

Chlorination of water containing bromide and formation of the bromine - substituted trihalomethanes

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Abstract—Based on the experiments, it is evident that the formation of bromine - substituted trihalomethanes was due to hypobromous acid formed in oxidation of the bromide in water by chlorine, and these chlorine and bromine could chlorinate or/and brominate humic acid. Although the chlorine atoms in chloroform can be directly substituted by bromine, this reaction is only the secondary route.

Keywords: chlorination; bromination; bromine - substituted THMs.

1 Introduction

The presence of bromide in raw water before chlorination has been shown not only to increase the total yield of trihalomethanes (THMs), but also to change the distribution of species (Rook, 1974; Oliver, 1978; Lange, 1978; Symons, 1987). Bull *et al.* (Bull, 1985) reported that bromine - substituted trihalomethanes (Br - THMs), including CHBrCl_2 , CHBr_2Cl and CHBr_3 , had the effects of hepatotoxic and renal toxicity. Animal studies indicated that both CHCl_3 and CHBr_3 were carcinogenic to rats and mice (Theiss, 1977; USNCl, 1977). CHBrCl_2 , CHBr_2Cl and CHBr_3 , with the exception of CHCl_3 , had been shown to be positive in the Ames *Salmonella* assay, and gave a dose - related mutagenic response (Simmon, 1977; Uehleke, 1977). Morimoto *et al.* (Morimoto, 1983) reported that the potential of THMs inducing sister chromatid exchange in human lymphocytes in vitro and mouse bone marrow cells in vivo increased with the number of bromine atoms in THMs, i. e., $\text{CHBr}_3 > \text{CHBr}_2\text{Cl} > \text{CHBrCl}_2 > \text{CHCl}_3$. Moreover, it is difficult to control Br - THMs in water by air stripping, because the volatility of Br - THMs is rather lower than CHCl_3 (Symons, 1981).

Compared with CHCl_3 , the studies on Br - THMs were limited, Rook *et al.* (Rook, 1978) and Luong *et al.* (Luong, 1982) proposed that chlorine preferentially acts as an oxidant, bromide in water is oxidized by chlorine to hypobromous acid (HOBr) which more effectively acts as a halogen - substituting agent, and hence HOBr substitutes the chlorine atom(s) in chloroform to form CHBrCl_2 , CHBr_2Cl and CHBr_3 . Unfortunately, there is very little information from experiment to support this hypothesis.

The primary objective of the current research was to conduct a systematic analysis of the halogenation reactions of a well known model compound - humic acid (HA), to help explaining

the formation pathways for Br - THMs.

2 Experimental

2.1 Halogen solution

Chlorine came from the saturation solution of $\text{Ca}(\text{OCl})_2$, and bromine from the dilution of Br_2 water. The concentration of chlorine and bromine was measured by iodometry.

2.2 Purification of HA

The commercial HA (the Second Chem, Reagent Co., Shanghai) was purified using the procedure outlined by Narkis *et al.* (Narkis, 1975).

2.3 Chlorination conditions

Except specially mentioned, chlorination conditions of HA were: free chlorine 10.0 mg/L; HA concentration 2.0 mg/L; bromide 1.0 mg/L; temperature 25°C, pH range 6.5–7.0; reaction time 24 hours. Vit. C was used to quench the reactions.

2.4 Analytical method

Samples were incubated in the dark at $40 \pm 2^\circ\text{C}$ for 40 min before analysis. The concentration of THMs was determined by the head space method which was recommended by Urano *et al.* (Urano, 1983) with slight modifications. A gas chromatograph, HP5890 series II, equipped with an electron capture detector and a glass column. A column with 7% OV-101 as stationary phase on chromosorb A HP AW DMCS (80–100 mesh) was employed for separation of THMs. N_2 was used as carrier with a flow rate of 35 ml/min. The temperature of the column, injection port and detector were kept at 80, 160 and 250°C, respectively.

3 Results and discussion

3.1 Effect of bromide on the total THMs yield and species distribution

CHBrCl_2 increased with increasing bromide concentration up to 0.1 mg/L, and thereafter decreased. CHBr_2Cl behaved in a similar manner except that the maximum concentration occurred at a higher bromide concentration 0.5 mg/L. In contrast, chloroform decreased significantly as a nonlinear function of bromide concentration. When bromide concentration was equal to or higher than 0.5 mg/L, CHBr_3 was produced (Table 1). The trends for THMs formation were in accordance with the result from Luong *et al.* (Luong, 1982).

Table 1 Effect of bromide concentration on THMs yield and distribution of species

THMs, $\mu\text{g/L}$	Br ⁻ added, mg/L					
	0.00	0.025	0.05	0.10	0.50	1.00
CHCl_3	140.06	134.20	122.40	118.91	20.81	12.50
CHBrCl_2	—	12.32	37.20	91.94	89.37	36.37
CHBr_2Cl	—	—	5.30	25.66	236.41	183.89
CHBr_3	—	—	—	—	134.88	256.81
THMs	140.06	146.52	164.90	236.51	481.47	489.57
Br - THMs	0.00	12.32	42.50	117.60	460.66	477.07

* : not detected

For waters with low levels of bromide (< 0.5 mg/L), the predominant THMs species were CHCl_3 , CHBrCl_2 and CHBr_2Cl . In contrast, at high concentration of bromide, CHBr_3 was formed, and Br - THMs were the dominant species ($> 95\%$).

Table 2 shows the proportions of chlorine and bromide incorporated into THMs. A recovery of 24.03%—70.58% of the added bromide was as Br—THMs, but only 0.48%—1.50 % of the initial chlorine was recovered in THMs. This result showed no difference to the previous studies (Cooper, 1983; Arguello, 1979; Minear, 1978).

It was apparent that most of the initial bromide that was activated by chlorine was changed into THMs. On other words, Br - THMs were formed preferentially when water containing bromide was chlorinated.

Table 2 Chlorine and bromide percentage conversion observed in THMs

Atom	Br ⁻ added, mg/L					
	0.00	0.25	0.05	0.10	0.50	1.00
Cl	1.25	1.25	1.26	1.50	0.97	0.48
Br	—	24.03	44.42	64.53	70.58	44.60

3.2 Changes of THMs concentration and species distribution with time

The yield and distribution of THMs with reaction time are shown in Table 3. The concentration of THMs increased as a function of the reaction time, but the increasing rates differed significantly. From 15 minutes to 24 hours, CHCl_3 was increased by 68%, while Br - THMs was 8.7 folds as much. In the initial 15 minutes, Br - THMs consisted of 87% of the total THMs, and at 24 hours, it attained up to 96%. It was further proved that Br - THMs were formed prior to CHCl_3 .

Table 3 THMs yield and species distribution with reaction time

THMs, $\mu\text{g/L}$	Reaction time, h							
	0.00	0.25	0.50	1.00	3.00	6.50	9.00	24.00
CHCl_3	0.17	7.44	7.96	8.74	10.05	10.22	11.44	12.51
CHBrCl_2	—	9.80	11.35	13.81	20.20	27.23	30.38	40.27
CHBr_2Cl	—	17.45	22.11	32.08	60.91	106.35	110.41	154.42
CHBr_3	—	15.75	19.94	33.17	70.04	137.13	144.77	179.27
THMs	0.17	50.45	61.37	87.82	161.22	280.94	297.03	386.48
Br - THMs	—	43.01	53.41	79.08	151.17	270.72	285.58	373.97

3.3 Reaction of bromine with HA

HA solution (2.0 mg/L) was brominated for 24 hours at pH 6.5 by various dosing of Br_2 water. The result is portrayed in Fig. 1. CHBr_3 was the predominant species of THMs. Simultaneously, CHCl_3 , CHBrCl_2 and CHBr_2Cl with much lower concentration were formed through the chlorination of HA by the trace chlorine in Br_2 water (0.002 %).

3.4 Chlorine atoms in THMs were substituted by bromine

Various amount of Br_2 water was added to the distilled water spiked to about 110 $\mu\text{g/L}$ CHCl_3 , to react for 24 hours. Table 4 summarized the results of bromine substituted CHCl_3 .

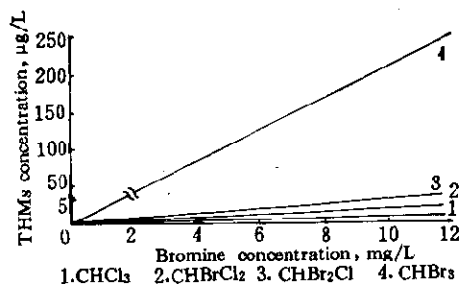


Fig. 1 Reaction of bromine with HA

CHCl_3 concentration reduced slightly, and Br - THMs, i. e. , CHBrCl_2 etc. were formed with the rising of bromine concentration, nevertheless, the yield of Br - THMs was insignificant. It was found that, in all cases, expressed in terms of micromoles per liter Br - THMs remained nearly constant although some changes in speciation were observed. Similar trends were observed as shown in Table 5.

Table 4 Formation of bromine substituted compounds of CHCl_3 with variation of Br_2 concentration

THMs	Br ₂ added, mg/L					
	0.0	0.1	0.5	1.0	2.0	5.0
CHCl_3 , µg/L	108.54	109.32	107.42	107.78	106.11	106.16
CHBrCl_2 , µg/L	—	—	0.74	0.82	1.06	1.61
CHBr_2Cl , µg/L	—	—	—	—	1.61	2.58
CHBr_3 , µg/L	—	—	—	—	—	8.50
THMs, µg/L	108.54	109.32	108.16	108.60	109.32	118.85
THMs, µmol/L	0.90	0.91	0.90	0.90	0.90	0.94

Table 5 Formation of bromine substituted compounds of CHCl_3 with variation of Cl_2/Br^- ratio

THMs	Chlorine/bromide*					
	0.0	2.0	6.0	10.0	20.0	40.0
CHCl_3 , µg/L	140.41	139.43	138.41	131.43	121.54	118.50
CHBrCl_2 , µg/L	—	—	2.43	3.72	11.26	15.12
CHBr_2Cl , µg/L	—	—	—	4.77	18.85	20.94
THMs, µg/L	140.41	139.43	140.84	139.92	151.65	154.56
THMs, µmol/L	1.17	1.16	1.17	1.14	1.17	1.18

* bromide concentration: 1.0 mg/L

As the ratio of chlorine/bromide increased, CHCl_3 concentration declined gradually, while the yield of Br - THMs increased slightly, however, there was no CHBr_3 formed.

According to these experiments, it was realized that Br_2 or HOBr can substitute the chlorine atoms in CHCl_3 to form Br - THMs. The sequence of formation is as follows: $\text{CHBrCl}_2 > \text{CHBr}_2\text{Cl} > \text{CHBr}_3$. However, the extent of CHCl_3 reduced or the yield of Br - THMs was limited, and this result can not explain the phenomena observed in experiments (Table 1).

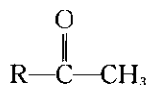
3.5 Reaction of chlorine with CHBr_3

Although the sequence of oxidizing power is $E_{\text{O}_{\text{HCl}}} (1.49 \text{ V}) > E_{\text{O}_{\text{HOBr}}} (1.33 \text{ V})$, and the order of electrophilic substitution reaction is $\text{S}_{\text{Cl}_2} > \text{S}_{\text{Br}_2}$ (Dore, 1982), chlorine can not replace the bromine atoms in CHBr_3 to form CHBr_2Cl , CHBrCl_2 or CHCl_3 , based on our experiments.

3.6 Formation pathways for Br - THMs

On the basis of the experiments, the formation routes of Br - THMs are summarized in Fig.

2. The precursor of THMs was expressed as



(Morris, 1977).

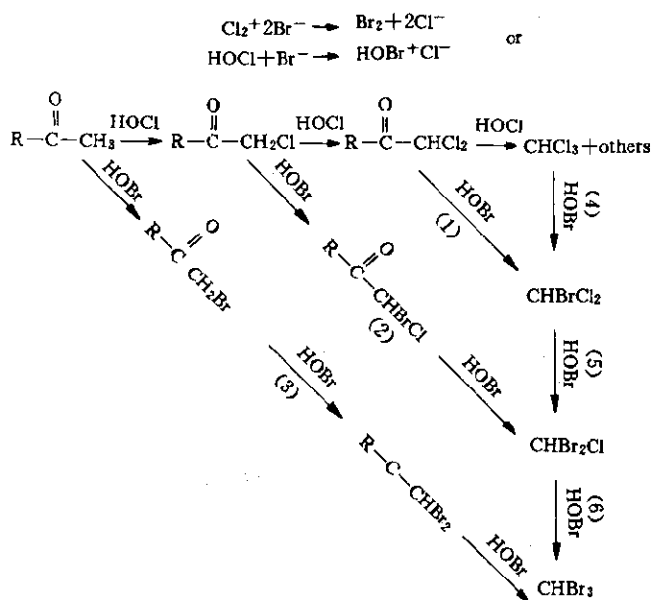


Fig. 2 Proposed formation pathways for Br - THMs

The reactions from (1) to (3) are the principal pathways for the formation of Br - THMs. When the concentration of bromide is lower than 0.5 mg/L, (1) and (2) are preponderant; while $\text{Br}^- \geq 0.5 \text{ mg/L}$, (2) and (3) are the preferential reaction routes. (4) to (6), (i.e. substitution reaction) are the secondary pathways for the formation of Br - THMs.

4 Summary

The presence of bromide in water before chlorination not only greatly increased the total yields of THMs and Br-THMs, but also shifted the distribution of species.

The bromide was oxidized by chlorine to Br_2 or HOBr, then they all reacted with HA to form Br-THMs preferentially, and these were the principal pathways of the formation of Br-THMs.

The chlorine atoms in CHCl_3 can be substituted by Br_2 or HOBr to form Br - THMs. However, it is not the major route for Br-THMs formation.

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