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BROMINATED TRIHALOMETHANE FORMATION IN HALOGENATION OF HUMIC ACID IN THE COEXISTENCE OF HYPOCHLORITE AND HYPOBROMITE IONS

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Abstract—Brominated trihalomethanes (Br-THMs) such as $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$ are produced by the reaction of hypobromite with humic acid in the presence of hypochlorite. In the presence of excess NaOCl, addition of NaOBr enhanced the formation of Br-THMs but reduced the formation of CHCl_3. The product distribution of THMs was affected by the ratio of [NaOBr]/[NaOCl] and was independent of pH and reaction time. In the presence of excess NaOBr, the yield of CHBr_3 only increased linearly with the NaOCl concentration added. However, the other three THMs were hardly-produced even though NaOCl concentration was increased up to 0.5 of the [NaOCl]/[NaOBr] molar ratio. Our results suggest that in the process of THM formation, hypochlorite ion reacts effectively with humic acid in the oxidation reaction and hypobromous acid plays a predominant role in the electrophilic substitution when both of hypohalites are present. © 1998 Elsevier Science Ltd. All rights reserved

Key words: brominated trihalomethane, redox reaction, hypochlorite, hypobromite, humic acid.

INTRODUCTION

In 1974, brominated trihalomethanes (Br-THMs) formation, i.e., CHCl₂Br, CHClBr₂, and CHBr₃ in addition to CHCl₃ as main product, was first reported by Rook (1974) and Bellar *et al.* (1974) in the practical water disinfection process using chlorine. Since then researchers have made intensive efforts to clarify source of bromide of Br-THMs and also to elucidate the reaction mechanisms.

In contrast, a variety of the candidate for the source material of bromide can be considered. Hence, although much important knowledge has already been accumulated concerning reaction mechanisms of Br-THM formation. (Cooper *et al.*, 1985; Krasner *et al.*, 1994; Symons *et al.*, 1994), there are still uncertainties for the most probable mechanism.

Aiming at contribution to the mechanistic studies, we chose a model reaction system with combination of humic acid and sodium hypobromite (NaOBr). The idea of using NaOBr is based on mainly two types of important observation. First, Br-THMs were produced even at a considerably lower concentration of bromide relative to chloride concentration (Cooper *et al.*, 1985; Krasner *et al.*, 1994). Second, the amounts of Br-THMs formed were pH dependent when KBr was used as a source material of bromide (Aizawa *et al.*, 1989). This information seemed to match with a concept of hypobromite ion (OBr⁻) and hypobromous acid (HOBr) acting as reactive entity (Farkas *et al.*, 1949; Rook, 1977). The reasons are that bromide can be oxidized readily to highly reactive OBr⁻ or HOBr species, and the composition of these two species is pH-dependent, and in addition, OBr⁻ or HOBr species may be formed also from KBr and NaOCl.

Hence, we tested chlorination of the system of humic acid and NaOBr (in the presence or absence of NaOCl) at first time to obtain new elementary information about (1) product distribution of THMs formed, (2) effect of concentration ratio of NaOBr to NaOCl, (3) effect of pH, (4) outline of reaction time-profiles, all of which will be helpful for more detailed mechanistic studies in the future. On the basis of our information, the difference in the role of NaOBr from NaOCl is briefly discussed.

EXPERIMENTAL SECTION

Reagents and materials

Sodium salt of humic acid was obtained from Aldrich. This humic acid was composed of 51.85% C, 5.08% H and 0.67% N by elemental analysis. It was observed by potentiometric titration of humic acid with NaOCH₃ in methanol/benzene in dimethyl sulfoxide (Yonebayashi and

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Hattori, 1985) that the humic acid had the carboxyl group (4.01 milli equivalent mol/g humic acid) and phenolic hydroxyl group (1.4 milli equivalent mol/g humic acid). The 10 mg/L humic acid solution was used as a precursor of THMs. This concentration of the humic acid corresponded to 5.2 mg/L of total organic carbon (TOC) by TOC measurement (TOC-5000A Shimazu). The concentration of TOC was within the range of 0.1 to 10 mg/L dissolved organic carbon contained in groundwater (Gaffrey et al., 1996). Concentrations of NaOCl (5% solution, Kanto) and NaOBr (5% solution, Kanto) solutions were determined by titration with 0.01 M sodium thiosulfate solution after addition of potassium iodide and sulfuric acid. These solutions were diluted to given concentrations just before use. Potassium bromide was used as the bromide ion source. The 0.258 mmol/L NaOCl corresponded to 18.29 mg/L chlorine (Cl₂). This concentration of hypochlorite was two times that of humic acid solution. Solution of hydrochloric acid (0.02 M) and sodium hydroxide (0.02 M) were used to adjust the pH of the reacting solution. A 50 g/L solution of sodium L-ascorbate and 2 M HCl were used to quench the reaction. All of these chemicals i.e., sodium thiosulfate, potassium iodide, sulfuric acid, potassium bromide, hydrochloric acid, sodium hydroxide, and sodium L-ascorbate, were reagent grade and obtained from Wako. Glass-distilled and deionized water was employed to dilute the solutions of humic acid, reagents and reaction mixtures.

Halogenation procedure

The solution of known concentration of NaOCl and NaOBr or KBr was added to the humic acid solution and the pH values of the mixed solutions were adjusted under stirring by using 0.02 M HCl or 0.02 M NaOH solution as quick as possible. The pH values were measured by an HM-40V pH meter (Toa Electrics). The initial pH value was adjusted to be 8, at which the surface water was disinfected by chlorination for water supply (Krasner et al., 1994). The pH 8 decreased little in 60 min to 7.62-7.75 for using NaOCl and to 7.96-7.98 for using NaOBr. So, the adjusting the initial pH was used for the following result and discussion in this paper. Rook (1977) and Norwood et al. (1980) already reported that the two kinds of slope of the curve for chloroform formation rate were distinguished. During the first 15 min, a rapid start was observed followed by a much slower secondary phase which continued for 24 h. The linear relationship of CHBrCl₂ produced to reaction time at pH 8 was observed until 60 min (Fig. 7). So, 60 min was adopted for the reaction time to investigate the initial reaction mechanism of THMs formation. Aliquots of the solutions were poured into 43 mL vials, which were closed immediately by screw stoppers fitted with Teflon septa. After allowing for an appropriate reaction time, ascorbic acid solution (0.5 mL) and 2 M HCl (0.5 mL) were added to the vials to quench the halogenation reaction. The series of experiments was carried out at room temperature (22-24°C).

Analysis of THM

THMs formed were analyzed by the fully automated analytical method of purge and cold trapping/gas chromatography (GC)/mass spectrometry (MS). This method has been described in detail previously (Ichihashi *et al.*, 1995). Then the vials were placed in an AquaTek-50 automatic vial sampler (Tekmer) connected to an automatic concentrator (LSC 2000, Tekmer) by purging and trapping to a precolumn. GC/MS measurements of the THMs were carried out with a Hewlett Packard 5890 series II gas chromatograph interfaced to a Hewlett Packard 5972A mass spectrometer. The column used was a fused silica capillary (60 m × 0.25 mm i.d. × 1 μ m) supplied by J and W Scientific. The mass acquisition mode was selected ion



Fig. 1. Changes in concentration of CHCl₃ and CHBr₃ formed in the reaction of humic acid with NaOCl or NaOBr alone, respectively. - ♦ - CHCl₃ (NaOCl); - ○ - CHBr₃ (NaOBr). Humic acid: 10 mg/L, pH: 8.0, Reaction time: 60 min.

monitoring (SIM), and the ionization mode was electron impact (70 eV).

RESULTS

THMs formed by the reaction of NaOCl or NaOBr with humic acid

Figure 1 shows the relationship between the amount of THM formed and the concentration of NaOCl or NaOBr added to the humic acid solution. It is well known that CHCl₃ is formed in the reaction of humic acid with NaOCl and CHBr3 with NaOBr, and the amounts of CHCl3 and CHBr3 depend on the concentration of NaOCl and NaOBr, respectively. The concentration of CHCl₃ formed by using a 0.258 mM NaOCl solution was 0.456 µM after reacted for 60 min at pH 8.0. In contrast, the concentration of CHBr₃ was only 0.218 µM by using a 0.258 mM NaOBr solution under the same reaction conditions. Thus, it was defined that twice the amount of CHCl3 was yielded compared with CHBr₃ for the reaction employing the same amounts of the two hypohalites for humic acid.

Effect of NaOBr concentration on the product distribution of THMs in the presence of excess NaOCl

Effects of varying the concentration of NaOBr (from 0 to 0.03 mM) on the distribution of THMs formed in the reaction with 0.258 mM of NaOCl and 10 mg/L humic acid at pH 8 were examined (Fig. 2). When the concentration of NaOBr was less than 0.005 mM, i.e., the ratio of [NaOBr]/[NaOCl] being less than 0.04, CHCl₃ was formed predominantly. Lower concentrations of other brominated THMs (Br-THMs, CHCl₂Br > CHClBr₂ > CHBr₃) were detected. This order is the same as the number of Br atoms in the Br-THMs by which Cl atoms in CHCl₃ were replaced. However, the profile of product distribution of THMs changes as the [NaOBr]/



Fig. 2. Distribution of THM species as function of concentration of NaOBr added to a reaction mixture of humic acid and NaOCl. $- - CHCl_3$; $- \Box - CHCl_2Br$; $- \bigtriangleup - CHClBr_2$; $- \circlearrowright - CHBr_3$; $- \blacksquare - Br-THMs$. Humic acid: 10 mg/L, NaOCl: 0.258 mM, pH: 8.0, Reaction time: 60 min.

[NaOCl] ratio increases. Over the molar ratio [NaOBr]/[NaOCl] = 0.1, the most predominant species among the four THMs formed was CHBr₃, followed by CHClBr₂, CHCl₂Br, and CHCl₃ in the decreasing order. This is opposite to the order observed at the ratio of [NaOBr]/[NaOCl] < 0.04. These results suggest that the ratio of [NaOBr]/ [NaOCl] regulates the product distribution of THMs intensely. As the concentration of NaOBr increases, the amount of CHCl3 decreases continuously, and those of CHCl2Br and CHClBr2 have maxima. On the other hand, CHBr3 begins to increase almost linearly with the concentration of NaOBr being higher than 0.003 mM. The finding that in spite of the presence of a high concentration of NaOCl larger amounts of CHBr₃ and CHClBr₂ are formed compared with those of CHCl₃ and CHCl₂Br suggests that the rate of substitution of bromide by NaOBr is greater than that of chloride by NaOCl. The addition of KBr in the reaction of NaOCl and humic acid gave profiles of the product distribution of THMs similar to the case of addition of NaOBr as shown in Fig. 3. These findings strongly suggest that Br⁻ is first oxidized to OBr⁻ by OCl- (Farkas et al., 1949) and the resultant OBr⁻ reacts with humic acid.

Effect of NaOCl concentration on THM formation in the presence of excess NaOBr

Effects of the varying concentration of NaOCl (from 0 to 0.129 mM) added to a reaction mixture of 0.258 mM NaOBr and 10 mg/L humic acid solution at pH 8.0 was also examined (Fig. 4). The yield of CHBr₃ as solely major product, increases almost linearly with the concentration of NaOCl. Small amount of CHClBr₂ is formed, but no significant formation of CHCl₃ and CHCl₂Br is observed under the conditions where both of OCl⁻ and OBr⁻ ion can react with humic acid. The concentrations of CHBr₃, CHClBr₂, CHCl₂Br, and CHCl₃ observed at 0.129 mM NaOCl were 1.468, 0.063, 0.007, and 0.006 μ M, respectively. Surprisingly, the



Fig. 3. Distribution of THM species as function of concentration of KBr added to a reaction mixture of humic acid and NaOCl. $- \blacklozenge - CHCl_3; -\Box - CHCl_2Br; - \bigtriangleup - CHClBr_2; -\bigcirc - CHBr_3$. Humic acid: 10 mg/L, NaOCl: 0.258 mM, pH: 8.0, Reaction time: 60 min.

concentration of CHBr₃ is seven times higher than that observed in the reaction with the same concentration of NaOBr in the absence of NaOCl. Such a highly attractive result was first observed here, and we suggest that NaOCl and NaOBr differ in oxidation ability and in rate of substitution in the course of THM formation from humic acid. If the oxidation potential and rate of halogenation for OCl^- are equal to those of OBr^- , increase of CHCl₃ should be observed with increasing NaOCl concentration under our conditions. Our results clearly shows that NaOCl promotes the formation of CHBr₃. Namely, NaOCl in the reaction system promotes mainly the oxidation of humic acid to prepare a precursors for THM formation.

Effect of pH on the amount and composition of THMs

The amount of THM formed in disinfection of natural water depends on the dose of the disinfectant Cl_2 , concentration of organic substrates, pH, and the water temperature (Urano *et al.*, 1983; Amy *et al.*, 1987; Adin *et al.*, 1991). We investigated the influence of pH on the formation of Br-THMs by using the reaction mixture of 0.0258 mM NaOBr





Fig. 5. Dependence of pH on the total brominated THM concentration formed by the addition of NaOBr or KBr.
- ◆ - NaOCl 0.258 mM + NaOBr 0.026 mM; - ○ - NaOCl 0.258 mM + KBr 0.026 mM. Humic acid: 10 mg/L, Reaction time: 60 min.

or 0.0258 mM KBr, 0.258 mM NaOCl and humic acid (Fig. 5). The total concentration of Br-THMs is found to be the same as those of using either NaOBr or KBr at up to pH 9.0. This means that the amount of Br-THMs formed is almost constant independent of pH in a range from 4 to 6, and increases with pH in a range from 6 to 9.0, and then decreases at pH above 9.5 in both cases. These behaviors correspond to those shown by Boyce and Hornig (1983). The increases of Br-THMs with the pH in the range of 6.0 to 9.0 is thought to be attributed to the increment of alkaline hydrolysis of the Br-THMs intermediates by OH⁻ (Peters et al., 1980). And also, these decreases at pH above 9.0 may be due to the following disproportionation of hypobromite ion (Bard et al., 1985).

$$OBr^- + 2HOBr \longrightarrow BrO_3^- + 2Br^- + 2H^+$$

From this equation, the OBr⁻ is disproportionated to bromate and bromide ions, neither of which reacts with humic acid. The disproportionation in the case of KBr proceeds slower than in the case of NaOBr. When NaOBr was used, the magnitude of the decrease was larger than that when KBr was used. This large decrease may be due to the magnitude of the proceeding of above disproportionation reaction. Since this disproportionation may proceed as fast as the decrease of the concentration of Br⁻ in the reaction systems of our experiment. Therefore, the degree of decrease in the amount of THMs with KBr relative to that with NaOBr is less than that of the case where NaOBr is used.

Yields of each THMs formed at various pH are listed in Table 1. The proportions of each THM



Fig. 6. Time dependencies of THM concentrations formed by the addition of OBr⁻ or Br⁻ at pH 5. (A) CHCl₃, (B) CHCl₂Br, (C) CHClBr₂, (D) CHBr₃, $-\phi$ - NaOCl 0.258 mM + NaOBr 0.01 mM, pH 4.9; $-\bigcirc$ - NaOCl 0.258 mM + KBr 0.01 mM, pH 4.8. Humic acid: 10 mg/L.

remained relatively constant. These results suggest that the amount of THMs produced depends on the pH values, while the THM composition, including CHCl₃, is almost independent of pH.

Effect of reaction time on the composition of THM products

Figure 6 shows the relationships between the yield of THMs and the reaction time when 0.01 mM NaOBr or 0.01 mM KBr coexisted with 0.258 mM NaOCl and humic acid at pH 5. The rate of production of each THM species by using NaOBr is similar to that using KBr. Under the low pH range, the amount of CHCl₂Br produced was linearly increased with reaction time until 180 min. The product distribution of four THMs is fairly unchanged at the reaction time ranging from 5 to 180 min. The order of magnitude of the rate of initial reaction for the formation of THMs (CHClBr₂>CHCl₂Br>CHBr₃) is the same as the order of the amounts of individual Br-THM formed when [NaOBr]/[NaOCl] or [KBr]/[NaOCl] was 0.04

Table 1. PH dependency of the distribution of THM species formed by addition of NaOBr

		pH	CHCl ₃ (µM%)	CHClBr (µM%)	CHClBr ₂ (µM%)	CHBr ₃ (µM%)	Total THM
NaOBr	0.0258 mM	4.9	3.1	10.5	42.0	44.4	100
		6.8	3.4	11.7	40.4	44.5	100
		8.0	2.7	11.7	41.0	44.6	100
		9.0	2.3	9.7	34.3	53.7	100
		9.9	4.2	13.3	33.3	49.1	100
		10.7	5.8	10.7	42.7	40.8	100

Humic acid: 10 mg/L, NaOCl: 0.258 mM, Reaction time: 60 min.



Fig. 7. Time dependencies of THM concentrations formed by the addition of NaOBr or KBr at pH 8. (A) CHCl₃,
(B) CHCl₂Br, (C) CHClBr₂, (D) CHBr₃, (E) Br-THMs.
- ◆ - NaOCl 0.258 mM + NaOBr 0.026 mM, pH 8.4;
- ○ - NaOCl 0.258 mM + KBr 0.026 mM, pH 8.1. Humic acid: 10 mg/L.

at pH 8 for 60 min reaction (Figs 2 and 3). As shown in Fig. 7, on the other hand, at [NaOBr]/[NaOCI] of 0.1 and pH 8, the initial rate of reaction for CHBr₃ formation is the highest and that for CHCl₃ is the lowest among the four THMs. The initial rates of the formation of four THMs increase with the number of Br atoms incorporated in the THM. These results suggests that the product distribution of the THM is controlled almost solely by the [NaOBr]/[NaOCI] molar ratio, but not by the reaction time.

DISCUSSION

There have been many investigations to elucidate the mechanism of THM formation in the disinfection of natural water by using dihydroxybenzenes as model compounds of humic acid and Cl_2 or Br_2 as halogenation reagent. This work has aimed to reveal the mechanism of brominated THM formation particularly in the coexistence of chlorine and bromine. Both of halogens (X₂) undergo rapid hydrolysis and disproportionation reaction to yield the corresponding halide ion (X⁻) and hypohalous acid (HOX) which can dissociate into hypohalite anion (OX⁻). The composition of halogen-containing species in the resulting solutions is largely pH dependent.

The two redox reactions consisting of Cl(+I)/Cl(0)/Cl(-I) redox couples are expressed by equations 1 and 2. The redox potential for equation 2, $E_{(2)}^{\circ}$, is referred to "Standard Potentials in Aqueous solution" (Bard *et al.*, 1985). The redox potential for equation 1, $E_{(1)}^{\circ}$, and the acid dissociation constant for HOCl, K_a , can be calculated on the basis of the data in the same book.

$$2\text{HOCl}+2\text{H}^{+}+2\text{e}^{-}=\text{Cl}_{2}(\text{aq})+\text{H}_{2}\text{O}$$
$$\text{E}_{(1)}^{\circ}=1.592\text{ V} \tag{1}$$

$$Cl_2(aq) + 2e^- = 2Cl^- E_{(2)}^\circ = 1.396 V$$
 (2)

$$HOCl = H^{+} + OCl^{-} pK_a = 7.543$$
 (3)

These available values readily give the potentialpH diagram for the HOCl–OCl⁻/Cl₂/Cl⁻ system, which is represented in Fig. 8(a).

Analogously, Fig. 8(b) shows the potential-pH diagram for the HOBr-OBr $^{-}/Br_{2}/Br^{-}$ system, which is obtained from the following three equations.

$$2HOBr+2H^{+}+2e^{-} = Br_{2}(aq) + H_{2}O$$
$$E_{(3)}^{\circ} = 1.582V$$
(4)

 $Br_2(aq) + 2e^- = 2Br^- \quad E_{(4)}^\circ = 1.087 V$ (5)

$$HOBr = H^{+} + OBr^{-} pK_a = 8.558$$
 (6)

The redox potential of the Cl_2/Cl^- couple is more positive than that of the Br_2/Br^- couple in the full pH range, which means that the humic acid is oxidized more readily by NaOCl than by NaOBr.

At pH 8, the species of OCl⁻ and HOBr in the X(+I) state predominate thermodynamically. The OCl⁻ species is 73.3 mol% of NaOCl and HOBr is 80.6 mol% of NaOBr: the ratio of the molar concentrations of OCl⁻ to HOBr is 0.909 under an equimolar amount of NaOCl and NaOBr. The concentration of OCl⁻ is about nine times higher than that of HOBr at pH 8 when the amount of NaOCl is ten molar times higher than that of NaOBr.

In the presence of excess NaOCl, $0.60 \ \mu\text{M}$ CHCl₃ was formed by $0.191 \ \text{mM}$ OCl⁻ ion in the reaction with humic acid in the absence of NaOBr (Fig. 2). The mixture of $0.191 \ \text{mM}$ OCl⁻ and $0.0242 \ \text{mM}$



Fig. 8. Redox potential (E°) -pH diagrams. (A) chlorine system, (B) bromine system.

HOBr, however, yielded $1.61 \,\mu\text{M}$ of total THM products including $0.134 \,\mu\text{M}$ of CHCl₃.

It has been reported (Tee et al., 1989) that HOX is more effective than OX⁻ ion for electrophilic substitution of humic acid. Hence, HOCl and HOBr might control the substitution reaction similarly. In our study, however, the amount of CHBr3 formed was found to be 6 times larger than that of CHCl₃ in spite of the ratio of [HOCl]/[HOBr] of 2.87. These observations suggest that HOBr becomes an electrophile stronger than HOCl when the two species compete in the substitution reaction. In other words, the oxidation ability of NaOCl is twice larger than that of NaOBr, but the rate of substitution by HOBr is 17 times higher than by HOCl. Accordingly, it can be assumed that humic acid is first oxidized by OCl- to give monohalogenated carbanion(I), and the resultant carbanion is substituted by HOBr faster than by HOCl to dihalogenated carbanion (II) as follows:

Humic acid
$$\xrightarrow{\text{Oxidation}}$$

(NaOX)

Humic acid <u>Substitution</u> Halogenated Humic acid (NaOX) (II)

The tentative reaction mechanism for the organic chemistry is as follows:

In the presence of excess of NaOBr, 0.149 μ M of CHBr₃ was formed by the reaction of 0.210 mM HOBr and humic acid in the absence of NaOCl. The amount of CHBr₃ formed was 0.369 μ M by the addition of 0.0191 mM of OCl⁻ to the 0.210 mM HOBr solution, and increased in parallel with the amount of OCl⁻ added. As the molar ratio of [HOBr]/[HOCl] corresponded to be 32 in this case of excess NaOBr, it is reasonable that CHBr₃ was a predominant product relative to CHCl₃. However, only by addition of a little amount of OCl⁻, the amount of CHBr₃ formed under the condition was larger than 2 times of CHBr₃ formed by 0.210 mM HOBr alone.

These evidences suggest that the OCl⁻ promoted the formation of the monohalogenated carbanions which have been postulated (Rebenne *et al.*, 1996) as initial intermediates of THM formation from humic acid, and that faster electrophilic substitution of the intermediates of THM is caused by HOBr subsequently.

The results of our experiments support the importance of the existence of mono halogenated carbanion formed by OCl⁻ as oxidant, predominantly through the pathways of formation of THM from humic acid.

From this work, we propose a new concept that when hypochlorite and hypobromite coexist, the hypochlorite reacts more effectively with humic acid in the oxidization reaction to produce precursors,



and then the hypobromite reacts predominantly in the subsequent electrophilic substitution reaction.

CONCLUSION

The results observed by the reaction of humic acid with NaOBr as bromination reagent in the presence of NaOCl were as follows;

(1) The product distribution of the THM is governed almost only by the [NaOBr]/[NaOCl] molar ratio, but within 60 min hardly by the reaction time and pH.

(2) The amount of THMs formed in the coexistence of NaOCl and NaOBr was larger than the sum of the CHCl₃ and CHBr₃ formed in the respective reactions of NaOCl and NaOBr alone with humic acid.

(3) In the presence of an excess amount of HOBr to OCl⁻, the amount of CHBr₃ formed increased with the concentration of OCl⁻, and was 7 times larger than that formed in the reaction of NaOBr alone with humic acid.

(4) These observations suggest that OCI^- ion in the THM formation reaction promotes the oxidation of humic acid, and that the rate of the subsequent substitution by HOBr seems higher than that of HOCl.

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REFERENCES

- Adin A., Katzhendler J., Alkaslassy D. and Rav-Acha C. (1991) Trihalomethane formation in chlorinated drinking water: A kinetic model. *Wat. Res.* 25, 797–805.
- Aizawa T., Magara Y. and Musashi M. (1989) Effect of bromide ions on trihalomethane (THM) formation in water. Aqua 38, 165–175.
- Amy G. L., Minear R. A. and Cooper W. J. (1987) Testing and validation of a multiple nonlinear regression model for predicting trihalomethane formation potential. *Wat. Res.* 21, 649–659.
- Bard A. J., Parsons R. and Jordan J. (1985) Standard Potentials in Aqueous Solution. Marcel Dekker, Inc., New York and Basel, pp. 70–83.

- Bellar T. A., Lichtenberg J. J. and Kroner R. C. (1974) Occurrence of organohalides in chlorinated drinking waters. J. Am. Wat. Wks. Ass. 66, 703–706.
- Boyce S. D. and Hornig J. F. (1983) Reaction pathways of trihalomethane formation from the halogenation of dihydroxyaromatic model compounds for humic acid. *Envir. Sci. Technol.* **17**, 202–211.
- Cooper W. J., Zika R. G. and Steinhauer M. S. (1985) Bromide-oxidant interactions and THM formation: A literature review. J. Am. Wat. Wks. Ass. 77, 116–121.
- Farkas L., Lewin M. and Bloch R. (1949) The reaction between hypochlorite and bromides. J. Am. Chem. Soc. 71, 1988–1991.
- Gaffrey J. S., Marley N. A. and Clark S. B. (1996) *Humic* and *Fulvic Acids*. American Chemistry Society, Washington, DC, pp. 2.
- Ichihashi K., Kanazawa Y., Isomura K. and Teranishi K. (1995) Examination of a full automated analytical method for volatile organic compounds in tap water with purge and trap/gas chromatography/mass spectrometer. J. Wat. Waste 37, 5–10in Japanese.
- Krasner S. W., Sclimenti M. J. and Means E. G. (1994) Quality degradation: Implications for DBP formation. J. Am. Wat. Wks. Ass. 86, 34–47.
- Norwood D. L., Johnson J. D., Christman R. F., Hass J. R. and Bobenrieth M. J. (1980) Reactions of chlorine with selected aromatic models of aquatic humic material. *Envir. Sci. Technol.* 14, 187–190.
- Peters C. J., Young R. J. and Perry R. (1980) Factors influencing the formation of haloform in the chlorination of humic materials. *Envir. Sci. Technol.* 14, 1391–1395.
- Rebenne L. M., Gonzalez A. C. and Olson T. M. (1996) Aqueous chlorination kinetics and mechanism of substituted dihydroxybenzenes. *Environ. Sci. Technol.* **30**, 2235–2242.
- Rook J. J. (1974) Formation of haloforms during chlorination of natural waters. *Water Treat. Exam.* 23, 234– 243.
- Rook J. J. (1977) Chlorination reactions of fulvic acids in natural waters. *Envir. Sci. Technol.* **11**, 478–482.
- Symons J. M., Speitel J. G. E., Diehl A. C. and Sorensen J. H. W. (1994) Precursor conyrol in waters containing bromide. J. Am. Wat. Wks. Ass. 86, 48–60.
- Tee O. S., Paventi M. and Bennett J. M. (1989) Kinetics and mechanism of the bromination of phenols and phenoxide ions in aqueous solution. Diffusion-controlled rates. J. Am. Chem. Soc. **111**, 2233–2240.
- Urano K., Wada H. and Takemasa T. (1983) Empirical rate equation for trihalomethaneformation with chlorination of humic acid. *Wat. Res.* **17**, 1797–1802.
- Yonebayashi K. and Hattori T. (1985) Nonaqeous titration of functional groups in humic acid. *Org. Geochem.* **8**, 47–54.