

## Brominated-trihalomethane Formation from Phenolic Derivatives as a Model of Humic Materials by the Reaction with Hypochlorite and Hypobromite Ions

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Among the 21 phenolic derivatives tested for the model system of the disinfection process in the natural water containing humic acid, 2-hydroxytoluene and 2,6-dihydroxybenzoic acid produced high yields of  $\text{CHBr}_3$  under the co-existence of NaOCl and NaOBr. In the study of distribution of THMs produced, the amount of  $\text{CHBr}_3$  increased with the relative concentration of NaOCl added to NaOBr. These results were similar to the case of halogenation of the humic acid under the co-existence of NaOCl and NaOBr.

The chemical mechanism of formation of the brominated trihalomethanes (Br-THMs) through the disinfection process in the natural water containing humic acid substances has been a worldwide environmentally important puzzle. This communication refers to the halogenation of phenolic model compounds.

Previously<sup>1</sup> we reported that  $\text{CHBr}_3$  was produced in preference to the other three THMs;  $\text{CHCl}_3$ ,  $\text{CHCl}_2\text{Br}$  and  $\text{CHClBr}_2$ , when humic acid reacted with both hypochlorite ion ( $\text{OCl}^-$ ) and hypobromite ion ( $\text{OBr}^-$ ) which was thought to be formed from bromide ion in natural water by  $\text{OCl}^-$ . However, this observation could not be completely explained with the mechanism reported by other investigators who used 1,3-dihydroxybenzene as a model compound of the molecular moieties of humic substances.<sup>2,3</sup> So, we investigated the THM formation using 21 selected phenolic derivatives which contain two or three substituents such as hydroxy, methyl and/or carboxyl group as model compound of humic substances.

The phenolic compounds studied are listed in Figure 1. 2,4-Dihydroxytoluene (7) was prepared from 5-amino-*o*-cresol through diazotization and purified by recrystallization. This compound was identified by the mp and <sup>1</sup>H-NMR(400 MHz) spectra.<sup>4</sup> The other compounds were of commercial reagent

**Table 1.** The amounts of  $\text{CHCl}_3$  and  $\text{CHBr}_3$  formed in the halogenation of phenolic compounds with NaOCl or NaOBr alone

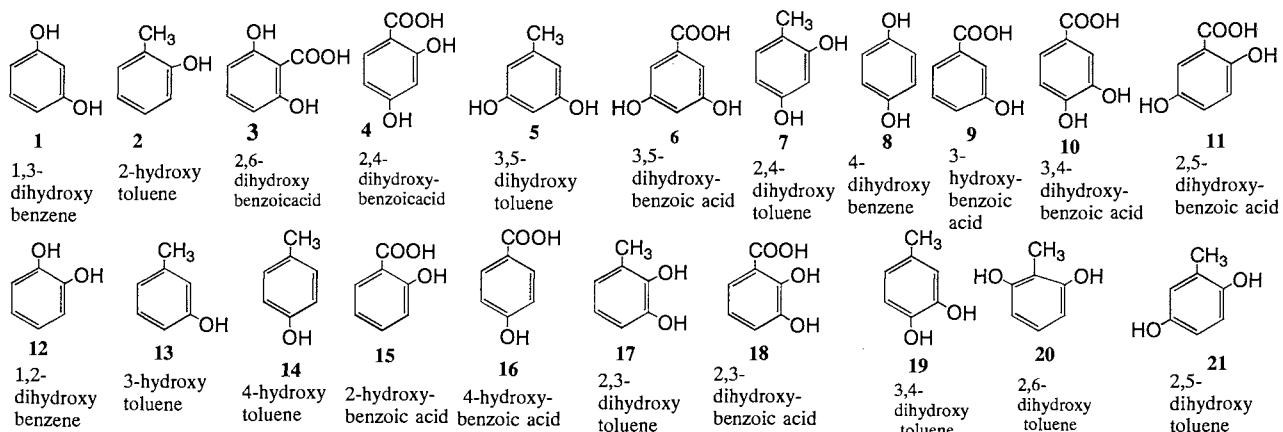
phenolic substrate	NaOCl $\text{CHCl}_3$ / $\mu\text{M}$	NaOBr $\text{CHBr}_3$ / $\mu\text{M}$
1	7.83	0.68
2	1.03	0.05
3	11.3	1.19
4	7.45	1.02
5	5.90	0.20
6	3.80	1.11
7	4.44	1.02

Phenolic substrate (10  $\mu\text{M}$ ), NaOX (200  $\mu\text{M}$ ), 60 min, pH 8.

grade and used without further purification. Halogenation of chemicals was carried out as reported previously.<sup>1</sup>

Table 1 shows the amounts of  $\text{CHCl}_3$  and  $\text{CHBr}_3$  formed in the reaction of the phenolic compounds with NaOCl or NaOBr alone. The phenols 1-7 (group A) produced much higher amounts of  $\text{CHCl}_3$  or  $\text{CHBr}_3$  than phenols 8-21 (group B) under the same condition. Table 2 shows the product distribution and total amounts of THMs formed by the reaction of each phenolic compound with the mixture of NaOCl and NaOBr. All of the phenols except for 20 produced THMs by this halogenation reaction. The phenols of group B except for 9 produced relatively small amounts of total THMs composed of  $\text{CHBr}_3$  mainly. For group A, the main THM product from 1, 4, 5 and 6 was  $\text{CHClBr}_2$ , but that from 2 and 3 was  $\text{CHBr}_3$ .

The phenomena that  $\text{CHBr}_3$  was a main product are similar to those of the case of humic acid as previously reported.<sup>1</sup> In the case of 2, 7.30  $\mu\text{M}$  amount of total THMs was produced by the



**Figure 1.** The phenolic type compounds tested as model of humic acid.

**Table 2.** The distribution and total amounts of trihalomethanes produced in the halogenation of phenolic compounds listed in Figure 1 with the mixture of NaOCl and NaOBr

Entry		CHCl <sub>3</sub> / %	CHCl <sub>2</sub> Br / %	CHClBr <sub>2</sub> / %	CHBr <sub>3</sub> / %	THM / μM
A	1	2.8	14.1	65.5	17.6	8.80
	2	4.9	4.1	14.7	76.2	7.30
	3	0.4	2.2	15.7	81.6	7.30
	4	2.1	7.6	53.5	36.7	11.0
	5	11.7	13.2	41.3	33.7	2.0
	6	5.4	7.8	56.1	30.7	6.31
	7	39.5	21.2	9.5	29.7	3.67
B	8	0.0	0.0	15.8	84.2	0.38
	9	0.0	0.0	1.5	98.5	2.60
	10	0.0	0.0	5.3	94.7	0.19
	11	0.0	0.0	0.0	100	0.43
	12	0.0	0.0	29.4	70.6	0.17
	13	0.0	0.0	0.0	100	0.27
	14	0.0	0.0	0.0	100	0.08
	15	0.0	0.0	3.1	96.9	0.96
	16	0.0	0.0	4.0	96.0	0.75
	17	0.0	0.0	0.0	100	0.09
	18	0.0	0.0	8.9	91.1	0.45
	19	0.0	0.0	13.3	86.7	0.15
	20	0.0	0.0	0.0	0.0	0.00
	21	0.0	0.0	0.0	100	0.05

Phenolic substrates (10 μM), halogenation reagents (NaOCl 200 μM and NaOBr 200 μM), 60 min, pH 8. A and B denote the group of phenols.

reaction with the mixture of NaOCl and NaOBr. This is about seven times higher than the total amount of CHCl<sub>3</sub> and CHBr<sub>3</sub> produced by the reaction with NaOCl or NaOBr alone.

All the phenols of group A except for **2** have two hydroxyl substituents in the meta position. But, a meta dihydroxy compound **20** (group B) did not form THMs at all. In compound **20**, the carbon atom in benzene ring being between the two OH groups was occupied by a methyl group. This fact suggests that the carbon atom hindered by the methyl group may be the key active site of chlorination in meta dihydroxybenzenes.<sup>2,3</sup> On the other hand in phenol **3**, the carbon atom between the two OH groups is substituted by a carboxyl group, but this phenol formed a higher amount of THM. Details of the role of the carboxyl group in this position should

be studied in future.

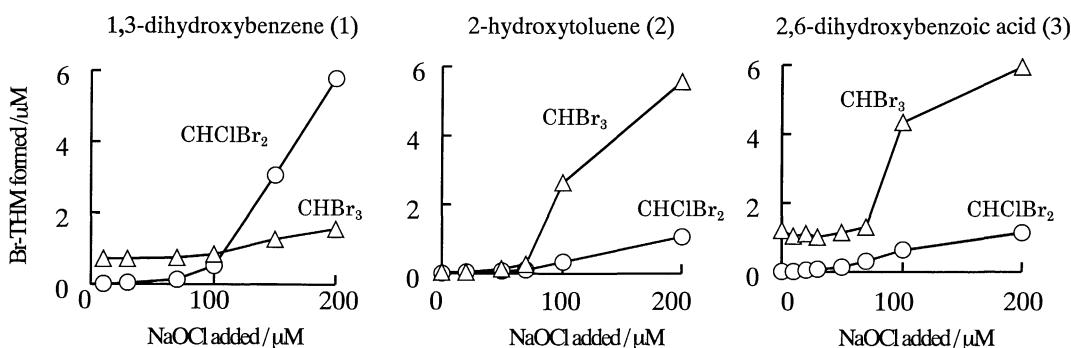
The relationships between the amount of THMs formed and the relative concentration of NaOCl added to 200 μM NaOBr were investigated for three phenols of **1**, **2** and **3**. The results are shown in Figure 2. The phenols **2** and **3** formed mainly CHBr<sub>3</sub>, which increased with the relative concentration of NaOCl. The trend of results are almost the same as that of the case of using humic acid.<sup>1</sup> However, CHClBr<sub>2</sub> was formed predominantly from **1** when the concentration of NaOCl exceeded 100 μM.

The results of phenols **2** and **3** are similar to that of the corresponding cases of using humic acid previously reported.<sup>1</sup> Hence, it seems that the phenols **2** and **3** are oxidized by OCl<sup>-</sup> to the monochlorinated carbanions in the first step, and subsequently are substituted by HOBr to give CHBr<sub>3</sub> in the presence of a mixture of the two hypohalites at pH 8. Phenols of the group B except for **20** seem to produce THMs through the same pathway of the THM formation as the cases of **2** and **3**. In contrast, **1** may be oxidized to bis-chlorinated carbanion directly in the first step under the same conditions, and then substituted by HOBr. Phenols **4**, **5** and **6**, which produce CHClBr<sub>2</sub> predominantly, may be oxidized and then substituted by almost the same mechanisms as in the case of **1**. Since Rook hypothesized that dihydroxybenzene moieties in the humic materials were responsible for the formation of chloroform,<sup>2</sup> many investigators<sup>3</sup> have used the phenol **1** and its derivatives in discussing the mechanisms of THM formation. However, from our new results, it can be proposed that 2-hydroxytoluene (**2**) and 2,6-dihydroxybenzoic acid (**3**) would be more effective than 1,3-dihydroxybenzene (**1**) as aromatic model for the aquatic humic acid in mechanistic studies of THM formation.

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#### References and Notes

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**Figure 2.** The effect of NaOCl added to the mixture of phenolic compounds and NaOBr on the formation of brominated trihalomethane. Concentration of substrates: 10 μM, Concentration of NaOBr: 200 μM, Reaction time: 60 min at pH 8.