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CHEMICAL CHANGES OF ORGANIC COMPOUNDS IN CHLORINATED WATER

IX*. FORMATION OF POLYCHLORINATED PHENOXYPHENOLS DURING THE REACTION OF PHENOL WITH HYPOCHLORITE IN DILUTE AQUEOUS SOLUTION

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SUMMARY

Aqueous phenol solutions were treated with hypochlorite at 20°C under various experimental conditions. Changes in the composition of the chlorination products in water were determined by using gas chromatographic (GC) and GC–mass spectrometric analyses of diethyl ether extracts. Chlorination of phenol in dilute aqueous solution produced a series of highly chlorinated compounds, including chlorophenols, chlorobenzoquinones and chlorinated carboxylic acids. Tentative identifications were also made for other compounds with the following proposed molecular formulae: $C_{12}H_8Cl_2O_2$, $C_{12}H_7Cl_3O_2$, $C_{12}H_6Cl_4O_2$ and $C_{12}H_5Cl_5O_2$. On the basis of thin-layer chromatographic and GC behaviour, these compounds are considered to be chlorinated phenoxyphenols. Production of some of these compounds is dependent on the equivalents of chlorine per mole 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.

INTRODUCTION

Polychlorinated aromatic compounds are environmental contaminants which may cause risks to human health. An important group for investigation are the chlorinated dimers and trimers formed during the industrial production of chlorophenolic compounds and the combusion of chlorine-containing materials. Chlorinated phenoxyphenols are chlorophenol dimers, forming the main impurities in commercial chlorophenol formulations[2,3] which are widely used as bactericides, fungicides, herbicides and wood preservations. Recent attention has especially been focused on chlorinated 2-phenoxyphenols (predioxins), which are precursors of the highly toxic

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* For Part VIII, see ref. 1.

chlorinated dibenzo-*p*-dioxins[4]. According to Deinzer *et al.*[5], certain polychlorinated 2-phenoxyphenols may be as toxic as the most toxic polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans.

The discussion of the origin of polychlorinated phenoxyphenols has been focused on two potential sources, namely the amount of the phenoxyphenols present as impurities in commercial products and the formation of chlorophenoxyphenols from chlorophenols by thermal decomposition or irradiation. Recently we have, however, observed that treatment with hypochlorite of phenolic compounds in water produces compounds corresponding to the chlorinated dimers[6,7]. The data presented here show the possible formation of polychlorinated phenoxyphenols during the chlorination of water contaminated with phenol, under the conditions utilized for water treatment.

EXPERIMENTAL

Materials
     Phenol was obtained from Tokyo Chemicals (Tokyo, Japan). Several chlorinated phenols and benzoquinones, which may be expected to be formed during the reaction of phenol 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 subsequently dilution. 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 Na$_2$HPO$_4$–KH$_2$PO$_4$ buffer solution. The hypochlorite concentrations were determined by iodimetric titration.

Treatment with hypochlorite of aqueous phenol solution and extraction of reaction mixture
     Aqueous phenol solutions (50 μmol/l) were treated with hypochlorite at 20°C for 1 h with stirring at varying pH values and with various equivalents of chlorine per mole of compound. After the desired reaction time, the unreacted chlorine was removed by addition of sodium thiosulphate solution to the solutions. 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) and GC–mass spectrometric (GC–MS) analyses.

Product resolution and characterization
     A Shimazu GC-6A gas chromatograph equipped with a flame-ionization detector and 2 m × 0.3 mm I.D. glass column packed with 10% Apiezon L on Chromosorb 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 Shimazu Model Chromatopac-1A data system was used to determine the retention times and areas of peaks on the chromatograms.
     A Hitachi M-80 combined mass spectrometer–gas chromatograph equipped with a Hitachi M-003 data processing system was used under the following conditions

for the qualitative analyses of samples. The ion source was operated at 250°C with a trap current of $70\mu A$ and an electron energy of 70 eV. A glass column (2 m × 0.3 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. products were identified by comparison of their retention times and mass spectra with those of authentic compounds.

RESULTS AND DISCUSSION

In the reactions of phenolic compounds with hypochlorite in aqueous solutions, it has been established[8-15] that chlorophenols and chloroquinones–quinols are the principal intermediate products and oxidation-ruptured compounds of the aromatic ring are the end products in chlorinated water. Our current studies concerning the phenol–hypochlorite reaction[16] have demonstrated that trichloroacetic and chloromaleic acids are constituents of the end products, yielding only 25 mol-% of each acid per mole of compound after reaction for 24 h at 20°C. Consequently, this result
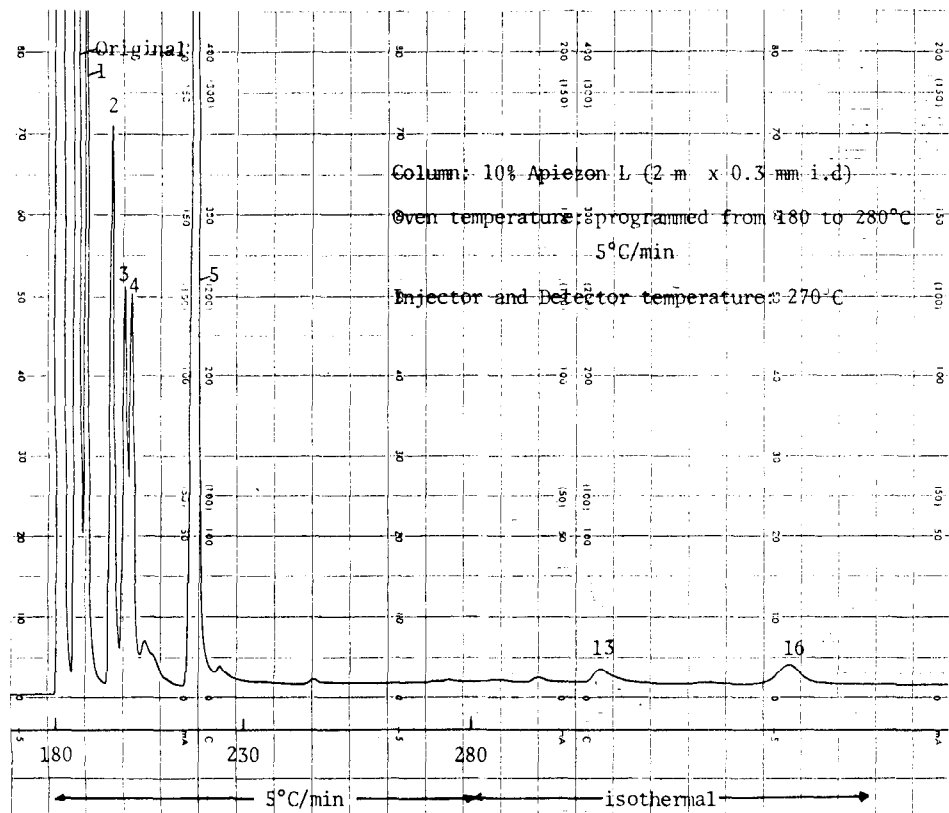

Fig. 1. Typical gas chromatogram (with flame-ionization detection) of diethyl ether extract of phenol solution (50 μmol/l) after treatment with hypochlorite at 5 equiv. of chlorine per mole of compound and 20°C for 1 h. Compounds as in Table I. For GC conditions, see Experimental.

suggests the presence of more stable phenolic compounds in chlorinated water, other than these carboxylic acids. In the present work, further studies were carried out to determine the chlorination products, especially the higher chlorinated and oxidized substances or chlorophenol dimers, of phenol with hypochlorite in dilute aqueous solution.

Production of chlorophenol dimers

Typical GC (with flame-ionization detection) and GC–MS (total ion) traces of diethyl ether extract of phenol solution after treatment with hypochlorite at 5 equiv. of chlorine per mole of compound are shown in Figs. 1 and 2. Some of the peaks were identified on the basis of the retention times of known substances.

Compounds corresponding to other peaks were determined from the mass spectrum of each peak (Figs. 3–5). In addition, to investigate the detailed mass fragment patterns for these chlorination products, the extract was further separated on Polyamid 11 F 254 [pre-coated thin-layer chromatography (TLC) plates; E. Merck, Darmstadt, F.R.G.] using chloroform as the developing solvent, and the separated components were then analysed by mass spectrometry.

The mass spectra of the chlorinated compounds show some peaks with typical chlorine clusters arising from the presence of ^{35}Cl and ^{37}Cl isotopes in the natural ratio of 3:1. Thus, for ions containing n chlorine atoms, a cluster of $n + 1$ peaks
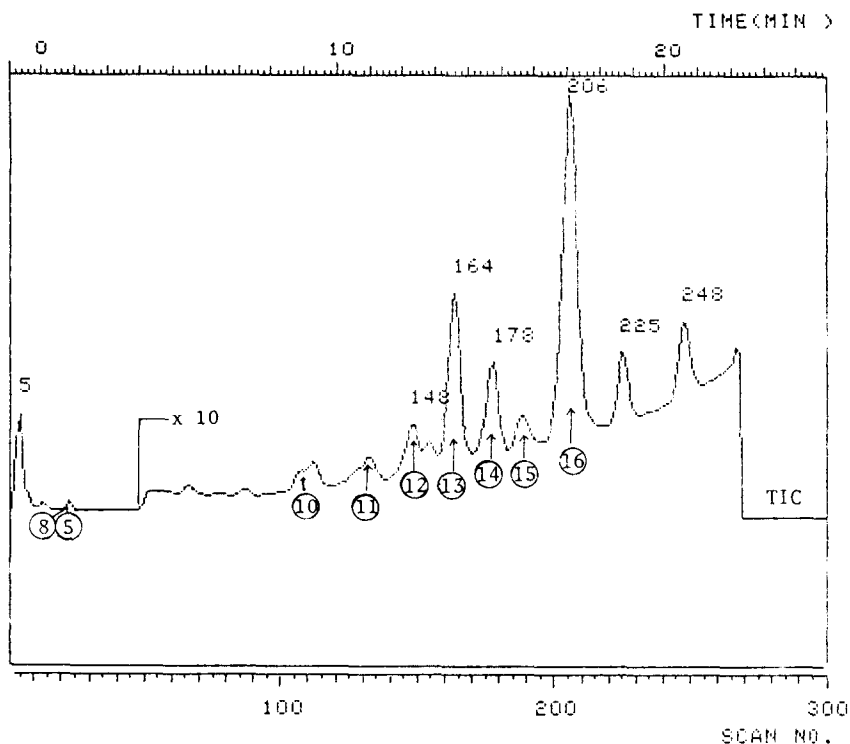

Fig. 2. Mass chromatogram (total ion current) of diethyl ether extract of phenol solution (50 μmol/l) after treatment with hypochlorite at 5 equiv. of chlorine per mole of compound and 20°C for 1 h. Compounds as in Table I. For GC–MS conditions, see Experimental.
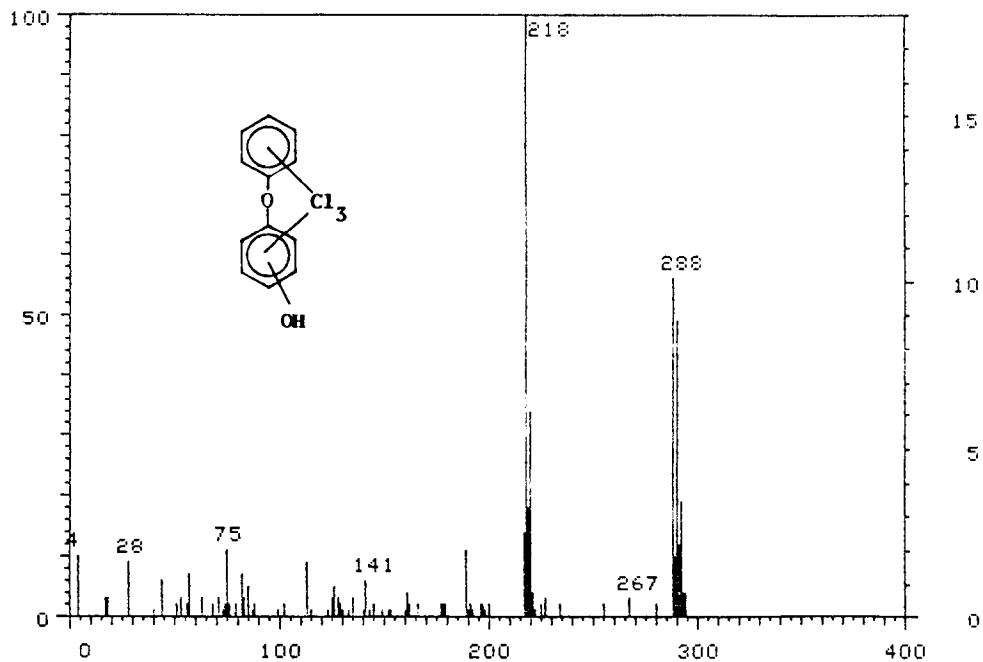
Fig. 3. Mass spectrum of trichlorinated phenol dimer obtained from peak 11 (*cf.*, Fig. 2).
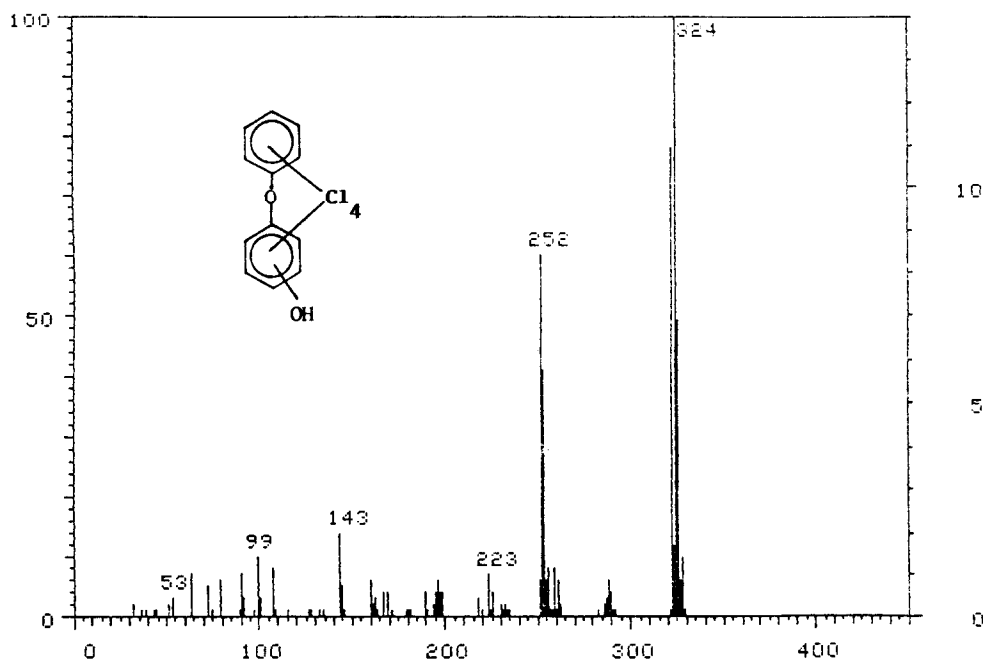

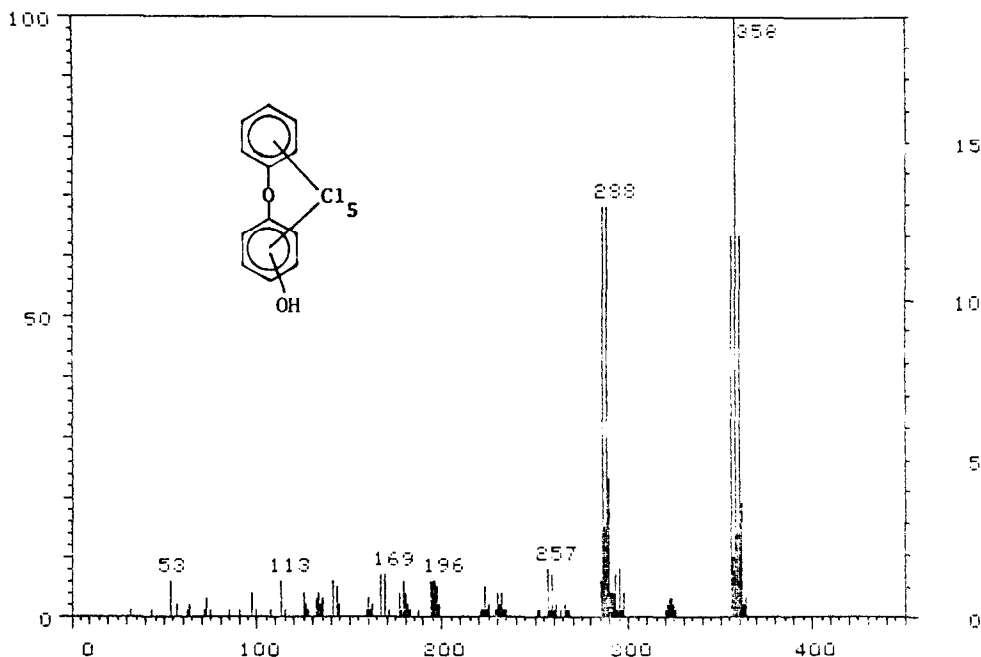Fig. 4. Mass spectrum of tetrachlorinated phenol dimer obtained from peak 13 (*cf.*, Fig. 2).

Fig. 5. Mass spectrum of pentachlorinated phenol dimer obtained from peak 16 (*cf.*, Fig. 2).

should be obtained with an m/e difference of 2, the ratio of the relative intensities corresponding to the coefficient of the polynomial $(3x + 1)$ for $x = 1$.

For example, Fig. 3 illustrates the mass spectrum of a trichlorinated compound occurring in the diethyl extract from chlorine-treated phenol solution with a scan number of 148, which is due to peak 12 (Fig. 2). The molecular ion (M^+) is at m/e 288 and the most abundant fragment is at m/e 218, which arises by the loss of two chlorine atoms from the molecular ion, indicating the occurrence of a phenol dimer with three chlorine atoms in the extract. Peak 11 (Fig. 2) gave a similar fragmentation pattern, with three chlorine atoms, to that of peak 12, which also suggests the oc-currence of an isomer of a phenol dimer with three chlorine atoms in the extract.

The mass spectrum of peak 13 was interpreted as being that of a phenol dimer with four chlorine atoms (Fig. 4). The same molecular ion and fragmentation pat-terns, with four chlorine atoms, as those of peak 13 were also observed for peaks 14 and 15, respectively. This leads to the conclusion that three isomers of a phenol dimer with four chlorine atoms are present in the diethyl ether extract from chlorine-treated phenol solution. Fig. 5 shows that peak 16, with the molecular ion at m/e 356, which is the most abundant among the chlorinated phenol dimers (Fig. 2), is a phenol dimer with five chlorine atoms.
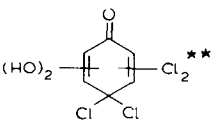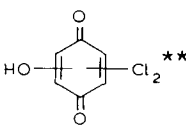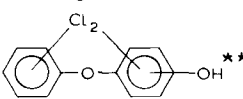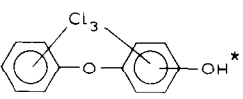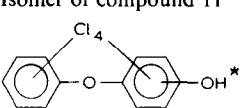
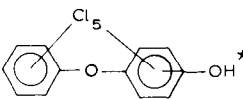Several compounds corresponding to the chlorinated phenol dimers were ob-served on the mass chromatograms of the diethyl ether extract of the reaction mixture of phenol with hypochlorite in water (Figs. 1 and 2). However, earlier workers[17,18] demonstrated the presence of the corresponding chlorinated 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 detected in the mass spectra of the chlorinated phenols. Therefore, it is concluded that the production of several chlorinated phenol dimers occurs during the reaction of phenol with hypochlorite in dilute aqueous solution.

A summary of these chlorination products identified or determined from their GC retention times and mass spectrometric interpretations is presented in Table I.

TABLE I

REACTION PRODUCTS OF PHENOL WITH HYPOCHLORITE IN DILUTE AQUEOUS SOLUTION AT 20°C

No.	Compound	Scan No.	m/e (order of ion intensity)
1	2-Chlorophenol*	—	128 (M^+)
2	4-Chlorophenol*	—	128 (M^+)
3	2,4-Dichlorophenol*	—	162 (M^+)
4	2,6-Dichlorophenol*	—	162 (M^+)
5	2,4,6-Trichlorophenol*	25	196 (M^+)
6	Chloro-p-benzoquinone*	—	142 (M^+)
7	2,6-Dichloro-p-benzoquinone*	—	176 (M^+)
8		22	143 (M^+ − CHO − Cl − 2CO), 199 (M^+ − CHO − Cl), 170 (M^+ − 2CHO − Cl), 262 (M^+)
9		40	163 (M^+ − CHO), 192 (M^+)
10		107	254 (M^+), 184 (M^+ − 2Cl)
11		135	288 (M^+), 218 (M^+ − 2Cl)
12	Isomer of compound 11**	148	218 (M^+ − 2Cl), 288 (M^+)
13		164	322 (M^+), 252 (M^+ − 2Cl)
14	Isomer of compound 13**	178	252 (M^+ − 2Cl), 322 (M^+)
15	Isomer of compound 13**	189	252 (M^+ − 2Cl), 322 (M^+)
16		206	356 (M^+), 286 (M^+ − 2Cl)

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

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

On the basis of TLC, GC and GC–MS (Figs. 1 and 2), and mass spectrometric characterization (Figs. 3–5), these phenol dimers containing different numbers of chlorine atoms are considered to be chlorinated phenoxyphenols, but their exact structures are not clear. Although chlorophenols, chlorobenzoquinones and chlorinated cyclohexadienones and cyclohexenones[8–15] have been identified to be present in the reaction mixture of phenol with hypochlorite in aqueous solution, this seems to be the first recorded production of chlorinated phenol dimers.

GC determination of residual amounts of chlorinated phenol dimers in water

GC analysis of the diethyl ether extracts indicated that a marked reduction in the amount of original phenol in water occurs with an increase in the molar ratio of hypochlorous acid to the compound (Fig. 6). The chlorophenols were identified to be present at higher concentrations in water at low molar ratios of hypochlorous acid to the compound. At moderate molar ratios (5–10), both further oxychlorinated products of chlorophenols (*m/e* 142, 176, 192 and 262, in Table I) and polychlorinated phenol dimers (*m/e* 254, 288, 322 and 356, in Table I) were now detected as the reaction intermediates of phenol with hypochlorite in water. Treatment at molar ratios of hypochlorous acid to the compound over 20 gave a small amount of these chlorinated intermediates (Fig. 6).

Table II shows the results of GC determinations of the diethyl ether extracts from the phenol solutions after treatment with an excess of hypochlorite at varying pH for 1 h. Several chlorophenols, further oxychlorinated products of chlorophenols
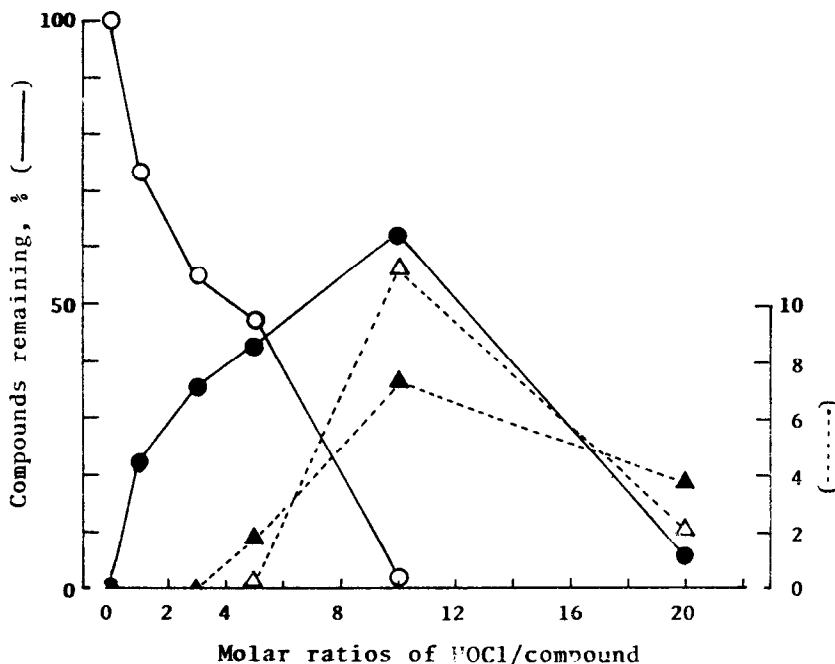

Fig. 6. Residual amounts of reaction products in aqueous phenol solutions (50 μmol/l) after treatment with hypochlorite at various equivalents of chlorine per mole of compound and 20°C for 1 h. Yields derived from GC peak areas, relative to the peak area of starting material. ○, Phenol; ●, chlorophenols; △, polychloropolyhydroxyphenols; ▲, chlorophenol dimers.

TABLE II

CHLORINE CONSUMPTION AND CHLORINATION PRODUCTS OF PHENOL IN WATER AFTER TREATMENT WITH AN EXCESS OF HYPOCHLORITE AT 20°C FOR 1 h, AS A FUNCTION OF pH

A, Phenol; B, chlorophenols; C, polychloropolyhydroxyphenols; D, chlorophenol dimers; and E, unknown compounds.

Reation pH	Cl consumption (moles of HOCl/ moles of compound)	Product yield (%)*				
		A	B	C	D	E
4	8.50	ND**	5.50	16.50	10.50	0.50
6	12.50	ND	3.80	3.50	5.50	2.00
7	13.50	ND	5.00	2.00	3.50	2.80
8	12.50	ND	1.50	trace	0.50	2.30
10	10.50	ND	trace	0.10	0.05	0.80

    * Yields derived from GC peak areas, relative to the area of starting material.
    ** Not detected by GC analysis.

and the chlorinated phenol 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 phenol obtained at various pH values (Table II).

From the results presented above and those obtained in earlier investigations[8-16], it may be conducted that the chlorination with hypochlorite of phenol in dilute aqueous solution takes place by the following competing reactions:
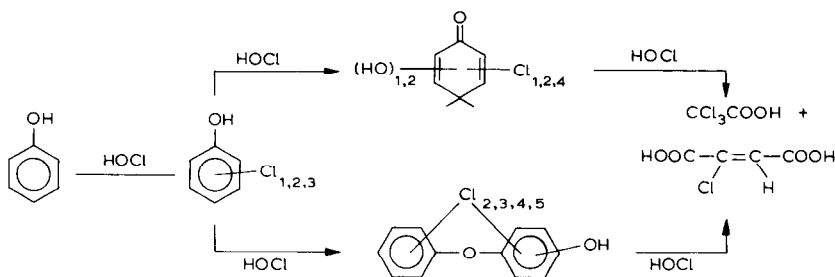
Aqueous chlorine is used to disinfect sewage water and raw water that are destined for human consumption. Phenol has been shown to produce many chlorinated aromatic compounds after reaction with hypochlorite in water (Table I). The production of these compounds is greatly dependent on the molar ratios of hypochlorous acid to the compound and the reaction pH, with higher concentrations at moderate chlorine doses (Fig. 6) and acidic conditions (Table II). Acidic chlorinated waters are generally adjusted to neutral conditions or diluted in the receiving water at the water treatment station. Therefore, most of the chlorinated aromatic compounds are destroyed by this process and the public health hazard may be substantially decreased. However, the chlorinated phenol dimers are particularly interesting, as they are present in the chlorine-treated phenol solution and they are also precursors of the highly toxic chlorinated dioxins.

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