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## Contribution of brominated organic disinfection by-products to the mutagenicity of drinking water

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**Abstract** The activity inducing chromosomal aberrations of the mixture of brominated disinfection by-products (DBPs) was approximately three times higher than that of the chlorinated counterparts for the same hypohalous acid dose. With the combination of chromosomal aberration test and a new analytical technique to differentiate total organic chlorine (TOCl) and total organic bromine (TOBr), it was found that TOBr was correlated to the mutagenicity of chlorinated waters. It was also implied that for a bromide-to-TOC ratio of 0.1 (mg/mg C), brominated DBPs could account for at least 29% of the total toxicity of DBPs formed during chlorination. On the other hand, bromate ion, a major ozonation DBP, was not a major contributor to the activity inducing chromosomal aberrations of the water treated with an ozone/chlorine sequential process. Therefore, ozonation is one possible option to reduce the health risk caused by DBPs even in the presence of bromide.

**Keywords** Brominated disinfection by-products; chlorination; chromosomal aberration test; ozonation

### Introduction

When a source water is chlorinated in drinking water treatment process, not only chlorinated disinfection by-products (DBPs) but also brominated DBPs are produced. Naturally occurring bromide ion ( $\text{Br}^-$ ) in source waters is easily oxidized to hypobromous acid (HOBr) (Pinkernell *et al.*, 2001), and then HOBr reacts with natural organic matter (NOM) to form brominated compounds (Richardson *et al.*, 1999a). These brominated DBPs have been gathering more attention recently because studies have suggested that small brominated compounds such as bromoacetic acids are much more mutagenic to mammalian cells than their chloro counterparts (Plewa *et al.*, 2002). Also, Nobukawa and Sanukida (2001) demonstrated that genotoxicity of chlorinated water greatly increases with  $\text{Br}^-$  using Ames test and micronuclei formation assay.

However, while the above results imply the importance of controlling brominated DBPs during drinking water treatment processes, many questions on the contribution of brominated DBPs to the toxicity of finished water remain unanswered. One of these questions is the relative toxicity of the mixture of brominated DBPs to that of chlorinated DBPs. Past studies only consisted of comparative studies on simple DBPs or toxicity evaluation of a mixture that contained both chlorinated and brominated DBPs. It is of practical importance to quantitatively identify raw water characteristics and treatment conditions with which the contribution of brominated DBPs is of concern.

Ozonation is commonly used to decompose the precursors of chlorinated DBPs (Richardson *et al.*, 1999b). Studies have suggested that preozonation can destroy reaction sites in NOM for chlorinated DBP formation, and reduce the toxicity of finished water (Patterson *et al.*, 1995). However, little information is available on the effect of  $\text{Br}^-$  on the toxicity of water treated by an ozone/chlorine sequential process. Also, the relative toxicity of ozonation DBPs in the presence of  $\text{Br}^-$  (e.g., bromate ion ( $\text{BrO}_3^-$ )) to the entire toxicity of finished water is not fully understood.

The main objective of this study is to answer the two unanswered questions mentioned above. This study consisted of three sets of experiments. First, chromosomal aberration test was performed to compare the mutagenicity of brominated DBPs with that of chlorinated DBPs. These two mixtures were separately prepared by the reactions between humic acid and corresponding hypohalous acids (i.e., HOBr and hypochlorous acid (HOCl)), so that the activity inducing chromosomal aberrations of brominated and chlorinated DBPs could be evaluated separately. In the second part of this study, total organic bromine (TOBr) and total organic chlorine (TOCl) of the mixtures of DBPs formed during chlorination in the presence of  $\text{Br}^-$  were measured by the combination of a combustion furnace and an ion chromatograph, and were compared to the results of chromosomal aberration test. With this new analytical technique, it was possible to determine the contribution of TOBr and TOCl to TOX. Lastly, the activity inducing chromosomal aberrations of the DBPs formed during the ozone/chlorine sequential treatment both with and without  $\text{Br}^-$  was evaluated. Of particular concern was the effect of pH during ozonation on the toxicity and the contribution of  $\text{BrO}_3^-$ , an ozonation DBP, to the total toxicity of finished water.

## Experimental

### Sample preparation

**Humic acid solution.** Concentrated humic acid solutions (TOC = 750–1,000 mg/L) were used as model NOM solutions to perform the chromosomal aberration test without concentrating samples after reactions. The concentrated humic acid solutions were prepared by dissolving approximately 3 g of humic acid (Aldrich) in 1 L of 0.01 N NaOH solution for 24 hr with vigorous mixing, readjusting pH to 7.0, and filtering through a glass fiber filter (GS25, Advantec).

**HOBr solution.** To minimize the effect of liquid bromine ( $\text{Br}_{2(\text{aq})}$ ), a bromide-free HOBr solution for direct bromination was prepared by oxidizing  $\text{Br}^-$  (0.23 M KBr solution) with a NaOCl solution (Wako). The concentration of the stock solution was measured by direct UV absorbance at 266 nm (Beckwith *et al.*, 1996). A commercial NaOBr solution could not be used for this purpose because it contains approximately equal amount of  $\text{Br}^-$  and thus  $\text{Br}_{2(\text{aq})}$  was not negligible at a high dose around pH7.0 (Snoeyink and Jenkins, 1980). Similar consideration was not necessary for HOCl solution because the equilibrium constant for hydration is much lower than that for  $\text{Br}_{2(\text{aq})}$ .

**Chlorination and bromination.** Chlorination and bromination were performed by adding NaOCl solution (Wako) or the HOBr stock solution to the mixture of the concentrated humic acid solution, a phosphate buffer solution (final concentration = 50–175 mM), and a KBr (Wako) solution (if necessary). The samples were stored in dark place at 20°C for 24 hours before chromosomal aberration test and chemical analysis unless otherwise noted.

**Ozone/chlorine sequential treatment.** Concentrated humic acid solutions (pH 6.0, 7.0 or 8.0) were ozonated in an impinger (inner volume = 30 mL) in semi-batch mode. Ozone was generated from ultrapure oxygen using a Mitsubishi OS-1N-A ozone generator. The flow rate of ozone was 1.5 mg/min. After ozonation, the pH of the solution was readjusted to 7.0 with NaOH or  $\text{H}_2\text{SO}_4$ , and the solution was chlorinated following the procedure described above. The readjustment of pH was necessary to evaluate the effect of pH during ozonation.

### Chromosomal aberration test

Chromosomal aberration test using Chinese hamster lung cells (CHL/IU, Dainihon Pharmaceutical) was performed to evaluate the initiating activity in the carcinogenesis process of humic acid solutions treated by chlorination, bromination, and an ozone/chlo-

rine sequential treatment. The details of the test procedure is described elsewhere (Itoh *et al.*, 1996). The number of abnormal cells was counted by visual observation under a microscope. For each sample, 100 metaphases were analyzed. The ratio of the sample volume to the media volume was fixed to 1/6. The incubation time after contacting with sample solutions was 24 hr. To minimize the decomposition of DBPs, no quenching reagent was added to the samples since chlorine and bromine concentrations were less than the concentration range where cytotoxicity on CHL cells is significant.

#### Chemical analysis

**TOX analysis.** TOX (TOBr+TOCl) was analyzed by following the Standard Methods (1995). A Mitsubishi Chemical TOX-10Σ TOX analyzer was used for the analysis.

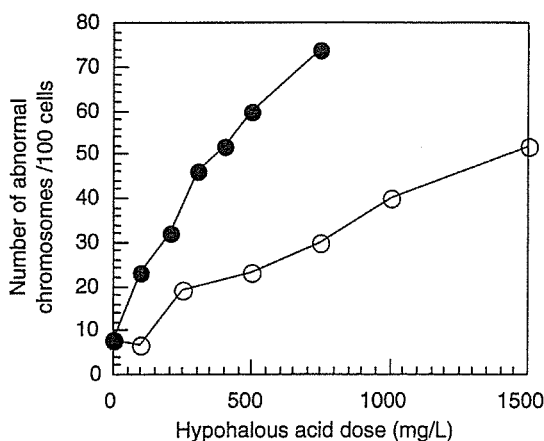
**Differentiation of TOBr and TOCl.** The detail of the procedure is described elsewhere (Echigo *et al.*, 2000). But, briefly, the off gas from a TOX furnace that contains HCl and HBr corresponding to TOCl and TOBr was trapped into distilled water, and these Cl<sup>-</sup> and Br<sup>-</sup> were separately quantified by an ion chromatograph. A TOX analyzer (TOX-10Σ, Mitsubishi Chemical) was used as a furnace. A Shimdzu VP-10 system was used for ion chromatographic analysis.

**Bromate analysis.** Bromate ion concentration was determined by ion chromatography with a post-column derivatizing method (Wagner *et al.*, 1999). Samples were diluted prior to the analysis.

## Results and discussion

#### Activity inducing chromosomal aberrations of the brominated and chlorinated DBPs

The activity inducing chromosomal aberrations of the mixture of brominated DBPs was approximately three times higher than that of chlorinated DBPs at the same doses of hypohalous acids (Figure 1). For example, at 750 mg Cl/L, the number of abnormal chromosomes was 60 per 100 cells for the mixture of brominated DBPs, while the number for chlorinated DBPs were 23 per 100 cells. Two explanations are possible for this result. One is the difference of the toxicity between brominated DBPs and chlorinated DBPs on molar basis (i.e. TOX basis). The other one is the difference of the amount of halogenated compounds produced by the two hypohalous acids. To test these hypotheses, the number of



**Figure 1** Comparison of the activity inducing chromosomal aberrations of brominated DBPs from the reaction between HOBr and humic acid with that of chlorinated DBPs from the reaction between HOCl and humic acid. Conditions: humic acid concentration, 1,000 mg C/L; reaction time, 24 hours; temperature, 20°C. The ratios of the hypohalous acid doses to TOC were similar to a chlorine-to-DOC ratio in actual drinking water treatment practice

chromosomal aberrations per unit TOX (mmol) was calculated (Table 1). From this result, it can be clearly seen that the activity inducing chromosomal aberrations of the mixture of brominated DBPs per unit TOX is roughly two to six times higher than that of chlorinated DBPs, while the TOX formation per unit hypohalous acid addition was almost identical for HOBr and HOCl. Thus, it can be said that the mixture of the brominated DBPs is more toxic than that of chlorinated DBPs.

With this difference on the magnitude of the activity inducing chromosomal aberrations between brominated DBPs and chlorinated DBPs shown in Table 1, rough estimation of the contribution of brominated DBPs to the total mutagenicity is possible for a model raw water. For example, Echigo *et al.* (2000) reported that the TOBr-to-TOX ratio of a model chlorinated water ( $\text{Br}^- = 100 \mu\text{g/L}$ ; chlorine dose = 4.0 mg Cl/L; DOC = 3.0 mg/L) was approximately 7%. Hence, assuming the effect of all the DBPs are additive and the chemical structures of both NOMs are similar, it is estimated that brominated DBPs account for roughly 12–30% of the activity inducing chromosomal aberrations of the model drinking water.

#### Activity inducing chromosomal aberrations of chlorination DBPs in the presence of $\text{Br}^-$

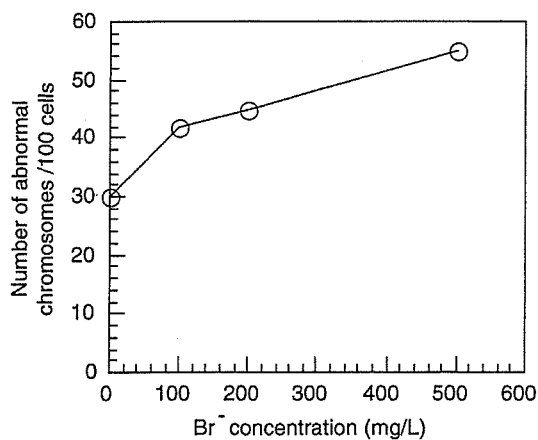
*Effect of  $\text{Br}^-$  concentration on the activity inducing chromosomal aberrations of chlorinated water.* The implication from the comparison of the toxicity of brominated DBPs and chlorinated DBPs led us to investigate more realistic situations. That is, chlorination in the presence of  $\text{Br}^-$ . Figure 2 illustrates that with increasing  $\text{Br}^-$  concentration, the number of abnormal chromosomes increases. This tendency was in agreement with the results of Ames assay and micronuclei formation test (Nobukawa and Sanukida, 2001). Also, this increase of the number of abnormal chromosomes corresponded to the formation of TOBr (Figure 3).

For the initial  $\text{Br}^-$  concentration of 100 mg/L ( $\text{Br}^-/\text{TOC} = 0.1 \text{ mg/mg}$ ), the number of abnormal chromosomes was 1.4 times higher than that without  $\text{Br}^-$ . Hence, at least 29% (=  $0.4/1.4$ ) of the activity inducing chromosomal aberrations could be attributed to brominated DBPs under this condition. This percentage fell in the range estimated from the relative activity inducing chromosomal aberrations of brominated DBPs and chlorinated DBPs given in the previous section and the TOBr and TOCl data (17–39%).

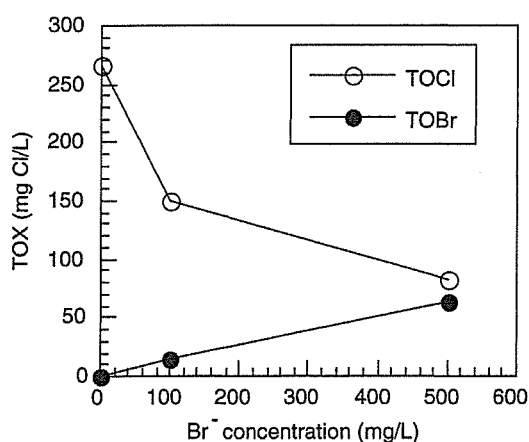
Assuming that TOC of a typical source water is 2 mg/L, the corresponding  $\text{Br}^-$  concentration to the  $\text{Br}^-/\text{TOC}$  ratio = 0.1 is 200  $\mu\text{g/L}$ . Average  $\text{Br}^-$  concentration in the United States is 100  $\mu\text{g/L}$  (Westerhoff *et al.*, 1998), and 200  $\mu\text{g/L}$  is relatively high but not uncommon. Serious attention should be paid to brominated DBPs for the raw waters that contains  $\text{Br}^-$  above this level. Also, a linear interpolation suggested a 7–20% increase of chromosomal aberrations for the  $\text{Br}^-/\text{TOC}$  ratio of 0.05 (100  $\mu\text{g/L}$  for TOC = 2 mg/L) compared to the number of abnormal cells without  $\text{Br}^-$ .

**Table 1** Activity inducing chromosomal aberrations of the reaction products of the reaction between HOBr and humic acids and those between HOCl and humic acid on TOX basis. See the caption of Figure 1 for the reaction conditions

Halogenating reagent	Dose (mg Cl/L)	TOX (mg Cl/L)	TOX/dose (mg/mg)	Number of abnormal chromosomes per TOX (count/100 cells mmol)
HOBr	100	14.4	0.14	56.7
	200	21.3	0.11	53.3
	500	60.8	0.12	35.0
HOCl	250	35.0	0.14	19.3
	750	97.1	0.13	11.0
	1,500	185.7	0.12	9.9

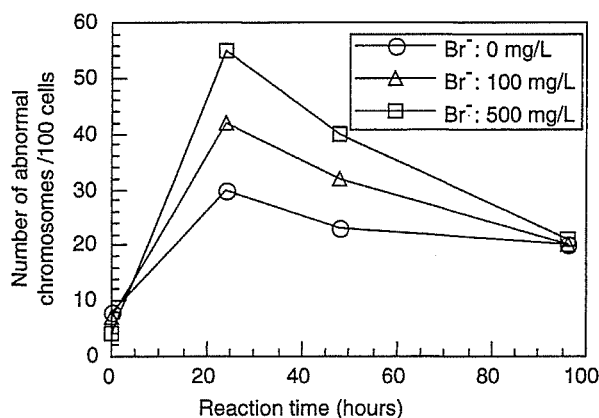


**Figure 2** Effect of initial Br<sup>-</sup> concentration on the activity inducing chromosomal aberrations of chlorinated humic acid solution. Conditions: humic acid concentration, 1,000 mg C/L; reaction time, 24 hours; temperature, 20°C; chlorine dose, 1,500 mg/L



**Figure 3** Effect of initial Br<sup>-</sup> concentration on the distribution of TOBr and TOCl during chlorination of a concentrated humic acid solution. See the caption of Figure 2 for reaction conditions

The effect of reaction time on the activity inducing chromosomal aberrations was also investigated (Figure 4). The number of abnormal chromosomes was highest after 24 hours, and then decreased regardless the initial concentration of Br<sup>-</sup>. After 96 hours, the numbers of abnormal chromosomes were almost identical with and without Br<sup>-</sup>. This result appears to be in agreement with a general observation that hydrolysis of brominated compounds is faster than chlorinated counterparts (Larson and Weber, 1994).



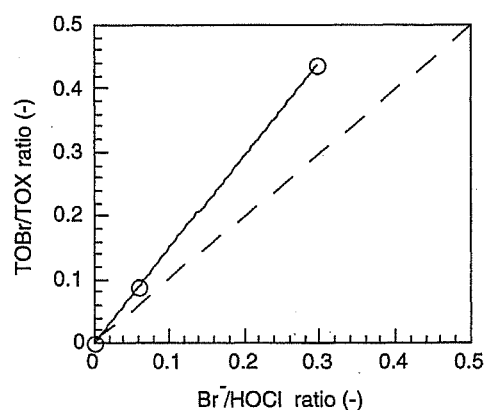
**Figure 4** Effect of reaction time on the activity inducing chromosomal aberrations of chlorinated humic acid solution. Conditions: humic acid, 1,000 mg C/L; temperature, 20°C; chlorine dose, 1,500 mg/L

*Competition between HOBr and HOCl to humic acid.* In Figure 5, the ratio of  $\text{Br}^-$  to HOCl and the ratio of TOBr to TOX are compared. The latter was higher than the former, though certain reaction time is required for the formation of HOBr before reacting with NOM. If the reactivities of HOBr and HOCl to humic acid are similar, the Br-to-HOCl ratio should be less than the TOBr-to-TOX ratio (i.e., below the dashed line in the figure). Thus, bromination of humic acid by HOBr has to be kinetically preferential to chlorination. Indeed, it is known that the reactions between phenolic compounds and HOBr are much faster than those with HOCl (Echigo and Minear, 2001; Gallard *et al.*, 2003). Also, it was indicated that bromination of humic acid is faster than chlorination (Qualls and Johnson, 1983; Echigo, 2002).

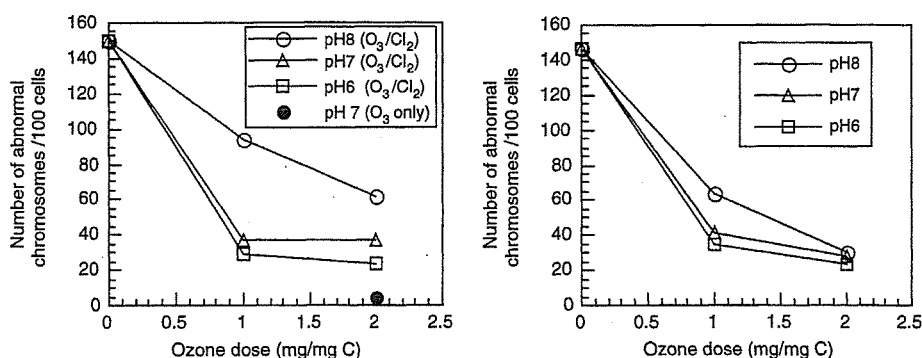
#### Effect of preozonation on the activity inducing chromosomal aberrations of chlorinated humic acid

The effect of preozonation on the chlorinated humic acid with and without  $\text{Br}^-$  is shown in Figure 6. Regardless the presence of  $\text{Br}^-$  and pH (6–8), the number of abnormal chromosomes decreased with ozonation. Therefore, the ozone/chlorine sequential treatment is an effective way to improve the safety of finished water with and without  $\text{Br}^-$  compared to chlorination.

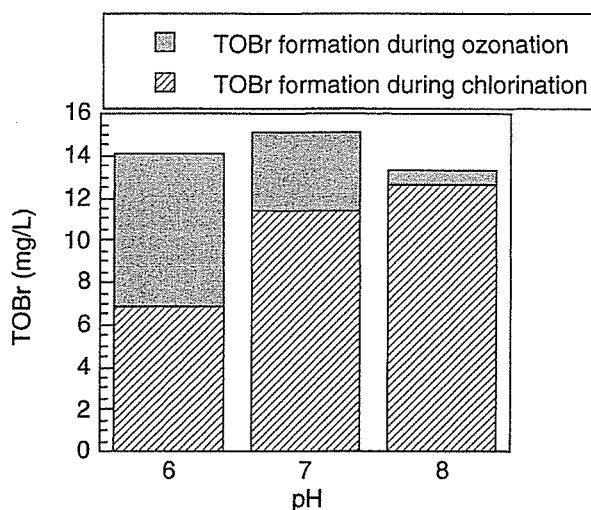
The effect of pH during ozonation (note: chlorination was conducted at pH7.0) was not as evident as the pH effect during chlorination (Kowbel *et al.*, 1984). But the number of abnormal chromosomes was slightly higher at higher pH, especially with  $\text{Br}^-$ . The first possible explanation would be the contribution of  $\text{BrO}_3^-$  since in general higher  $\text{BrO}_3^-$  formation is observed for higher pH (Pinkernell *et al.*, 2001). However, comparing  $\text{BrO}_3^-$  concentration range (0.0–1.1 mg/L) in this experiment with a reported dose-response curve



**Figure 5** Comparison of the  $\text{Br}^-$ -to-HOCl ratio with the TOBr-to-TOX during chlorination of a concentrated humic acid solution. See the caption of Figure 4 for the reaction conditions. Dashed line is the hypothetical line for  $\text{Br}^-/\text{HOCl} = \text{TOBr}/\text{TOX}$



**Figure 6** Effect of ozonation on the activity inducing chromosomal aberrations of chlorinated humic acid solution with (left,  $\text{Br}^-/\text{TOC} = 0.05$  mg/mg) and without (right)  $\text{Br}^-$ . Conditions: humic acid concentration, 750 mg DOC/L; reaction (chlorination) time, 24 hours; temperature, 20°C; chlorine dose, 1,500 mg/L



**Figure 7** Effect of pH on the formation of TOBr during the ozone/chlorine sequential treatment. Ozone dose was 2 mg/mg C. See the caption of Figure 6 for other reaction conditions

(Life-science Information Center, 1998), it was implied that  $\text{BrO}_3^-$  could not be a major contributor to the activity inducing chromosomal aberrations of this solution. Also, the contribution of reaction products during ozonation (i.e., without chlorine addition) was small (see the solid circle in Figure 6 (left)). Thus, main contributors to the activity inducing chromosomal aberrations of the water treated with the ozone/chlorine sequential treatment are the DBPs formed during the chlorination stage.

TOX formation decreased by approximately 20% with preozonation (data not shown in figures). Also, while no clear pH dependence was observed for TOX and TOBr formed in the ozone/chlorine sequential treatment, the TOBr formed during the chlorination stage in the ozone/chlorine sequential treatment did depend on pH and higher TOBr observed for high pH (Figure 7). This may be related to the difference of the activity inducing chromosomal aberrations for different pH during ozonation.

## Conclusions

This study demonstrated that brominated organic DBPs can be major contributors to the activity inducing chromosomal aberrations of the finished water. Other major findings from this study are listed below.

- The activity inducing chromosomal aberrations of the reaction products of the reaction between humic acid and HOBr was two to six times higher than those between humic acid and HOCl on TOX basis.
- For a bromide-to-TOC ratio of 0.1 (mg/mg), brominated DBPs accounted for at least 29% of the activity inducing chromosomal aberrations of DBPs formed during chlorination.
- With increasing initial  $\text{Br}^-$  concentration, both TOBr and the number of abnormal chromosomes increased. That is, TOBr formation corresponded to the toxicity of the chlorinated water.
- With the differentiation technique between TOBr and TOCl, it was implied that bromination of humic acid is dominant over chlorination in the initial phase of chlorination process.
- Bromate ion, a major ozonation DBP, was not a major contributor to the activity inducing chromosomal aberrations of the water treated with the ozone/chlorine sequential treatment.
- Ozonation is a possible option to reduce the health risk caused by chlorination DBPs even in the presence of  $\text{Br}^-$ .



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## Bromide Removal by Hydrotalcite-Like Compounds

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### ABSTRACT

Bromide removal from aqueous phase was attempted using hydrotalcite-like compounds (HTCs) to minimize the formation of brominated disinfection by-products (DBPs) in drinking water treatment processes. The anion selectivity and anion exchange capacity of HTCs depended on synthesis conditions. In particular, the type of cations and the molar ratio of trivalent ions to divalent ions had strong impact on the anion-exchange characteristics of HTCs. Among the HTCs synthesized in this study, MgAlFe-HTCs prepared with a cation molar ratio of Mg : Al : Fe = 8 : 1 : 1 was effective for bromide removal. While both column tests and batch tests demonstrated that HTCs are effective for bromide removal, the anion-exchange characteristics in a continuous system was different from those in batch experiments. It is necessary to run column tests for predicting the performance of HTCs in drinking water treatment system.

**Keywords:** Bromide, Disinfection by-products, Hydrotalcite-like compounds, Layered double hydroxide, Ion exchange, Drinking water treatment

### INTRODUCTION

The formation of brominated disinfection by-products (DBPs) is of great concern both in chlorination and ozonation in drinking water treatment (Fig. 1). In chlorination, bromide ion rapidly reacts with hypochlorous acid (HOCl) to form hypobromous acid (HOBr). (Larson and Weber, 1994). The source of bromide can be both natural (by geological formation or intrusion of seawater) and anthropogenic (Siddiqui *et al.*, 1995). In Japan, bromide concentration in source waters falls in the range between 0 to 450  $\mu\text{g/L}$ , and mostly around or slightly below 50  $\mu\text{g/L}$  (Shimazaki *et al.*, 2004). Hypobromous acid formed rapidly reacts with natural organic matter (NOM) in source water (Westerhoff *et al.*, 1998) to form brominated organic compounds. Recent toxicological studies have suggested the importance of controlling brominated DBPs in drinking water treatment. For example, Echigo *et al.* (2004) showed that the products of the reaction between hypobromous acid and humic acid are five to ten times more mutagenic than the ones between hypochlorous acid and humic acid on TOX basis.

During ozonation, the formation of bromate ion ( $\text{BrO}_3^-$ ) is the primary concern among various DBPs produced. Bromate is classified as Group 2B (possibly carcinogenic to human) by International Agency for Research on Cancer, and is regulated at 10  $\mu\text{g/L}$  by the Japanese drinking water quality standards. Considering that 10 to 50 % of bromide in raw water is converted to bromate ion, this regulation poses a difficult situation to many water utilities.

Given the toxicological importance of controlling brominated DBPs, many attempts have been made to minimize brominated DBPs. These attempts are

categorized into four groups: (1) use of alternative disinfectants, (2) modification of chlorination and/or ozonation processes, (3) removal of DBPs, (4) removal of precursors *i.e.*, reactive components in dissolved organic matters (DOM), and bromide. Each option has its advantage and disadvantage. Switching to other disinfectants is effective to reduce trihalomethanes (THMs) and bromate ion. However, as long as a chemical disinfectant is used, the formation of DBPs is unavoidable because both NOMs and microorganisms to be inactivated are organic compounds.

Modifications of chlorination and ozonation processes are widely used. Among many operating conditions, disinfectant dose and reaction pH are most commonly modified to reduce the formation of regulated DBPs (*e.g.*, THMs). However, it should be noted that these modifications may sacrifice the disinfection capability of the system, or may enhance the formation of different types of DBPs.

As the third option, adsorption by activated carbon is most commonly used. However, activated carbon treatment is not effective for hydrophilic compounds.

The last option is the removal of precursors.

#### Chlorination

NOM	+	HOCl/OCl	→	Organic chlorines
Br	+	HOCl/OCl	→	HOBr/OBr
NOM	+	HOBr/OBr	→	Organic bromines

#### Ozonation

Br	+	$\text{O}_3$	→	HOBr/OBr
NOM	+	HOBr/OBr	→	Organic bromines
HOBr/Obr	+	$\text{O}_3/\text{HO}\cdot$	→	$\text{BrO}_3^-$

Fig. 1 Formation of brominated DBPs.

Relatively hydrophobic components of NOMs can be removed by activated carbon treatment, but hydrophilic fractions are difficult to remove. Recently, a magnetic ion-exchange resin was found to be effective for the removal of hydrophilic fractions of NOM (Singer and Bilyk, 2002). The removal of bromide has been also attempted by several researchers. Amy and Siddiqui (1999) reported that activated carbon treatment, coagulation, and softening are not practical for bromide removal. Reverse osmosis (RO) treatment is capable of removing bromide, but not cost effective if used solely for bromide removal. Ion-exchange process can remove bromide ion (Amy and Siddiqui, 1999), but may not be cost effective as conventional ion-exchange resins also remove other ions and use up ion exchange sites for bromide ion. However, recent advances in material chemistry suggested some possibility of controlling ion selectivity of inorganic ion-exchangers (*e.g.*, Tezuka *et al.*, 2004). This technique may lead to the synthesis of a bromide-selective ion-exchanger. One promising class of compounds in this area is hydrotalcite-like compounds (HTCs). The present study investigates the possibility of bromide removal by HTCs.

HTCs are known to have anion exchange capability, and are classified as layered double hydroxides (LDHs) in clay mineralogy. Fig. 2 shows the crystal structure of HTCs. The backbone structure of HTCs consists of brucite-like sheets ( $\text{Mg}(\text{OH})_2$ ) of which divalent cations (*e.g.*,  $\text{Mg}^{2+}$ ) are randomly substituted by trivalent cations (*e.g.*,  $\text{Al}^{3+}$ ). The net positive charge in the backbone structure requires anions to be placed between the cation sheets. The unique anion selectivity of HTCs is caused by "ion sieve" effect; that is, the gap between guest layers rejects large anions. Also, some HTCs are

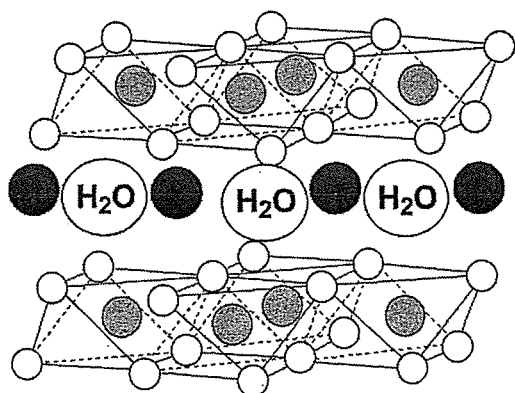


Fig. 2 Crystal Structure of HTCs.

○, -OH groups; ●, bromide ion; ⊙, metal ions (tri- or divalent).

unique in that their ion-exchange capacity is enhanced by calcination. Anions consisting of "guest layers" (anion layers between cation layers) are easily volatilized at high temperature, and the structure of calcinated HTCs with a larger ion-exchange capacity is reconstructed in water (Miyata, 1983). HTCs have been applied to the removal of various ions *i.e.* dyes (Cavani *et al.*, 1991), fluoride (Daset *et al.*, 2003), nitrate (Tezuka *et al.*, 2004), but few attempt was made on bromide removal by HTCs.

The purpose of the present study is to evaluate the anion exchange characteristics of various HTCs, including calcinated HTCs. The competition among common anions in source waters (*i.e.*, bromide, chloride, nitrate, and sulfate) was evaluated by a series of batch experiments. Also, anion removal experiments by HTCs in real source water were conducted. In addition, column experiments were performed to evaluate the anion removal characteristics of HTCs in a continuous system.

## MATERIAL AND METHODS

### Material

**Chemicals.** All the chemical reagents used in this study were of reagent grade or better (mostly analytical grade), were purchased from Wako unless otherwise noted, and used without further purification. All the aqueous solutions used in this study were prepared with ultra pure water treated by a Millipore Elix10 system.

**Source water.** For the experiments with real source water, Lake Biwa water was used. The water was sampled on the west shore of South Lake of Lake Biwa on January 31, 2005. Lake Biwa is the largest lake in Japan, and serves more than ten million people in the Kansai area as a water source.

### Synthesis of HTCs

HTCs used in this study were synthesized by the following hydrothermal method. First, the divalent and trivalent cation sources (chloride salts were used unless otherwise noted) were mixed in approximately 100 mL of ultra pure water. The types and ratios of cations used were shown in Table 1. The total amount of cations was set to 0.125 mol.

Second, the cation mixture and 25 % ammonia solution or 1N NaOH solution were added dropwise to approximately 200 mL of ultra pure water in a 500 mL beaker with micro tube pumps (EYELA MICROTUBEPUMP MP-3, Tokyo Rikakikai). The flow rates of the pumps were adjusted so that the pH of

Table 1 Conditions of HTCs synthesis.

HTC Type	MgAl	MgAlFe
divalent cation	$\text{Mg}^{2+}$	$\text{Mg}^{2+}$
trivalent cation	$\text{Al}^{3+}$	$\text{Al}^{3+}, \text{Fe}^{3+}$
molar ratios of cations	$[\text{Mg}^{2+}] : [\text{Al}^{3+}]$ = 2 : 1, 3 : 1, 4 : 1	$[\text{Mg}^{2+}] : [\text{Al}^{3+}] : [\text{Fe}^{3+}]$ = 4 : 1 : 1, 6 : 1 : 1, 8 : 1 : 1
calcination time and temperature	1 hr, 450°C	

the mixture could be kept in alkali region (pH 10 to 11) to obtain the precipitation of mineral hydroxide. During the addition of the two solutions, the mixture in the flask was stirred with a magnetic stirrer and a stirrer bar. The final volume of the suspension was approximately 500 mL.

Third, hydrothermal treatment was conducted to improve the crystallization of the suspension; the mineral hydroxide obtained was transferred into a 1-L Teflon-tube container (10 cm i.d.). The container was placed in a hydrothermal reactor (TEM-D1000M, Taiatsu Techno), heated at 120°C for 24 hr with mild stirring (120 rpm), and left quietly for aging at room temperature for 24 hr.

Fourth, the suspension was washed with ultra pure water and vacuum-filtered with 1 µm glass fiber filter, and dried at 80°C for 1 day in a desiccator (SH-OMT, Nitto Kagaku). Then, the dried HTC were ground to powder with a mortar. Some of the synthesized HTCs were calcinated at 450 °C for 1 hr to evaluate the effect of the calcination on the anion-exchange characteristics of HTCs.

#### Evaluation of the anion-exchange property of HTCs

To identify HTCs having the "good" anion-exchange property for bromide removal, a series of anion exchange experiments was conducted in batch mode. In these experiments, both dried and calcinated HTCs were tested (see Figs. 4 and 5 for HTCs tested). Considering the ion content in natural water, the test solution was prepared with chloride, nitrate, sulfate, and bromide (100 µM each).

Each anion removal test was initiated by adding 0.1 g of a dried HTC or 0.05 g of a calcinated HTC to 100 mL of the test ion solution in a 100 mL beaker. The mixture was stirred for 24 hr with a magnetic stirrer and stirrer bar. The aqueous phase was separated from the HTC phase by passing through 0.45 µm filter (GL chromato disk, GL Science). Anion concentrations were determined by ion chromatography (LC-VP, Shimadzu) with a Shim-pack IC-A3 analytical column (Shimadzu) protected by a Shim-pack IC-GA3 guard column (Shimadzu). The mobile phase was 50 mM boric acid/ 8 mM *p*-hydroxybenzoic acid/ 3.2 mM bis-tris. Anion removals were calculated by subtracting the remaining concentrations in aqueous phase from the initial concentrations.

#### Experiments on practical aspects of ion exchange treatment by HTCs

To apply an ion-exchange process using HTCs to drinking water treatment, it is necessary to collect the information on the effects of the various co-existing substances in natural water on bromide removal. For this reason, batch experiments were conducted in a real source water matrix with several HTCs which were found to be effective for bromide removal in terms of both selectivity and ion-exchange capacity in the series of batch experiments described in the previous subsection. Also column experiments were conducted to

evaluate bromide-exchange characteristics of HTCs in continuous mode.

#### Bromide removal from a real source water.

In the batch experiments, both dried and calcinated HTCs (see Fig. 6 and 7 for the types of HTCs used) were used. Lake Biwa water was used for this series of experiments (note that because the ambient concentration of bromide in Lake Biwa water was too low to accurately determine, bromide concentration was adjusted to 100 µM by adding potassium bromide). The procedure of the experiments was almost the same as the batch experiments with the synthesized anion solution (see the previous subsection) *i.e.*, each test was initiated by adding 0.1 or 0.2 g of a dried HTC, or 0.05 or 0.2 g of a calcinated HTC to the Lake Biwa water in a 100 mL beaker. In addition, dissolved organic carbon (DOC) before and after the addition of HTCs was measured with a Shimadzu 5000A TOC analyzer.

#### Bromide removal in a continuous system.

Column tests were also conducted with both dried and calcinated HTCs. For this series of experiments, the synthesized anion solution was prepared based on the compositions of anions in Lake Kasumigaura because the bromide concentration of this Lake is the highest among major Lakes in Japan.

The schematic of the system is shown in Fig. 3. The gap between the spacers in the column (Millipore Vantage™ L column) was approximately 10 cm, and 0.2 g of a HTC was placed in the gap. The glass fiber filters at the top and the bottom of the gap were to prevent the leakage of HTCs. The ion solution was continuously pumped to the column by a Sep-Pak Concentrator Plus pump (Waters) at a flow rate of 1 mL/min.

Effluent was sampled at every 0.5 or 1 hr for 20 hr. Anion concentrations of the samples were determined as average concentrations by ion chromatography (LC-VP, Shimadzu) after passing through 0.45 µm filter (see the previous subsection for analytical conditions). In paral-

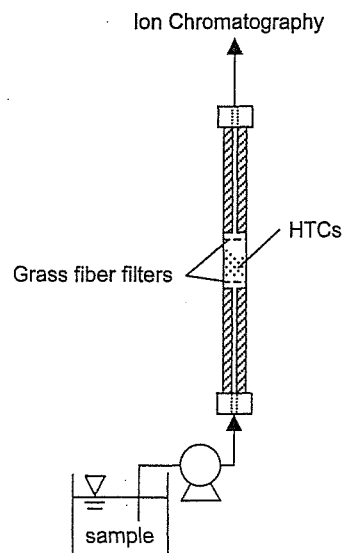


Fig. 3 Schematic flow of the column test.

lel, pH was monitored with the rest of the samples.

## RESULTS AND DISCUSSION

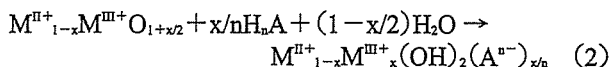
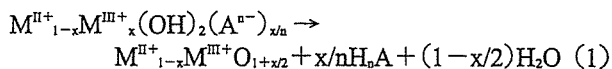
### Anion Selectivity Test with a Synthesized Anion Solution

The removals of anions from the synthesized ion solution by dried HTC are shown in Fig. 4. While bromide removals were more than 50 % in most cases, the removal of sulfate was the highest among the four anions tested for most of the HTCs. This is a common observation for many ion exchangers including organic anion-exchange resins. However, MgAlFe(8:1:1) and MgAl(4:1) showed higher removal ratios to nitrate than sulfate, and bromide removal ratios are relatively high compared to other HTCs (note that the ratios in parenthesis indicate the molar ratio of cations).

Two important remarks can be made from the results above. First, MgAlFe(8:1:1) and MgAl(4:1) containing higher divalent cations than other HTCs appeared to have the high selectivity to bromide. The exact relationship between the ratio of divalent cation to trivalent cation and the structure of HTCs in aqueous phase is still unknown, but this is useful information for synthesizing a HTC effective to monovalent anion removal. Second, MgAlFe(8:1:1) was less selective to divalent anions (sulfate in this case). This is a unique feature of HTCs and very important for monovalent anion removal from fresh waters because sulfate concentration is usually much higher than monovalent anions. In short, the results from this experiment suggest a possibility of synthesizing a HTC more selective to monovalent anions, bromide in particular, by refining synthesis conditions.

Figure 5 shows the removals of the anions by calcinated HTCs. The anion exchange capacity of HTCs was greatly enhanced by calcinations. This is mainly because chloride ions in the crystal structures of HTCs were volatilized by calcination, and HTCs were converted to metallic oxide (1). Then, metallic oxide reconstructed HTC structure in solution, and removed more

anions than non-calcinated HTCs (2). However, the unique anion selectivity of some HTCs (e.g., MgAlFe(8:1:1)) to monovalent anions were lost by calcination. This result indicates that calcinated MgAlFe(8:1:1) is effective for removing anions from water if anion selectivity is not required.



For efficient anion removal, both selectivity and total anion exchange capacity are important factors. Keeping these factors in mind, dried MgAlFe(8:1:1), which showed relatively high selectivity to bromide, and calcinated MgAlFe(8:1:1), which had large ion-exchange capacity, were selected for the experiments in the following subsections.

### Bromide Removal from Lake Biwa water

The effects of natural organic and inorganic anions contained in Lake Biwa water on bromide removal by HTCs were evaluated in batch mode. Figure 6 shows the removal ratios of anions and TOC in Lake Biwa water by 1 g/L of dried MgAlFe(8:1:1) and 0.5 g/L of calcinated MgAlFe(8:1:1). Anion uptakes by both dried MgAlFe(8:1:1) and calcinated MgAlFe(8:1:1) considerably were lower than those from the synthetic anion solution in the previous sections, and the bromide removals were around 20 %. These low bromide removals could be attributed to carbonate ion and natural organic ions in Lake Biwa water. The removal ratio of TOC was 17-19 %, approximately 0.3 mg/L. The uptake of TOC not only consumed the sites for anion exchange, but also expanded the interlayer distance of HTCs. It has been known that the change of interlayer distance has a great impact on the anion-exchange properties of HTCs. For example, Millange *et al.* (2000) re-

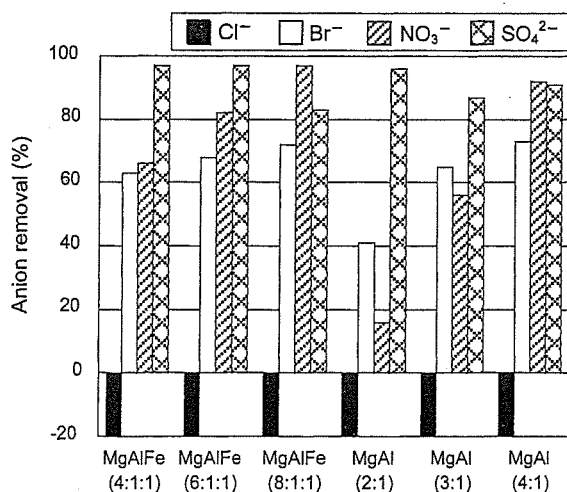


Fig. 4 Removal ratios of anions by 1 g/L of dried HTCs in a model solution (Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>; 100 μM).

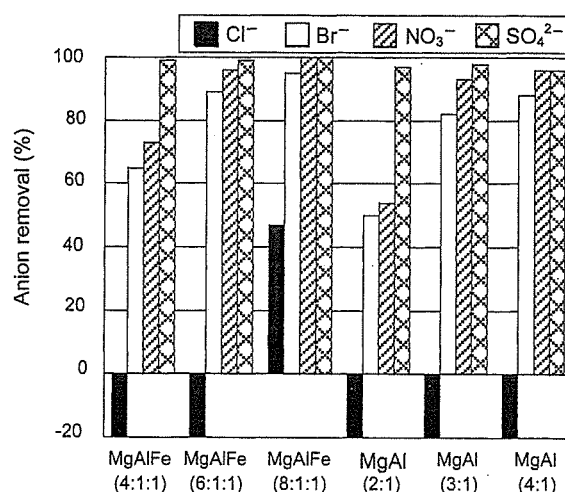


Fig. 5 Removal ratios of anions by 0.5 g/L of calcinated HTCs in a model solution (Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>; 100 μM).

ported that a calcinated HTC with carbonate ions in its guest layer has the  $d_{003}$  value of 0.788 nm, but the  $d_{003}$  value changes to the 1.36 nm by the adsorption of trinitrophenol to the interlayer. From this  $d_{003}$  value (1.36 nm), the corresponding interlayer distance is calculated to be 0.88 nm. However, this gap between the cation layers is too wide to hold the target anions of this study (note that the diameters of the bromide, chloride, and nitrate are approximately 0.35 nm).

Figure 7 shows the removals of the anions by 2 g/L of dried and calcinated MgAlFe(8 : 1 : 1) to evaluate whether the increase of the amount of HTC lead to sufficient anion removal. In this case, 91 % of bromide ion was removed by calcinated MgAlFe(8 : 1 : 1). From this result, it can be said that the anion-exchange reaction by HTCs is inhibited by NOM in raw waters, but sufficient bromide removal is achieved by adding proper amounts of HTCs. Also, the calcinated MgAlFe(8 : 1 : 1), which has larger ion exchange capacity, found to be better than the dried one under the condition of this experiment.

**Anion Removal by HTCs in a Continuous System**

In the previous two experiments, the bromide-exchange property of HTCs was evaluated by a series of batch experiments, but the characteristics of HTCs in a continuous system must be evaluated in order to apply HTCs to real drinking water treatment systems. For this purpose, removal ratio of bromide in column test was monitored. Dried MgAlFe(8 : 1 : 1) and calcinated MgAlFe(8:1:1) were used in this experiment.

Figure 8 showed the time-removal profiles of the four anions when treated by dried MgAlFe(8 : 1 : 1). The pH values of the effluent were at  $10.0 \pm 0.3$ . The removal ratio of bromide was almost 100 % in the initial six hours despite its lower initial concentration than other anions. Then, the removal ratio gradually decreased and dropped to 0 % or below, but it was higher than 60 % in the initial fourteen hours.

After a certain period of time, the removal ratio of

bromide and nitrate went down to below 0 %, in other words, “desorption” from the interlayer structure of dried MgAlFe(8 : 1 : 1) occurred. The primary reason for this is likely to be the effect of sulfate, that is, sulfate exchanged from the solution expanded the interlayer distance of dried MgAlFe(8 : 1 : 1) because the diameter of sulfate (0.516 nm) is larger than that of the initial anion, chloride (0.344 nm). The “widen” interlayer cannot hold smaller monovalent anions (i.e., bromide, nitrate, and chloride) any longer. Also, it is of note that the anion selectivity in the continuous mode was different from that in batch mode. In the batch experiment, the selectivity of the anions was in the following order: nitrate > sulfate > bromide. However, in the continuous mode, the removal of nitrate was much lower than those of bromide and sulfate, indicating that this HTC is effective for bromide removal even with relatively high concentration of nitrate. This difference in the anion selectivity implies the dependence of the anion selectivity of HTCs on the composition of the water to be treated at the configuration of the reactor. Thus, it is recommended to run a column test with target waters to evaluate the applicability of this HTC.

Figure 9 showed the time-removal profiles of the four anions when treated by calcinated MgAlFe(8 : 1 : 1). The effluent pH was at  $11.2 \pm 0.3$ . The removal ratio of bromide was sufficiently over 60 % in the initial fourteen hours, but sharply went down to 0 % after sixteen hours. After that, the captured bromide ions were gradually released from the interlayer of MgAlFe(8 : 1 : 1) to the solution. From the point of water quality management, such a sudden decrease of removal ratio of bromide is difficult to respond. Thus, judging from both removal ratio of bromide and “stability” of removal, dried MgAlFe(8 : 1 : 1) is suitable to drinking water treatment.

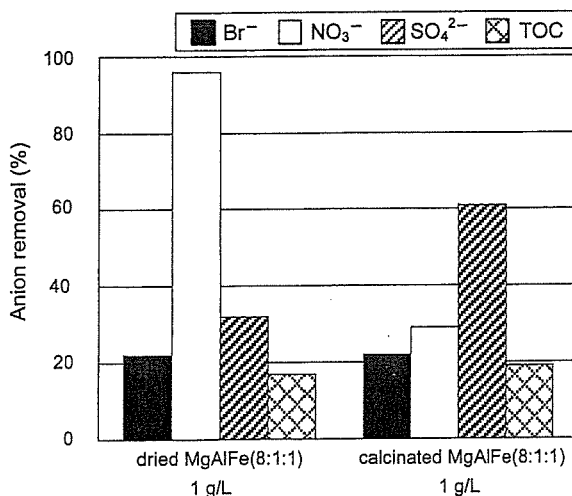


Fig. 6 Removal ratios of anions by 1 g/L of dried MgAlFe(8 : 1 : 1) and 0.5 g/L of calcinated MgAlFe(8 : 1 : 1) in Lake Biwa water. Bromide concentration was adjusted to 100 μM.

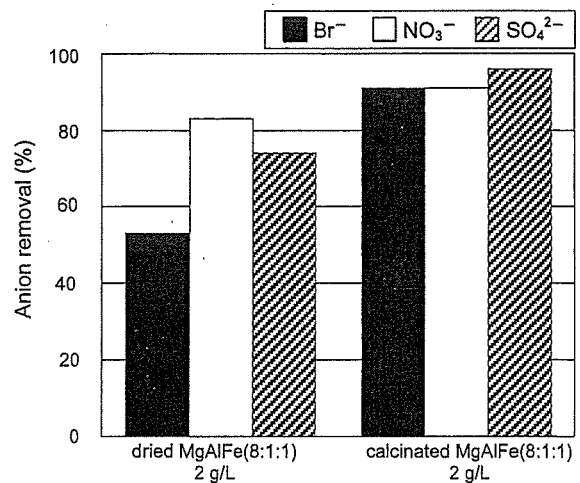
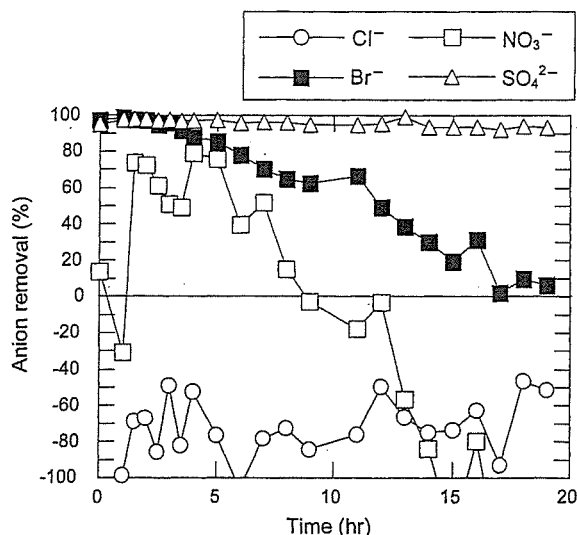


Fig. 7 Removal ratios of anions by 2 g/L of dried MgAlFe(8 : 1 : 1) and calcinated MgAlFe(8 : 1 : 1) in Lake Biwa water. Bromide concentration was adjusted to 100 μM.



**Fig. 8** Time-removal profiles of the four anions when treated by dried MgAlFe(8 : 1 : 1).  
Condition: Cl<sup>-</sup>, 10 mg/L; Br<sup>-</sup>, 200 μg/L; NO<sub>3</sub><sup>-</sup>, 850 μg/L; SO<sub>4</sub><sup>2-</sup>, 10 mg/L; dried MgAlFe(8 : 1 : 1) 0.2 g.

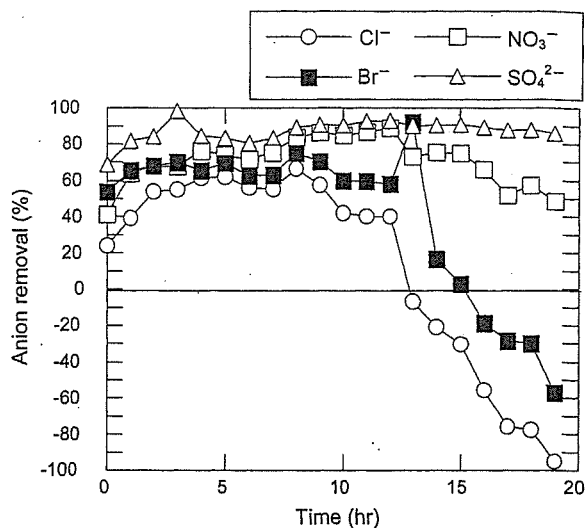
**CONCLUSIONS**

In this study, bromide removal was attempted by HTC to minimized brominated DBPs formation in drinking water treatment. The major findings from this study are listed below.

- 1) The anion selectivity and anion exchange capacity of HTCs changed with synthesis conditions. In particular, the type of cations and the molar ratio of trivalent ions to divalent ions had strong impact on the anion-exchange characteristics of HTCs. Among the HTCs synthesized in this study, dried MgAlFe (8 : 1 : 1) showed the highest selectivity to bromide ion, and calcinated MgAlFe (8 : 1 : 1) showed the largest anion-exchange capacity in an aqueous solution containing 100 μM of chloride, bromide, nitrate, and sulfate.
- 2) Anion-exchange reactions by HTCs were interfered by NOM in Lake Biwa water, but sufficient bromide removal was achieved by increasing HTC dose.
- 3) While both column tests and batch tests demonstrated that HTCs are effective for bromide removal, the anion-exchange characteristics in a continuous system were different from those in batch experiments. It is recommended to run column tests for predicting the performance of HTCs in drinking water treatment system.

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**Fig. 9** Time-removal profiles of the four anions when treated by calcinated MgAlFe(8 : 1 : 1).  
Condition: Cl<sup>-</sup>, 10 mg/L; Br<sup>-</sup>, 200 μg/L; NO<sub>3</sub><sup>-</sup>, 850 μg/L; SO<sub>4</sub><sup>2-</sup>, 10 mg/L; calcinated MgAlFe(8 : 1 : 1) 0.2 g.

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## 〈特集論文〉

# 浄水プロセスにおける NOM およびフェノール性化合物の臭素化反応の速度論

## Bromination Kinetics of Phenolic Compounds and NOM by Hypobromous Acid in Drinking Water Treatment

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### Abstract

Kinetic information on the reactions between hypobromous acid (HOBr) and phenols and the reactions between HOBr and natural organic matter (NOM) was collected by sequential stopped-flow technique. The observed second-order rate constants ( $k_2^{obsd}$ ) of 15 phenols at pH7.0 ranged from  $3.3 \times 10^2$  to  $6.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ , indicating higher reactivity than other unsaturated organic compounds. The rate constants of the reactions between HOBr and 14 phenolates ( $k_2'$ ), the major reaction pathway in the common pH range in drinking water treatment practice, were correlated to Hammett's  $\sigma$  values and  $k_2'$  for chlorination of phenols by HOCl. Multiple reaction phases were found during the reaction between HOBr and NOMs. The number of reaction sites for the fast reaction phase of NOM from three different sources ranged from 0.20 to  $0.92 \mu\text{mole (mg C)}^{-1}$ , and was linked to specific phenolic contents. Also, the apparent second-order rate constants for the initial reaction phase between HOBr and NOM were similar that of vanillin. A chemical quenching method using 2-chlorophenol confirmed that bromination is a dominant reaction pathway during the reaction between NOM and HOBr over oxidation.

**KeyWords** : NOM, bromide, hypobromous acid, disinfection byproducts, sequential stopped-flow analysis, bromination

## 1. はじめに

水道原水中の天然有機物 (Natural Organic Matter, NOM) は、浄水プロセスの各单位操作により一部は系外に取り除かれるが、溶存成分の多くは凝集沈殿・砂ろかプロセスでは除去されず、消毒剤または酸化剤などによって化学的変換作用を受ける。この化学反応により生成した化合物を一般に消毒副生成物 (Disinfection Byproducts, DBPs) という。DBPsの一部は、発がん性などの慢性毒性を示すとされ、この制御が水道工学上の大きな課題となっている。臭素系DBPsは、近年特に多くの注目を集めている。これは、最近の毒性学的研究により、有機臭素系DBPsはTOX基準で有機塩素系DBPs

に比べて毒性が高い可能性が示されたためである<sup>1,2)</sup>。

有機臭素系DBPsは、(1)消毒剤等の酸化剤と水道原水中に数  $\mu\text{g/L}$  から数100  $\mu\text{g/L}$  の濃度範囲で存在<sup>3,4)</sup>している臭化物イオン(Br<sup>-</sup>)の酸化による次亜臭素酸(HOBr)の生成、(2)HOBrとNOMの反応、という2段階を経て生成する。後段のHOBrとNOMの反応速度論は有機臭素系DBPsの生成特性を理解する上で必要不可欠なものであるが、十分な速度論情報が集積されているとはいえない。

NOMとHOBrの反応速度論に関する情報が欠如している最大の理由は、この反応が極端に速いためである。これまでの多くの試みでは、特に中性付近において、通常の回分式の実験では、反応の初期段階のHOBr濃度を追跡することが非常に困難であるということが示されてきたに過ぎない<sup>5)</sup>。

NOMの化学構造の様々な構成要素のうち、HOBrとの反応を考える上でフェノール性化合物は特に注目に値

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する。これは、フェノール性化合物が様々なハロゲン化剤に対して高い反応性を示し、特に水溶液中の臭素分子( $\text{Br}_{2(\text{aq})}$ )には拡散律速あるいはそれに近い速度で反応することが知られているためである<sup>6)</sup>。したがって、NOM分子中のフェノール性水酸基を持つ芳香環もHOBrに対して高い反応性を示し、有機臭素系DBPsの生成に大きく関与するものと推定される。また、HOBrとフェノール性化合物の反応生成物は毒性学的にも重要なものであると考えられている。例えば、フェノール性化合物はハロ酢酸類(HAAs)の主な前駆体の一つであるとされている<sup>7)</sup>。以上のことから、フェノール性化合物を浄水プロセス(より具体的にはオゾンおよび塩素処理過程)におけるNOMとHOBrの高速反応に関与する主たる反応部位の一つと仮定することは妥当であり、またこの反応に関する速度論情報を整理することは工学的にも意義があるといえる。

HOBrと不飽和化合物の高速反応中でのHOBr濃度の測定に関しては、いくつかの技術的問題点がある。まず、HOBrと多くの不飽和化合物の紫外スペクトルが重なるため、通常の高速溶液反応の速度論実験で用いる吸光度の直接測定<sup>8)</sup>は困難である。また、有機化合物の紫外スペクトルが問題にならなかったとしてもHOBrの初期濃度に関して制約条件がある。すなわち、十分な感度を得ようとするためにHOBr初期濃度を高く設定することはできない。これは、化学平衡により、HOBr濃度に対する $\text{Br}_{2(\text{aq})}$ および $\text{Br}_3^-$ 濃度が無視できなくなる、つまりフェノール性化合物と $\text{Br}_{2(\text{aq})}$ や $\text{Br}_3^-$ の反応が無視できなくなるためである<sup>6,9)</sup>。 $\text{Br}_{2(\text{aq})}$ と $\text{Br}_3^-$ は反応性が高い化学種ではあるが、実際の浄水プロセスの条件下では系内に存在し得ないため、分析上の理由からHOBrの濃度を高く設定することは妥当性を欠く。

これらの問題を回避するためにGallardら<sup>10)</sup>は、フローチューブリアクターを用いてDPD法によりHOBr濃度の経時変化測定を行い、3種類のフェノール性化合物(フェノールについては塩素化体についても若干検討)とHOBrの反応速度定数を決定した。この結果から、構造が比較的単純なフェノール性化合物については、塩素処理過程においてはHOBrによる臭素化がHOClによる塩素化に優先することが示された。また、オゾン処理では、オゾンによる酸化の方が臭素化よりも速いことを速度論的に示した。

以上のGallardらによる研究成果は、浄水プロセスにおいて臭素化反応に注目する必要性を指摘した点で重要なものと評価できる。しかしながら、NOM分子中のフェノール性化合物は、この研究で検討されたものより複

雑な構造を有しており、さらに多様な置換基の影響について検討する必要がある。特にカルボキシル基はNOM分子中に普遍的に含まれていることが知られており、その影響は必須の検討課題といえる。また、実際のNOMとHOBrの反応速度についても測定し、フェノール性化合物とHOBrの反応速度と比較する必要がある。これまでに、Westerhoffら<sup>11)</sup>が若干の検討を試みているが時間解像度が不十分であり、速度論的パラメーターが得られているとはいえない。

以上のことを踏まえ、本稿では中性付近でのフェノール性化合物とHOBrの高速溶液反応に関する速度論情報を整理し、さらにNOMとHOBrの反応速度パラメーターと比較を行う。本研究では、この分野での技術的問題点であった時間解像度と検出感度の問題を、ABTS法<sup>12)</sup>と多段ストップ・フロー分析を組み合わせることで解決する。本方法は時間解像度とデータ数確保の容易さの両面で、従来の方法よりも優れている<sup>10,11)</sup>。ABTS法では2,2-azino-bis(3-ethylbenzthiazoline)-6-sulfonic acid-diammonium 塩(ABTS)が酸性条件下でHOBrに高い反応性を示し、なおかつ生成物が可視域で高い吸光度を示すことを応用している。多段ストップ・フロー分析システムはHOBr水溶液と反応対象となる水溶液さらにABTS試薬を正確にごく短時間のうちに混合することができる。

## 2. 実験方法

### 2.1 試薬

実験に用いた試薬は全てAnalytical Gradeかそれ以上の純度で、特に断りのない場合には全てAldrich (Milwaukee, WI) から購入したものをを用いた。水溶液の調製には脱イオン蒸留水(DDI)を用いた。

本実験でHOBrとの反応速度を測定したフェノール性化合物は、フェノール、2-ヒドロキシ安息香酸、3-ヒドロキシ安息香酸、4-ヒドロキシ安息香酸、2-プロモフェノール、4-プロモフェノール、2-クロロフェノール、4-クロロフェノール、2-ニトロフェノール、バニリン、*o*-クレゾール、*m*-クレゾール、*p*-クレゾール、バニリン酸、レゾルシノール、4-メトキシフェノールの16種類であった。また、比較のためにアニソール(メトキシベンゼン)についても同様の実験を行って反応速度定数を算出した。

また、HOBrのNOMに対する反応性に関する実験では、2種類の単離されたNOMと1種類の水道原水を用いた。これらの基本的な化学的性状をTable 1にまとめる。表中

Table 1. Characteristics of the water and NOM samples tested.

code	DOC (mg L <sup>-1</sup> )	NH <sub>4</sub> <sup>+</sup> (μmole (mg C) <sup>-1</sup> )	SUVA <sup>a</sup> (L cm <sup>-1</sup> mg <sup>-1</sup> )	phenolic content <sup>b</sup> (μmole(mg C) <sup>-1</sup> )
SRFA	-	0.2	0.042	1.93
LBJ	-	0.7	0.014	0.37
LKA <sup>e</sup>	12.8	0.3	0.011	0.43

<sup>a</sup> Specific UV absorbance. <sup>b</sup> as phenol equivalent. <sup>c</sup> Suwannee River fulvic acid.

<sup>d</sup> Lake Biwa NOM, <sup>e</sup> a lake water from the Midwest region, USA.

のLBJは琵琶湖南湖水から逆浸透膜により分離された NOMで、京都大学工学研究科附属環境質制御研究センターより提供を受けたものである。Suwannee河フルボ酸 (SRFA) は International Humic Substance Society より購入したものをそのまま用いた。LKA はアメリカ合衆国中西部の湖沼より採取した湖沼水である。LKA に関しては Pellicon 0.22 μm PVDF 膜 (Millipore) により粒子状物質を除去した後、実験に供した。また、これら3試料中に含まれるフェノール性化合物の総量は、Folin法<sup>13)</sup>により推定した。

HOBr 保存液は Pinkernell ら<sup>12)</sup>による方法にしたがって、オゾンにより KBr 水溶液を当量で pH4 付近にて酸化することにより調製した。オゾン水は Song ら<sup>14)</sup>と同様の方法で調整した。この方法による HOBr の収率は常に 90% 以上であり、未反応の Br<sup>-</sup> は 3% 以下であった。このため、Br<sub>2(aq)</sub> と Br<sub>3</sub><sup>-</sup> の濃度は、化学平衡から考えて<sup>9)</sup>HOBr および OBr<sup>-</sup> の濃度に対して無視でき、臭素化反応に関与する化学種は HOBr と OBr<sup>-</sup> のみであるとしてよい。残りの数%の一部は臭素酸イオン (BrO<sub>3</sub><sup>-</sup>) として検出されたが、予備実験により BrO<sub>3</sub><sup>-</sup> の存在はフェノール性化合物と HOBr の反応に影響を及ぼさないことを確認した。また、残りの数%は脱気操作中に失われたものと考えられた。なお、HOBr 保存液の濃度は直接波長 266 nm の吸光度を測定することで確認した (HOBr のモル吸光係数は 97 cm<sup>-1</sup> M<sup>-1</sup> とした<sup>15)</sup>)。測定には、Beckman DU-500 紫外可視吸光度計を用いた。Br<sup>-</sup> と BrO<sub>3</sub><sup>-</sup> 濃度は、フェノールで HOBr をプロモフェノールとして除去した後、イオンクロマトグラフィー (システム, Dionex DX-300; カラム, AS9-HC column)<sup>16)</sup>により分析した。

ABTS は Sigma (St. Louis, MO) より購入した。ABTS 酸性溶液は、2 mM ABTS 保存液 5 mL と 1.8 M 硫酸 1 mL を DDI で混合、希釈し 100 mL としたものをを用いた。この ABTS 酸性溶液は 3 時間ごとに調製した。また、2 mM ABTS 保存液は 2 日ごとに新しく調製した。

## 2.2 多段ストップ・フロー分析による HOBr 濃度の測定法

反応はすべて SX. 18MV-R 連続ストップ・フロー分析システム (Applied Photophysics, UK) で行った (Fig. 1)。まず HOBr とフェノール性化合物 (50 mM リン酸緩衝液中に溶解) または NOM 水溶液 (以下簡単のため LKA も含めて Table 1 に示した NOM を含む 3 種の試料を NOM 水溶液と表記する) を第 1 ミキサーで混合し、このミキサーとセルの間のテフロンチューブ内に一定時間保持する (この保持時間が反応時間となる)。その後、セル内 (第 2 ミキサーは吸光度セルを兼ねる) でこの溶液と ABTS 酸性溶液<sup>12)</sup>を混合し直ちに 417 nm または 728 nm にて HOBr 濃度に対応する ABTS<sup>+</sup> ラジカルの吸光度を測定した。反応は 20 °C にて行った。なお、このシステムで実現可能な最短反応時間 (第 1 ミキサーで混合した後に第 2 ミキサーで混合するまでの最短時間) は 10 ms であった。第 2 ミキサー内の吸光度測定用セルの光路長は 10 mm とした。なお、擬 1 次反応条件を実現するために、フェノール性化合物と HOBr の反応ではフェノール性化合物初期濃度は HOBr 初期濃度の 10 倍以上に設定した。また、本システムによる HOBr の定量限界は 0.2 μM であった。

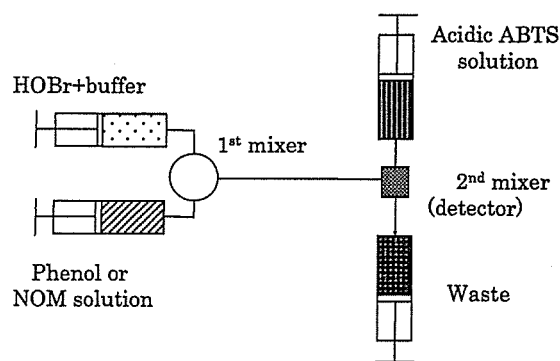


Fig. 1. Schematic of the sequential stopped-flow system.

なお、第2ミキサー内におけるフェノール性化合物およびNOMとHOBrの反応は、HOBrとABTSの反応よりかはるかに遅く、今回の実験条件ではセル内に到達したHOBrのうち少なくとも95%がABTSと反応した。このことは、ABTS溶液とフェノール性化合物(あるいはNOM)の混合液とHOBr水溶液を混合したときの吸光度と、ABTS溶液(フェノール類を含まない)と同じHOBr水溶液の混合液の吸光度に差がないことにより間接的に確認した。クレゾール類だけは例外的にこの予備実験におけるHOBr回収率が100%に満たず、95-98%の範囲であった。ただし、この場合もHOBrの未回収率がクレゾールの濃度に比例し、HOBr濃度には無関係であったので擬1次反応速度定数の決定に際しては補正計算を行う必要はなかった。

### 2.3多段ストップ・フロー分析による反応タイプの決定

HOBr濃度に加えて、HOBrとNOMの反応の様式についても推定を試みた。すなわち、反応後のBr濃度を測定することで臭素化反応以外の酸化還元反応に消費されたHOBrの量を算出した。

ストップ・フロー分析システムの設定条件は第3シリンジで注入する反応停止剤を除いて同様である。2.1では反応停止剤兼発色試薬としてABTS酸性試薬を注入したが、この実験ではpH7.0に調節した500 μM 2-クロロフェノールによりHOBrをプロモクロロフェノール類として捕捉した。残存しているBrは臭素化反応以外の酸化還元反応により消費されたHOBrの量に対応すると見なすことができるので、このBrをイオンクロマトグラフにより測定した(システム、Dionex DX-300; カラム、AS9-HC)。

## 3. 実験結果と考察

### 3.1 HOBrとフェノール性化合物の反応速度論

16種類のフェノール類とHOBr反応は見かけ上それぞれの濃度に対し1次で、2次反応と見なすことができた。その結果のうちpH7.0における見かけの2次反応速度定数( $k_2^{obsd}$ )をTable 2に示す。ただし、HOBrとレゾルシノールの反応はpH7.0においては速すぎて測定することができなかった(pH4.0では  $k_2^{obsd}$  は  $1.7 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  であった)。

置換基をもつフェノール性化合物の多くが、フェノール自体よりも反応サイトの数(すなわち求電子置換反応

**Table 2.**  $k_2^{obsd}$  of the reaction of HOBr and phenols at pH 7.0 at 20 °C. Conditions: buffer, 25 mM phosphate buffer; initial HOBr concentration, 2.0-7.0 μM; phenol concentration, 20-45 μM. Each compound was tested at least at three different HOBr concentrations and three phenolic compound concentrations (i.e., at least nine runs) to determine  $k_2^{obsd}$ .

No.	compound	$k_2^{obsd} (\text{M}^{-1}\text{s}^{-1})$
1	phenol	$(4.1 \pm 0.1) \times 10^4$
2	2-hydroxybenzoic acid	$(3.3 \pm 0.2) \times 10^2$
3	3-hydroxybenzoic acid	$(5.1 \pm 0.2) \times 10^4$
4	4-hydroxybenzoic acid	$(5.2 \pm 0.1) \times 10^4$
5	2-nitrophenol	$(2.0 \pm 0.3) \times 10^4$
6	2-bromophenol	$(2.3 \pm 0.1) \times 10^5$
7	4-bromophenol	$(2.1 \pm 0.1) \times 10^4$
8	2-chlorophenol	$(2.0 \pm 0.1) \times 10^5$
9	4-chlorophenol	$(2.5 \pm 0.1) \times 10^4$
10	vanillic acid	$(1.3 \pm 0.1) \times 10^5$
11	vanillin	$(6.0 \pm 0.4) \times 10^5$
12	4-methoxyphenol	$(3.1 \pm 0.1) \times 10^4$
13	<i>o</i> -cresol	$(4.5 \pm 0.2) \times 10^4$
14	<i>m</i> -cresol	$(2.7 \pm 0.2) \times 10^5$
15	<i>p</i> -cresol	$(7.4 \pm 0.2) \times 10^4$
16	resorcinol	$>(1.7 \pm 0.2) \times 10^6$

に関与するオルト位、パラ位のC-H結合)が少ないにもかかわらず、大きな $k_2^{obsd}$ を示すことは注目に値する。NOM中のフェノール性化合物は様々な置換基を有するので、NOM分子中のフェノール性化合物についてもHOBrに対して高い反応性をもつ化学構造が存在するものと考えられる。

$k_2^{obsd}$ のpH依存性については多くのフェノール性化合物についてはGallardらの報告<sup>10)</sup>と同様の傾向を示した。すなわち、2-ヒドロキシ安息香酸と2-ニトロフェノールの場合を除き、 $k_2^{obsd}$ はpH5.0-8.0の範囲で単位pHあたり10倍に増加し(Fig. 2)、中性付近においてはフェノレートイオンとHOBrの反応がHOBrの減少速度を支配していると考えられた。また、この傾向は、HOCl<sup>17,18)</sup>、Br<sub>2(aq)</sub><sup>9)</sup>およびHOI<sup>19)</sup>によるフェノール性化合物のハロゲン化の速度と共通のものであった。なお2-ヒドロキシ安息香酸はカルボキシル基とフェノール性水酸基の相互作用によりpKaが13.6と他のフェノールに比べて異常に高いため<sup>20)</sup>、本実験のpH領域ではフェノレートの寄与は明確には認められなかった。また、2-ニトロフェノールについては非解離のものとHOBrの反応も無視できないものと考えられた。

以上の結果から、実際の反応の主体である各フェノール性化合物のフェノレートとHOBrの反応速度定数( $k_2$ )を算定することとした。HOBrとフェノレートおよび

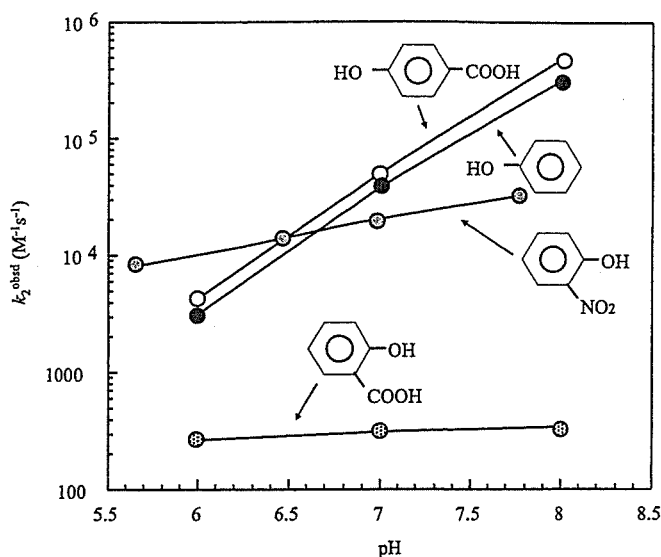


Fig. 2. Effect of pH on the observed second-order rate constant of the reaction between selected phenols and HOBr. 25 mM phosphate buffer was used to adjust pH. For other conditions see the caption of Table 1.

HOBrと非解離のフェノール性化合物の反応以外は無視できる, すなわち $\text{Br}_{2(\text{aq})}$ や $\text{Br}_3^-$ の濃度は無視でき $\text{OBr}^-$ はHOBrよりも反応性が低く無視できると仮定すると, HOBrの濃度を支配する微分方程式は式(1)のようになる。

$$-\frac{d[\text{Br}(\text{I})]}{dt} = k_2[\text{HOBr}][\text{phenol}] + k_2'[\text{HOBr}][\text{phenolate}] \quad (1)$$

ここで,  $\text{Br}(\text{I})$ は酸化数+Iの臭素を表す。また,  $k_2$ はHOBrと非解離のフェノール性化合物の2次反応速度定数である。ここで, 酸塩基平衡<sup>21-23)</sup>の関係式から右辺を整理すると,  $k_2^{\text{obsd}}$ と $k_2$ および $k_2'$ の関係式が得られる。

$$k_2^{\text{obsd}} = \frac{[\text{H}^+](k_2[\text{H}^+] + k_2'K_{a2})}{([\text{H}^+] + K_{a1})([\text{H}^+] + K_{a2})} \quad (2)$$

ここで $K_{a1}$ と $K_{a2}$ はそれぞれHOBrと各フェノール性化合物の酸解離定数である。pH5.0-8.0の範囲で単位pHあたり10倍に増加するものについては,  $k_2[\text{H}^+]$ は無視でき,

$$k_2^{\text{obsd}} = \frac{[\text{H}^+]k_2'K_{a2}}{([\text{H}^+] + K_{a1})([\text{H}^+] + K_{a2})} \quad (2')$$

と簡略化できる。この関係式に基づき算出した $k_2'$ をTable 3に示す。なお2-ニトロフェノールとHOBrの反応では前述の通り中性付近であっても非解離の分子の反応も無視できなく,  $k_2$ も $7.8 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ と他のフェノールよりも高い値を示した(例えばフェノールの $k_2$ は $480 \text{ M}^{-1} \text{ s}^{-1}$ )。

フェノール, 4-クロロフェノールおよび $p$ -クレゾールについては, DPD法とフローチューブ分析による既報と

Table 3.  $k_2'$  of the reactions between HOBr and phenols at 20 °C.

No.	compound	$k_2'$ ( $\text{M}^{-1}\text{s}^{-1}$ )	source
1	phenol	$(4.1 \pm 0.1) \times 10^7$	this study
3	3-hydroxybenzoic acid	$(4.4 \pm 0.2) \times 10^7$	this study
4	4-hydroxybenzoic acid	$(1.3 \pm 0.1) \times 10^7$	this study
5	2-nitrophenol	$(4.0 \pm 0.6) \times 10^4$	this study
6	2-bromophenol	$(6.7 \pm 0.3) \times 10^6$	this study
7	4-bromophenol	$(4.9 \pm 0.2) \times 10^6$	this study
8	2-chlorophenol	$(7.5 \pm 0.4) \times 10^6$	this study
9	4-chlorophenol	$(6.5 \pm 0.3) \times 10^6$	this study
10	vanillic acid	$(3.3 \pm 0.3) \times 10^7$	this study
11	vanillin	$(2.1 \pm 0.1) \times 10^6$	this study
12	4-methoxyphenol	$(5.0 \pm 0.2) \times 10^7$	this study
13	<i>o</i> -cresol	$(8.8 \pm 0.4) \times 10^7$	this study
14	<i>m</i> -cresol	$(3.3 \pm 0.3) \times 10^8$	this study
15	<i>p</i> -cresol	$(1.3 \pm 0.1) \times 10^8$	this study
17	phenol	$(1.8 \pm 0.2) \times 10^8$	ref. 10 <sup>a</sup>
18	4-chlorophenol	$(7.0 \pm 0.8) \times 10^6$	ref. 10 <sup>a</sup>
19	4-acetylphenol	$(4.1 \pm 0.5) \times 10^6$	ref. 10 <sup>a</sup>
20	2,4-dichlorophenol	$(8.8 \pm 0.9) \times 10^5$	ref. 10 <sup>a</sup>
21	<i>p</i> -cresol	$(2.1 \pm 0.5) \times 10^8$	ref. 10 <sup>a</sup>
22	2,4,6-trichlorophenol	$(3.0 \pm 1.0) \times 10^8$	ref. 10 <sup>a</sup>

の比較が可能である(Table 3)。3物質と限られたデータ数ではあるが, DPD法による $k_2'$ の方が本実験の結果よりも最大で4.4倍大きかった(フェノールの場合)。これらの速度定数の違いは, 高速反応の実験においてはよく見受けられる程度のものであり, またこの違いが浄水プロセスにおける臭素化反応の重要性を考察する上で大きな違いを引き起こすとは考えにくい。ただし, DPD法とフローチューブ分析による速度定数の決定<sup>10)</sup>については, DPD添加後のHOBrの回収率に関する考察が不十分であることが指摘できる。また, 多段ストップ・フロー分析システムの方が, 反応時間の設定の容易さと必要試料量の観点からも優れているといえる。

次に様々な有機物とHOBrの2次反応速度定数をTable 4に示す。フェノール性化合物は2-ヒドロキシ安息香酸を除けば, 他の不飽和化合物よりもHOBrに対してはるかに高い反応性を示す物質群であることがわかる。

Fig. 3に $k_2'$ と $\sigma$ 定数との線型自由エネルギー関係(LFER)を示す。 $k_2'$ は置換基の電子吸引効果( $\sigma$ 定数)の増大とともに減少する傾向が認められた。図中の回帰式より $\sigma$ 定数からフェノール性化合物とHOBrの反応性がある程度推定できると考えられる。また,  $\text{p}K_a$ と $k_2'$ の間にもある程度の相関が認められた(Fig. 4)。 $\sum \sigma_{o,m,p}$ と $k_2'$ との関係は以下の式(3)の用に表現される。