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CHEMICAL CHANGES OF ORGANIC COMPOUNDS IN CHLORINATED WATER

XVI. GAS CHROMATOGRAPHIC–MASS SPECTROMETRIC STUDIES OF REACTIONS OF TRICYCLIC AROMATIC HYDROCARBONS WITH HYPOCHLORITE IN DILUTE AQUEOUS SOLUTION

SUKEO ONODERA*, KIYOSHI IGARASHI, ATSUKO FUKUDA, JUNKO OUCHI and SHIZUO SUZUKI

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

SUMMARY

The products of aqueous chlorination reactions of tricyclic aromatic hydrocarbons (fluorene, carbazole, dibenzofuran, anthracene, phenanthrene and some methyl derivatives) with hypochlorite have been determined by gas chromatography–mass spectrometry. They included chloro-substituted, oxygenated (quinones) and hydroxylated (phenols) compounds, and products of addition which were readily formed at ambient temperature. The extent of the reactions was shown to depend on the chlorine dose, the solution pH, the initial concentrations of both compounds and the structures. Monochlorinated compounds and quinones were shown to be present in chlorinated water under the conditions utilized for water treatment.

INTRODUCTION

The disinfection of water and waste-water with chlorine is a well established procedure. However, the increasing presence and variety of aquatic pollutants raises the question of the chemical fate of these contaminants when subjected to aqueous chlorination[1].

Even the numerous studies of phenol, which established the intermediate formation of mono-, di- and trichlorophenols[2–9], leave the question of the end-products of this reaction unresolved[10].

Several polynuclear aromatic hydrocarbons (PAHs) in aqueous solution are degraded by addition of chlorine[11,12], chlorine dioxide[13,16] or sodium hypochlorite[17–22]. These reactions may occur at the site of chlorine addition and through the water distribution system[23]. PAHs have been suggested as the precursors of at least a portion of the mutagens produced in some chlorination processes[23]. The levels of these ubiquitous compounds may be increased by the presence of coal tar coating inside pipes and water storage tanks[24,25].

In order to provide further insight into the possible rôle of organic compounds in the formation of chlorine-substituted compounds and of chlorine-induced mutagens, this laboratory has continued the study of the aqueous chlorination chemistry of organic compounds[26]. The present report describes a detailed study of the product distributions of several tricyclic aromatic hydrocarbons (TCAHs) which were chosen because of their previous identification in unpurified water[27] and drinking water[28-30].

EXPERIMENTAL

Materials

The tricyclic aromatic hydrocarbons (TCAHs) were obtained from Wako Pure Chemical Industry (Osaka, Japan), Tokyo Chemical Industry (Tokyo, Japan) and Nakarai Chemical (Kyoto, Japan). Chloro-substituted, oxygenated (quinones) and hydroxylated (phenols) compounds of TCAHs, which are expected to be formed during chlorination of TCAHs with aqueous chlorine, were commercially available. The chemical names and gas chromatographic–mass spectrometric (GC–MS) data for these compounds are summarized in Table I.

Hypochlorite solution was prepared by diluting sodium hypochlorite solution (*ca.* 10% available Cl, Nakarai Chemical) in 0.1 *M* disodium hydrogenphosphate–potassium dihydrogenphosphate buffer solution, pH 7. The hypochlorite concentrations were determined by iodometric titration.

TABLE I

GAS CHROMATOGRAPHIC AND MASS SPECTROMETRIC DATA FOR TRICYCLIC AROMATIC HYDROCARBONS

Compound	Relative retention time[a]	Molecular ion, m/z	Compound	Relative retention time[a]	Molecular ion, m/z
Fluorene	0.741	166	Anthraquinone	1.203	208
Fluorenone	0.935	180	1,4-Anthraquinone	1.339	208
9-Chlorofluorene	0.944	200	1-Chloroanthraquinone	1.454	242
Carbazole	1.055	167	2-Chloroanthraquinone	1.383	242
Dibenzofuran	0.663	168	1,5-Dichloroanthraquinone	1.680	276
2-Chlorodibenzofuran	0.861	202	1,8-Dichloroanthraquinone	1.663	276
2,7-Dichlorodibenzofuran	1.100	236	1-Hydroxyanthracene	1.328	194
Dibenzo-*p*-dioxin	0.668	184	2-Methylanthracene	1.148	192
1-Chlorodibenzo-*p*-dioxin	0.908	218	2-Methylanthraquinone	1.358	222
2-Chlorodibenzo-*p*-dioxin	0.895	218	9-Methylanthracene	1.199	192
2,3-Dichlorodibenzo-*p*-dioxin	1.150	252	9-Chloromethylanthracene	1.402	226
2,7-Dichlorodibenzo-*p*-dioxin	1.135	252	9,10-Dimethylanthracene	1.387	206
Anthracene	1.000[b]	178	Phenanthrene	1.000	178
1-Chloroanthracene	1.241	212	Phenanthrenequinone	1.517	208
2-Chloroanthracene	1.228	212	1-Methylphenanthrene	1.171	192
9,10-Dichloroanthracene	1.449	246	2-Methylphenanthrene	1.146	192

[a] GC conditions: column, 2% OV-1/Uniport HP (60–80 mesh), glass (2 m × 2 mm); column temperature, programmed from 120 to 260°C at 5°C/min; nitrogen gas flow-rate; 50 ml/min.
[b] The retention time of anthracene under these conditions was 15.78 min.

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

A mixture of 100 ml of hypochlorite solution and each TCAH compound dissolved in 1 ml of methanol was stirred in a stoppered conical flask using a magnetic stirrer at 20°C for 24 h. After the desired reaction time, the residual chlorine was removed by addition of an equivalent volume of sodium thiosulphate solution. The reaction mixture was then acidified to pH 2 with 0.1 M hydrochloric acid before extraction with two 30-ml volumes of diethyl ether. The solvents were dried over anhydrous sodium sulphate and 2 ml of *n*-hexane–acetone (1:1, v/v) were added to prevent evaporation of the reaction products during concentration under vacuum at 40°C to suitable volumes for GC and GC–MS analyses.

Product resolution and characterization

A Shimadzu GC-6A gas chromatograph equipped with a flame ionization detector and 2 m × 2 mm I.D. glass column packed with 2% OV-1 on Uniport HP (60–80 mesh) was programmed from 120 to 260°C at 5°C/min. The nitrogen carrier gas flow-rate was 40 ml/min. A Shimadzu 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-008 data processing system was used for the qualitative analyses of samples under the following conditions: temperature of ion source, 250°C; trap current, 70 μA; electron energy, 70 eV. A glass column (2 m × 3 mm I.D.) packed with 2% OV-1 on Uniport HP (60–80 mesh) was used for the GC separation of the diethyl ether extracts. The oven temperature of the gas chromatograph was programmed from 120 to 240°C at a rate of 5°C/min. The products were identified by comparison of their retention times and mass spectra with those of authentic compounds.

RESULTS AND DISCUSSION

In a preliminary examination of the reaction of individual TCAHs with hypochlorite in dilute aqueous solution, the decrease in the concentration of the active chlorine during contact with each of these compounds was followed by iodometric titration. A much slower decrease occurred at low concentration, less than 1 mg/l, of TCAH compounds with two exceptions, in comparison with aqueous phenolic solutions[7,31–33]. In the present work, therefore, each TCAH (10^{-4} M) was allowed to react with hypochlorite (10^{-2} M) and the products identified.

GC–MS analysis of chlorination products of fluorene

A typical GC–MS (total ion current) trace of a diethyl ether extract of aqueous fluorene solution (0.3 mmol/l, pH 5) after treatment with hypochlorite (20 equiv. of chlorine per mol of compound) at 20°C for 24 h is shown in Fig. 1. At least fifteen reaction products can be seen on the chromatogram. Some of the peaks were identified on the basis of their retention times and mass spectra as compared with those of authentic compounds. Compounds corresponding to other peaks were determined from the mass spectra of each peak (Fig. 2).

Fig. 2A shows the mass spectrum of the peak at scan 128 which is the main reaction product when fluorene was treated with less than 5 equivalents of chlorine per
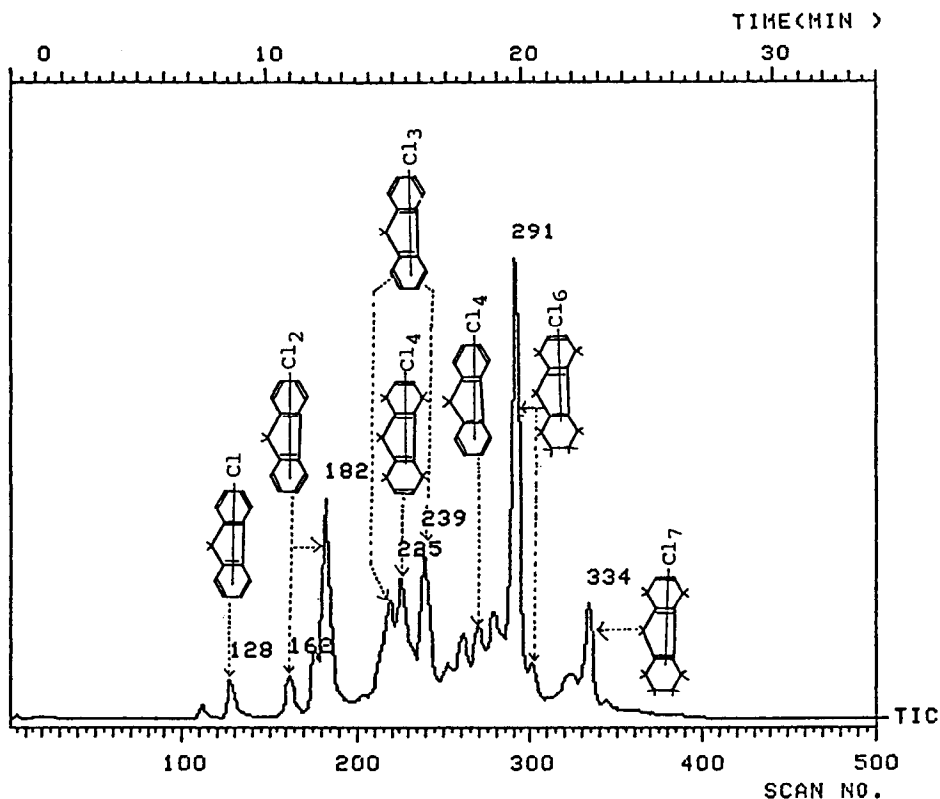
Fig. 1. Mass chromatogram (total ion current) of a diethyl ether extract of a fluorene solution (0.3 mmol/l) after treatment with hypochlorite (40 equiv. of chlorine per mol of compound) at 20°C and pH 5 for 24 h. Mass spectrum for each peak as in Fig. 2. The GC column temperature was raised from 120 to 250°C at 5°C/min. For other GC–MS conditions, see Experimental.

mol of compound for 24 h. The molecular ion (M^+) of the peak at scan 128 occurs at m/z 200, indicating one chlorine atom, and a fragment ion occurs at m/z 165, which arises by the loss of one chlorine atom from the molecular ion. The mass spectrum and retention time of this compound were in agreement with those of 9-chlorofluorene.

The compound corresponding to the peak at scan 182 in Fig. 1 gave a molecular ion at m/z 234 (Fig. 2B), indicating two chlorine atoms, and two fragment ions at m/z 199 ($M^+ - Cl$) and 163 ($M^+ - Cl - HCl$). The molecular ion and its fragmentation pattern indicate the occurrence of dichlorofluorene in the diethyl ether extract. The peak at scan 162 in Fig. 1 gave a similar fragmentation pattern, with two chlorine atoms, to that of the peak at scan 182, which also suggests the occurrence of an isomer of a dichlorofluorene in the extract.

Fig. 2C and D show the mass spectra of the peak at scans 225 and 291 in Fig. 1, respectively, which are the reaction products when fluorene was treated with hypochlorite at high molar ratios of chlorine per mol of compound (over 20 equivalents) for 24 h. The compound corresponding to the peak at scan 225 in Fig.
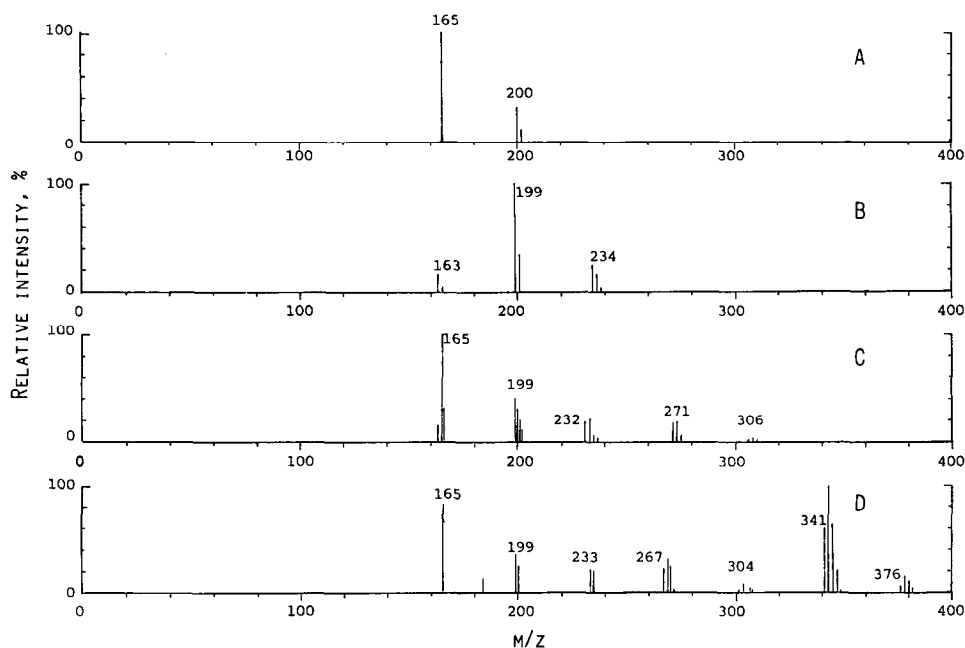
Fig. 2. Mass spectra of peaks of scans 128 (A), 182 (B), 225 (C) and 291 (D) in Fig. 1.

1 gave a molecular ion at m/z 306, having four chlorine atoms, and four fragment ions at m/z 271 (M^+ − Cl), 235 (M^+ − Cl − HCl), 199 (M^+ − Cl − 2HCl) and 165 (M^+ − 3Cl − HCl). The molecular ion of the peak at scan 291 occurs at m/z 376, having six chlorine atoms, and six fragment ions occur at m/z 341 (M^+ − Cl), 302 (M^+ − 2HCl − 2H), 267 (M^+ − 3HCl − H), 233 (M^+ − Cl − 3HCl), 199 (M^+ − 3Cl − 2HCl) and 165 (M^+ − 6Cl − H). These molecular ions and their mass fragmentation patterns indicate the compounds to be tetrahydrotetrachlorofluorene and hexahydrohexachlorofluorene, respectively, but their exact structures could not be determined.
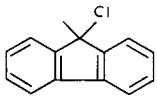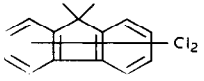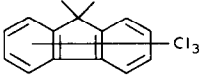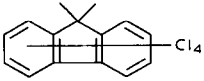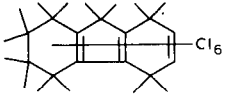
A summary of the chlorination products identified or determined from their relative retention times and mass spectra is presented in Table II. These findings lead to the conclusion that chlorination of aqueous fluorene solutions with hypochlorite produces not only products of substitution, but also those of addition.

The occurrence of mono- and dichlorofluorenes and fluorenone in chlorine-treated fluorene solution has been confirmed by Oyler et al.[20] by GC–MS analysis of a acetonitrile–dichloromethane extract, using C_{18} Porasil B and XAD-2 adsorption, from the reaction solution. Similar compounds have also been shown to be present in chlorinated leachate from a commercial coal tar[24,25] and in drinking water[30]. However, no products of addition have been reported in the literature[12,20,24,25,30], although it has been shown that chlorination of methylnaphthalene by molecular chlorine in acetic acid produces both products of substitution and addition[34].

TABLE II

PRODUCTS OF REACTION OF FLUORENE WITH HYPOCHLORITE IN ACIDIC AQUEOUS
SOLUTION AT 20°C FOR 24 h[a]

MS data for each compound appearing in Tables II–V are available from the authors.

Proposed structure	Scan no. in Fig. 1	Relative retention time $(GC)^b$	Molecular ion, m/z
1 [c]	128	0.945	200
2	162	1.084	234
3 Isomer of compound 2	182	1.165	234
4	219	1.321	268
5	225	1.346	306
6 Isomer of compound 4	239	1.402	268
7	271	1.545	302
8	291	1.626	376
9 Isomer of compound 8	302	1.664	376
10	334	1.844	410

[a] pH 5, [fluorene]$_0$ = $0.3 \cdot 10^{-3}$ M, [hypochlorous acid]$_0$ = $6 \cdot 10^{-2}$ M.
[b] Reference = anthracene.
[c] Relative retention time and mass spectrum are identical to those of the authentic compound.

Chlorination products of carbazole, dibenzofuran and dibenzo-p-dioxin

Typical GC–MS (total and mass fragment ion currents) traces of diethyl ether extracts from carbazole, dibenzofuran and dibenzo-*p*-dioxin solutions (pH 5) after treatment with an excess of hypochlorite at 20°C for 24 h are shown in Fig. 3. Some of the peaks were identified on the basis of GC retention times and mass spectra compared with those of authentic compounds. Compounds corresponding to other peaks were determined from the mass spectrum of each peak in the same manner as described for the fluorene products.

Fig. 3 shows that treatment of carbazole, dibenzofuran and dibenzo-*p*-dioxin with an excess of hypochlorite in aqueous solutions (pH 5) produces several chloro-substitution products. The reaction in low concentrations of both compounds (less than 1 mg/l) gave mono- and, occasionally, dichloro-substituted compounds, while higher chlorinated products were detected in the reactions at high concentrations.

A summary of the chlorination products identified or determined from the GC retention times and mass spectra is presented in Table III. Monochlorodibenzofuran has been identified to be present in chlorine-treated dibenzofuran solution[12,20], in chlorinated leachate from commercial coal tar[24,25] and in drinking water[30].

Chlorination products of anthracene, phenanthrene and their methyl derivatives

As can be seen in Fig. 4A, treatment of 2-methylanthracene with an excess of hypochlorite in the buffered solution of pH 5 produced 2-methylanthraquinone as the predominant product, minor products being chloro-2-methylanthraquinone and chloro-substituted derivatives. This product distribution was the similar to that of the anthracene–hypochlorite reaction (Table IV).

Fig. 4B shows that treatment of 9-methylanthracene with an excess of hypochlorite in the buffered solution of pH 5 produces several reaction products
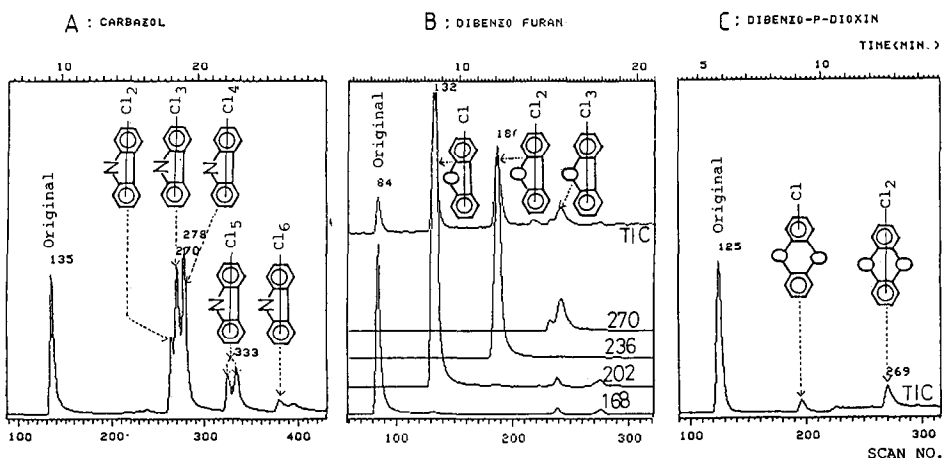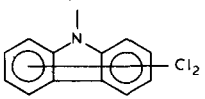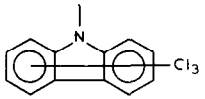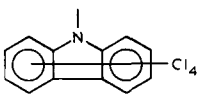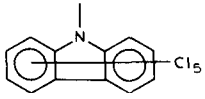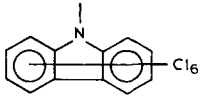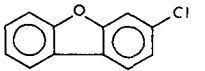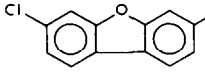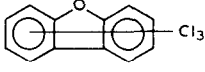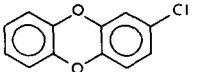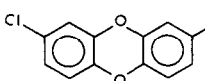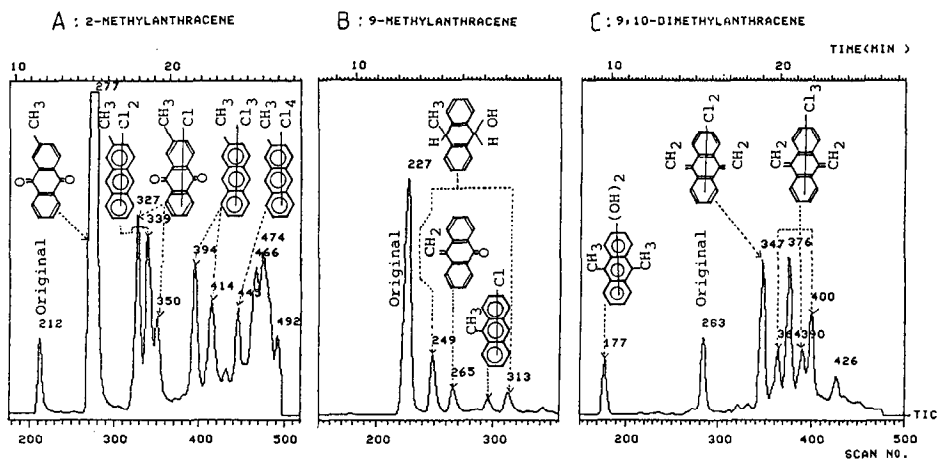

Fig. 3. Mass chromatograms (total or fragment ion current) of diethyl ether extracts from carbazole, dibenzofuran and dibenzo-*p*-dioxin solutions (0.3 mmol/l) after treatment with hypochlorite (40 equiv. of chlorine per mol of compound) at 20°C and pH 5 for 24 h. GC column temperature as in Fig. 1. For other GC–MS conditions, see Experimental. Mass spectral data for each peak as in Table III.

TABLE III

PRODUCTS OF REACTION OF CARBAZOLE, DIBENZOFURAN AND DIBENZO-*p*-DIOXIN
WITH HYPOCHLORITE IN ACIDIC AQUEOUS SOLUTION AT 20°C FOR 24 h[a]

Proposed structure	Scan no. in Fig. 3	Relative retention time (GC)[b]	Molecular ion, m/z
Carbazole products			
1	263	1.570	235
2	270	1.610	269
3	278	1.640	303
4	325	1.830	337
5 Isomer of compound 4	333	1.870	337
6	395	2.050	371
Dibenzofuran products			
1 [c]	132	0.858	202
2 [c]	186	1.102	236
3	241	1.323	270
Dibenzo-p-dioxin products			
1 [c]	195	0.908	218
2 [c]	269	1.149	252

[a] pH 5, [compound]$_0$ = 0.3 · 10^{-3} *M*, [hypochlorous acid]$_0$ = 6 · 10^{-2} *M*.
[b] Reference = anthracene.
[c] Relative retention time and mass spectrum are identical to those of the authentic compound.

Fig. 4. Mass chromatograms (total ion current) of diethyl ether extracts from 2- and 9-methylanthracene and 9,10-dimethylanthracene solutions (0.3 mmol/l) after treatment with hypochlorite (40 equiv. of chlorine per mol of compound) at 20°C and pH 5 for 24 h. GC–MS conditions as in Fig. 1. Mass spectral data for each peak as in Table IV.

including hydroxylated (phenols), oxygenated (9-methyleneanthracenone) and chlorine-substituted compounds. 9-Chloromethylanthracene exhibits a mass spectrum which is nearly identical to that of its ring substituted isomer, chloro-9-methylanthracene. A difference in relative retention times (1.402 *versus* 1.437, respectively) allowed the conclusion that the latter compound occurs in the chlorinated 9-methylanthracene solution.

Treatment of 9,10-dimethylanthracene with an excess of hypochlorite in the buffered solution of pH 5 has been shown to produce hydroxylated (phenol) and chlorinated 9,10-dimethyleneanthracenes (Fig. 4C and Table IV). A summary of chlorination products identified or determined from the retention times and mass spectra is presented in Table IV.

Fig. 5 shows that treatment of 1- and 2-methylphenanthrenes with an excess of hypochlorite in the buffered solution of pH 5 at 20°C for 24 h produces several reaction products including chlorine-substituted derivatives and products of addition. The reactions in low concentrations of both compounds (less than 1 mg/l) gave only monochlorinated derivatives, while products of addition were detected in the high concentration reactions. A summary of the chlorination products identified or determined from retention times and mass spectra is shown in Table V.

Oxygenated (quinones), hydroxylated (phenols) and monochlorinated compounds have been identified in chlorine-treated anthracene or phenanthrene solutions[12,20], in a chlorinated leachate from commercial coal tar[24,25] and in drinking water[30].

Effect of the experimental conditions on the TCAH–hypochlorite reactions in aqueous solution

GC analysis of the diethyl ether extracts indicates that the reactions of TCAHs with hypochlorite in neutral aqueous solution are strongly dependent on structural

TABLE IV

PRODUCTS OF REACTION OF ANTHRACENE AND ITS METHYL DERIVATIVES WITH HYPOCHLORITE IN ACIDIC AQUEOUS SOLUTION AT 20°C FOR 24 h[a]
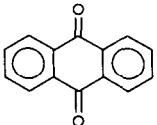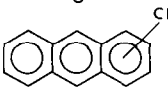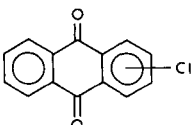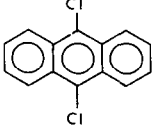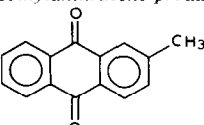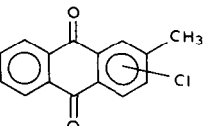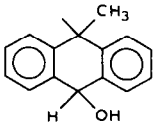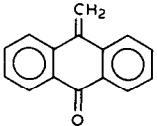
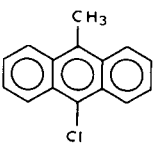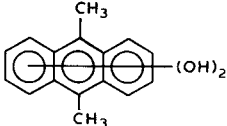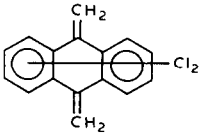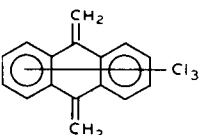| Proposed structure	Scan no. in Fig. 4	Relative retention time (GC)[b]	Molecular ion, m/z	
Anthracene products				
1 (anthraquinone) [c]		1.203	208	
2 (chloroanthracene)		1.236	212	
3 (chloroanthraquinone)		1.405	242	
4 (dichloroanthracene) [c]		1.450	246	
5 (trichloroanthracene, Cl$_3$)		1.670	280	
2-Methylanthracene products				
1 (2-methylanthraquinone, CH$_3$)	270	1.358	222	
	327	1.555	256	
2 (methyl-chloroanthraquinone, CH$_3$, Cl)	329	1.600	260	
3 (methyl-dichloroanthracene, CH$_3$, Cl$_2$)				
4 Isomer of compound 2	350	1.630	256	
5 (methyl-trichloroanthracene, CH$_3$, Cl$_3$)	414	1.867	294	

TABLE IV (continued)

Proposed structure	Scan no. in Fig. 4	Relative retention time (GC)[b]	Molecular ion, m/z
9-Methylanthracene products			
1	249	1.301	210
2	265	1.363	206
3	296	1.437	226
4 Isomer of compound 1	313	1.536	210
9,10-Dimethylanthracene products			
1	177	0.991	238
2	347	1.656	272
3	364	1.713	306
4 Unknown	376	1.756	—
5 Isomer of compound 3	400	1.855	306

[a] pH 5, [compound]$_0$ = 0.3 · 10^{-3} M, [hypochlorous acid]$_0$ = 6 · 10^{-2} M.
[b] Reference = anthracene.
[c] Relative retention time and mass spectrum are identical to those of the authentic compound.

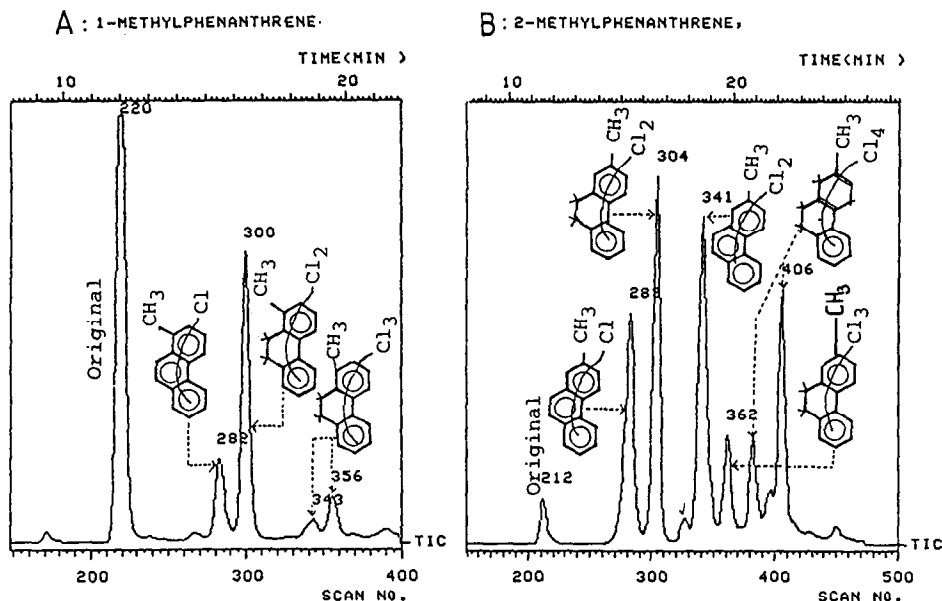A : 1-METHYLPHENANTHRENE·   B : 2-METHYLPHENANTHRENE,

Fig. 5. Mass chromatograms (total ion current) of diethyl ether extracts from 1- and 2-methylphenanthrene solutions (0.3 mmol/l) after treatment with hypochlorite (40 equiv. of chlorine per mol of compound) at 20°C and pH 5 for 24 h. GC–MS conditions as in Fig. 1. Mass spectral data for each peak as in Table V.
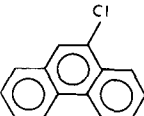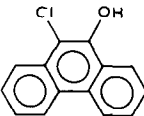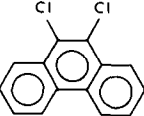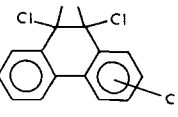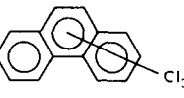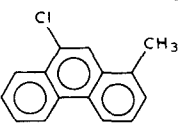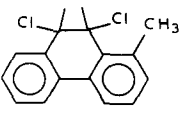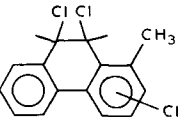
features (Fig. 6). Carbazole and 9-methylanthracene readily reacted with hypochlorous acid in water. A moderate reactivity was found for the anthracene, 2-methylanthracene and 9,10-dimethylanthracene solutions, and low reactivity for the fluorene, dibenzofuran, phenanthrene, 1-methyl- and 2-methylphenanthrene solutions.

Oxygenated (quinones) and hydroxylated (phenols) compounds were present at high concentrations in water when anthracene, 2-methyl- and 9-methylanthracenes were treated with hypochlorite at high molar ratios of hypochlorous acid to compound (Fig. 6B). Monochloro-9-methylanthracene and dichlorocarbazole were also detected at high concentrations in water when 9-methylanthracene and carbazole were treated with hypochlorite at moderate and high molar ratios of hypochlorous acid to compound (Fig. 6C). These reactions at high molar ratios of hypochlorous acid to compound may occur at the site of chlorine addition, as compared with those observed at a terminal water supplying system or in the presence of other substances reactive to chlorine in water.

Fig. 7 shows the results of GC determinations of diethyl ether extracts from aqueous solutions of TCAHs after treatment with an excess of hypochlorite at various pH values for 24 h. Oxygenated (quinones), hydroxylated (phenols) and chlorine-substituted compounds were detected at high concentrations under acidic and neutral conditions (Fig. 7B and C). Low concentrations of these oxygenated and chlorinated compounds were detected when TCAH compounds were treated with an excess of hypochlorite at pH 9. An exception was observed for the reaction of 9-methylanthracene with hypochlorite in water (Fig. 7).
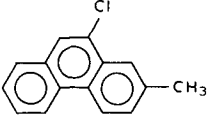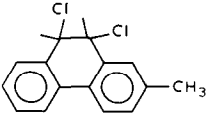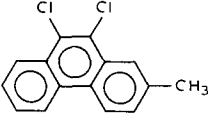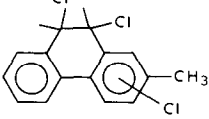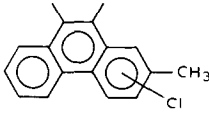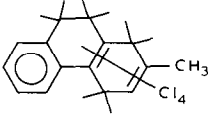
TABLE V

PRODUCTS OF REACTION OF PHENANTHRENE AND ITS METHYL DERIVATIVES WITH HYPOCHLORITE IN ACIDIC AQUEOUS SOLUTION AT 20°C FOR 24 h[a]

Proposed structure	Scan no. in Fig. 5	Relative retention time (GC)[b]	Molecular ion, m/z
Phenanthrene products			
1		1.270	212
2		1.380	228
3		1.56	246
4		1.700	282
5		1.740	280
6 Isomer of compound 5		1.76	280
1-Methylphenanthrene products			
1	282	1.446	226
2	300	1.506	262
3	343	1.652	296
4 Isomer of compound 3	356	1.711	296

TABLE V (continued)

Proposed structure	Scan no. in Fig. 5	Relative retention time (GC)[b]	Molecular ion, m/z
2-Methylphenanthrene products			
[structure: chloro-methylphenanthrene]	283	1.436	226
2 [structure: dichloro-methyldihydrophenanthrene]	304	1.516	262
3 [structure: dichloro-methylphenanthrene]	341	1.666	260
[structure: trichloro-methyldihydrophenanthrene]	362	1.735	296
5 [structure: trichloro-methyldihydrophenanthrene]	396	1.873	294
6 [structure: tetrachloro product, Cl₄]	406	1.896	332

[a] pH 5, [compound]$_0$ = 0.3 · 10^{-3} M, [hypochlorous acid]$_0$ = 6 · 10^{-2} M.
[b] Reference = anthracene.

At the typical ranges of pH found during the course of most water treatment processes (pH 5–9), the activated chlorine species can range from entirely hypochlorite ($^-$OCl) to entirely hypochlorous acid (HOCl, pK_a = 7.5 at 20°C). It has been observed that chlorine is more readily incorporated into aromatic systems at low pH values[22,35], a result which parallels the observation of increasing disinfection ability with decreasing pH[36]. Thus it seems that higher concentrations of chlorine-incorporated compounds would be formed when acidic industrial water effluents were treated with an excess of hypochlorite.

In order to confirm whether similar reactions take place under conditions
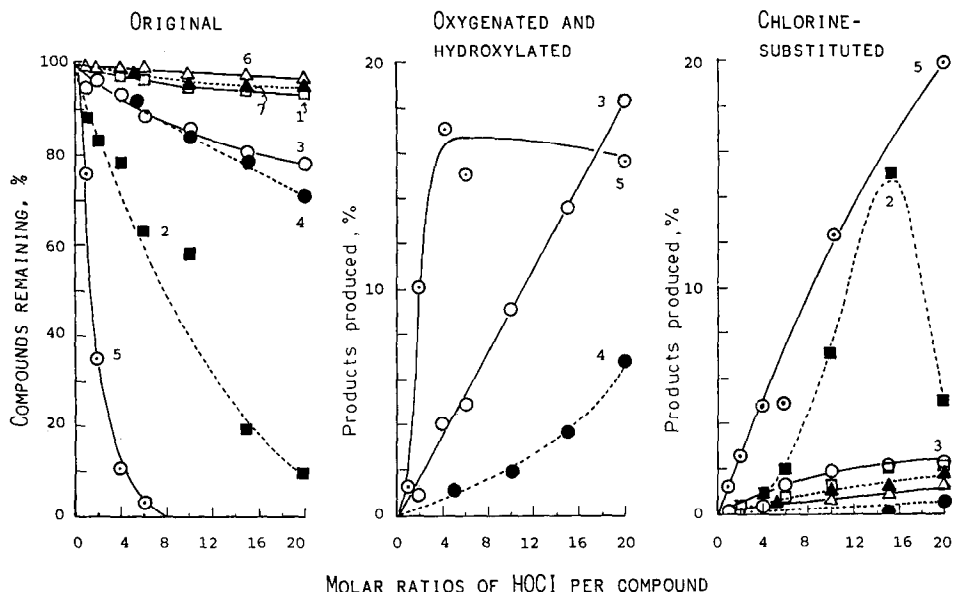
Fig. 6. Effect of the chlorine dose on the reactions of TCAHs (0.3 mmol/l) with hypochlorite in neutral aqueous solutions at 20°C for 24 h. The yields were derived from GC peak areas, relative to the area of each starting material. 1 (□), fluorene; 2 (■), carbazole; 3 (○), anthracene; 4 (●), 2-methylanthracene; 5 (⊙), 9-methylanthracene; 6 (½), phenanthrene and 7 (▲), 2-methylphenanthrene as the starting material.
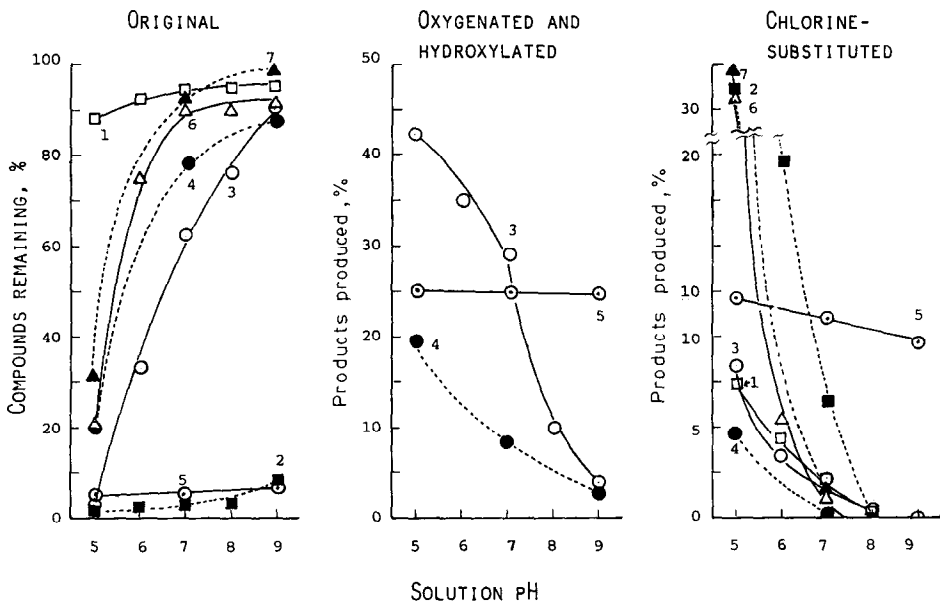

Fig. 7. Effect of the solution pH values on the reactions of TCAHs (0.3 mmol/l) with hypochlorite (6 mmol/l) in aqueous solutions at 20°C for 24 h. Other details as in Fig. 6.
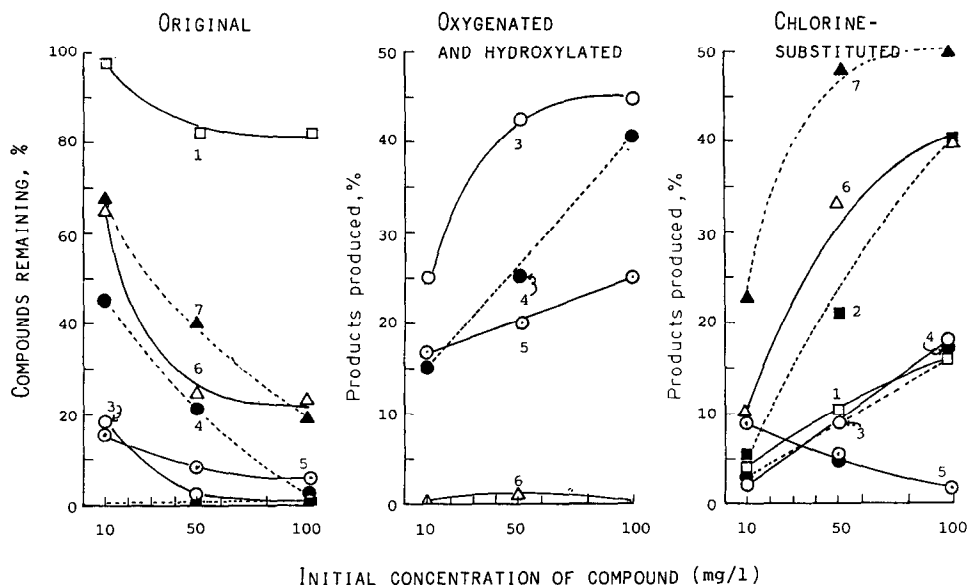
Fig. 8. Effect of the initial concentrations of compounds on the reactions of TCAHs with hypochlorite (20 equiv. of chlorine per mol of compound) in an acidic aqueous solution (pH 5) at 20°C for 24 h. Other details as in Fig. 6.

present during water treatment, different initial concentrations of TCAHs were treated with an excess of hypochlorite at pH 5 for 24 h. The results of GC determinations of the diethyl ether extracts from the chlorinated waters of TCAHs are shown in Fig. 8. It was observed that reactions of TCAHs with hypochlorite in water proceed more rapidly with increasing initial concentrations of both compounds. Oxygenated (quinones) and monochlorinated compounds were detected at comparatively high concentrations after treatment of even lower concentrations of TCAHs with an excess of hypochlorite under neutral and acidic conditions.

The higher concentrations of organic compounds and the corresponding high active chlorine levels described above have been found to represent extreme cases of contamination, such as encountered in some industrial water effluents[36,37] and in disinfection of the water mains and storage tanks after installation and maintenance[38].

It is worth stressing the relationship between the results reported here and the customary chemical treatment of waste-water. Industrial waste-waters are frequently treated with heavy doses of chlorine to destroy odours, to disinfect the waste-water and to improve sedimentation and filtration behaviour. As already mentioned, TCAHs are common components in such waste-water[29], unpurified water[27] and coal-tar coatings of water-supply systems[24,25] and this has led to the suggestion that oxygenated and chlorinated TCAHs may be generated during the chlorine treatment of such waters and in the water-supply system. This suggestion was clearly supported by an earlier report[30] in which several chlorinated and oxygenated TCAHs were found to be present in drinking water.

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