

Characterization of Polyhalogenated 4-Methylphenol Dimers (Br/Cl-Predioxins) Formed during Aqueous Chlorination of 4-Methylphenol Solution in the Presence of Bromide Ion

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Aqueous 4-methylphenol solution with bromide ion was treated with hypochlorite at 20°C under various experimental conditions. Changes in the composition of the halogenated products in water were determined by gas chromatographic (GC) and GC-mass spectrometric (GC/MS) analyses of diethyl ether extracts. 4-Methylphenol was shown to produce a variety of halogenated compounds, including polybrominated/chlorinated phenoxyphenols (Br/Cl-predioxins), having one to four halogen atoms, as by-products in the chlorine-treated water. Production of these predioxins is dependent on the number of equivalent of chlorine atoms per mole of compound and on the reaction pH. These results suggest that the chlorine treatment of water contaminated with 4-methylphenol and bromide ion leads to the formation of Br/Cl-predioxins, which are precursor of the highly toxic halogenated dibenzo-*p*-dioxins.

Key words — polyhalogenated phenoxyphenol, methylated predioxin, water chlorination

INTRODUCTION

Polychlorinated phenoxyphenols (PCPPs) are the main contaminants of technical chlorophenol formulations.¹⁾ The chemical structures of the PCPPs isomers are presented in Fig. 1. These compounds have attracted considerable attention because their 2-hydroxy isomers (predioxins) have been shown to undergo both thermal and photochemically ring closure to form polychlorinated dibenzo-*p*-dioxins (PCDDs). In addition, the chlorophenols themselves may react photochemically to yield PCDDs. Although the discussion of the origin of PCPPs and PCDDs have been focused on in the two above mentioned potential sources, several works have demonstrated the presence of PCDDs in municipal sewage sludge²⁾ and sedimentation-basin sludge from water treatment plants.³⁾

Chlorination is used extensively in wastewater treatment to disinfect and deodorize effluents prior to discharge, particularly in place where wastewater may subsequently be used for recreational pur-

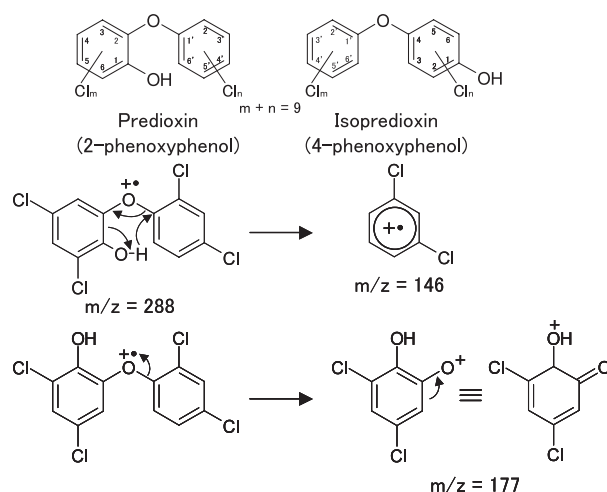


Fig. 1. Chemical Structure of Polychlorinated Phenoxyphenols (above) and Example of Characteristic Fragment Ions Occurring in Electron Ionization of Chlorinated 2-Phenoxyphenol (below)

poses or as a source of potable water. Therefore, it appears that PCPPs and PCDDs are formed mainly due to condensation reactions that occur after the chlorination of the phenolic substances in the water supplies and wastes.^{2,3)} This hypothesis has been directly supported by our previous findings that demonstrated that phenolic compounds react with chlorine to form the condensation products of their

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chlorinated compounds.⁴⁻⁸⁾

Recently, polybrominated diphenyl ethers (PBDEs) and dibenzo-*p*-dioxins (PBDDs) have attracted attention because the presence of these compounds in human milk has been shown.⁹⁾ Further, they exhibit high toxicity in the early life stages of fish.¹⁰⁾ We now presented more detailed findings on the characteristics of the condensation products [polyhalogenated phenoxyphenols (PXPPs), refer to Fig. 1] formed due to the reaction of chlorine with 4-methylphenol in dilute aqueous solution containing bromide ion. These aqueous solutions were selected because they were previously identified in environmental water systems.¹¹⁻¹⁵⁾ 4-Methylphenol was also chosen in this work because this compound has been used as an intermediate in the production of important industrial chemicals and also identified as being present in aquatic samples.¹⁶⁾

MATERIALS AND METHODS

Chemicals—4-Methylphenol was purchased from Tokyo Kasei Kogyo Co., Ltd. (Tokyo, Japan). Several halogenated 4-methylphenols, benzoquinones, and carboxylic acids, which may be expected to form during the reaction of 4-methylphenol with chlorine in an aqueous solution, were commercially available reagents. 5-Chloro-(2,4-dichlorophenoxy)phenol (commercial name, triclosan) was commercially available (purity 99.3%) and was used as a typical predioxin standard. Standard of these compounds both individually and as a mixture were prepared by dissolving the compounds in methanol and performing subsequent dilutions. The organic solvent (diethyl ether, methanol and chloroform) used in this study for pesticide residue analysis were of analytical-reagent grade (Cika-Merck, Tokyo, Japan).

Hypochlorite solutions were prepared by diluting sodium hypochlorite solution (*ca.*, 10% available chlorine; Nacalai Tesque, Kyoto, Japan) with distilled water. Their pHs were adjusted to the required level by adding a 0.1 M phosphate buffer solution. The hypochlorite concentrations were determined by iodometric titration. Polyamide 11 F₂₅₄ (20 × 20 cm, thickness 0.15 mm) pre-coated thin-layer chromatographic (TLC) plates (Merck, Darmstadt, Germany) were used to fractionate the diethyl ether extracts. Other chemicals (KBr and anhydrous Na₂SO₄) were used as reagents of ana-

lytical special grade.

Chlorination of 4-Methylphenol and Solvent Extraction—A mixture of 100-ml of buffered 4-methylphenol solution (0.5 mmol/l) containing bromide ion (2.5 mmol/l) and 1-ml of hypochlorite solution was shaken in a separatory funnel at room temperature (*ca.*, 20°C). After the desired reaction time, the un-reacted chlorine or bromine was removed adding a 1 M sodium thiosulfate solution. The reaction mixture was then acidified to pH 2 with 6 M hydrochloric acid before extraction with 20-ml portions of diethyl ether. The extracts were dried over anhydrous sodium sulfate and concentrated under reduced pressure at 40°C to volumes suitable for polyamide TLC, gas chromatographic (GC) and GC-mass spectrometric (GC/MS) analyses.

Fractionation of Diethyl Ether Extract by TLC—The diethyl ether extracts were fractionated into several fractions by TLC on the polyamide 11 F₂₅₄ using chloroform as a developing solvent. UV irradiation was used to detect spots on the plates. The separated zones were scraped off using special recovery tubes (Wako Pure Chemical Co., Osaka, Japan) and the adsorbed substances were then eluted with diethyl ether. The diethyl ether eluates were then analyzed by GC and GC/MS analyses.

Product Resolution and Characterization—A Shimadzu GC 14B gas chromatograph (Shimadzu, Kyoto, Japan) equipped with a flame ionization detector and a GC-SIL 8CB capillary column, 30 m × 0.32 mm *i.d.*, and 0.12 μm film thickness (Chromatopack, Amsterdam, Netherlands) was programmed from 80 to 270°C at the rate of 10°C/min. The injector and detector temperatures were 270°C. The helium gas flow-rate was 1 ml/min. A Shimadzu C-R6A Chromatopac system was used to determine the retention times and the peak areas of the chromatograms.

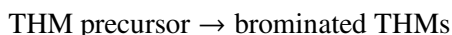
Qualitative analyses were performed using an HP model 5890 II gas chromatograph (Yokogawa-Hewlett-Packard Ltd., Tokyo, Japan) equipped with a JEOL Automass 50 mass spectrometer (JEOL Ltd., Tokyo, Japan). The analytical column and chromatographic conditions were the same as described above. Splitless injection of sample (1 μl) into the GC/MS was performed at 270°C. The electron ionization conditions were as follows: ion energy, 70 eV; ion source temperature, 250°C; *m/z* = 50–600 full scan for qualitative analysis. The presence of polyhalogenated 2-phenoxyphenols (predioxin) and 4-phenoxyphenols (isopredioxin) in the

condensation products of 4-methylphenol was confirmed from their mass fragmentation (refer to Fig. 1), according to the method reported in the previous paper.¹⁷⁾

RESULTS AND DISCUSSION

Fractionation of Diethyl Ether Extracts by TLC

The condensation products of chlorinated phenolic substances (PCPPs and PCDDs) have been shown to be formed during the treatment with H₂O₂/peroxidase or ozone in water containing chlorophenols.^{18,19)} Our previous papers⁴⁻⁸⁾ have also demonstrated that these PCPPs are formed in the reactions of phenolic compounds with chlorine in aqueous solutions. In addition, several researchers have demonstrated that chlorination or ozonation of surface and ground water containing bromide ion produces high concentrations of brominated trihalomethanes (THMs),^{12,13)} according to the following reactions:



On the basis of the findings described above, formation of PXPPs should be expected to occur after treatment with chlorine from an aqueous phenol solution containing bromide ion. Further investigations conducted on the reactions of chlorine with the aqueous 4-methylphenol solution in the presence of bromide ion showed PXPPs to be present in the diethyl ether extracts. However, earlier researchers demonstrated the presence of corresponding chlorinated dimers (ethers and PCDDs) in the mass spectra of the chlorinated phenols and concluded that these dimers are formed by the pyrolysis of the chlorinated compounds.²⁰⁾

Diethyl ether extracts of chlorinated 4-methylphenol solutions in the presence of bromide ion are, therefore, fractionated into several fractions by polyamide TLC before the GC/MS analyses. Figure 2 shows a typical thin-layer chromatogram of diethyl ether extracts from acidic (pH 6.0) and alkaline 4-methylphenol solutions (pH 9.5) in the presence of bromide ion after treatment with five equivalents of chlorine atoms per mol of compound. Several compounds including original material, bromo/chloro-substituted products, their oxygenated compounds (quinines)⁴⁾ and unknown substances were observed in the chromatogram. These unknown compounds occurring in the ex-

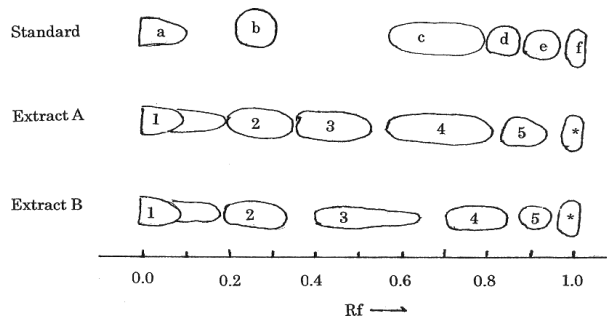


Fig. 2. Typical Thin-layer Chromatograms of Diethyl Ether Extracts from Chlorine-treated 4-Methylphenol Solutions Containing Bromide Ion, on a Polyamide Plates with Chloroform as the Developing Solvent

Mixture of tichloroacetic acid (a), 4-methylphenol (b), 2-bromo-4-methylphenol (c), triclosan (d), 2,6-dibromo-4-methylphenol (e) and polychlorinated 4-methylphenol dimers (f). Extract A obtained from the chlorinated acidic solution (pH 6.0). Extract B obtained from the chlorinated alkaline solution (pH 9.5). The asterisk indicates the targeted unknown compounds.

tracts of chlorine-treated 4-methylphenol solutions containing bromide ion yielded Rf values similar to that of chlorinated 4-methylphenol dimers⁴⁾ on the polyamide TLC plates. However, the GC/MS behavior of the unknown compounds differed from that of chlorinated 4-methylphenol dimers: this was observed in the extracts obtained from the chlorine-treated 4-methylphenol solution in the presence of bromide ion.

Characterization of PXPPs Formed in an Acidic Solution

A typical mass chromatogram (total ion current) of the unknown compounds occurring in the polyamide TLC fraction of a diethyl ether extract from a chlorinated acidic 4-methylphenol solution in the presence of bromide ion, and mass spectra of the peaks are shown in Fig. 3. The mass spectrum of the compound corresponding to the peak 1 in Fig. 3 yielded a molecular ion (M^+) at m/z 214 (proposed formula, $C_{14}H_{14}O_2^+$) and several fragment at m/z 199 ($C_{13}H_{11}O_2^+$), 171 ($C_{12}H_{11}O^+$) and 128 ($C_{10}H_8^+$). Since no characteristic fragment ion was observed at m/z 92 ($C_7H_8^+$) in the mass spectrum, this compound is considered to be dimethylated 4-phenoxyphenol (DM-4-PP).⁴⁻⁸⁾

The compounds corresponding to the peaks 2 and 3 in Fig. 3 yielded the same molecular ion at m/z 292 ($C_{14}H_{13}BrO_2^+$) and several fragment ion. Since no characteristic fragment ions were observed in the mass spectra at m/z 170 ($C_7H_7Br^+$) or 92 ($C_7H_8^+$), these compounds are considered to be Br-

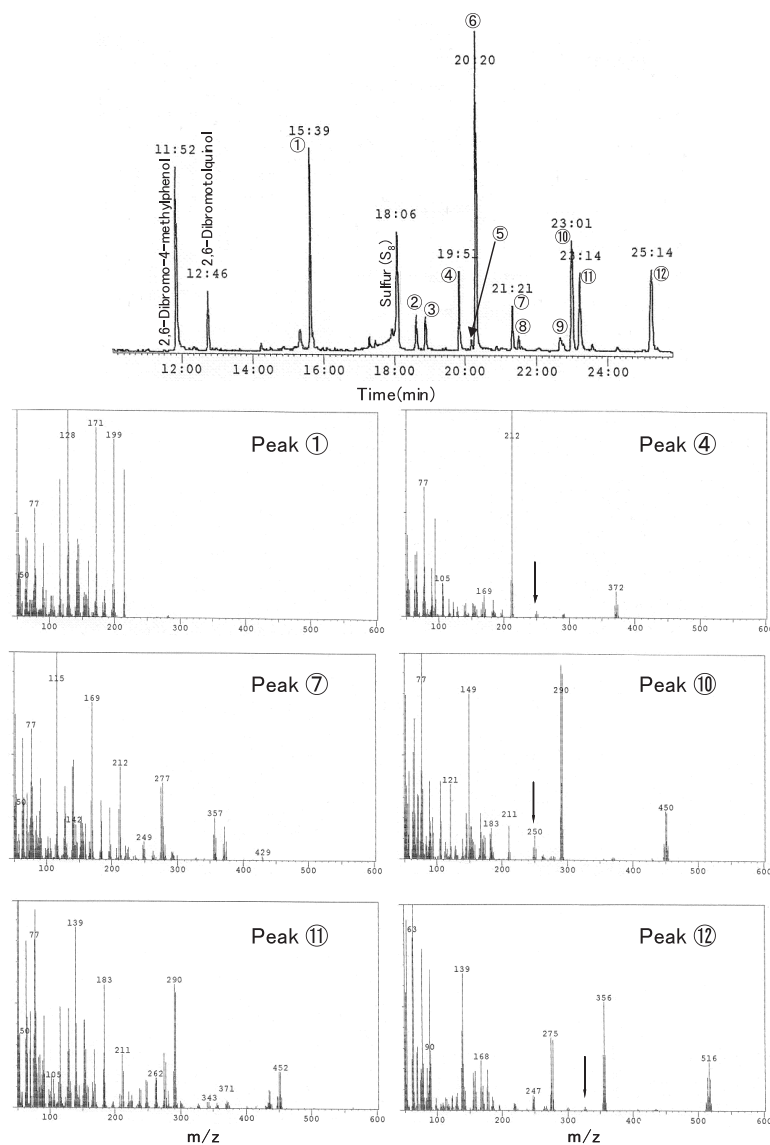


Fig. 3. Mass Chromatogram (Total Ion Current) of Polyamide TLC-separated Fraction (Unknown Compound Zone) of a Diethyl Ether Extract from the Chlorine-treated 4-Methylphenol Solution (pH 6.0) in the Presence of Bromide Ion and Mass Spectra of the Peaks

DM-4-PP. The mass spectra of the compounds corresponding to the peaks 4, 6, 7 and 8 yielded the same molecular ion at m/z 370 ($C_{14}H_{12}Br_2O_2^+$), but with different fragment patterns. These findings indicate the occurrence of DMPP isomers containing two Br atoms in the diethyl ether extract. A characteristic fragment ion at m/z 248 ($C_7H_6Br_2^+$ for the peak 4) is indicative of a dimethylated 2-phenoxyphenol (DM-2-PP), since the hydrogen transfer rearrangement from the OH group to the nearest ring is typical of the fragmentation of an ortho hydroxyl ether.¹⁷⁾

The mass spectra of the compounds corresponding to the peaks 10 and 11 in Fig.3 yielded the

same molecular ion at m/z 448 ($C_{14}H_{11}Br_3O_2^+$), but different fragment patterns. These findings indicate the occurrence of DMPP isomers containing three Br atoms in the diethyl ether extract. A characteristic fragment ion at m/z 248 ($C_7H_6Br_2^+$ for the peak 10) is indicative of a 2-phenoxyphenol. In addition, the compound corresponding to the peak 12 in Fig.3 yielded a molecular ion at m/z 512 ($C_{13}H_8Br_4O_2^+$) and several fragment ions at m/z 354 ($C_{13}H_8Br_2O_2^+$), 275 ($C_{13}H_8BrO_2^+$) and 196 ($C_{13}H_8O_2^+$). This finding also indicates the occurrence of monomethylated phenoxyphenol (MMPP) containing four Br atoms in the diethyl ether extract. The characteristic fragment ion at m/z 326

Table 1. Summary of GC/MS Data and Proposed Formulae of the Halogenated Phenoxyphenols Formed by Reactions of 4-Methylphenol (0.5 mmol/l) with Chlorine (Molar Ratio of Cl per Compound = 5) in Dilute Aqueous Solution Containing Bromide Ion (2.5 mmol/l) at pH 6.0 for 1 hr at 20°C

Peak no.	Retention time (min)	Molecular ion (M^+)	No. of halogen atoms in M^+	Proposed formulae	Chemical name
1	15.39	214	no halogen	$C_{14}H_{14}O_2$	DMPP
2	18.38	292	Br	$C_{14}H_{13}BrO_2$	Br-DMPP
3	18.54	292	Br	$C_{14}H_{13}BrO_2$	isomer of peak 2
4	19.52	370	2Br	$C_{14}H_{12}Br_2O_2$	Br_2 -DMPP*
5	20.13	356	2Br	$C_{13}H_{10}Br_2O_2$	Br_2 -MMPP*
6	20.20	370	2Br	$C_{14}H_{12}Br_2O_2$	isomer of peak 4
7	21.21	370	2Br	$C_{14}H_{12}Br_2O_2$	isomer of peak 4
8	21.31	370	2Br	$C_{14}H_{12}Br_2O_2$	isomer of peak 4
9	22.42	434	3Br	$C_{13}H_9Br_3O_2$	Br_3 -MMPP
10	23.02	448	3Br	$C_{14}H_{11}Br_3O_2$	Br_3 -DMPP*
11	23.14	448	3Br	$C_{14}H_{11}Br_3O_2$	isomer of peak 10
12	25.14	512	4Br	$C_{13}H_8Br_4O_2$	Br_4 -MMPP*

The asterisk indicates a 2-phenoxyphenol (predioxin). DMPP = dimethylphenoxyphenol. MMPP = monomethylphenoxyphenol.

($C_7H_5Br_3^+$) suggests this compound to be a 2-phenoxyphenol.

A summary of these bromination products identified or determined from their retention times and mass spectrometric interpretation is presented in Table 1. These GC/MS findings, therefore, indicate that di-, tri- and tetra-brominated 2-phenoxyphenols and mono-, di-, tri- and tetra-brominated 4-phenoxyphenols are present in the TLC-separated fractions of the 4-methylphenol reaction products under an acidic condition. The GC/MS analysis also suggests that MMPPs are present in the chlorine-treated 4-methylphenol solution. Furthermore, these results suggest that the chlorine treatment of water contaminated with 4-methylphenol and bromide ion leads to the formation of Br-predioxins, which have been shown to be mutagenic,⁸⁾ and are also precursor of the highly toxic PBDDs.¹⁰⁾

Characterization of PXPPs Formed in an Alkaline Solution

Figure 4 shows a typical mass chromatogram (total ion current) of the unknown compounds occurring in the polyamide TLC fraction of a diethyl ether extract from a chlorinated alkaline 4-methylphenol solution in the presence of bromide ion, and the mass spectra of several peaks. The mass spectra of the compounds corresponding to the several peaks in Fig. 4 were interpreted to be Cl-DMPP for the peak 1, Cl_2 -DMPP isomers for the peaks 2 and 3, Cl_3 -DMPP isomers for the peaks 8 and 9, and Cl_4 -DMPP for the peak 14, respec-

tively, as compared with those reported in the previous papers.⁴⁻⁸⁾ The compound corresponding to the peak 9 in Fig. 4 yielded a characteristic fragment ion at m/z 160 ($C_7H_6Cl_2^+$), suggesting this compound to be a 2-phenoxyphenol. The mass spectrum of the compound corresponding to the peak 4 in Fig. 4 yielded a molecular ion at m/z 292 ($C_{14}H_{13}BrO_2^+$), indicating the occurrence of DMPP containing one Br atom in the diethyl ether extract.

The mass spectra of the compounds corresponding to the peaks 5, 6 and 7 in Fig. 4 yielded the same molecular ion at m/z 326 ($C_{14}H_{12}BrClO_2^+$), but with different fragment patterns. These findings indicate the occurrence of DMPP isomers containing Br/Cl atoms in the diethyl ether extract. A characteristic fragment ion at m/z 204 ($C_7H_6BrCl^+$ for the compound corresponding to the peak 5) is indicative of a 2-phenoxyphenol. The compounds corresponding to the peaks 12 and 13 in Fig. 4 yielded the same molecular ion at m/z 360 ($C_{14}H_{11}BrCl_2O_2^+$), but with different fragment patterns. These findings also indicate the occurrence of DMPP isomers containing Br/ Cl_2 atoms in the diethyl ether extract. The characteristic fragment ions at m/z 204 ($C_7H_6BrCl^+$ for the compound corresponding to the peak 12) and at m/z 160 ($C_7H_6Cl_2^+$ for the compound corresponding to the peak 13) are also indicative of a 2-phenoxyphenol.

The compound corresponding to the peaks 15 and 16 in Fig. 4 yielded the same molecular ion at m/z 404 ($C_{14}H_{11}Br_2ClO_2^+$), but different fragment patterns. These findings indicate the occurrence of DMPP isomers containing Br_2/Cl atoms in the di-

Table 2. Summary of GC/MS Data and Proposed Formulae of the Halogenated Phenoxyphenols Formed by Reactions of 4-Methylphenol (0.5 mmol/l) with Chlorine (Molar Ratio of Cl per Compound = 5) in Dilute Aqueous Solution Containing Bromide Ion (2.5 mmol/l) at pH 9.5 for 1 hr at 20°C

Peak no.	Retention time (min)	Molecular ion (M^+)	No. of halogen atoms in M^+	Proposed formulae	Chemical name
1	17.44	248	Cl	$C_{14}H_{13}ClO_2$	Cl-DMPP
2	18.29	282	2Cl	$C_{14}H_{12}Cl_2O_2$	Cl ₂ -DMPP
3	18.36	282	2Cl	$C_{14}H_{12}Cl_2O_2$	isomer of peak 2*
4	18.54	292	Br	$C_{14}H_{13}BrO_2$	Br-DMPP
5	19.04	326	Br/Cl	$C_{14}H_{12}BrClO_2$	Br/Cl-DMPP*
6	19.21	326	Br/Cl	$C_{14}H_{12}BrClO_2$	isomer of peak 5
7	19.28	326	Br/Cl	$C_{14}H_{12}BrClO_2$	isomer of peak 5
8	19.48	316	3Cl	$C_{14}H_{11}Cl_3O_2$	Cl ₃ -DMPP
9	20.25	316	3Cl	$C_{14}H_{11}Cl_3O_2$	isomer of peak 8*
10	20.39	Over lapping two compounds with m/z 316 and 326			
11	20.49	356	2Br	$C_{14}H_{11}Br_2O_2$	Br ₂ -DMPP
12	21.12	360	Br/2Cl	$C_{14}H_{11}BrCl_2O_2$	Br/Cl ₂ -DMPP*
13	21.19	360	Br/2Cl	$C_{14}H_{11}BrCl_2O_2$	isomer of peak 12
14	21.27	350	4Cl	$C_{14}H_{10}Cl_4O_2$	Cl ₄ -DMPP
15	22.00	404	2Br/Cl	$C_{14}H_{11}Br_2ClO_2$	Br ₂ /Cl-DMPP*
16	22.08	404	2Br/Cl	$C_{14}H_{11}Br_2ClO_2$	isomer of peak 15
17	22.19	394	Br/3Cl	$C_{14}H_{10}BrCl_3O_2$	Br/Cl ₃ -DMPP

The asterisk indicates a 2-phenoxyphenol (predioxin). DMPP = dimethylphenoxyphenol.

ethyl ether extract. The characteristic fragment ion at m/z 204 ($C_7H_6BrCl^+$ for the compound corresponding to the peak 16) suggests the product to be a 2-phenoxyphenol. In addition, the compound corresponding to the peak 17 in Fig. 4 yielded a molecular ion at m/z 394 ($C_{14}H_{10}BrCl_3O_2^+$) and several fragment ions. This finding also indicates the occurrence of DMPP with Br/Cl₃ atoms in the diethyl ether extract. The presence of very small fragment ions at m/z 126 ($C_7H_7Cl^+$), 170 ($C_7H_7Br^+$), 160 ($C_7H_6Cl_2^+$), 204 ($C_7H_6BrCl^+$) and 248 ($C_7H_6Br_2^+$) suggest the compound to be Br/Cl₃-DMPP (isopredioxin).

A summary of these halogenation products identified or determined from their retention times and MS interpretation is presented in Table 2. On the basis of TLC (Fig. 2) and GC/MS (Fig. 4) findings, these 4-methylphenol dimers containing different numbers of bromine and chlorine atoms are considered to be PXPPs. The GC/MS findings indicate the 2-phenoxyphenols (predioxins) containing Br/Cl, Br/Cl₂ and Br₂/Cl atoms are present in the TLC-separated fraction of the 4-methylphenol reaction products under the alkaline solution. In addition, the GC/MS analysis showed the presence of DMPP isomers containing Br₂/Cl₂ and Br₃/Cl atoms in the 4-methylphenol reaction products (data not shown). Recently, several researchers have

reported that polyhalogenated dibenzo-*p*-dioxins (PXDDs) and dibenzofurans (PXDFs) were found in pulp mill sludges, crustacean samples living near the plant and human adipose and milk.^{21–23)}

Effect of Experimental Conditions on the PXPP Formation

GC analyses of the diethyl ether extracts indicated that a marked reduction in the original amount of 4-methylphenol in water containing an excess bromide ion occurs with an increase in the molar ratios of hypochlorite to a compound. Figure 5 shows the results of GC determinations of PXPPs in aqueous 4-methylphenol solutions in the presence of an excess bromide ion after treatment with chlorine at various molar ratios of hypochlorite to the compound for 1 hr. PXPPs were found to be present at high concentrations in water at three equivalents of the molar ratios of hypochlorite to the compound.

At molar ratios of hypochlorite to 4-methylphenol exceed five, a small amount of polyhalogenated 4-methylphenol dimers was found. The amounts of PXPPs formed and their chemical compositions were strongly dependent on the molar ratios of hypochlorite to the compound in water. In general, lower PXPP (Br/Cl) were detected in a chlorine-treated 4-methylphenol solution containing bromide ion at molar ratios

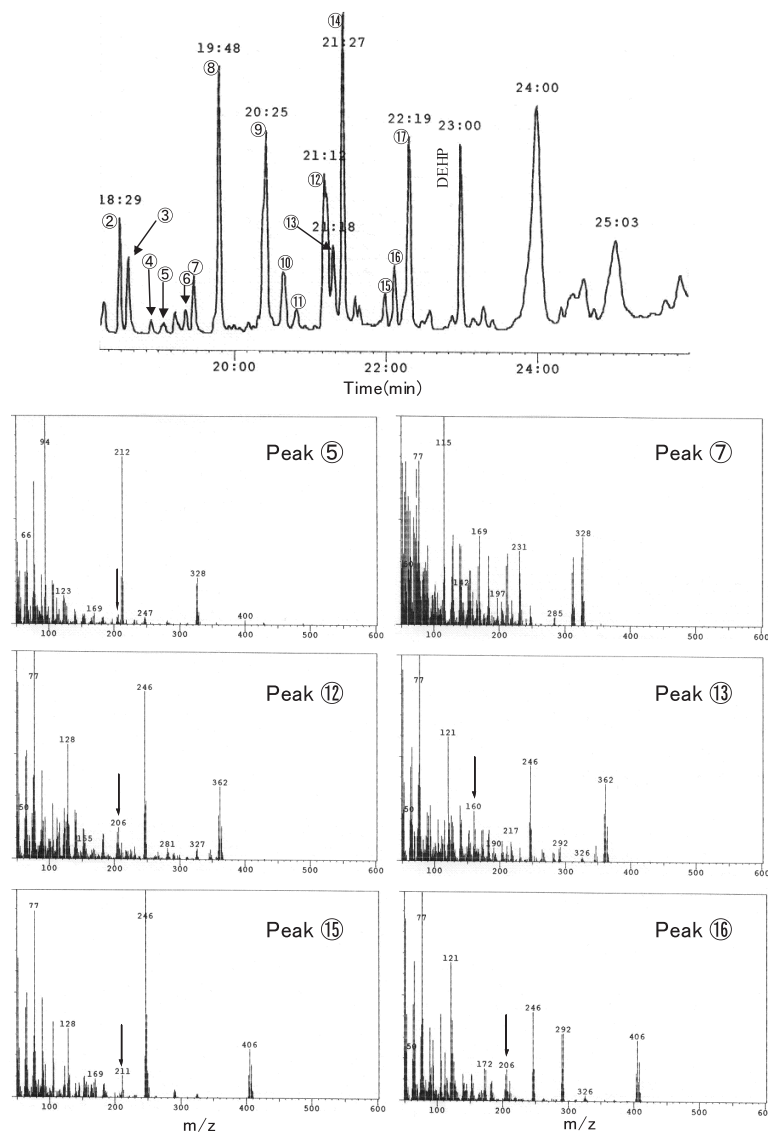


Fig. 4. Mass Chromatogram (Total Ion Current) of Polyamide TLC-separated Fraction (Unknown Compound Zone) of a Diethyl Ether Extract from the Chlorine-treated 4-Methylphenol Solution (pH 9.5) in the Presence of Bromide Ion and Mass Spectra of the Peaks

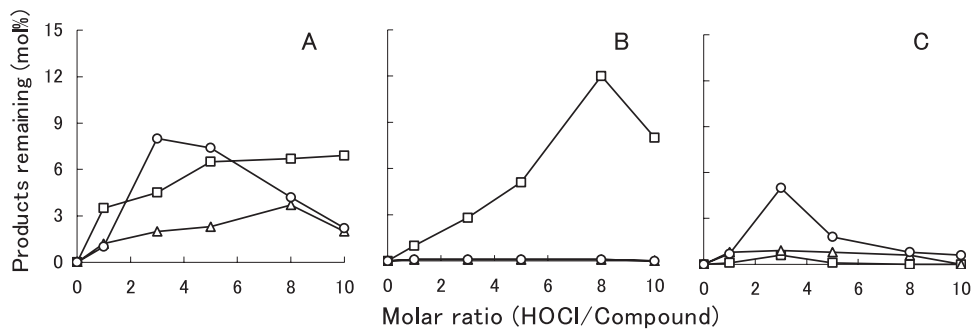
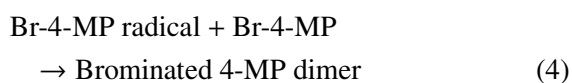
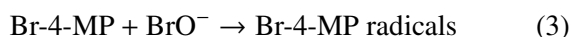
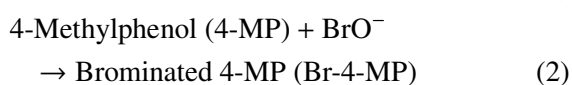
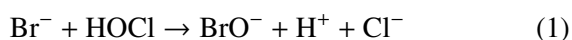


Fig. 5. Residual Amounts of Reaction Products in Aqueous 4-Methylphenol Solutions (0.5 mmol/l) Containing Bromide Ion (2.5 mmol/l) after Treatment with Chlorine at Various Molar Ratios of Active Chlorine to the Compound for 1 hr at 20°C. The yields were derived from GC peak areas, relative to the area of 4-methylphenol. (A) 2,6-dibromo-4-hydroxy-4-methylcyclohexa-2,5-dien-1-one (2,6-dibromo-4-tolquinol), (B) halogenated 4-methylphenols and (C) polyhalogenated 4-methylphenol dimers. □, pH 6.0; △, pH 8.5 and ○, pH 9.5.

lower than 2, while higher PXPPs (Br/Cl₂ and Br₂/Cl) were observed at molar ratios greater than 4. Similar distribution patterns have also been observed for the chlorine-treated 4-methylphenol solution without bromide ion.^{4–8)}

Figure 5 also shows the results of GC determinations of PXPPs in an aqueous 4-methylphenol solution with an excess bromide ion after treatment with chlorine (4 NaOCl/compound) at pH 6.0, 8.5 and 9.5 for 1 hr. The PXPPs found in the reaction of 4-methylphenol with chlorine were detected at high concentrations in a weak alkaline solution of pH 9.5, although small amounts of PXPPs were obtained in neutral and acidic solutions. This could be explained by the presence of active species of bromine and chlorine in water. At the typical ranges of pH found during most of the water treatment processes (pH 5–10) the active bromine species can range from entirely sodium hypobromite (NaOBr, greater than pH 9.5) to entirely hypobromous acid (HOBr, pK_a = 8.5 at 20°C).

On the basis of the results presented above and those obtained previously,^{4–8)} it may be concluded that the chlorination with hypochlorite of aqueous 4-methylphenol solutions in the presence of bromide ion takes place according to the following competing reactions,



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