

CHROM. 13,082

GAS CHROMATOGRAPHIC IDENTIFICATION AND DETERMINATION OF CHLORINATED QUINONES FORMED DURING CHLORINATION OF DIHYDRIC PHENOLS WITH HYPOCHLORITE IN DILUTE AQUEOUS SOLUTION

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(First received May 12th, 1980; revised manuscript received July 1st, 1980)

SUMMARY

This paper describes gas chromatographic identification of chlorinated quinones present in water on the basis of plots of $\log t_R$ against number of chlorine atoms in the molecule. The plots for each homologous series of chlorinated phenols, hydroquinones (HQ) and *p*-benzoquinones chromatographed on polar and non-polar columns are found to be linear, with few exceptions. Mono-, di- and trichlorinated quinones are the principal intermediate products during chlorinations of catechol, resorcinol, HQ and methyl-HQ with aqueous hypochlorite. The residual intermediate compounds formed from resorcinol and methyl-HQ are present in higher concentrations in chlorinated water than those of other dihydric phenols.

INTRODUCTION

Chlorination is extensively practised in waste-water treatment to disinfect the effluent prior to discharge, particularly where the water may subsequently be used for recreational purposes or as a source of potable water. Recently, the chlorination of municipal waste-water has been demonstrated to increase its toxicity to aquatic life¹. In view of the known high toxicity of many chlorinated organic compounds, it is desirable to determine the products formed by chlorination of waste-water and drinking water. It has now become evident that a variety of organochlorine compounds are formed, haloforms, chlorinated phenols and phenolic acids, chlorinated quinones and heterocyclic compounds being only a few of the many structural types which have been identified²⁻¹¹. Much attention is also now being paid to the behaviour of volatile halocarbons in water ultimately used for human consumption; however, many of the less volatile compounds have not been fully characterized.

Although a number of studies have been made of the chromatographic separation of substituted quinones¹²⁻¹⁶, there are few reports of the gas-liquid chromatography (GLC) of chlorinated derivatives of quinones¹⁶. Three papers describe the separation and identification of some chlorinated quinones by paper¹² and thin-layer

chromatography^{13,14,16}. The identification of the separated compounds is a complex problem, and requires the use of many known standards or the combination of gas chromatography and mass spectrometry (GC-MS). Some attempts to identify the components being chromatographed on the basis of their relative retention times t_R have been made, and it has been found that plots of $\log t_R$ for many alkylphenols, paraffins and organometallic compounds against the number of carbon atoms in the molecule give straight lines¹⁷⁻²³. The corresponding relationships for organochlorine compounds have not yet been established.

The aim of our investigation is to identify the chlorinated quinones in water on the basis of a plot of $\log t_R$ against the number of chlorine atoms in the molecule, and also to determine the residual concentrations of these compounds formed during chlorination of catechol, resorcinol, hydroquinone (HQ) and methyl-HQ with aqueous hypochlorite, under those conditions utilized for water renovation.

EXPERIMENTAL

Materials

Chlorinated derivatives of phenol, HQ and *p*-benzoquinone (BQ), used for the study of their chromatographic behaviour on polar and non-polar stationary phases, and dihydric phenols, used for the model study of chlorination of the water contaminated with these compounds, were obtained from Tokyo Chemical (Tokyo, Japan), Wako (Osaka, Japan), Aldrich (Milwaukee, WI, U.S.A.) and Eastman-Kodak (Rochester, NY, U.S.A.). All compounds were checked by GLC and MS, and distilled before use, if necessary. Standard solutions of these compounds both alone and as mixtures were prepared by dissolving the compounds in methanol, with subsequently serial dilutions.

GLC

A Model 20-KE gas chromatograph (Japan Electron Optic Laboratory) equipped with electron-capture detector (ECD, 10 mCi ⁶³Ni) and a Shimadzu GC-6A gas chromatograph equipped with flame ionization detector (FID) were used with nitrogen as the carrier gas. The columns were coiled glass tubes (2 m × 3 mm I.D.) packed with Chromosorb W AW DMCS (60-80 mesh) coated with 10% Apiezon L as non-polar stationary phase and an other coated with 5% DEGS (diethylene glycol succinate polyester) + 1% H₃PO₄ as polar stationary phase. These columns were conditioned according to the usual method before use. Other conditions were: oven temperature, see Table I; injector and detector temperatures, 240°C; carrier gas (nitrogen) flow-rate, 50 ml/min.

Chlorination of aqueous dihydric phenols

Test solutions containing 3.5, 7.0, 10.5, 17.5 and 35 ppm active chlorine were prepared by diluting sodium hypochlorite solution (*ca.* 10% available chlorine; Nakarai Chemicals, Kyoto, Japan) with distilled water and acidifying with sulphuric acid to the required pH. The hypochlorite concentrations were determined by the use of Active-Cl Test (Wako) and iodometric titration. A 100-ml volume of each test solution and a 1 ml of a solution of a dihydric phenol (10 μmol) dissolved in methanol were mixed in a 200-ml separation-funnel and shaken at room temperature. The

reaction was then terminated by addition of a volume of sodium disulphite equal to that of the chlorinating reagent, and the products were extracted from the acidified reaction mixture with 20 ml of diethyl ether. The products were chromatographed on both the polar and non-polar columns.

Recovery data were obtained by spiking water with the chlorinated dihydric phenols and benzoquinones and carrying them through the entire analytical procedure except for the chlorination. The recoveries were over 85%.

RESULTS AND DISCUSSION

Chromatographic behaviour

In order to reveal the detailed gas chromatographic behaviour of chlorinated aromatic compounds, both polar and non-polar stationary phases were tested for the direct chromatography of the chlorinated derivatives of phenol, HQ and *p*-BQ. Relative retention times t_R and FID and ECD response data for these compounds on both columns are summarized in Table I and presented graphically in Fig. 1 as a plot of $\log t_R$ against number of chlorine atoms in the molecule. Although the paper and thin-layer chromatography of some chlorinated HQ and *p*-BQ have been reported by Taimr and Pospíšil¹² and Švec and co-workers^{13,14,16}, the present results appear to be the first detailed GC data for these compounds.

TABLE I

GAS CHROMATOGRAPHIC BEHAVIOUR OF SOME CHLORINATED DERIVATIVES OF PHENOL, HYDROQUINONE AND *p*-BENZOQUINONE ON POLAR AND NON-POLAR STATIONARY PHASES

Sensitivities expressed by peak area (cm² per μ g of sample injected) for FID and cm²/ng for ECD. ND = Not detected in spite 5 μ g sample injected.

Compound	5% DEGS + 1% H ₃ PO ₄ (160°C)		10% Apiezon L (200°C)	
	t_R (min)	Sens. (FID/ECD)	t_R (min)	Sens. (FID/ECD)
1 Phenol	1.00	3.76/ ND	1.00	3.40/ND
2 2-Chlorophenol	0.60	2.43/ 0.005	1.40	2.56/0.005
3 4-Chlorophenol	4.00	2.15/ 0.005	2.90	2.30/0.005
4 2,4-Dichlorophenol	1.70	2.00/ 2.40	3.35	1.90/0.50
5 2,6-Dichlorophenol	1.60	1.95/ 2.50	3.55	1.90/0.65
6 2,4,6-Trichlorophenol	3.00	1.50/45.00	7.80	1.30/8.60
7 2,3,4,6-Tetrachlorophenol	6.50	0.65/40.00	19.00	1.15/8.60
8 2,3,4,5,6-Pentachlorophenol	15.00	0.30/48.50	43.00	0.30/2.00
9 Hydroquinone	36.00	1.30/ ND	3.30	1.50/ND
10 Chlorohydroquinone	28.00	1.00/ 0.01	5.40	1.00/0.01
11 2,5-Dichlorohydroquinone	15.00	1.20/ 1.70	6.80	0.85/1.50
12 2,3,5-Trichlorohydroquinone	40.00	0.85/ 2.50	22.50	0.50/2.00
13 2,3,5,6-Tetrachlorohydroquinone	68.00	0.20/ 2.00	47.00	0.30/2.50
14 <i>p</i> -Benzoquinone	0.50	1.80/ ND	3.30	1.65/ND
15 Chloro- <i>p</i> -benzoquinone	0.85	1.55/ 0.005	5.40	1.35/0.01
16 2,5-Dichloro- <i>p</i> -benzoquinone	1.70	1.30/ 2.40	6.80	1.00/3.00
17 2,6-Dichloro- <i>p</i> -benzoquinone	1.60	1.30/ 2.50	18.00	0.85/2.30
18 2,3,5-Trichloro- <i>p</i> -benzoquinone	4.00	0.80/ 2.00	22.00	0.50/3.50
19 2,3,5,6-Tetrachloro- <i>p</i> -benzoquinone	8.60	0.30/ 4.00	50.00	0.10/5.50

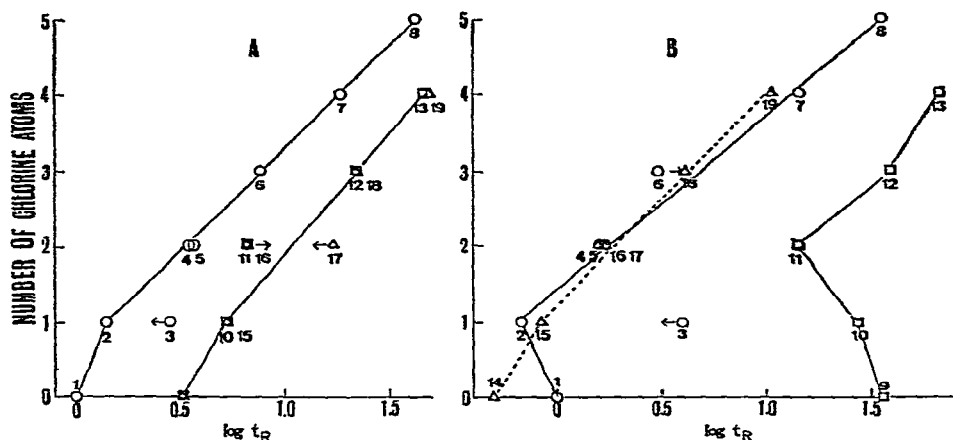


Fig. 1. Plot of $\log t_R$ against number of chlorine atoms. A, Non-polar column packed with 10% Apiezon L and Chromosorb W AW DMCS (60–80 mesh); B, polar column packed with 5% DEGS + 1% H_3PO_4 and Chromosorb W AW DMCS (60–80 mesh). \circ , Chlorophenols; \triangle , chloro-hydroquinones; \square , chloro-*p*-benzoquinones. Compound numbers, as in Table I.

Since it is known that plots of $\log t_R$ for many organic compounds on non-polar columns against their boiling points give approximately straight lines²⁴, the t_R values of compounds with lower numbers of chlorine substituents and having low boiling points are expected to be smaller than those of compounds with higher numbers and high boiling points, when these compounds are chromatographed on a non-polar column. Fig. 1 shows that the chlorinated derivatives of phenol, HQ and *p*-BQ chromatographed on the 10% Apiezon L column are usually eluted in the order of increasing number of chlorines on the aromatic ring. The plots of $\log t_R$ against number of chlorine atoms in the aromatic ring are found to be linear for each homologous series, with few exceptions. Unfortunately, a poor separation of the chlorinated HQ from the corresponding *p*-BQ is observed using the non-polar column, because these compounds have similar boiling points.

When the chlorinated derivatives of phenol, HQ and *p*-BQ were chromatographed on 5% DEGS + 1% H_3PO_4 (the polar column), some non-polar compounds among these derivatives are eluted prior to some polar compounds, although the same order of elution as obtained on 10% Apiezon L is observed for the chlorinated phenols and *p*-BQ. A poor separation of the chlorinated derivatives of phenol from the corresponding *p*-BQ is observed using the polar column (Fig. 1B) because these compounds have similar polarities. Fig. 1B also shows that the smallest t_R values are found for 2-chlorophenol (point 2), 2,5-dichloro-HQ (point 11) and *p*-BQ (point 14) in among each homologous series. Large t_R values occurred for 4-chlorophenol (point 3) and HQ with free chlorine (point 9) chromatographed on the polar column in comparison with those of corresponding compounds having higher numbers of chlorine substituents. These results could be explained by steric shielding of hydroxy groups in phenol and HQ by chlorine atoms substituted in the aromatic ring, which prevents hydrogen-bond formation between the polar stationary phase and the chlorinated compounds.

Response data given in Table I show that the sensitivities of the FID for the chlorinated derivatives of phenol, HQ and *p*-BQ became smaller with increase in the number of chlorine atoms in the aromatic ring, but those of the ECD became larger. Similar relative ECD responses have been reported previously²⁵⁻²⁷ for other aromatic halogeno and nitro compounds. These results could be explained in terms of a reduction of the flame ionization current with organochlorine compounds, or as an increase in electron-capture reactions with these compounds²⁸.

The apparent differences in the FID and ECD sensitivities for the chlorinated derivatives of phenol, HQ and *p*-BQ chromatographed on both polar and non-polar columns shown in Table I also arise as a result of peak broadening or narrowing associated with increases or decreases of t_R .

The results obtained suggest that both the plots of $\log t_R$ against number of chlorine atoms and the differences in ECD responses can be used to investigate the chemical structure of chlorinated aromatic compounds formed during chlorinations of mono- and dihydric phenols with aqueous hypochlorite.

Identification of residual chlorinated quinones formed during chlorinations of some dihydric phenols with hypochlorous acid

In the reactions of many phenolic compounds with hypochlorite in aqueous solutions it has been established^{2-4,8,9,11,29-31} that chlorinated phenols and quinones/quinols are the principal intermediate products and oxidation-ruptured compounds of the aromatic ring are the end products in chlorinated water. Further studies of these reactions by Eliasek and Jungwirt² and Onodera *et al.*¹¹ have confirmed that the chlorination processes of phenol at the ppm level in water are as follows. In the first step, phenol is readily chlorinated in the presence of excess of hypochlorite by a substitution mechanism to give 2,4,6-trichlorophenol. Then the chlorine atom in the *para*-position of chlorinated phenol is hydrolyzed and subsequently oxidized with hypochlorite giving 2,6-dichloro-*p*-BQ, which is not stable in chlorinated water at pH 7-8, but somewhat more stable in acidic solution. Therefore, an examination of the fates of various quinones in chlorinated water could provide valuable information on the chlorination of drinking water and waste-water polluted with phenols.

In a preliminary examination of the reactions of several dihydric phenols 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 Resi-chlocorder (Bionics Instrument) at 20°C and an initial pH of 7.0. It was observed that a large consumption of active chlorine and a decrease in the initial pH occurred during the first 15 min, followed by much slower secondary reactions. These results may indicate that the formation of chlorinated quinones and oxidation-ruptured compounds of the aromatic ring occur during the reactions of several dihydric phenols with hypochlorite, under those conditions utilized for water renovation. In these experiments, the greatest chlorine demand was observed for the resorcinol solution after reaction for 1 and 24 h, while the smallest value was obtained for the methyl-HQ solution. The chlorine demand for individual dihydric phenols and the changes of pH in these solutions after reaction for 1 and 24 h are summarized in Table II.

In order to identify the residual chlorinated products formed during chlorinations of individual dihydric phenols with aqueous hypochlorite, the ether extracts

TABLE II

CHLORINE DEMANDS OF SOME DIHYDRIC PHENOLS IN A $5 \cdot 10^{-5}$ MOLAR SOLUTION AND CHANGES OF pH IN THE SOLUTION AFTER REACTIONS FOR 1 h AND 24 h WITH EXCESS OF HYPOCHLORITE

Initial pH 7.0; temperature 20°C.

Substituent No.	2	3	4	5	6	pH after		Cl demand (moles/mol) after	
						1 h	24 h	1 h	24 h
1	H	H	H	H	H	5.3	3.7	5.5	8.3
2	OH	H	H	H	H	5.1	4.8	4.6	8.4
3	OH	H	Cl	H	H	4.8	4.3	4.6	7.4
4	H	OH	H	H	H	5.5	5.0	7.7	8.8
5	H	OH	Cl	H	H	4.9	4.8	7.4	7.8
6	H	OH	Cl	H	Cl	4.6	4.4	6.2	7.2
7	H	H	OH	H	H	5.9	4.8	3.6	5.7
8	Cl	H	OH	H	H	5.0	4.3	4.0	6.7
9	Cl	H	OH	Cl	H	4.5	4.0	4.6	7.6
10	Cl	Cl	OH	Cl	H	4.3	4.1	4.9	7.7
11	Cl	Cl	OH	Cl	Cl	4.3	4.0	5.4	7.7
12	CH ₃	H	OH	H	H	6.0	5.4	3.5	4.1

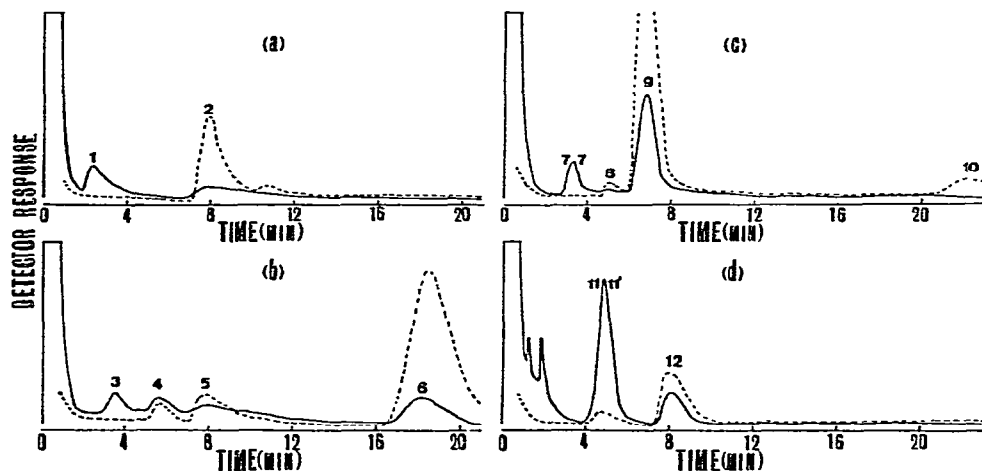


Fig. 2. Typical FID (—) and ECD (---) gas chromatograms of ether-extracted products of catechol (a), resorcinol (b), hydroquinone (c) and methyl-hydroquinone (d) solutions treated with hypochlorite. Column, 10% Apiezon L; oven temperature, 200°C. See text for identification of peaks.

from these reaction mixtures were chromatographed on the polar and non-polar columns. Typical gas chromatograms of some ether extracts are shown in Fig. 2, where some of the peaks appearing were identified according to the t_R of known compounds. Compounds corresponding to other peaks on the chromatograms were assigned on the basis of plots of $\log t_R$ against number of expected chlorine atoms and also identified purely on the mass spectra of the ether extracts.

During the reactions of dihydric phenols with hypochlorite in dilute aqueous solution it is expected that the formation of some chlorinated quinones by substitution

of hydrogen atoms on the aromatic ring with chlorine would occur readily in chlorinated water since their aromatic rings are activated by electron-donating substituents (OH groups). 4-Chlorocatechol (2) was the principal product of the catechol (1), whereas resorcinol (3) gave a mixture of 4-chloro- (4), 4,6-dichloro- (5), and trichlororesorcinol (6). *Ortho*- and *meta*-BQ were not detected in these ether extracts. A mixture of *p*-BQ (7'), chloro-*p*-BQ (8), 2,5-dichloro-*p*-BQ (9) and 2,3,5-trichloro-*p*-BQ (10) was produced when HQ was chlorinated. Methyl-HQ (11) gave a mixture of methyl-*p*-BQ (11') and chloromethyl-*p*-BQ (12). The end products, chloroform and oxidation-reptured compounds of the aromatic ring, were not tested in the present work.

Determination of residual concentrations of chlorinated quinones in water under various experimental conditions

In order to investigate in more detail the effect of the molar ratio of HOCl/compound and of pH on the reactions of dihydric phenols in low concentration with aqueous hypochlorite, the ether extracts obtained during chlorinations of catechol, resorcinol, HQ and methyl-HQ with hypochlorite under various experimental conditions were subsequently chromatographed and then analysed. The results obtained for the resorcinol and methyl-HQ solutions are summarized in Table III.

A marked reduction in the amount of each dihydric phenol occurred with

TABLE III

RESIDUAL AMOUNTS OF CHLORINATED DERIVATIVES OF RESORCINOL AND METHYL-HYDROQUINONE IN WATER AFTER REACTION FOR 1 h AT 20°C, AS FUNCTIONS OF pH AND MOLAR RATIO OF THE COMPOUND *versus* HYPOCHLORITE

Yields derived from GLC peak areas, relative to the area of starting material. ND = Not detected by ECD-GLC.

<i>Experimental conditions</i>				<i>Residual product (%)</i>			
<i>Compound (ppm)</i>	<i>Chlorine (ppm)</i>	<i>Initial pH</i>	<i>Final pH</i>	<i>Cl₀-deriv.</i>	<i>Cl₁-deriv.</i>	<i>Cl₂-deriv.</i>	<i>Cl₃-deriv.</i>
Resorcinol (100)	35	7.00	4.50	29.2	0.1	2.0	5.0
	70	7.00	4.35	17.5	0.1	5.0	3.5
	105	7.00	4.15	13.4	0.5	5.0	7.5
	175	7.00	4.75	11.0	1.0	7.5	10.5
	350	7.00	3.65	1.0	0.5	3.0	15.5
	350	4.00	3.00	0.5	0.3	2.0	14.3
	350	6.00	3.15	0	0.3	2.0	16.4
	350	8.00	10.50	0.1	1.0	0.1	22.3
	350	10.00	11.30	0	0.5	0.1	11.3
Methyl-HQ (100)	35	7.00	3.50	33.0	0.1	trace	trace
	70	7.00	5.35	26.5	0.1	trace	ND
	105	7.00	3.60	34.5	0.5	trace	ND
	175	7.00	3.50	25.0	1.5	trace	ND
	350	7.00	4.80	20.1	2.8	trace	ND
	350	4.00	3.20	42.1	1.5	trace	ND
	350	6.00	3.30	23.0	0.5	trace	ND
	350	8.00	7.40	0	ND	ND	ND
	350	10.00	8.90	0	ND	ND	ND

increase in the molar ratio HOCl/compound, with the exception of methyl-HQ solution. Table III shows that methyl-*p*-BQ formed from methyl-HQ remained in high concentration even in the presence of excess of hypochlorite. On the other hand, the concentrations of residual chlorinated derivatives of these dihydric phenols formed during the reactions reached maxima when the molar ratio was 3 or 5. In the presence of excess of hypochlorite, the concentrations of these residual products were relatively high in acidic solutions, but the ether-extracted products were not detected in basic solutions, with the exception of the products of resorcinol. When resorcinol was treated with excess of hypochlorite for 1 h, 2,4,6-trichlororesorcinol remained in high concentration in both acidic and basic solutions (Table III).

It is concluded from these results that the concentrations of residual chlorinated quinones in chlorinated water may be dependent on the molar ratio, pH and contact time, and also on the molecular structure of the original phenolic pollutants.

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