

CHROM. 18 338

CHEMICAL CHANGES OF ORGANIC COMPOUNDS IN CHLORINATED WATER

X*. FORMATION OF POLYCHLORINATED METHYLPHENOXYMETHYLPHENOLS (PREDIOXINS) DURING CHLORINATION OF METHYLPHENOLS IN DILUTE AQUEOUS SOLUTION

SUKEO ONODERA*, KAORI YAMADA, YOKO YAMAJI, SHUNJI ISHIKURA and SHIZUO SUZUKI

Faculty of Pharmaceutical Sciences, Tokyo University of Science, 12, Ichigaya-funagawara-machi, Shinjuku-ku, Tokyo 162 (Japan)

(First received October 22nd, 1985; revised manuscript received November 12th, 1985)

SUMMARY

Aqueous methylphenol (*o*-, *m*- and *p*-isomers) solutions were treated with hypochlorite at 20°C under various experimental conditions. Changes in the compositions of the chlorination products in water were determined by using gas chromatographic (GC) and GC-mass spectrometric analyses of diethyl ether extracts. The chlorination of methylphenols in dilute aqueous solutions produced a series of highly chlorinated compounds, including chloromethylphenols, chloromethylbenzoquinones and chlorinated carboxylic acids. Tentative identifications were also made for other compounds with following molecular formulae: $C_{14}H_5Cl_2O_2$, $C_{14}H_4Cl_3O_2$ and $C_{14}H_3Cl_4O_2$. On the basis of the thin-layer chromatographic and GC behaviour and mass fragmentation patterns, these compounds are considered to be chlorinated methylphenoxyethylphenols. The production of some of these compounds is dependent on the number of equivalents of chlorine per mol of compound and the reaction pH. These results show that treatment with chlorine of water contaminated with phenolic compounds leads to the production of chlorinated phenoxyphenols (predioxins), which are precursors of the highly toxic chlorinated dibenzo-*p*-dioxins.

INTRODUCTION

Polychlorinated phenoxyphenols (PCPPs) occur as the main contaminant of technical chlorophenol formulations^{1,2}. Attention has been drawn to such compounds because their 2-hydroxy isomers (predioxins) have been shown to undergo both thermal and photochemical ring closure to form polychlorinated dibenzo-*p*-dioxins (PCDDs)³⁻⁵. In addition, the chlorophenols themselves may react photo-

* For Part IX, see ref. 13.

chemically to give PCDDs⁶⁻⁸. Although the discussion of the origin of PCDDs and PCPPs has been focused on the above two potential sources, recently Lamparski *et al.*⁹ and Weerasinghe *et al.*¹⁰ have demonstrated the presence of PCDDs in municipal sewage sludges.

Chlorination is used extensively in waste-water treatment in order to disinfect and deodorize effluents prior to discharge, particularly where the water may subsequently be used for recreational purposes or as a source of potable water. It seems, therefore, that PCPPs and PCDDs are formed mainly by condensation reactions after chlorination of phenolic substances in the water supplies and wastes^{9,10}. Direct support for this hypothesis has been provided by our recent findings which demonstrate that phenolic compounds react with chlorine to form the condensation products of their chlorinated compounds¹¹⁻¹³. We now present more detailed findings on the characteristics of the condensation products formed upon reaction of chlorine with methylphenols in dilute aqueous solution.

EXPERIMENTAL

Materials

Methylphenols (*o*-, *m*- and *p*-isomers) were obtained from Tokyo Chemicals (Tokyo, Japan). Several chlorinated methylphenols, benzoquinones and carboxylic acids, which may be expected to be formed during the reaction of each methylphenol with hypochlorite in dilute aqueous solution, were commercially available reagents. Standard solutions of these compounds both alone and as mixtures were prepared by dissolving the compounds in methanol, with subsequent dilutions. Hypochlorite solutions were prepared by diluting sodium hypochlorite solution (*ca.* 10% available chlorine; Nakarai Chemicals, Kyoto, Japan) in distilled water and were adjusted to the required pH by addition of 0.1 *M* disodium hydrogenphosphate-potassium dihydrogenphosphate buffer solution. The hypochlorite concentrations were determined by iodometric titration.

Treatment of aqueous methylphenol solutions with hypochlorite and extraction of reaction mixture

Aqueous methylphenol solutions (50 $\mu\text{mol/l}$) were treated with hypochlorite at 20°C for 1 h with stirring at various pH values and with various equivalents of chlorine per mol of compound. After the desired reaction time, the unreacted chlorine was removed by addition of sodium thiosulphate solution. The reaction mixture was then acidified to pH 2.0 with 0.1 *M* hydrochloric acid before extracting with three 200-ml volumes of diethyl ether. The solvents were dried over anhydrous sodium sulphate and concentrated under vacuum at 40°C to suitable volumes for gas chromatographic (GC), GC-mass spectrometric (GC-MS) and thin-layer chromatographic (TLC)-MS analyses. More detailed results of TLC-MS studies of diethyl ether extracts from a chlorine-treated methylphenol solution will be presented subsequently.

Product resolution and characterization

A Shimadzu GC-6A gas chromatograph equipped with a flame ionization detector and 2 m \times 3 mm I.D. glass column packed with 10% Apiezon L on Chro-

mosorb W AW DMCS (60–80 mesh) was programmed from 180 to 280°C at 5°C/min. The nitrogen carrier gas flow-rate was 50 ml/min. A Shimadzu Model Chromatopac-1A data system was used to determine the retention times and peak areas on the chromatograms.

An Hitachi M-80 mass spectrometer–gas chromatograph equipped with an Hitachi M-003 data processing system was used for the qualitative analyses of samples under the following conditions. The ion source was operated at 250°C with a trap current of 70 μ A and an electron energy of 70 eV. A glass column (2 m \times 3 mm I.D.) packed with 5% SE-30 on Chromosorb W AW DMCS (60–80 mesh) was used for the GC separation of the diethyl ether extracts. The oven temperature of the gas chromatograph was programmed from 220 to 300°C at 5°C/min. The products were identified by comparison of their retention times and mass spectra with those of authentic compounds.

RESULTS AND DISCUSSION

Production of chlorinated methylphenol dimers

Typical GC (with flame ionization detection) and GC–MS (total ion) traces of diethyl ether extracts of methylphenol solutions after treatment with hypochlorite at 5 equiv. chlorine per mol of compound are shown in Figs. 1 and 2. Some of the peaks were identified on the basis of the retention times of known compounds.

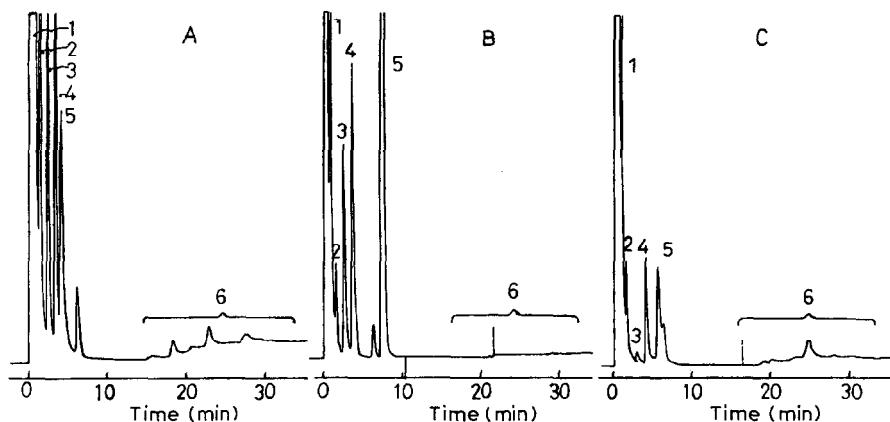


Fig. 1. Typical gas chromatograms (with flame ionization detection) of diethyl ether extracts of 2- (A), 3- (B) and 4-methylphenol (C) solutions (50 μ mol/l) after treatment with hypochlorite (5 equiv. of chlorine per mol of compound) at 20°C for 1 h. For GC conditions, see Experimental. Peaks: (A) 1 = 2-methylphenol, 2 = 6-chloro, 3 = 4-chloro, 4 = 4,6-dichloro, 5 = quinone body, 6 = 2-methylphenol dimers; (B) 1 = 3-methylphenol, 2 = 6-chloro, 3 = 4-chloro, 4 = 4,6-dichloro, 5 = 2,4,6-trichloro, 6 = 3-methylphenol dimers; (C) 1 = 4-methylphenol, 2 = 2-chloro, 3 = quinone body, 4 = 2,6-dichloro, 5 = quinone body, 6 = 4-methylphenol dimers.

Compounds corresponding to other peaks were determined from the mass spectrum of each peak (Figs. 3 and 4). In addition, in order to investigate the detailed mass fragment patterns for these chlorination products, the extract was further separated on Polyamid 11 F 254 pre-coated TLC plates (E. Merck, Darmstadt, F.R.G.)

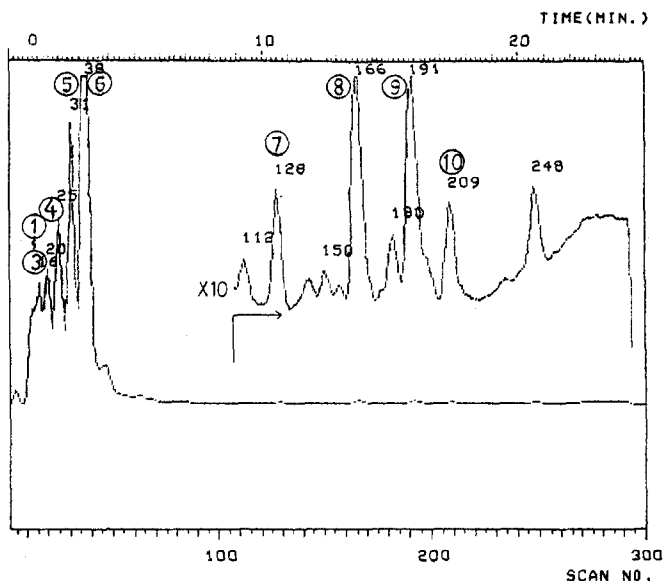


Fig. 2. Mass chromatogram (total ion current) of a diethyl ether extract of a 2-methylphenol solution (50 $\mu\text{mol/l}$) after treatment with hypochlorite (5 equiv. of chlorine per mol of compound) at 20°C for 1 h. Compounds as in Table I. For GC-MS conditions, see Experimental.

using chloroform as the developing solvent (Fig. 5), and the separated components were then analyzed by mass spectrometry.

Fig. 3A shows the mass spectrum of the dichlorinated compound, peak 7 in Fig. 2, occurring in the diethyl ether extract from a chlorine-treated 2-methylphenol solution. The molecular ion (M^+) is at m/e 282 and the most abundant fragment ion is at m/e 212, which arises by the loss of two chlorine atoms from the molecular ion. Other fragment ions at m/e 247 ($M^+ - \text{Cl}$), 142 ($M^+ - 2\text{Cl} - \text{C}_4\text{H}_6\text{O}$) and 77 ($M^+ - 2\text{Cl} - \text{C}_8\text{H}_7\text{O}_2$) are observed. The same molecular ion with two chlorine atoms was also observed for peak 9 (Fig. 4A), but the fragmentation pattern of this compound is different from that of peak 7. This seems to indicate that two isomers of a methylphenol dimer with two chlorine atoms are present in the diethyl ether extract from chlorine-treated 2-methylphenol solution.

The mass spectrum of peak 8, which was the most abundant among the chlorinated 2-methylphenol dimers (Fig. 2), was interpreted as being that of a 2-methylphenol dimer with three chlorine atoms (Fig. 3B). The molecular ion at m/e 316 and three fragment ions at m/e 246 ($M^+ - 2\text{Cl}$), 142 ($M^+ - 3\text{Cl} - \text{C}_4\text{H}_5\text{O}$) and 77 ($M^+ - 3\text{Cl} - \text{C}_8\text{H}_6\text{O}_2$) were observed. Fig. 4B shows that peak 10 is a 2-methylphenol dimer with four chlorine atoms. The molecular ion is at m/e 350 and the most abundant fragment ion at m/e 280, which arises by the loss of two chlorine atoms from the molecular ion. Other fragment ions at m/e 142 ($M^+ - 4\text{Cl} - \text{C}_4\text{H}_4\text{O}$) and 77 ($M^+ - 4\text{Cl} - \text{C}_8\text{H}_5\text{O}_2$) were observed.

The GC-MS trace (not shown) of the diethyl ether extract of a chlorine-treated 4-methylphenol solution showed the occurrence of 4-methylphenol dimers with two, three and four chlorine atoms.

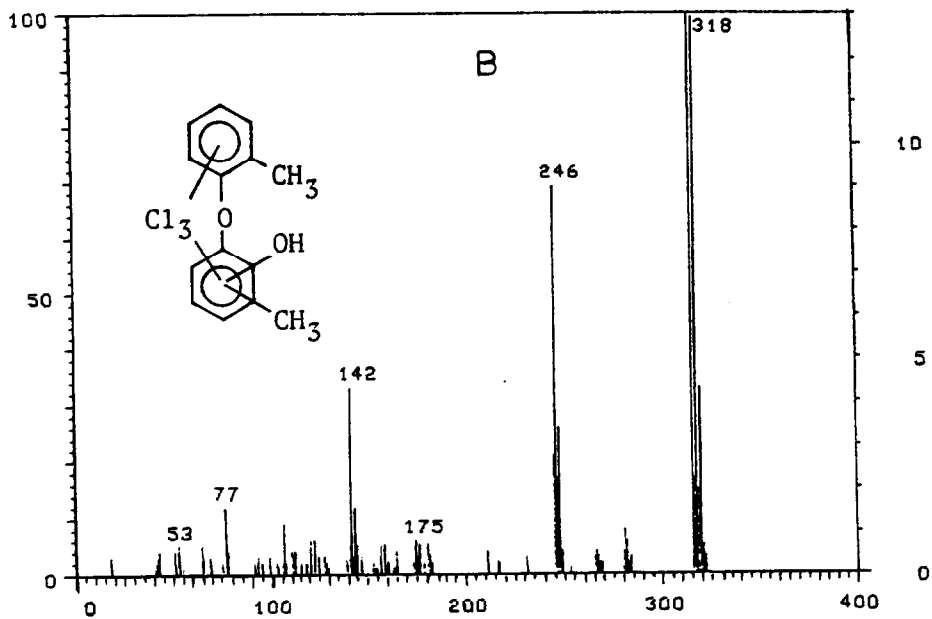
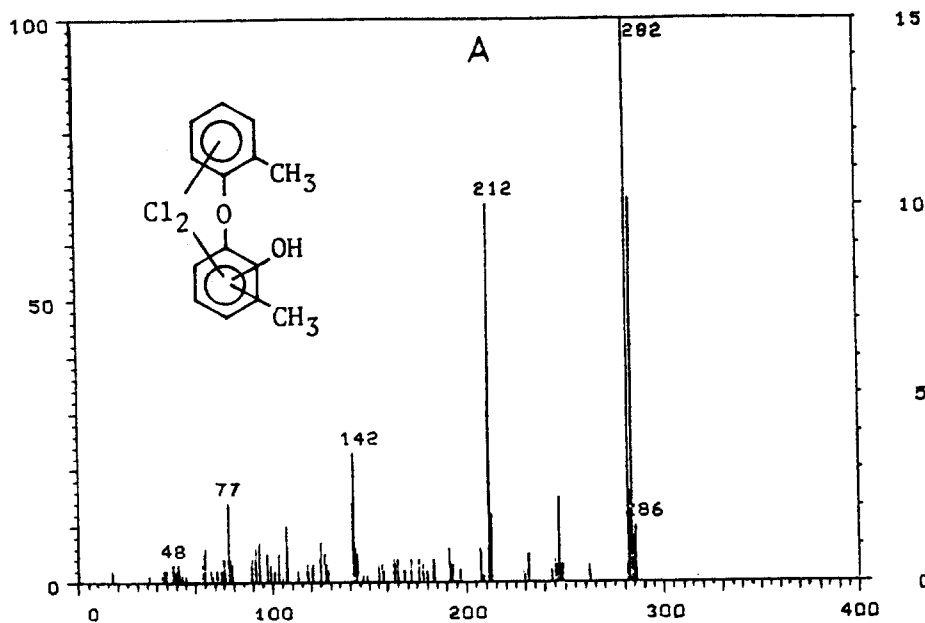


Fig. 3. Mass spectra of dichlorinated (A) and trichlorinated 2-methylphenol (B) dimers obtained from peaks 7 and 8, respectively (*cf.*, Fig. 2).

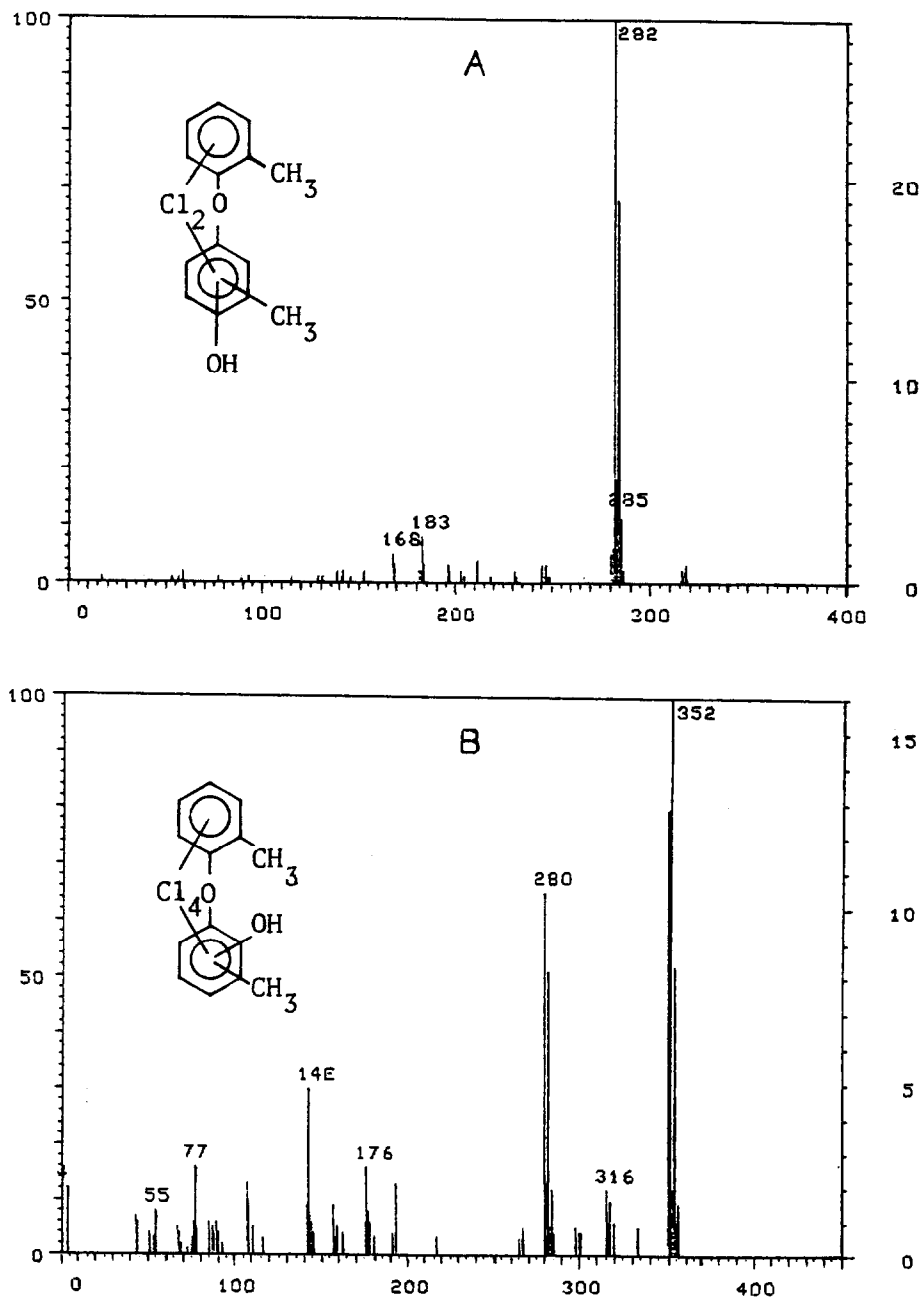


Fig. 4. Mass spectra of dichlorinated (A) and tetrachlorinated 2-methylphenol (B) dimers obtained from peaks 9 and 10, respectively (*cf.*, Fig. 2).

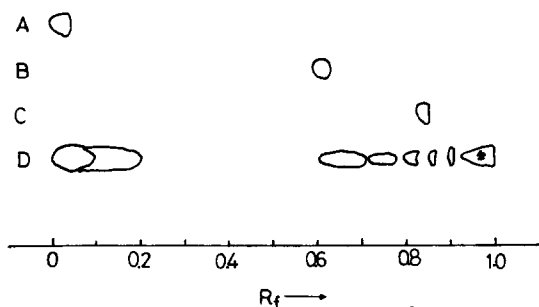


Fig. 5. Typical thin-layer chromatogram of a diethyl ether extract of the products from a chlorine-treated 4-methylphenol solution, on a Polyamid plate with chloroform as the developing solvent. A, Trichloroacetic acid B, 4-methylphenol; C, 2,6-dichloro-4-methylphenol; D, diethyl ether extract. The asterisk indicates chlorinated 4-methylphenol dimers. Based on the R_f values, each separated component was scraped from the plate with diethyl ether and then analyzed by GC-MS.

Several compounds corresponding to the polychlorinated methylphenol dimers were observed on the gas and mass chromatograms of diethyl ether extracts of mixtures obtained upon reaction of methylphenols with hypochlorite in water (Figs. 1 and 2). However, earlier workers^{14,15} demonstrated the presence of the corresponding chlorinated phenol dimers (ethers and dioxins) in the mass spectra of polychlorinated phenols and concluded that these dimers are formed by pyrolysis of the chlorinated compounds. In this work, the corresponding dimers could not be detected in the mass spectra of the chlorinated methylphenols. Therefore, it is concluded that the production of several chlorinated methylphenol dimers occurs during the reactions of methylphenols with hypochlorite in dilute aqueous solution.

A summary of these chlorination products identified or determined from their GC retention times and mass spectrometric interpretation is presented in Tables I and II. On the basis of TLC, GC and GC-MS (Figs. 1, 2 and 5), and mass spectrometric characterization (Figs. 3 and 4), these methylphenol dimers containing different numbers of chlorine atoms are considered to be chlorinated methylphenoxy-methylphenols, but their exact structures are not clear.

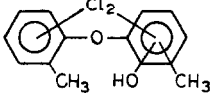
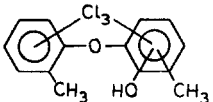
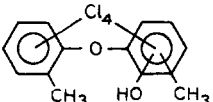
GC determinations of residual amounts of chlorinated methylphenol dimers in water

GC analysis of the diethyl ether extracts indicated that a marked reduction in the original amount of methylphenols in water occurs with an increase in the molar ratio of hypochlorous acid (Fig. 6). The chlorinated methylphenols were found to be present at high concentrations in water at low molar ratios of hypochlorous acid. At moderate molar ratios, chlorinated methylbenzoquinones and polychlorinated methylphenol dimers (m/e 282, 316 and 350 in Tables I and II) were detected as the intermediates of reaction of methylphenol solutions with hypochlorite in water. At molar ratios of hypochlorous acid to the compound of > 20 only a small amount of these chlorinated intermediates was found (Fig. 6).

Polychlorinated dibenzo-*p*-dioxins were recently found in dried municipal sludge from Milwaukee (Milorganite)⁹ sampled in 1933, 1981 and 1982 and it was speculated that their presence may have resulted from condensation reactions after

TABLE I

REACTION PRODUCTS OF 2-METHYLPHENOL WITH HYPOCHLORITE IN DILUTE AQUEOUS SOLUTION AT 20°C

No.	Compound	Scan No.	<i>m/e</i> (order of ion intensity)
1	6-Chloro-2-methylphenol*	—	142 (M ⁺), 107 (M ⁺ - Cl)
2	4-Chloro-2-methylphenol*	—	142 (M ⁺), 107 (M ⁺ - Cl)
3	Chloromethyl- <i>p</i> -benzoquinone*	—	158 (M ⁺), 123 (M ⁺ - Cl)
4	4,6-Dichloro-2-methylphenol*	13	141 (M ⁺ - Cl), 176 (M ⁺)
5	Dichloromethyl- <i>p</i> -benzoquinone*	30	192 (M ⁺), 157 (M ⁺ - Cl)
6	Unknown	38	165, 163, 43, 145, 89, 101
7	C ₁₄ H ₁₂ Cl ₂ O ₂ **	128	282 (M ⁺), 212 (M ⁺ - 2Cl), 142 (M ⁺ - 2Cl - C ₄ H ₆ O), 247 (M ⁺ - Cl), 77 (M ⁺ - 2Cl - C ₈ H ₇ O ₂)
			
8	C ₁₄ H ₁₁ Cl ₃ O ₂ **	166	316 (M ⁺), 246 (M ⁺ - 2Cl), 142 (M ⁺ - 3Cl - C ₄ H ₅ O), 77 (M ⁺ - 3Cl - C ₈ H ₆ O ₂)
			
9	Isomer of compound 7**	191	282 (M ⁺)
10	C ₁₄ H ₁₀ Cl ₄ O ₂ **	209	350 (M ⁺), 280 (M ⁺ - 2Cl), 142 (M ⁺ - 4Cl - C ₄ H ₄ O), 77 (M ⁺ - 4Cl - C ₈ H ₅ O ₂), 315 (M ⁺ - Cl)
			

* Complete identification based on mass spectral interpretation and confirmed by comparison with a reference spectrum and the retention time of the substance.

** Tentative structure; identification based on mass spectral interpretation.

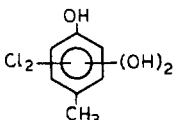
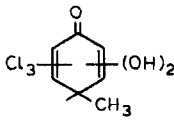
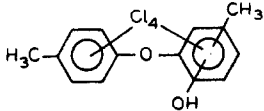
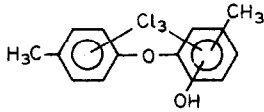
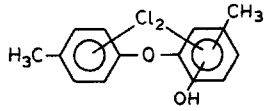
chlorination of phenolic substances in the water supply and wastes. Although a reduction in the amounts of chlorinated methylphenol dimers in water was observed with increasing molar ratio of hypochlorous acid to the compound (Fig. 6), the formation of polychlorinated methyl-dibenzo-*p*-dioxins in chlorine-treated water was not tested in the present work. Further research would therefore be required to determine how the chlorinated methylphenol dimers are converted into other chlorinated substances.

Fig. 7 shows the results of GC determinations of diethyl ether extracts from methylphenol solutions after treatment with an excess of hypochlorite at various pH values for 1 h. Several chlorinated methylphenols, further oxychlorinated products of chlorinated methylphenols and the chlorinated methylphenol dimers were detected at high concentrations in acidic solutions, although small amounts of these chlorinated compounds were obtained under neutral and alkaline conditions. These results were also in agreement with the values of the chlorine demands of methylphenols obtained at various pH values (data not shown).

Under acidic and neutral conditions, chlorinated products of 4-methylphenol formed upon treatment with hypochlorite in water were detected at higher concen-

TABLE II

REACTION PRODUCTS OF 4-METHYLPHENOL WITH HYPOCHLORITE IN DILUTE AQUEOUS SOLUTION AT 20°C

No.	Compound	Scan No.	<i>m/e</i> (order of ion intensity)
1	2-Chloro-4-methylphenol*	—	142 (M ⁺)
2	C ₇ H ₆ Cl ₂ O ₃ ** 	19	89 (M ⁺ - 2Cl - 3CO), 53 (M ⁺ - 2Cl - 3CO - C ₃ H), 123 (M ⁺ - 2CO - CHO), 208 (M ⁺)
3	2,6-Dichloro-4-methylphenol*	12	141 (M ⁺ - Cl, 176 (M ⁺), 77 (M ⁺ - 2Cl - CHO)
4	C ₇ H ₅ Cl ₃ O ₃ ** 	25	123 (M ⁺ - COCl - 2CO), 87 (M ⁺ - COCl - CHO - CO - Cl), 53 (M ⁺ - COCl - 2CO - 2Cl), 179 (M ⁺ - COCl), 242 (M ⁺)
5	Unknown	30	123, 53, 87, 179
6	C ₁₄ H ₁₂ Cl ₂ O ₂ ** 	144	146 (M ⁺ - 2Cl - C ₄ H ₂ O), 282 (M ⁺), 247 (M ⁺ - Cl), 212 (M ⁺ - 2Cl), 219 (M ⁺ - 2Cl - CO), 267 (M ⁺ - CH ₃)
7	C ₁₄ H ₁₁ Cl ₃ O ₂ ** 	172	316 (M ⁺), 246 (M ⁺ - 2Cl), 301 (M ⁺ - CH ₃), 281 (M ⁺ - Cl), 267 (M ⁺ - Cl - CH ₃), 146 (M ⁺ - 3Cl - C ₄ HO)
8	Isomer of compound 7***	187	180 (M ⁺ - 3Cl - CH ₃ O), 316 (M ⁺), 281 (M ⁺ - Cl), 246 (M ⁺ - 2Cl), 253 (M ⁺ - COCl)
9	C ₁₄ H ₁₀ Cl ₄ O ₂ ** 	214	350 (M ⁺), 280 (M ⁺ - 2Cl), 315 (M ⁺ - Cl), 335 (M ⁺ - CH ₃)

* Complete identification based on mass spectral interpretation and confirmed by comparison with a reference spectrum and the retention time of the substance.

** Tentative structure; identification based on mass spectral interpretation.

trations than those observed for 2- and 3-methylphenol solutions (Fig. 7). This could be explained by steric shielding of the *para*-position in the phenol by a methyl group substituent in the aromatic ring, which hinders the oxidative degradation of chlorinated methylphenols with hypochlorous acid in acidic aqueous solutions.

Aqueous chlorine is used to disinfect sewage water and raw water destined for

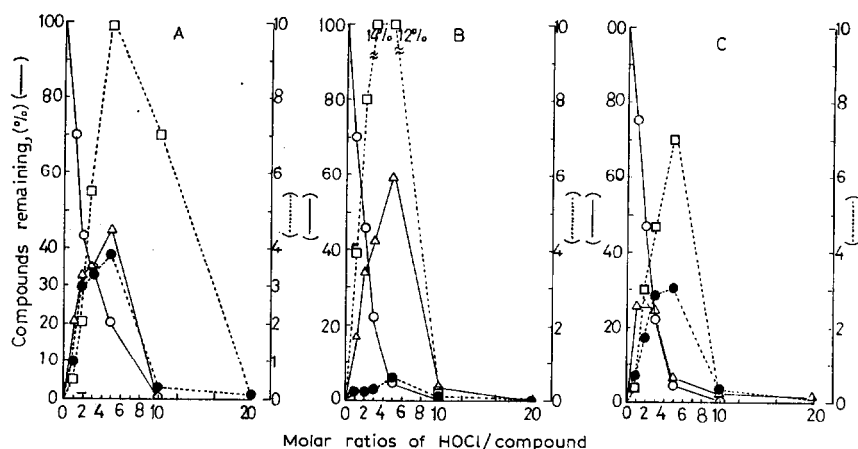


Fig. 6. Residual amounts of reaction products in aqueous 2- (A), 3- (B) and 4-methylphenol (C) solutions ($50 \mu\text{mol/l}$) after treatment with hypochlorite (various equivalents of chlorine per mol of compound) at 20°C for 1 h. The yields are derived from GC peak areas, relative to the peak area of each starting material. \circ — \circ , Starting material; \triangle — \triangle , chlorinated methylphenols; \square — \square , polychloropolyhydroxylated methylphenols; \bullet — \bullet , chlorinated methylphenol dimers.

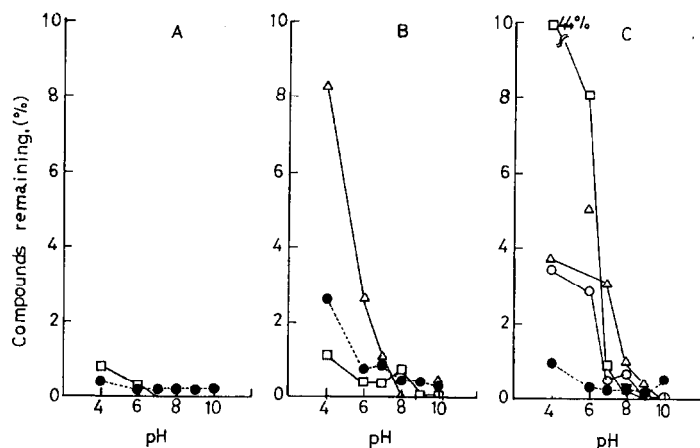


Fig. 7. Residual amounts of reaction products in aqueous 2- (A), 3- (B) and 4-methylphenol (C) solutions ($50 \mu\text{mol/l}$) after treatment with an excess of hypochlorite at various pH and 20°C for 1 h. Other details as in Fig. 6.

human consumption. Methylphenols have been shown to produce many chlorinated aromatic compounds upon reaction with hypochlorite in water (Tables I and II). The production of these compounds is greatly dependent on the molar ratio of hypochlorous acid and the reaction pH, with higher concentrations formed at moderate chlorine doses (Fig. 6) and under acidic conditions (Fig. 7). Acidic chlorinated waters are generally adjusted to neutral conditions or diluted in water at the water-treatment station. Therefore, most of the chlorinated aromatic compounds are destroyed by this process and the hazard to public health may be substantially decreased. However,

the chlorinated methylphenol dimers are particularly interesting, as they are present in chlorinated-treated methylphenol solutions and are also precursors of the highly toxic chlorinated dioxins.

REFERENCES

- 1 C.-A. Nilsson and L. Renberg, *J. Chromatogr.*, 89 (1974) 325.
- 2 W. P. Cochrane, J. Singh, W. Miles and B. Wakeford, *J. Chromatogr.*, 217 (1981) 289.
- 3 C.-A. Nilsson, K. Andersson, C. Rappe and S.-O. Westermark, *J. Chromatogr.*, 96 (1974) 137.
- 4 C. Rappe and C.-A. Nilsson, *J. Chromatogr.*, 67 (1972) 247.
- 5 J. Ress, G. R. Higginbotham and D. Firestone, *J. Assoc. Off. Anal. Chem.*, 53 (1970) 628.
- 6 M. Mansour and F. Korte, *Chemosphere*, 5 (1976) 383.
- 7 M. Mansour, H. Parlar and F. Korte, *Chemosphere*, 4 (1975) 235.
- 8 J. Olimmer and U. Klingebiel, *Science (Washington, D.C.)*, 174 (1971) 407.
- 9 L. L. Lamparski, T. J. Nestrick and V. A. Stenger, *Chemosphere*, 13 (1984) 361.
- 10 N. C. A. Weerasinghe, M. S. Gross and D. J. Lisk, *Chemosphere*, 14 (1985) 557.
- 11 S. Onodera, M. Matsuda, S. Ishikura and S. Suzuki, *J. Hyg. Chem.*, 28 (1982) 146.
- 12 S. Onodera, N. Iino, M. Matsuda and S. Ishikura, *J. Chromatogr.*, 265 (1983) 201.
- 13 S. Onodera, K. Yamada, Y. Yamaji and S. Ishikura, *J. Chromatogr.*, 288 (1984) 91.
- 14 M. Mulka, *Can. J. Chem.*, 39 (1961) 1973.
- 15 W. Sandermann, H. Stockman and R. Casten, *Chem. Ber.*, 90 (1957) 690.