguo@126.com (G. Guo),
fl@ecust.sdu.cn (F.Lin).

a faster substituting agent than hypochlorite with resorcinol and its derivatives, and the presence of bromide during chlorination increases the rate of formation of THMs [3,22,23]. Bromination of resorcinol and orcinol yielded mono-, di- and tribrominated electrophilic substitution products in meta and para positions [24]. For the reaction of hypobromous acid with phenol in aqueous solution in a batch reactor, an apparent second-order rate constant was $500 M^{-1} s^{-1}$ at pH 4 [25]. The kinetics of bromination of phenol was studied in the presence of high concentration of bromide and the rate constant was $1.2 \times 10^9 M^{-1} s^{-1}$ for the attack of bromine on phenoxide ion [26]. In the absence of bromide, the rate of bromination of aromatic compounds is proportional to the acidity of the media at low concentrations of acids [27], which can be explained if rate-limiting step is either the reaction of the effective bromine (H_2OBr^+) with organic compounds or the decomposition of a protonated transition state formed between hypobromous acid and the organic substrate. In the presence of high concentrations of bromide (dibromine (Br_2) and tribromide ion (Br_3^-) are the only brominating species), the kinetics of reaction of bromine with phenols was studied in aqueous solution at pH < 7 [26,28].

However, it is important to point out that for all these studies, pH is too low or the concentration of bromide too high to describe the reactivity of bromine with organic compounds in drinking water treatment. The literature lacks the study on the kinetics of bromine in aqueous solution at neutral and alkaline pH in the absence of bromide. The goal of this study was to determine the rate constants of bromination of selected phenolic compounds between pH 5 and pH 11.

2. Materials and methods

2.1. Materials and methods

All chemicals were of the purest available quality. Solutions of phenolic compounds, ammonia, chlorine and bromine were prepared with ultra-pure water produced from a US Filter Corporation. A total of six phenolic compounds was studied: phenol, p-aminophenol, p-nitrophenol, 3-methoxyphenol, 3-chlorophenol and 4-nitro-m-cresol. Stock solutions of chlorine were prepared by diluting a commercial solution of sodium hypochlorite (NaOCl, 4% active chlorine). Sodium hypochlorite was standardized by iodometry.

Stock solutions of bromine were prepared from a solution of ozone (5 °C, pH 4, 10 mM phosphate) by addition of 0.1 M solution of potassium bromide (KBr) [29]. After a day, ozone was purged by bubbling nitrogen for 30 min. The bromine solution was standardized by direct photometric determination of the hypobromite ion (BrO^-) at 329 nm $(\varepsilon = 332 M^{-1} cm^{-1}$ [30]) after adjusting the pH of the solution to 11. For a ratio $Br^-/O_3 = 0.9$, the yield of the reaction was ≥95% and the concentration of the bromine solution was typically 0.65 mM. The solution was stable for 4 weeks when stored at 4 °C.

All experiments were performed at room temperature (25 °C). pH measurements were carried out with a Mettler Toledo, which was calibrated with pH 4, 7 and 9 standard buffers. Solutions were buffered using phosphate (5 mM). Spectrophotometric measurements were performed on a SAFAS 190 DES spectrophotometer.

2.2. Reaction procedure

A preliminary study showed that the initial reaction of bromine with most of the phenolic compounds used in this study was too fast to be followed in a batch reactor. Therefore, the kinetics of bromination was studied using a continuous-flow reactor.

For the selected phenolic compounds the experimental setup consisted of two HPLC pumps (Constametric3200 LDC Analytical). The first one was used to pump the solution of oxidant (bromine or chlorine), the second one the solution of the tested molecule (phenolic compounds or ammonia). Both solutions were pumped with the same flow rate. Total flow rates in the reactor varied between 3 and 21 mL min^{-1}. The two solutions were mixed using a 1/15″ mixing tee, connected to a 79.8 cm or a 29.6 cm reaction tube (0.25-mm-ID Peek tube) where the reaction took place. The reaction solution was collected in a 8 cm long photometric cell containing 4 mL of a buffered (pH 7.0) solution of diethyl-p-phenylenediamine (DPD) method. The exact collected volume was determined using a precision balance (±0.1 mg). The DPD solution stopped the reaction and allowed analysis of the residual bromine (or chlorine) in solution at 510 nm [31]. Detection limit was 0.09 μM. The reaction time was defined based on the volume of the tube and the flux of the mixed solution. Reaction times ranged about from 10 to 150 ms.

3. Results and discussion

3.1. Preliminary experiments

For the study of kinetics of the fast reactions between bromine and selected phenolic compounds, preliminary kinetic experiments were conducted to test the suitability of the continuous-flow apparatus. To validate the measurements made using the continuous-flow apparatus, the confirmation of preliminary experiments of the kinetics of the reactions between chlorine and ammonia was used.

Saguiosin and Morris [32] and Gallard et al. [33] have reported the reaction of hypochlorous acid with ammonia (NH_3) is a second-order reaction (first-order with respect to chlorine and first-order with respect to ammonia). The fast reaction between HOCl and NH_3 produces NH_2Cl and $NHCl_2$. Between the two neutral molecules of hypochlorous acid and ammonia, the reaction rate constant (k_{cl}) was $5.6 \times 10^6 M^{-1} s^{-1}$ at 20 °C [32] and $5.97 \times 10^6 M^{-1} s^{-1}$ at 23 °C [33]. HOCl dissociates into OCl$^-$ with a pK_a of 7.54, and NH_4^+ dissociates into ammonia with a pK_a of 9.3. Accordingly, considering total concentrations of chlorine $([Cl]_t)$ and ammonia $([NH_3]_t)$ (Eqs. (1) and (2)), the rate of chlorine consumption is considered as follows (Eq. (3)):

$$[Cl]_t = [HOCl] + [OCl^-] \tag{1}$$

$$[NH_3]_t = [NH_3] + [NH_4^+] \tag{2}$$

$$\frac{d[Cl]_t}{dt} = k_a[Cl]_t[NH_3]_t \tag{3}$$

where k_a is the apparent second-order rate constant and $k_a = k_{cl}$ between pH 4 and pH 11.

Fig. 1 illustrated a plot of Ln $([Cl]_t/[Cl]_{t0})$ vs. time for four different pH values. Under pseudo-first-order kinetic experimental conditions, the total concentration of ammonia was much higher than chlorine. The initial concentration of ammonia $([NH_3]_{t0})$ varied from 0.5 to 2.0 mM, and the initial concentration of chlorine $([Cl]_{t0})$ was 10 μM. The pseudo-first-order rate constant (k') was indicated as the slope of the linear regression through data:

$$Ln \frac{[Cl]_t}{[Cl]_{t0}} = k't \tag{4}$$

where the pseudo-first-order rate constant

$$k' = k_a[NH_3]_{t0} \tag{5}$$

The experimental and theoretical profile of the apparent second-order rate constant (k_a) vs. pH was shown in Fig. 2. The preliminary experimental pH profile of the apparent second-order rate constant was determined in aqueous media over the pH range of
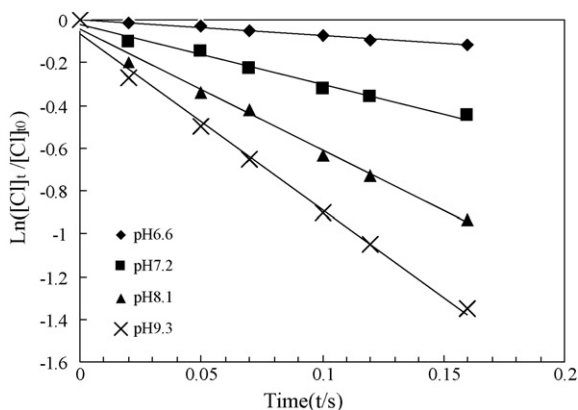
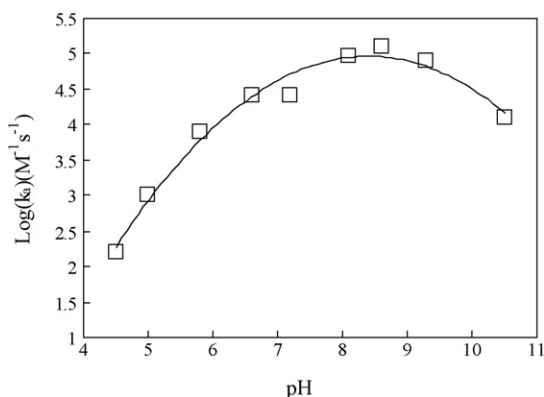**Fig. 1.** Pseudo-first-order kinetic plot of the reaction of chlorine with ammonia.

Fig. 2. Apparent second-order rate constant (k_a) pH profile of the reaction of chlorine with ammonia.

4.5–10.5. The apparent second-order rate constant depends on the individual reaction-rate constant k_{cl} and pH. The theoretical pH profile was determined by a non-linear least-squares regression of experimental data and the fit curve function of SigmaPlot 2000 software as a tool. The calculated value of k_{cl} was approximately $5.7 \times 10^6 \, M^{-1} \, s^{-1}$. This value was close to the value of $5.6 \times 10^6 \, M^{-1} \, s^{-1}$ observed by Saguiosin and Morris [32] and $5.97 \times 10^6 \, M^{-1} \, s^{-1}$ given by Gallard et al. [33]. Therefore, the continuous-flow apparatus in preliminary experiments could be used for the study of kinetics of the rapid reactions between bromine and selected phenolic compounds.

3.2. Rate constants of reactions between bromine and phenolic compounds

Bischel and Gunten [34] and Gallard and Gunten [18] studied the kinetics of reactions of hypoiodous acid (HOI) and hydrochlorous acid with phenolic compounds in aqueous solutions between pH 2 and pH 12, and reported that the initial iodination and chlorination of phenolic compounds were considered as second-order reactions. The apparent second-order rate constant showed a pH-dependence which could be explained by the species of both halogen and phenols in aqueous solutions. For hypobromous acid, a similar behavior is expected and it can be hypothesized that the initial bromination of phenolic compounds was a second-order reaction (first-order with respect to bromine and first-order with respect to phenolic compounds). Because hypobromous acid dissociates into hypobromite ion (BrO^-) with a pK_a of 8.89, and phenolic compounds dissociate into phenoxide ion (PhO^-), total concentrations of bromine ($[Br]_t$) and phenolic compounds ($[Phenols]_t$) can

be considered as follows:

$$[Br]_t = [HOBr] + [BrO^-] \tag{6}$$

$$[Phenols]_t = [PhOH] + [PhO^-] \tag{7}$$

Based on Eqs. (6) and (7), the second-order rate constant (k'') of the initial bromination of phenolic compounds will depend on the degree of dissociation of both bromine and phenolic compounds in aqueous solutions. For chlorine, apparent second-order rate constants showed a maximum in the pH region 8–9, which was explained that HOCl was the only active electrophile and the reactivity of OCl^- is negligible [18,34]. Similar to OCl^-, BrO^- was probably less reactive and might only react with phenoxide ion in alkaline solutions (Eq. (8)).

$$BrO^- + PhO^- \rightarrow Products, \quad k_1 \tag{8}$$
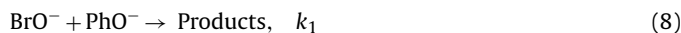
In neutral and alkaline solutions, hypobromous acid was probably the only active electrophilic species of bromine and exhibits a much higher reactivity than hypobromite ion, which could react with both undissociated phenolic species (PhOH) and phenoxide ion, respectively. The reaction of hypobromous acid with undissociated phenolic species and phenoxide ion can be depicted as follows:

$$HOBr + PhO^- \rightarrow Products, \quad k_2 \tag{9}$$

$$HOBr + PhOH \rightarrow Products, \quad k_3 \tag{10}$$
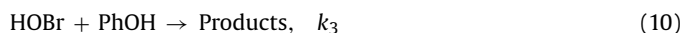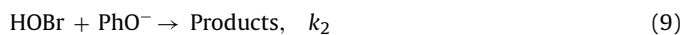
Based on previous studies in the literature, the contribution of dibromine (Br_2) species to the observed reaction rate was negligible in our proposed model. Gallard et al. [33] studied bromination of phenolic compounds under the same experimental conditions, and indicated the proportion of dibromine was calculated to be <0.08% at pH 5. Tee et al. [26] reported the kinetic constants of hypobromous acid were only one order of magnitude smaller than dibromine. These results reinforce our hypothesis and the reactions between dibromine and undissociated phenolic species and phenoxide ion were considered negligible. Also, in the literature, the reactions between XO^- (e.g. BrO^-) and phenoxide ion are generally not included into models because the contribution of the reaction seems to be significant only above pH 11. Furthermore, when the reaction between hypobromite ion and undissociated phenolic species was introduced into the model, the best fitting value of the rate constant was zero, which indicated the reaction was considered to be negligible. Therefore, the consumption of bromine can be written as follows:

$$\frac{d[Br]_t}{dt} = -k_1[BrO^-][PhO^-] - k_2[HOBr][PhO^-] - k_3[HOBr][PhOH] \tag{11}$$

$$\frac{d[Br]_t}{dt} = -(k_1\alpha_{Br}\alpha_{Phenols} + k_2(1-\alpha_{Br})\alpha_{Phenols} + k_3 \\ \times (1-\alpha_{Br})(1-\alpha_{Phenols}))[Br]_t[Phenols]_t \tag{12}$$

$$k_a = k_1\alpha_{Br}\alpha_{Phenols} + k_2(1-\alpha_{Br})\alpha_{Phenols} + k_3(1-\alpha_{Br})(1-\alpha_{Phenols}) \tag{13}$$

$$\alpha_{Br} = [BrO^-]/([HOBr] + [BrO^-]) \tag{14}$$

$$\alpha_{Phenols} = [PhO^-]/([PhO^-] + [Phenols]) \tag{15}$$

$$HOBr \rightleftharpoons BrO^- + H^+, \quad k_{a1} \tag{16}$$

$$PhOH \rightleftharpoons PhO^- + H^+, \quad k_{a4} \tag{17}$$

Table 1
Hammett constants and rate constants of OBr⁻ (k_1) and HOBr (k_2, k_3) with selected phenolic compounds.

Phenolic compounds	σ	k_1 (M⁻¹ s⁻¹)	k_2 (M⁻¹ s⁻¹)	k_3 (M⁻¹ s⁻¹)
Phenol	0	5.3×10^2	2.3×10^8	0.8×10^4
p-Aminophenol	−0.24	4.9×10^3	5.4×10^8	8.9×10^4
p-Nitrophenol	0.33	6.4×10^3	8.8×10^6	9.2×10^3
3-Methoxyphenol	−0.35	7.6×10^4	6.5×10^8	6.8×10^5
3-Chlorophenol	0.38	7.5×10^2	7.9×10^6	6.5×10^4
4-Nitro-m-cresol	−0.15	5.6×10^2	3.2×10^8	7.5×10^5

where α_{Br} and $\alpha_{Phenols}$ (reactions (14) and (15)) are the degrees of dissociation of hypobromous acid and phenolic compounds.

Hypobromous acid dissociates into hypobromite ion (reaction (16)) and phenolic compounds dissociate into phenoxide ion (reaction (17)). The degrees of dissociation can be calculated from the pH and the dissociation constants ($\alpha_{Br0} = k_{a1}/(k_{a1} + [H^+])$, $\alpha_{Phenols0} = k_{a4}/(k_{a4} + [H^+])$). Replacing α_{Br0} and $\alpha_{Phenols0}$ into reaction (13), the apparent second-order rate constant (k_a) depended on the individual reaction-rate constants (k_1, k_2, k_3), the pH, and the acid dissociation constants according to reaction (18). The individual rate constants were determined by a nonlinear least-squares regression of the experimental pH profile of k_a.

$$K_a = \frac{k_1 k_{a1} k_{a4} + k_2[H^+]k_{a4} + k_3[H^+]^2}{(k_{a1} + [H^+])(k_{a4} + [H^+])} \qquad (18)$$

Rate constants of initial brominations of phenol, p-aminophenol, p-nitrophenol, 3-methoxyphenol, 3-chlorophenol and 4-nitro-m-cresol were obtained in the pH range of 5–11 with the continuous-flow apparatus under experimental conditions developed for pseudo-first-order kinetics. The values of k_1, k_2, k_3 of the studied phenols were given in Table 1. The initial concentrations of phenols varied from 30 to 150 μM. The initial concentrations of bromine ranged from 1.5 to 7.5 μM. The bromination of 3-chlorophenol as representative reaction was described in detail.

For the bromination of a 150 μM solution of 3-chlorophenol, Fig. 3 illustrated a plot of Ln ($[Br]_t/[Br]_{t0}$) vs. time for four different pH values. The rate of bromination can be well linearized using a pseudo-first-order kinetic model. As shown in Fig. 4, the reaction order for 3-chlorophenol was examined at pH 8.3 by ranging the concentration of 3-chlorophenol. A close-fitting linear plot was obtained with our results for the pseudo-first-order rate constant vs. the initial concentration of 3-chlorophenol.

The experimental and theoretical profiles of the apparent second-order rate constant (k_a) vs. pH for the bromination of 3-chlorophenol are shown in Fig. 5. The experiments were conducted between pH 5 and pH 11. The solid line was a non-linear least-squares regression fit of k_1, k_2 and k_3 to the experimental
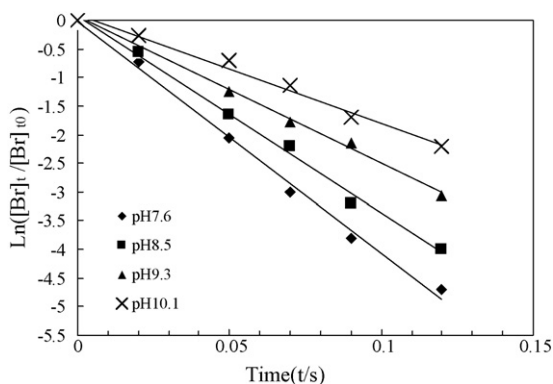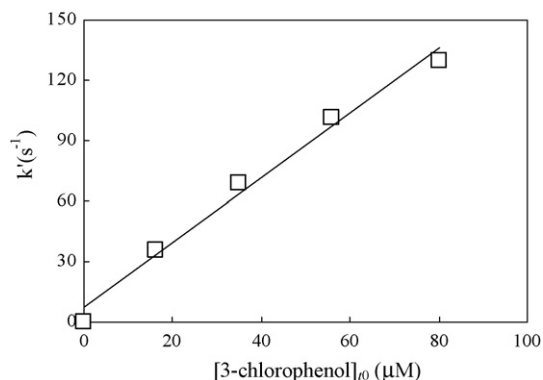

Fig. 4. Evolution of the pseudo-first-order rate constant (k') with the initial concentration of 3-chlorophenol at pH 8.3.
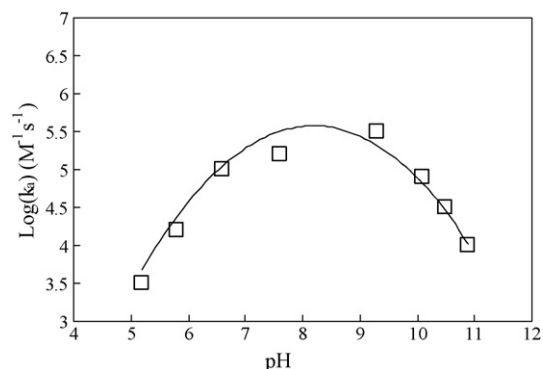

Fig. 5. Apparent second-order rate constant (k_a) pH profile of the initial bromination of 3-chlorophenol.

data. In near-alkaline media, rate constants showed a maximum, which was explained if hypobromous acid was the only electrophilic and the reactivity of hypobromite ion was negligible. Using the acid dissociation constants $k_{a1} = 10^{-8.9}$ and $k_{a4} = 10^{-7.85}$, the individual rate constants were calculated as $k_1 = 7.5 \times 10^2$ M⁻¹ s⁻¹, $k_2 = 7.9 \times 10^6$ M⁻¹ s⁻¹, $k_3 = 6.5 \times 10^4$ M⁻¹ s⁻¹.

The kinetic models of brominations of the other phenolic compounds were obtained using the same approach. The experimental and theoretical profiles of the apparent second-order rate constant vs. pH of the bromination of phenol are shown in Fig. 6. The experiments were conducted between pH 5 and pH 11 (the solid line was a non-linear least-squares regression fit of k_1, k_2 and k_3 to the experimental data). Gallard et al. [33] studied bromination kinetics of phenol under the same experimental condition. Also, Pinkernell and Gunten [25] studied the apparent second-order rate
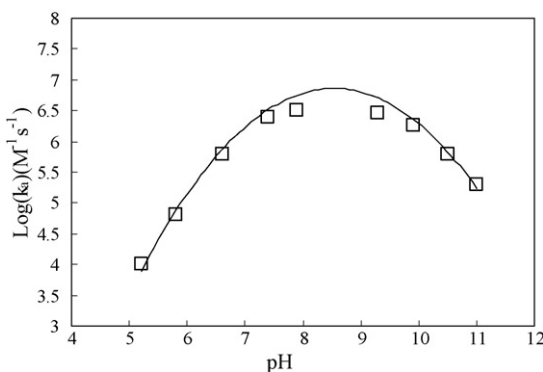

Fig. 3. Pseudo-first-order kinetic plots of the bromination of 3-chlorophenol.

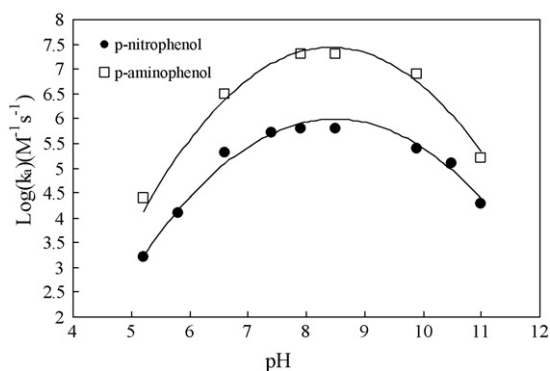**Fig. 6.** Apparent second-order rate constant (k_a) pH profile of the initial bromination of phenol.

Fig. 7. Apparent second-order rate constant (k_a) pH profiles of the initial bromination of p-aminophenol and p-nitrophenol.

Fig. 9. Hammett plots for the reaction of HOBr with phenoxide ions.

constant of the bromination of phenol in a batch reactor at pH 4. The experimental results showed that the pH profiles of the apparent second-order rate constant obtained in their studies were in good agreement with k_a in the present paper. The apparent second-order rate constant pH profiles of the initial bromination of both p-aminophenol and p-nitrophenol are shown in Fig. 7 and both 3-methoxyphenol and 4-nitro-m-cresol in Fig. 8, Similar to phenol, the proposed model fit well with the experimental profile. The values of k_1, k_2 and k_3 of the six selected phenolic compounds in our study were listed in Table 1.

The rate constants of the reaction of hypobromous acid with the phenoxide ions (k_2) ranged from 7.9×10^6 M^{-1} s^{-1} for 3-chlorophenol to 6.5×10^8 M^{-1} s^{-1} for 3-methoxyphenol. For phenol, the rate constant of hypobromous acid with phenoxide ion was 2.3×10^8 M^{-1} s^{-1}, which was close to the value of 1.8×10^8 M^{-1} s^{-1} given by Gallard et al. [33]. Tee et al. [26] reported the rate constant of dibromine with phenoxide ion was 1.2×10^9 M^{-1} s^{-1}, which was only one order of magnitude larger than hypobromous acid. Based on the very low dibromine concentration (<0.08%) under the same experimental conditions with the continuous-flow apparatus [33], this result could reinforce our hypothesis that the reactivity of dibromine species was considered as negligible. Because the rate constants of the reaction of hypobromous acid with the phenoxide ions were two to six orders of magnitude greater than the corresponding rate constants of the reaction between hypobromite ion and the phenoxide ions (k_1) and the rate constants of the reaction between hypobromous acid and the undissociated phenolic species (k_3), in the pH range of 7–9, the values of k_1 and k_3 were too small to affect the apparent second-order rate constant of bromination of the phenolic compounds. Therefore, the overall reaction was only controlled by the reaction of hypobromous acid with the phenoxide ions. Gallard et al. [33] studied the kinet-
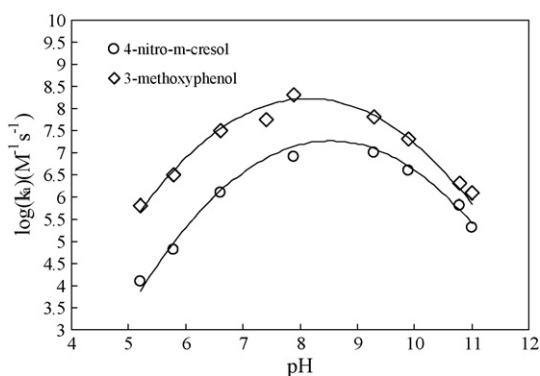

Fig. 8. Apparent second-order rate constant (k_a) pH profiles of the initial bromination of 3-methoxyphenol and 4-nitro-m-cresol.
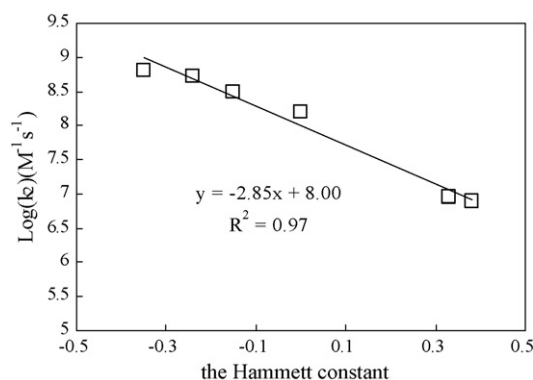
ics of bromination of phenolic compounds and found the initial bromination of p-methylphenol, p-chlorophenol, p-acetylphenol and 2,4-dichlorophenol was considered as a second–order reaction. However, kinetics of bromination of 2,4,6-trichlorophenol was first-order since 2,4,6-trichlorophenol exhibited a much lower reactivity toward bromine. Also, the reaction of hypobromous acid with the phenoxide ions controlled the reaction and the rate constants ranged from 1400 M^{-1} s^{-1} for 2,4,6-trichlorophenol to 2.1×10^8 M^{-1} s^{-1} for p-methylphenol.

3.3. The effect of substituents on rate constants

It is generally accepted that the Hammett correlation is classically used to predict the effect of substituents on reaction-rate constants between organic compounds and oxidants [18,34,35]. Both inductive effect and resonance effect determine substituents with an electron-withdrawing effect or an electron-donating effect. Substituents with an electron-withdrawing effect decrease the electron density of the aromatic ring, whereas substituents with an electron-donating effect increase the electron density of the aromatic ring. The Hammett constant (σ) reflects the effects of inductive and resonance effects on substituents. If $\sigma > 0$, substituents have an electron-withdrawing effect (e.g. –Cl, –NO$_2$), whereas if $\sigma < 0$ substituents exert an electron-donating effect (e.g. –CH$_3$, –NH$_2$). The non-substituted phenol was used as a reference compound ($\sigma = 0$). Because the reactions between hypobromite ion and the phenoxide ions and between hypobromous acid and the undissociated phenolic species were considered as negligible in the pH range of 7–9, the Hammett correlation was only tested for the reaction between hypobromous acid and phenoxide ions in natural waters (neutral pH). A linear plot could be drawn between log(k_2) and σ (Fig. 9). Values of σ were shown in Table 1 for the selected phenolic compounds. The linear regression for the bromination of the selected phenolic compounds was:

$$\log(k_2) = -2.85\sigma + 8.00, \quad r = 0.97, \quad n = 6. \tag{19}$$

The Hammett constant increased with the increase of the deactivating effect of the substituents, whereas the rate constants of the reaction of hypobromous acid with the phenoxide ions decreased with the deactivating effect of the substituents due to the electrophilic character of hypobromous acid. For example, for the bromination of 3-methoxyphenol, the Hammett constant was the smallest and the rate constant (k_2) was the largest. The negative sign of the Hammett slope of the linear regression was typical of electrophilic substitution reaction. Both p-aminophenol and 3-methoxyphenol with substituents having an electron-donating effect promoted the halogen substitution onto the para and meta position. However, p-nitrophenol and 3-chlorophenol with substituents having an electron-withdrawing effect hindered the

halogen substitution. The initial reaction of bromine with phenol compounds was the electrophilic substitution onto available 2, 4 and 6 ring positions leading to the formation of bromophenols [26]. With phenolic compounds the –OH and –O$^-$ substituents acted as activating substituents that promoted the halogen substitution onto the para and meta positions [33].

The Hammett correlation was also used to predict the kinetics of reactions of hypochlorous acid and hypoiodous acid with phenolic compounds in aqueous solutions by Bischel and Gunten [34] and Gallard and Gunten [18]. Rate constants of hypobromous acid were about three to four orders of magnitude higher than hypochlorous acid and 5 to 500-fold higher than hypoiodous acid, which indicated that HOBr was a more effective substituting halogen than HOCl and HOI. In agreement with the lowest electronegativity of iodine, the rate constants of the reaction of hypoiodous acid with the phenoxide ions should present the highest. However, the intermediate reactivity of iodine was not consistent with the order of electronegativity of halogens. Steric effect and the low stability of hypoiodous acid in aqueous solution might explain the unexpected reactivity of iodine. Hammett slopes of hypoiodous acid were smaller than Hammett slopes of hypochlorous acid and hypobromous acid, which could be explained by the lowest electronegativity of iodine [33].

3.4. Implications for drinking water treatment

To understand the behavior of hypobromous acid in drinking water treatment plants, the pseudo-first-order rate constants of reactions of HOBr with phenol and 3-chlorophenol were calculated at pH 8.0. The concentration of HOBr was 1.2 μM (about 100 μg/L of Br). Rate constants of reactions of HOBr with phenol and 3-chlorophenol were 2.6 and 0.34 s^{-1}, respectively. Pseudo-first-order rate constants of reactions of O_3 with phenol and 4-chlorophenol and reactions of HOCl with phenol and 4-chlorophenol were calculated at pH 8.0 for ozone ($[O_3] = 20$ μM, about 1 mg/L) and chlorine ($[HOCl] = 20$ μM, about 1.4 mg/L) from literature data [18,34]. Pseudo-first-order rate constant was 360 s^{-1} for reactions of O_3 with phenol and 1.2×10^{-3} s^{-1} for reactions of HOCl with phenol. Pseudo-first-order rate constant was 680 s^{-1} for reactions of O_3 with 4-chlorophenol and 6.0×10^{-4} s^{-1} for reactions of HOCl with 4-chlorophenol. Results showed that rate constants of bromination of phenol and 3-chlorophenol were about three orders of magnitude higher than rate constants of the reaction of chlorination of phenol and 4-chlorophenol when the concentration of bromine was much lower than chlorine. This verifies that during chlorination of natural waters, reactions of active bromine with phenol-like organic structures of NOM are much faster than reactions of chlorine, which leads to the formation of brominated and mixed chlorobromo by-products [33]. However, rate constants of bromination of phenol and 3-chlorophenol were about two to three orders of magnitude lower than rate constants of reactions of ozone with phenol and 4-chlorophenol. This result confirms that in ozonation step of natural waters, the high reactivity of ozone with phenols limits reactions of active bromine with phenol-like organic structures of NOM. Therefore, the formation of brominated organic compounds is considered as negligible [25].

4. Conclusion

The purpose of this paper was to determine bromination kinetics of phenolic compounds in aqueous solution between pH 5 and pH 11. The following conclusions were obtained from the study:

(1) The initial bromination of selected phenolic compounds was a second-order reaction. The reaction rates of hypobromous acid with phenoxide ions controlled the overall reaction rate between pH 7 and pH 9.
(2) Hammett correlation could be successfully used to predict the bromination kinetics of phenolic compounds. Hammett equation could be obtained to estimate the reactivity of active bromine with substituted phenols.
(3) In drinking water treatment plants, the high reactivity of bromine with phenol-like organic structures led to the formation of brominated disinfection by-products during chlorination. However, the reactions of bromine with phenols were negligible during ozonation.

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