

FORMATION OF POLYHALOGENATED 4-METHYLPHENOL DIMERS (Br/Cl-PREDIOXINS) DURING AQUEOUS CHLORINATION OF 4-METHYLPHENOL SOLUTION IN THE PRESENCE OF BROMIDE ION

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Introduction

Polychlorinated phenoxyphenol (PCPPs) occur as the main contaminants of technical chlorophenol formulation ¹. Attention has been drawn to such compounds because their 2-hydroxy isomers (predioxins) have been shown to undergo both thermal and photochemically ring closure to form PCDDs ². Although the discussion of the origin of PCPPs and PCDDs has been focused on the above two potential sources, several workers have demonstrated the presence of PCDDs in municipal sewage sludge ³ and sedimentation-basin sludge from water treatment plants ⁴. Chlorination is used extensively in wastewater treatment to disinfect and deodorize effluents prior to discharge. It seems, therefore, that PCPPs and PCDDs are formed mainly by condensation reactions after chlorination of phenols in the water supplies and wastes ^{3,4}. Direct support for this hypothesis has been provided by our recent findings which demonstrated that phenols react with chlorine to form the condensation products of their chlorinated compounds ⁵.

Recent attention has also been drawn to PBDEs and PBDDs because these compounds have been shown to be present in human milk ⁶ and to exhibit high toxicity to fish early life stages ⁷. We now presented more detailed findings on the characteristics of the condensation products (PXPPs) formed upon reaction of chlorine with 4-methylphenol in dilute aqueous solution containing an excess bromide ion. These aqueous solutions were chosen in this work because of their previous identification in surface water ⁸ and ground water ⁹.

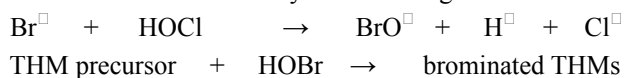
Materials and Methods

4-Methylphenol and its halogenated compounds were commercially available reagents. Standard solutions were prepared by dissolving the compounds in methanol and subsequent dilutions. Sodium hypochlorite solution was diluted with distilled water. The hypochlorite concentrations were determined by iodometric titration. The organic solvents used in this work were of analytical reagent grade. Polyamide 11 F₂₅₄ (20 x 20 cm, thickness 0.15 mm) pre-coated thin-layer chromatographic (TLC) plates were used to fractionate the diethyl ether extracts.

Aqueous 4-methylphenol solutions (0.5 mmol/l, 100 ml) containing bromide ion (5 mmol/l) were treated with hypochlorite in a separately funnel at 20°C for 1 h with shaking at various pH values and with various equivalents of chlorine per mol of compound. The unreacted chlorine or bromine was removed by addition of 1 N Na₂S₂O₃ solution. The reaction mixture was then acidified to pH 2 with 6 M HCl solution before extraction with two 20-ml volumes of diethyl ether. The extracts were dried over anhydrous Na₂SO₄ and concentrated under reduced pressure at 40°C to suitable volumes for polyamide TLC, GC and GC/MS analyses. The diethyl ether extracts were fractionated into several fractions by TLC on polyamide 11 F₂₅₄ using chloroform as a developing solvent. The detection of the spots on the plates were performed by UV irradiation. The separated zones were scraped off using special recovery tubes and the adsorbed substances were then eluted with diethyl ether. The diethyl ether eluates were analyzed by GC and GC/MS, according to the methods described in the previous papers⁵.

Results and Discussion

The condensation products of PCPPs and PCDDs have been shown to be formed during the treatment with H₂O₂/peroxidase or ozone of water containing chlorophenols^{10, 11}. Our previous papers⁵ have also demonstrated that production of these PCPPs occurs in the reaction of simple phenols with chlorine in aquatic solution. In addition, several workers have demonstrated that chlorination or ozonation of surface water and ground water containing bromide ion produces high concentrations of THMs^{8, 9} by the following reactions:



On the basis of these findings, production of PXPPs should be expected to occur upon treatment with chlorine of aqueous phenol solution containing bromide ion. Further investigation conducted on the reaction of chlorine with aqueous 4-methylphenol solution in the presence of bromide ion showed PXPPs to be present in the diethyl ether extracts. However, earlier workers 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 pyrolysis of the chlorinated compounds^{2, 12}.

Diethyl ether extracts of chlorinated 4-methylphenol solutions in the presence of bromide ion are, therefore, fractionated into several fractions by polyamide TLC before GC/MS analyses. Several compounds including original material, Br/Cl-substituted products, their oxygenated compounds (quinines)¹³ and unknown substances were observed on the chromatograms. These unknown compounds occurring in the extracts gave R_f value similar to that of chlorinated 4-methylphenol dimers¹³ on the polyamide TLC plates. However, different GC/MS behavior of the unknown compounds from that of the chlorinated dimers was observed in the extracts from the chlorine-treated solutions in the presence of bromide ion.

GC/MS determinations of the unknown compounds occurring in the polyamide TLC fractions showed that 12 compounds are present in a diethyl ether extract from the chlorinated acidic solutions, whereas over 17 substances occur in the extract from the alkaline solutions. The mass spectrum of the compound corresponding to peak 1 gave the molecular ion (M^+) at m/z 214 (no halogen atom) and several fragment ions, suggesting this compound to be methylphenoxymethylphenol [MPMP]¹⁴. The compounds corresponding to the peaks 4, 6, 7 and 8 gave the same molecular ion at m/z 370 (two Br atoms), but with different fragment patterns. These findings indicate the occurrence of MPMP isomers containing two Br atoms in the diethyl ether extract. Characteristic fragment ion at m/z 248 (two Br atoms for the peak 4) is indicative of a 2-phenoxyphenol (predioxin), since the hydrogen transfer rearrangement from the OH group to the nearest aromatic ring is typical of the fragmentation of an ortho hydroxyl ether¹⁴.

Table 1. GC Retention Times and Mass Spectral Data for PXPPs formed during Reactions of 4-Methylphenol with Chlorine in Water containing Bromide ion at pH 6 and 20°C for 1h

Peak no.	Retention time(min)	Mass fragmentation (m/z, EI-MS)	Proposed formulae
1	15.39	214 [M^+], 199 [$M^+ - CH_3$], 171 [$M^+ - CO$], 128 [$M^+ - 2(CH_3 - CO)$]	$C_{14}H_{14}O_2$
2	18.38	292 [M^+], 277 [$M^+ - CH_3$], 249 [$M^+ - CO$], 213 [$M^+ - Br$], 198 [$M^+ - CH_3 - Br$], 170 [$M^+ - CH_3 - Br - CO$]	$C_{14}H_{13}BrO_2$
3	18.54	292 [M^+], 277 [$M^+ - CH_3$], 249 [$M^+ - CO$], 213 [$M^+ - Br$], 198 [$M^+ - CH_3 - Br$], 170 [$M^+ - CH_3 - Br - CO$]	$C_{14}H_{13}BrO_2$
4	19.52	370 [M^+], 291 [$M^+ - Br$], 248*, 212 [$M^+ - 2Br$]	$C_{14}H_{12}Br_2O_2$
5	20.13	356 [M^+], 198 [$M^+ - 2Br$], 170*	$C_{13}H_{10}Br_2O_2$
6	20.20	370 [M^+], 355 [$M^+ - CH_3$], 291 [$M^+ - Br$], 275 [$M^+ - CH_3 - HBr$], 212 [$M^+ - 2Br$]	$C_{14}H_{12}Br_2O_2$
7	21.21	370 [M^+], 355 [$M^+ - CH_3$], 275 [$M^+ - CH_3 - HBr$], 212 [$M^+ - 2Br$]	$C_{14}H_{12}Br_2O_2$
8	21.31	370 [M^+], 355 [$M^+ - CH_3$], 276 [$M^+ - CH_3 - Br$], 212 [$M^+ - 2Br$]	$C_{14}H_{12}Br_2O_2$
9	22.42	434 [M^+], 355 [$M^+ - Br$], 276 [$M^+ - 2Br$]	$C_{13}H_9Br_3O_2$
10	23.02	448 [M^+], 290 [$M^+ - 2Br$], 248*, 221 [$M^+ - 3Br$]	$C_{14}H_{11}Br_3O_2$
11	23.14	448 [M^+], 433 [$M^+ - CH_3$], 369 [$M^+ - Br$], 221 [$M^+ - 3Br$]	$C_{14}H_{11}Br_3O_2$
12	25.14	512 [M^+], 354 [$M^+ - 2Br$], 326*, 275 [$M^+ - 3Br$], 196 [$M^+ - 4Br$]	$C_{13}H_8Br_4O_2$

The asterisk indicates the characteristic fragment ion of 2-phenoxyphenol (predioxin)

A summary of these bromination products identified or determined from their retention times and mass spectrometric interpretation is shown in Table 1. These GC/MS finding, therefore, indicate that brominated 2-phenoxyphenols (predioxins) and 4-phenoxyphenols (iso-predioxins) are present in the TLC-separated fraction of the 4-methylphenol reaction products under the acidic condition. In addition, GC/MS determinations showed the presence of brominated/chlorinated predioxins and iso-predioxins in the diethyl ether extracts from the chlorinated alkaline solutions (data not shown). Recently, several workers have reported that PXDDs/DFs were found in pulp mill sludge, crustacean samples living near the plant and human adipose tissue and milk^{15, 16}.

Conclusion

4-Methylphenol has been shown to produce a variety of polyhalogenated phenoxyphenols, including predioxins and iso-predioxins, upon reaction with chlorine in water containing bromide ion. The production of these compounds is strongly dependent on the molar ratios of hypochlorite to the compound and the pH with higher concentrations formed at moderate chlorine doses and a weak alkaline condition. The polyhalogenated 4-methylphenol dimers are particularly interesting, as they are present in chlorine-treated water and are also the precursors of the highly toxic halogenated dioxins.

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