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CHEMICAL CHANGES OF ORGANIC COMPOUNDS IN CHLORINATED WATER

VI*. GAS CHROMATOGRAPHIC AND MASS SPECTROMETRIC STUDIES OF THE REACTIONS OF PHENYLPHENOLS WITH HYPOCHLORITE IN DILUTE AQUEOUS SOLUTION

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SUMMARY

Diethyl ether-extracted products obtained from phenylphenol solutions after treatment with hypochlorite under various conditions have been investigated for their nature and contents of chlorination products in water. The ether extracts were chromatographed on polar and non-polar gas-liquid chromatographic (GLC) columns and the peaks were assigned on the basis of plots of $\log t_R$ against the number of expected chlorine atoms. They were subsequently identified from the mass spectra of the extracts. The GLC and mass spectral analyses of these products indicated that the reactions involve chlorination to chlorophenylphenols (A), oxidation of compounds A to chlorophenylquinones (B), oxidative degradation of compounds B to phenylcarboxylic acids and condensation of compounds A to the corresponding ethers and dioxins. The residual amounts of chlorinated compounds of phenylphenols in water were found to be dependent on the pH of the solution.

INTRODUCTION

Chlorination is used extensively in waste-water treatment in order to disinfect effluents prior to discharge, particularly where the water may subsequently be used for recreational purposes or as a source of potable water. Recently, it has become apparent that water chlorination is not only responsible for the formation of haloforms^{2–6} but it also has the potential to produce several high-molecular-weight mutagenic substances^{7–21}, some of which have been identified as organochlorines derived from natural products. It is, therefore, of interest to establish the nature of non-volatile compounds which may be present in waste-water effluents and drinking water after chlorination, under the conditions utilized for water treatment.

* For Part V, see ref. I.

One class of compounds recognized as a major source of pollutants in aquatic environments is phenols. Phenols are introduced into the environment in several ways: directly as industrial effluents and indirectly as transformation products from natural and synthetic chemicals. Phenol has also long proved problematical in disinfection of water supplies as it is readily chlorinated by free available chlorine, giving rise to compounds with increased taste and odour. Earlier workers have demonstrated that chlorine treatment of phenol in water leads to the formation of a variety of chlorinated phenolics and alicyclic compounds²²⁻³⁴; however, many of the less volatile compounds have not been fully characterized.

The aim of this work was to identify the chlorination products in water and also to determine the residual concentrations of these compounds formed during chlorination of phenylphenols, which are widely used as fungicides and bactericides, with aqueous hypochlorite, under the conditions utilized for water treatment.

EXPERIMENTAL

Materials

Phenylphenols (*o*-, *m*- and *p*-isomers), used in the model study of the chlorination of water, were obtained from Tokyo Chemicals (Tokyo, Japan). Several chlorinated derivatives of phenylphenols and phenylcarboxylic acids, which may be expected to be formed during reactions of phenylphenols 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 serial dilutions. Hypochlorite solutions were prepared by diluting sodium hypochlorite solution (*ca.* 10% available chlorine) (Nakarai Chemicals, Kyoto, Japan) with distilled water and were adjusted to the required pH by addition of 0.1 M Na₂HPO₄-KH₂PO₄ buffer solution. The hypochlorite concentrations were determined by means of iodimetric titration.

Treatment with hypochlorite solution containing phenylphenol

Reactions of phenylphenols with chlorine were observed by mixing 1000 ml of hypochlorite solution and 1 ml of a solution of phenylphenol dissolved in methanol at 20°C. The reaction was then terminated at the desired reaction time by addition of a volume of Na₂S₂O₃ solution equal to the equivalent chlorine added. The reaction mixture was acidified to pH 2.0 (1 M hydrochloric acid) before extraction with three 200-ml volumes of diethyl ether. The solvents were evaporated under vacuum at 40°C; half of the residues were resuspended in 1 ml of methanol for gas-liquid chromatographic (GLC) analysis and the other was investigated by means of mass spectrometry (MS).

Product resolution and characterization

A Shimadzu GC 6A gas chromatograph equipped with a flame-ionization detector (FID) and a Model Chromatopac-1A data system was used with nitrogen as the carrier gas. Two coiled glass columns (2 m × 3 mm I.D.), one packed with 10% Apiezon L-Chromosorb W AW DMCS (60-80 mesh) as the non-polar stationary phase and the other packed with 5% DEGS + 1% H₃PO₄-Chromosorb W AW DMCS (60-80 mesh) as the polar phase, were used for the separation and determina-

tion of the reaction products. The operating conditions were as described previously^{31,34,35}. A Hitachi M-80 mass spectrometer equipped with a Hitachi M-003 data processing system was used under the following conditions: the ion source was operated at 150°C with a trap current of 70 μ A and an electron energy of 79 eV. Sample introduction was by means of a heated direct probe inlet system (100°C).

Recovery data were obtained by spiking water with the chlorinated phenylphenols and phenylcarboxylic acids and carrying them through the entire analytical procedure except for the chlorination. The recovery were over 90% for the former and $80 \pm 5\%$ for the latter compounds.

RESULTS AND DISCUSSION

Kinetic studies of hypochlorite reaction

In a preliminary examination of the reactions of individual phenylphenols with hypochlorite in dilute aqueous solution, the reduction in concentration of the active chlorine during contact with each of these compounds was measured by using a Model RC-1 Resichlocorder (Bionics Instrument, Tokyo, Japan) at 20°C. Fig. 1 shows the time courses of consumption of chlorine with these compounds ($3.6 \cdot 10^{-5} M$) in unbuffered water at an initial pH of 7.0. It can be seen that a large consumption of active chlorine occurs during the first 15 min, followed by much slower secondary reactions. These reactions were accompanied by a rapid decrease in the initial pH of the solutions (5.5, 5.7 and 6.6 for *o*-, *m*- and *p*-isomers, respectively, after reaction for 1 h). About 60–70% of the active chlorine consumed after reaction for 24 h was obtained within the first 1 h for these compounds.

Table I summarizes the chlorine consumptions with individual phenylphenols in the absence and presence of buffer reagent in chlorinated water and the changes of pH in these solutions after reaction for 24 h at 20°C. Consumption of chlorine with simple phenol, as a reference substance, and change of pH in the solution are also presented in Table I. In the unbuffered conditions, the greatest consumption of chlorine was observed for *m*-phenylphenol in water after reaction for 24 h and the smallest value was obtained for the *p*-isomer. However, the consumptions of chlorine with these compounds, particularly the *o*- and *p*-isomers, in the buffered solution at pH 7.0 are greater than those obtained in the unbuffered conditions. These results

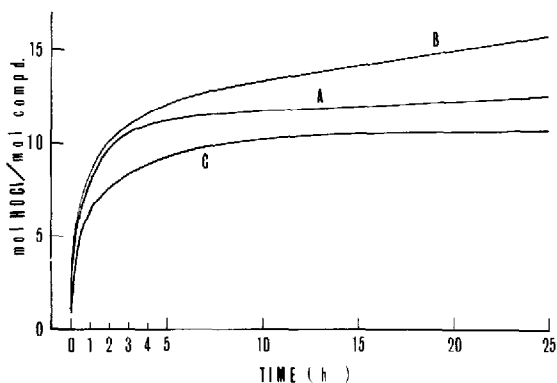


Fig. 1. Time courses of consumptions of active chlorine with phenylphenols ($3.6 \times 10^{-5} M$) in unbuffered water with an initial pH of 7.0 at 20°C. A, 2-Phenylphenol; B, 3-phenylphenol; and C, 4-phenylphenol.

TABLE I

CHLORINE DEMANDS OF PHENYLPHENOLS IN A 3.6×10^{-5} M SOLUTION AND CHANGES OF pH IN THE SOLUTION AFTER REACTIONS FOR 24 h WITH AN EXCESS OF HYPOCHLORITE AT 20°C

Compound	Water conditions	pH		Cl demand	
		Initial	Final	mol/mol	mol/carbon atom
o-Phenylphenol	Unbuffered	7.0	4.4	12.5	1.04
	Buffered	7.0	—	17.9	1.50
m-Phenylphenol	Unbuffered	7.0	4.3	15.6	1.30
	Buffered	7.0	—	18.0	1.50
p-Phenylphenol	Unbuffered	7.0	6.2	10.5	0.87
	Buffered	7.0	—	18.0	1.50
Phenol	Unbuffered	7.0	3.8	8.5	1.41
	Buffered	7.0	—	13.5	2.25

may indicate that the formation of chlorinated phenylphenols, chlorinated phenylquinones and compounds with oxidation-rupture of the aromatic ring occur more rapidly in the neutral solution than under acidic conditions.

Table I also shows that although the chlorine demands of phenylphenols are larger than that of simple phenol in both the absence and presence of buffer reagent in water, the amounts of the active chlorine per carbon atom in the former are smaller than those in the latter. A larger chlorine demand per compound, but smaller values per carbon atom in the molecule, have been observed for other substituted phenols³⁶. These results could be explained by steric shielding of the active sites in these phenylphenols by phenyl groups substituted in the phenol ring, which prevents the oxidative degradation of these compounds by hypochlorite in water.

Gas chromatographic and mass spectrometric identification of ether-extractable products

In order to identify the chlorination products present in phenylphenol solutions after treatment with hypochlorite, the diethyl ether extracts of these reaction mixtures were chromatographed on polar and non-polar columns. Typical gas chromatograms of the extracts from phenylphenol solutions treated with hypochlorite at a molar ratio of hypochlorous acid to compound of 2 are shown in Fig. 2. Some of the peaks were identified according to the retention times (t_R) of known substances. Compounds corresponding to other peaks were assigned on the basis of plots of $\log t_R$ against number of expected chlorine atoms^{31,35} and also identified purely from the mass spectra of the ether extracts (Figs. 3 and 5). The chlorinated derivatives of phenylphenols chromatographed on the 10% Apiczon L column are usually eluted in order of increasing number of chlorine atoms on the aromatic ring, whereas some of the non-polar derivatives, especially the isomers, chromatographed on the 5% DEGS + 1% H₃O₄ column are eluted prior to some polar compounds.

The mass spectra of the chlorinated compounds show some peaks with typical chlorine clusters arising from the presence of isotopes of ³⁵Cl and ³⁷Cl occurring naturally in the ratio 3:1. Thus, for ions containing n chlorine atoms, a cluster of $n + 1$ peaks should be obtained with an m/e difference of 2, the ratio of the relative

intensities corresponding to the coefficients of the polynomial $(3x + 1)^n$ for $x = 1$. Figs. 3 and 5 illustrate the mass spectra of the diethyl ether extracts of *o*- and *p*-phenylphenol solutions after treatment with hypochlorite under various conditions. A variety of molecular ions containing different numbers of chlorine atoms can be seen in the mass spectra of the diethyl ether extracts in Figs. 3 and 5. For example, the molecular ions appeared on the mass spectra in Fig. 3 are 204, 238 and 272, which may indicate mono-, di- and trichlorinated compounds, respectively. Other molecular ions are also observed at 122, 184 and 338 with no chlorine, 220, 268 and 372 with one chlorine atom, 254, 286 and 406 with two chlorine atoms and 440 with three chlorine atoms (Figs. 3 and 5).

To investigate the detailed mass fragment patterns for these chlorination products, the extracts were further separated on Polyamid 11 F 254 (pre-coated TLC plates; E. Merck, Darmstadt, G.F.R.) using chloroform as the developing solvent, and the separated components were then analysed by mass spectrometry. A summary

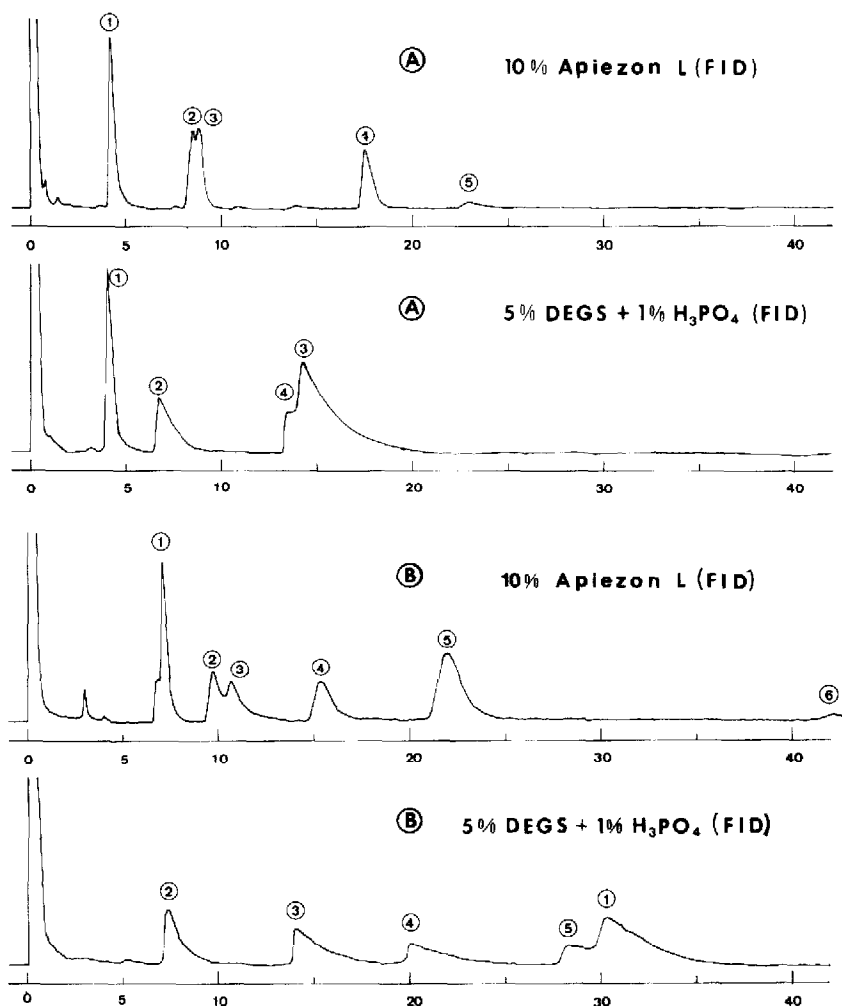


Fig. 2.

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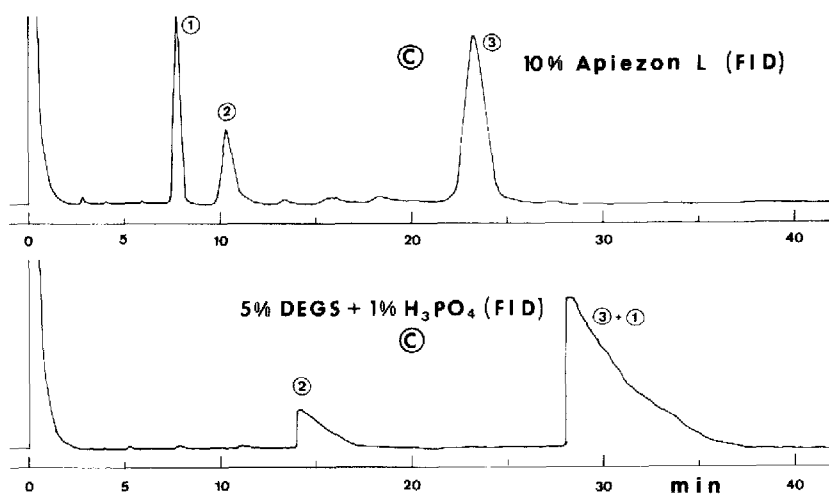


Fig. 2. Typical gas chromatograms (FID) of diethyl ether extracts on polar and non-polar columns. Each extract obtained from 2-phenylphenol (A), 3-phenylphenol (B) and 4-phenylphenol (C) solutions after treatment with hypochlorite at HOCl: compound molar ratio = 2 for 1 h was chromatographed under the following conditions: non-polar column, 10% Apiezon L, oven temperature 230°C; polar column, 5% DEGS + 1% H₃PO₄, oven temperature 160°C. Chromatograms A: (1) 2-phenylphenol; (2) 6-chloro-2-phenylphenol; (3) 4-chloro-2-phenylphenol; (4) 4,6-dichloro-2-phenylphenol; and (5) chloro-2-phenylhydroquinone. Chromatograms B: (1) 3-phenylphenol; (2) 6-chloro-3-phenylphenol; (3) 4-chloro-3-phenylphenol; (4) 4,6-dichloro-3-phenylphenol; (5) 2,4,6-trichloro-3-phenylphenol; and (6) unknown compound. Chromatograms C: (1) 4-phenylphenol; (2) 2-chloro-4-phenylphenol; and (3) 2,6-dichloro-4-phenylphenol.

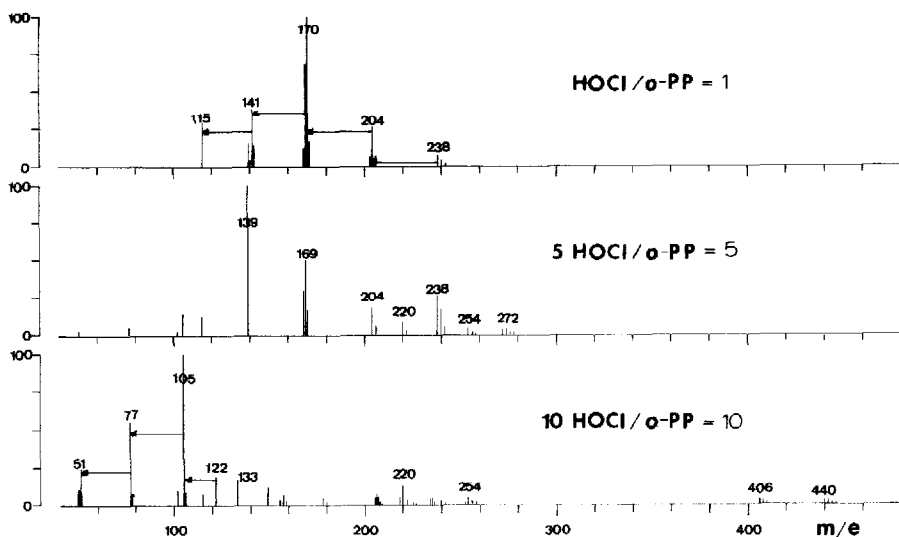


Fig. 3. Electron impact mass spectra of diethyl ether extracts of 2-phenylphenol solutions after treatment with hypochlorite at various molar ratios of HOCl to compound at a pH of 7.0. Mass spectrometric conditions: see Experimental.

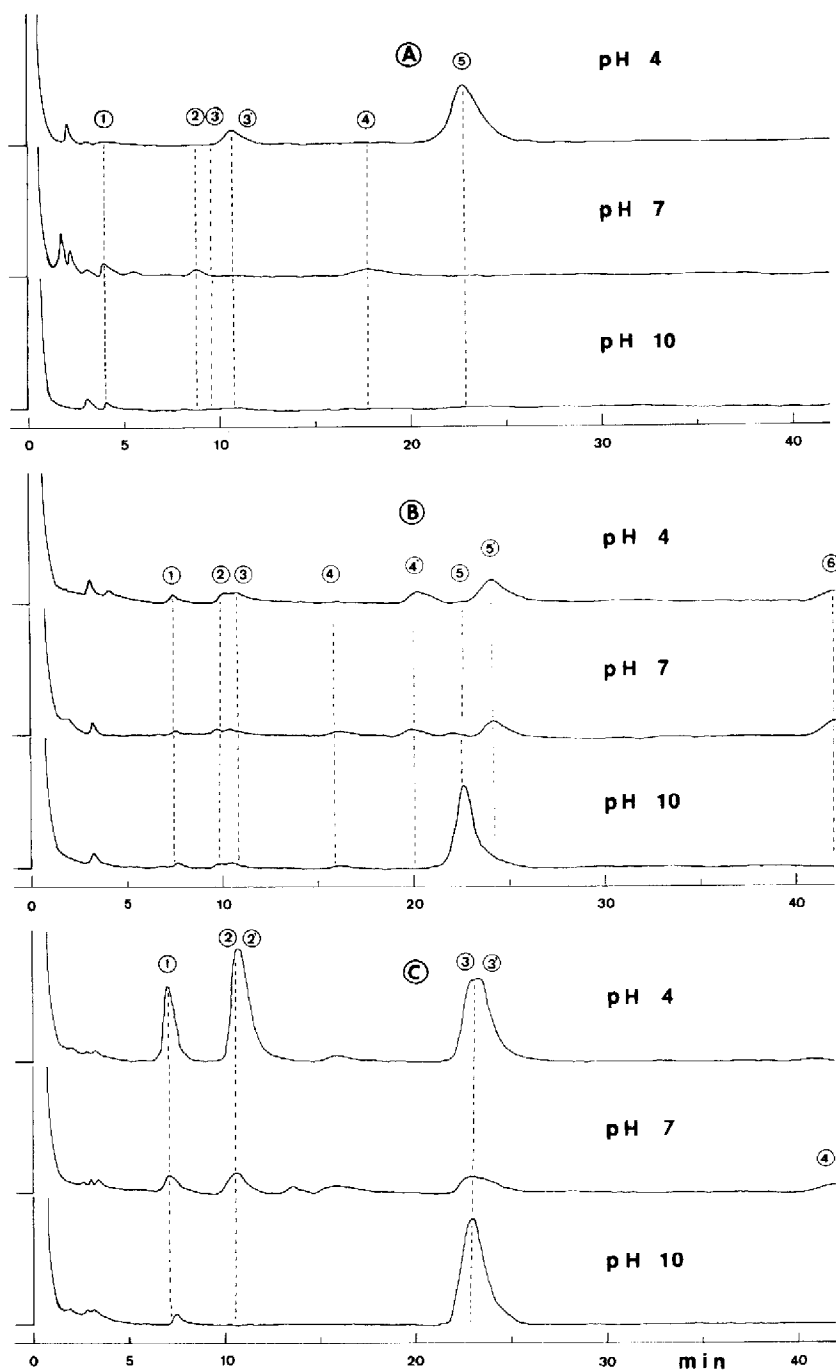
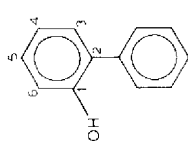
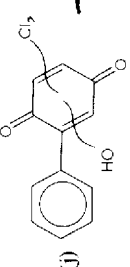
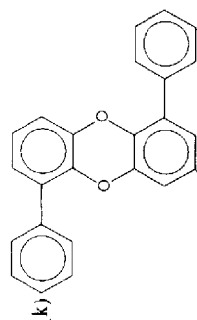
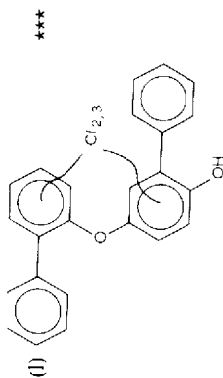


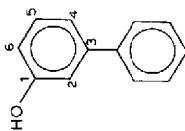
Fig. 4. Gas chromatograms (FID) of diethyl ether extracts of 2-phenylphenol (A), 3-phenylphenol (B) and 4-phenylphenol (C) solutions after treatment with an excess of hypochlorite at varying pH for 1 h. Column, 10% Apiezon L; oven temperature, 230°C. Chromatograms A: (3') 2-phenylhydroquinone; other compounds as in chromatograms A in Fig. 2. Chromatograms B: (4') chloro-3-phenylhydroquinone; (5') 2,6-dichloro-3-phenylhydroquinone; other compounds as in chromatograms B in Fig. 2. Chromatograms C: (2') 4-phenylhydroquinone; (3') 2-chloro-4-phenylhydroquinone; (4) unknown compound; other compounds as in chromatograms C in Fig. 2.

TABLE II
REACTION PRODUCTS OF PHENYLPHENOLS WITH HYPOCHLORITE IN DILUTE AQUEOUS SOLUTION AT 20°C

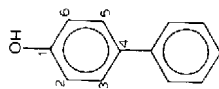
Reactant	Product identified or determined	GLC peak No.	m/e (order of ion intensity)
	(a) Original	1	170 (M ⁺), 169 (M ⁺ - H), 141 (M ⁺ - CHO), 115 (M ⁺ - CHO - C ₂ H ₅)
	(b) Benzoic acid*	2	105 (M ⁺ - OH), 77 (M ⁺ - COOH), 122 (M ⁺)
	(c) 6-Chloro-2-phenylphenol*	3	169 (M ⁺ - Cl), 204 (M ⁺), 140 (M ⁺ - Cl - CHO)
	(d) 4-Chloro-2-phenylphenol*	4	139 (M ⁺ - 2Cl - CHO), 168 (M ⁺ - 2Cl), 203 (M ⁺ - Cl), 238 (M ⁺)
	(e) 4,6-Dichloro-2-phenylphenol*	4	218 (M ⁺)
(f) Monochlorophenylbenzoquinone**			252 (M ⁺)
(g) Dichlorophenylbenzoquinone**			220 (M ⁺)
(h) Monochlorophenylhydroquinone**		3'	254 (M ⁺)
(i) Dichlorophenylhydroquinone**		5	268 (M ⁺)
			268 (M ⁺)
			370 (M ⁺)



- (a) Original
- (b) Benzoic acid*
- (c) 6-Chloro-3-phenylphenol*
- (d) 4-Chloro-3-phenylphenol*
- (e) 4,6-Dichloro-3-phenylphenol*
- (f) 2,4,6-Trichloro-3-phenylphenol*
- (g) Tetrachloro-3-phenylphenol**
- (h) Dichlorinated phenylhydroquinone**
- (i) Trichlorinated phenylhydroquinone**



- (a) Original
- (b) Benzoic acid*
- (c) 2-Chloro-4-phenylphenol*
- (d) 2,6-Dichloro-4-phenylphenol*
- (e) Trichloro-4-phenylphenol**
- (f) 4-Phenyl-o-quinone**
- (g) 4-Phenylcatechol**
- (h) Chloro-4-phenylcatechol**
- (i) Dichloro-4-phenylcatechol**



406 (M⁺) for dichlorinated compound
 440 (M⁺) for trichlorinated compound

1
 2
 3
 4
 5
 4'
 5'

170 (M⁺), 141 (M⁺ - CHO), 115 (M⁺ - CHO - C₂H₂)
 105 (M⁺ - OH), 77 (M⁺ - CHO), 122 (M⁺)
 204 (M⁺)
 238 (M⁺), 139 (M⁺ - 2Cl - CHO)
 272 (M⁺), 113 (M⁺ - 3Cl - CHO - C₂H), 173 (M⁺ - 2Cl - CHO), 138 (M⁺ - 3Cl - CHO), 202 (M⁺ - 2Cl)
 306 (M⁺)
 254 (M⁺)
 288 (M⁺)

474 (M⁺) tetrachlorinated compound
 508 (M⁺) pentachlorinated compound

1
 2
 3
 2'
 3'

170 (M⁺), 141 (M⁺ - CHO), 115 (M⁺ - CHO - C₂H₂)
 105 (M⁺ - OH), 77 (M⁺ - COOH), 122 (M⁺)
 204 (M⁺), 175 (M⁺ - CHO), 140 (M⁺ - Cl - CHO)
 238 (M⁺), 139 (M⁺ - 2Cl - CHO)
 272 (M⁺)
 184 (M⁺), 157 (M⁺ - CO), 128 (M⁺ - 2CO)
 77 (M⁺ - 2CHO - C₄H₃), 128 (M⁺ - 2CHO), 157 (M⁺ - CHO), 186 (M⁺)
 185 (M⁺ - Cl), 191 (M⁺ - CHO), 220 (M⁺)
 219 (M⁺ - Cl), 254 (M⁺), 198 (M⁺ - 2Cl)

TABLE II (continued)

Reactant	Product identified or determined	GLC peak No.	m/e (order of ion intensity)
	Compound or structure		
	(j)		233 (M ⁺ - Cl), 268 (M ⁺)
	(k)		286 (M ⁺)
	(l)		336 (M ⁺) for the compound with no Cl 370 (M ⁺) for monochlorinated compound 404 (M ⁺) for dichlorinated compound
	(m)		338 (M ⁺) for the compound with no Cl 372 (M ⁺) for monochlorinated compound 406 (M ⁺) for dichlorinated compound 440 (M ⁺) for trichlorinated compound

* Complete identification based on mass spectral interpretation and confirmed by comparison with a reference spectrum and retention time of the substance.
 ** Complete identification based on mass spectral interpretation and confirmed by comparison with a plot of log t_R against number of chlorine substituents in the molecule^{31,35}.
 *** Tentative structure; identification based on mass spectral interpretation.

of these chlorination products identified or determined from their GLC retention times (Figs. 2 and 4) and MS fragment patterns is presented in Table II. Table II shows that the extracts consist of four different types: chlorinated phenylphenols (A), chlorinated phenylquinones (B), phenylcarboxylic acids (C) and condensation products (D) of compounds A. Although GLC analyses of chlorinated phenols and benzoquinones in water have been widely investigated by a number of earlier workers^{22-34,36}, the present results appear to be the first detailed GLC and MS data for these reaction products of phenylphenols with hypochlorite in water.

Several compounds corresponding to the ethers and dioxins of polychlorinated phenylphenols were observed on the mass spectra of the ether extracts of the reaction mixtures of phenylphenols with hypochlorite in water (Fig. 5). However, earlier workers^{37,38} have demonstrated the presence of the corresponding chlorinated dibenzo-*p*-dioxins in the mass spectra of polychlorinated phenols and concluded that these dioxins are formed by pyrolysis of the chlorinated compounds. In the present work, the corresponding ethers and dioxins could not be detected in the mass spectra of the ether extracts containing mainly chlorinated phenylphenols. Therefore, it is concluded that the formation of several chlorinated ethers and dioxins occurs during the reactions of phenylphenols with hypochlorite in dilute aqueous solution. Similar ethers and dioxins that are formed by the reactions of other substituted phenols with hypochlorite in water were detected in the mass spectra of the ether extracts³⁹.

Gas chromatographic determination of residual amounts of chlorination products in water

GLC determinations of the diethyl ether extracts indicated that a marked reduction in the amount of original compounds in water occurs with an increase in the molar ratio of hypochlorous acid to compound. The chlorinated phenylphenols were identified to be present at higher concentrations in water at low molar ratios of

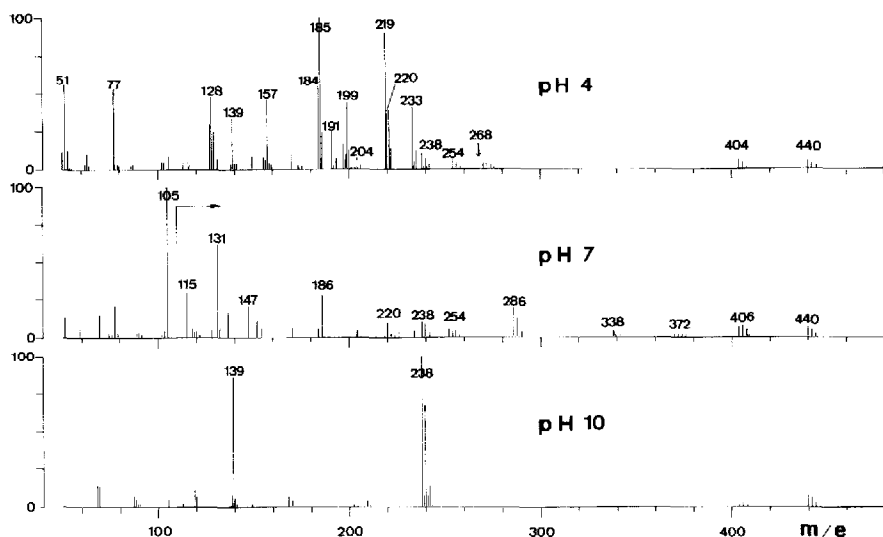


Fig. 5. Electron impact mass spectra of diethyl ether extracts of 4-phenylphenol solutions after treatment with an excess of hypochlorite at varying pH at 20°C. Mass spectrometric conditions: see Experimental.

hypochlorous acid to compound. At moderate molar ratios (3–5), these chlorophenylphenols and chlorinated phenylquinones (*m/e* 184, 220 and 254 in Figs. 3 and 5) were detected as the reaction intermediates of phenylphenols with hypochlorite in water. Treatment with molar ratios over 10 of hypochlorite to compound gave a small amount of these chlorinated intermediates, but phenylcarboxylic acids and condensation products of chlorinated phenylphenols were now detected in the extracts. These results indicate that the reactions involve chlorination to mono-, di- and trichlorinated phenylphenols (A), oxidation to chlorinated phenylquinones (B) and oxidative degradation of compounds B to phenylcarboxylic acids and dimerization of compounds A.

Fig. 4 shows the chromatograms of diethyl ether extracts from the phenylphenol solutions after treatment with an excess of hypochlorite at varying pH for 1 h. Several chlorinated phenylphenols were detected at high concentrations in acidic solutions, although a small amount of chlorinated products were obtained under neutral conditions (Table III). In this experiment, it was found that chlorinated phenylphenols formed from *m*- and *p*-isomers remained in high concentrations even in the presence of an excess of hypochlorite in the alkaline solutions. These results are also in agreement with the values of the chlorine demands of each phenylphenol obtained at various pHs (Table III).

Hypochlorous acid plays a multiple role in the degradation of a variety of organic compounds, especially when it is in equilibrium with hypochlorite at a pH near its pK_a (7.5). In the reactions of phenylphenols with chlorine in dilute aqueous solution, most of the active sites on the phenol ring rapidly undergo chlorine substi-

TABLE II

CHLORINE DEMANDS AND RESIDUAL CHLORINATION PRODUCTS OF PHENYLPHENOLS IN WATER AFTER REACTION WITH AN EXCESS OF HYPOCHLORITE FOR 1 h AT 20°C, AS A FUNCTION OF pH

Yields derived from FID–GLC peak areas, relative to the area of starting materials.

Compound	pH	Cl consumption (mol HOCl/ mol compound)	Residual product (%)			
			Original compound	Cl-substituted compounds	Chloroquinones	Others
2-Phenylphenol (6.1 mg/l)	4	8.32	0.27	ND	20.57	3.25
	6	12.40	0.32	0.65	17.52	4.69
	7	13.83	2.58	0.60	ND*	1.98
	8	12.40	1.66	0.26	ND	0.92
	10	10.80	0.94	0.42	ND	1.03
3-Phenylphenol (6.1 mg/l)	4	12.65	1.18	4.10	5.40	1.94
	7	17.51	0.48	ND	ND	2.40
	10	9.47	0.05	41.75	ND	1.71
4-Phenylphenol (6.1 mg/l)	4	8.03	9.89	28.10	28.10	0.37
	6	10.38	8.01	21.62	13.50	0.37
	7	13.26	2.33	8.13	1.00	0.59
	8	13.08	0.44	3.93	ND	0.79
	10	7.44	1.17	70.13	ND	0.26

* ND = Not detected by FID–GLC.

tution to form their chlorinated derivatives in an initial step of the reactions. This reaction is then followed by oxidation of these chlorinated derivatives to form the corresponding phenylquinones, which are not stable in chlorinated water at pH 7.0, but are stable under acidic conditions. These chlorine consumptions with phenylphenols and the residual amounts of their chlorination products in water were found to be dependent on the solution pH (Table III).

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