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CHEMICAL CHANGES OF ORGANIC COMPOUNDS IN CHLORINATED WATER

XII*. GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC STUDIES OF THE REACTIONS OF METHYLNAPHTHALENES WITH HYPOCHLORITE IN DILUTE AQUEOUS SOLUTION

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SUMMARY

The products of aqueous chlorination reactions of naphthalene, 1- and 2-methylnaphthalenes, 1,2-, 1,3-, 1,4-, 1,5-, 1,8-, 2,3- and 2,6-dimethylnaphthalenes and 2,3,5-trimethylnaphthalene with hypochlorite have been determined by gas chromatography-mass spectrometry. They included chloro-substituted, oxygenated (quinones) and hydroxylated (phenols) compounds which were readily formed at room temperature. The extent of the reactions was shown to depend on the pH, the initial concentrations of both compounds and the number of methyl substituents and their positions. Monochlorinated compounds were identified in the chlorinated water under those 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 chlorination¹. Even the numerous studies of phenol, which established the intermediate formation of mono-, di- and trichlorophenols²⁻⁹, leave the question of the end-products of this reaction unresolved¹⁰.

Several polynuclear aromatic hydrocarbons (PAHs) in aqueous solution are degraded by addition of chlorine^{11,12}, chlorine dioxide¹³⁻¹⁶ or sodium hypochlorite¹⁷⁻²¹. These reactions may occur at the site of chlorine addition as well as throughout a water distribution system²². PAHs have been suggested as the precursors of at least a portion of the mutagens produced in some chlorination processes²². The levels

* For Part XI, see ref. 33.

of these ubiquitous PAH compounds may be increased by the presence of coal-tar coatings inside pipes and water storage tanks^{23,24}.

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^{7,9,10,25-33}. The present report describes a detailed study of the product distributions of several methylated naphthalenes which were chosen for study because of their previous identification in unpurified water³⁴ and drinking water³⁵⁻³⁷.

EXPERIMENTAL

Materials

Naphthalene, methylnaphthalenes and ethylnaphthalenes were obtained from Tokyo Chemical Industry Co. (Tokyo, Japan), Nakarai Chemical Ltd. (Kyoto, Japan) and Wako Pure Chemical Industry Co. (Osaka, Japan). 1- and 2-chloronaphthalenes, 1,2- and 1,4-dichloronaphthalenes, 4-chlorophthalic acid and other compounds, which are expected to be formed during chlorination of naphthalenes with aqueous chlorine, were commercially available reagents. Hypochlorite solution was prepared by diluting sodium hypochlorite solution (*ca.* 10% available Cl, Nakarai Chemicals Ltd.) with 1 *M* disodium hydrogenphosphate-potassium dihydrogen phosphate buffer solution, pH 7. The hypochlorite concentrations were determined by iodometric titration.

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

A mixture of 200 ml of hypochlorite solution and each naphthalene compound dissolved in 1 ml of methanol was shaken in a separatory funnel at ambient temperature, in order to prevent leakage of the compound from the reaction system. 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 three 40-ml volumes of diethyl ether. The solvents were dried over anhydrous sodium sulphate and 2 ml of methanol were added to prevent evaporation of the reaction products during concentration under vacuum at 40°C to suitable volumes for gas chromatographic (GC) and GC-mass spectrometric (GC-MS) analyses.

Product resolution and characterization

A Shimadzu GC-6A gas chromatograph equipped with a flame ionization detector and 2 m × 3 mm I.D. glass column packed with 2% OV-1 on Uniport HP (60-80 mesh) was programmed from 60 to 240°C at 5°C/min. The nitrogen carrier gas flow-rate was 50 ml/min. A Shimadzu Model Chromatopac-1A data system was used to determine the retention times and peak areas on the chromatograms.

An Hitachi M-80 mass spectrometer-gas chromatograph equipped with an Hitachi M-003 data-processing system was used for the qualitative analyses of samples under the following conditions: ion source, temperature 250°C; trap current, 70 μ A; 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 (sometimes 60 or 80) to 240°C at 5°C/min. The products were identified by comparison of their retention times and mass spectra with those of authentic compounds.

RESULTS AND DISCUSSION

In a preliminary examination of the reaction of individual methylnaphthalenes 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. It was observed that a much slower decrease occurred at low concentration, less than 1 mg/l, of methylnaphthalenes, in comparison with aqueous phenolic solutions^{7,26,27,29}. In the present work, therefore, each methylnaphthalene (10^{-3} M) was allowed to react with 10^{-2} M hypochlorite and the products identified.

A small amount of methanol (less than 1%) was used in many reactions to provide sufficient quantities of methylnaphthalene products for analysis and to minimize the formation of methylnaphthalene crystals. The use of such small amounts of this solvent did not appear to alter the product distribution based on chromatographic comparison with reactions in the absence of methanol. In contrast, reaction solutions containing crystalline methylnaphthalene tended to yield only chloro products rather than both the chloro and oxygenated products observed in homogeneous solutions.

GC-MS analysis of chlorination products of naphthalene

A typical GC-MS (total ion current) trace of a diethyl ether extract of neutral naphthalene solution (3.9 mmol/l) after treatment with hypochlorite (20 equiv. of chlorine per mol of compound) for 24 h is shown in Fig. 1. At least ten 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 spectrum of each peak (Fig. 2).

Fig. 2B and D show the mass spectra of the peaks in scans 77 and 127, respectively, which are the major GC-MS peaks in the diethyl ether extract from chlorine-treated naphthalene solution. The molecular ion (M^+) of the peak of scan 77 occurs at m/z 162, having one chlorine atom, and a fragment ion occurs at m/z 127, which arises by the loss of one chlorine atom from the molecular ion. The compound corresponding to the peak of scan 127 gave a molecular ion at m/z 196, having two chlorine atoms, and two fragment ions at m/z 161 ($M^+ - Cl$) and at m/z 126 ($M^+ - 2 Cl$). The mass spectra and retention times of these compounds were in agreement with those of 1-chloronaphthalene and 1,4-dichloronaphthalene, respectively.

The mass spectrum of the compound (Fig. 2E) corresponding to the peak of scan 196 in Fig. 1 gave a molecular ion at m/z 262, having three chlorine atoms, and fragment ions at m/z 227 ($M^+ - Cl$), m/z 199 ($M^+ - COCl$), m/z 164 ($M^+ - Cl - COCl$) and m/z 136 ($M^+ - 2 COCl$). This suggests a formula $C_{10}H_5Cl_3O_2$. From the nature of the reaction of naphthalene with hypochlorite in water and the mass

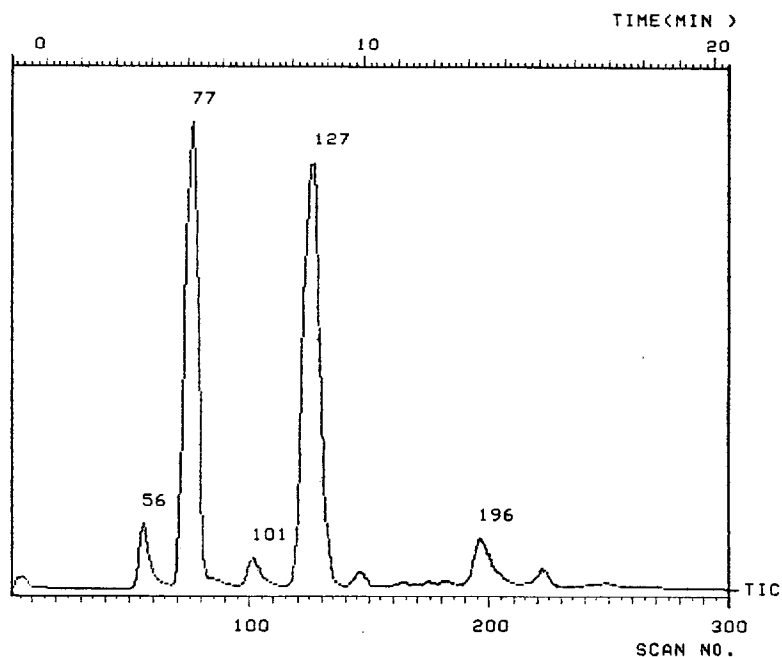


Fig. 1. Mass chromatogram (total ion current) of a diethyl ether extract of a naphthalene solution (3.9 mmol/l) after treatment with hypochlorite (20 equiv. of chlorine per mol of compound) at room temperature for 24 h. Mass spectrum for each peak as in Fig. 2. Compounds as in Table I. The GC column temperature was raised from 80 to 240°C at 5°C/min. For other GC-MS conditions, see Experimental.

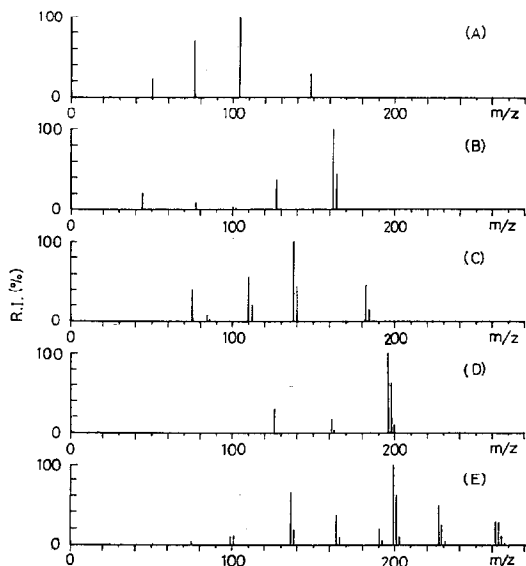


Fig. 2. Mass spectra of peaks of scan No. 56 (A), 77 (B), 101 (C), 127 (D) and 196 (E) in Fig. 1.

spectrum, this compound is considered to be a trichlorodihydroxynaphthalene. However, its exact nature could not be determined because authentic compounds were not available.

Fig. 2A shows the mass spectrum of the compound corresponding to the peak of scan 56 in Fig. 1. The molecular ion (M^+) is at m/z 148 and the most abundant fragment ion is at m/z 104, which arises by loss of carbon dioxide from the molecular ion. Other fragment ions occur at m/z 76 ($M^+ - CO_2 - CO$) and m/z 50 ($M^+ - CO_2 - CO - C_2H_2$). The retention time and mass fragmentation pattern of this compound are in agreement with those of anhydrous phthalic acid.

The compound corresponding to the peak of scan 101 in Fig. 1 gave a molecular ion at m/z 182, having one chlorine atom, and three fragment ions at m/z 138 ($M^+ - CO_2$), m/z 110 ($M^+ - CO_2 - CO$) and m/z 75 ($M^+ - CO_2 - CO - Cl$). This was interpreted as being due to an anhydrous phthalic acid with one chlorine atom. Since the GC retention time did not agree with that of anhydrous 4-chlorophthalic acid, the corresponding compound is probably the 3-chloro derivative. This result, in addition to the above finding, leads to the conclusion that chlorination of aqueous naphthalene solution with hypochlorite produces not only chloronaphthalenes and chlorohydroxynaphthalenes, but also chlorophthalic acids by oxidative cleavage of the aromatic ring.

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

The occurrence of mono-, di- and trichloronaphthalenes in chlorine-treated naphthalene solution has been confirmed by Smith *et al.*¹⁹ by GC analysis of a benzene and XAD-2 extract from the reaction solution. However, no oxidative ring-cleavage compounds (chlorophthalic acids) were reported, because such highly polar compounds could not be isolated from the aqueous solution by the benzene or XAD-2 extraction procedures. Other oxidizing reagents, *i.e.*, potassium permanganate, peracetic acid and hydrogen peroxide, have been reported to oxidize naphthalene under rather drastic conditions to form phthalic acid³⁸, *o*-carboxycinnamic acid³⁹ and 1- and 2-naphthols⁴⁰, respectively. Oxidation by chlorine dioxide is known to produce mono- and dichloronaphthalenes and phthalic acid¹⁴.

GC-MS analysis of chlorination products of methylnaphthalene

Typical GC-MS (total ion current) traces of diethyl ether extracts from individual methylnaphthalene solutions after treatment with an excess of hypochlorite at room temperature for 2 or 16 h are shown in Figs. 3-6. Some of the peaks were identified on the basis of the 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 naphthalene products.

Figs. 3-6 show that the treatment of methylnaphthalenes with hypochlorite in buffered solutions of pH 7 produces mono- and dichloro-substituted compounds as the predominant products, minor products being chlorinated polyhydroxy compounds (phenols) or quinones. (MS data for each compound appearing on the chromatograms in Figs. 3-6 are available from the authors). Unfortunately, the nature of the main peak of the diethyl ether extract from chlorine-treated 1,2-dimethylnaphthalene solution could not be determined because this compound gave a complex mass spectrum.

TABLE I
 PRODUCTS OF REACTION OF NAPHTHALENE WITH CHLORINE IN NEUTRAL WATER

Reaction conditions and GC-MS conditions as in Fig. 1.

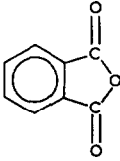

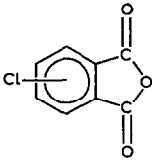
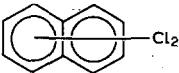




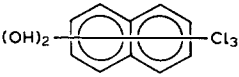
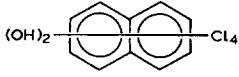
<i>Proposed structure</i>	<i>Scan No.</i>	<i>Molecular ion (m/z)</i>	<i>Amount*</i>	<i>m/z (relative intensity)</i>
	56	148	Minor	148(30), 104(100), 76(65), 50(21)
	77	162	Major	164(35), 162(100), 127(35), 77(5), 44(21)
	101	182	Minor	184(14), 182(44), 140(30), 138(100), 112(19), 110(6), 75(40)
	127	196	Major	200(10), 198(64), 196(100), 163(5), 161(17), 126(28)
	146	196	Minor	200(11), 198(64), 196(100), 163(7), 161(33), 126(29), 75(3)
$C_{10}H_8Cl_2O$	163	214	Trace	218(13), 216(58), 214(100), 142(13), 139(33), 123(73), 103(24), 76(29)
	172	212	Trace	216(8), 214(63), 212(100), 113(17)
	175	230	Trace	234(30), 232(90), 230(100), 195(20), 181(25), 162(8), 160(34), 133(88), 105(9)
	180	230	Trace	234(36), 232(91), 230(100), 195(91)

TABLE I (continued)

Proposed structure	Scan No.	Molecular ion (m/z)	Amount*	m/z (relative intensity)
	196	262	Minor	266(9), 264(28), 262(28), 229(25), 227(38), 203(9), 201(64), 199(100), 164(33), 136(54)
	222	296	Minor	302(1), 300(10), 298(25), 296(15), 265(12), 263(34), 261(36), 237(29), 235(93), 233(100), 199(31), 197(43), 163(50), 135(25), 127(12)

* Derived semiquantitatively from the GC-MS peak areas, relative to the area of starting material. Major, over 5%; minor, less than 5 to 0.5%; trace, near detection limit (0.05%).

Treatment of 1-methylnaphthalene with hypochlorite in water has been reported to produce over twenty chlorinated compounds including chloro derivatives, quinones, phenols and carboxylic acid¹². Hypochlorite treatment of C₂-naphthalenes present in the aromatic fraction of diesel fuel was shown to give monochloro-C₂-naphthalenes¹⁸. Mono- and dichloro-substituted compounds and phthalic acid have also been identified by Taymaz *et al.*¹⁴ when 1- and 2-methylnaphthalenes were treated with chlorine dioxide in aqueous solutions.

Effect of the experimental conditions on the reactions of methylnaphthalenes with hypochlorite in aqueous solution

GC analysis of the diethyl ether extracts indicated that a much slower decrease in the amount of the original compound in water occurs even though at longer reaction times (Fig. 7) and at higher molar ratios of hypochlorous acid to compound (Fig. 8), in comparison with those reactions observed for aqueous solutions of phenolic compounds^{7,27,29}. Monochloronaphthalene was present at higher concentrations in water when naphthalene was treated with hypochlorite for a long time and at high molar ratios of hypochlorous acid to compound. This was followed by the formation of a small amount of dichloro-substituted compounds, as is seen in Figs. 7 and 8. The fact that the monochloro-substituted compound is mainly formed can be explained by the deactivating effect of chlorine substituents. The amounts of ether-extractable and chromatographable compounds decreased with increasing contact time and increasing molar ratio of hypochlorous acid to compound. This indicates the formation of highly water-soluble and non-volatile compounds during the secondary reactions in chlorine-treated naphthalene solution.

In contrast to the naphthalene-hypochlorite reaction, it was found in the methylnaphthalene-hypochlorite reactions that a rapid decrease in the amount of the original compounds occurs with formation of monochloro-substituted compounds (Table II). This tendency was, however, strongly dependent upon the number of methyl substituents and their positions in the naphthalene ring. 2-Methyl-, 1,2- and 1,3-dimethyl- and 2,3,5-trimethylnaphthalenes readily reacted with hypochlorous acid in water. A moderate reactivity was found for the 1-methyl-, 2-ethyl- and 1,8-

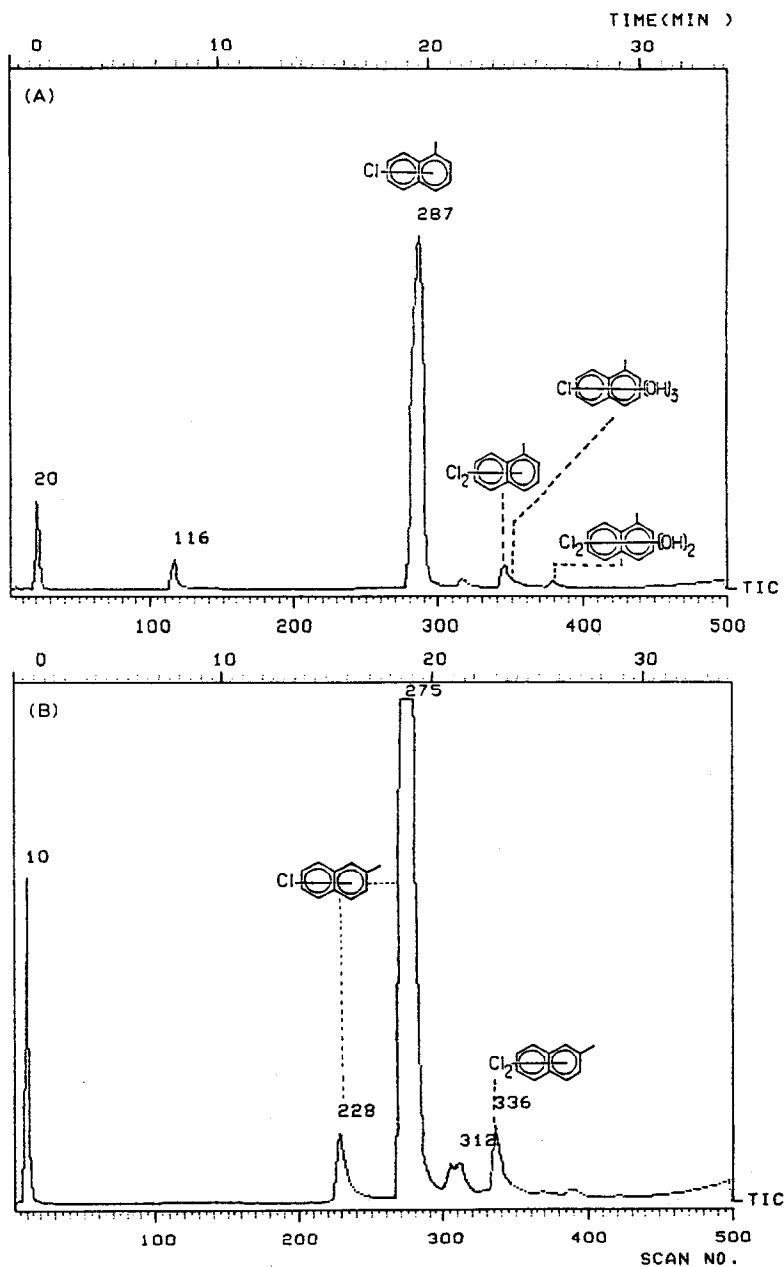


Fig. 3. Mass chromatograms (total ion current, TIC) of diethyl ether extracts of 1- (A) and 2-methylnaphthalene (B) solutions (3.5 mmol/l) after treatment with hypochlorite (20 equiv. of chlorine per mol of compound) at room temperature for 16 h. The GC column temperature was programmed from 60 (10-min hold) to 240°C at 5°C/min. For other GC-MS conditions, see Experimental.

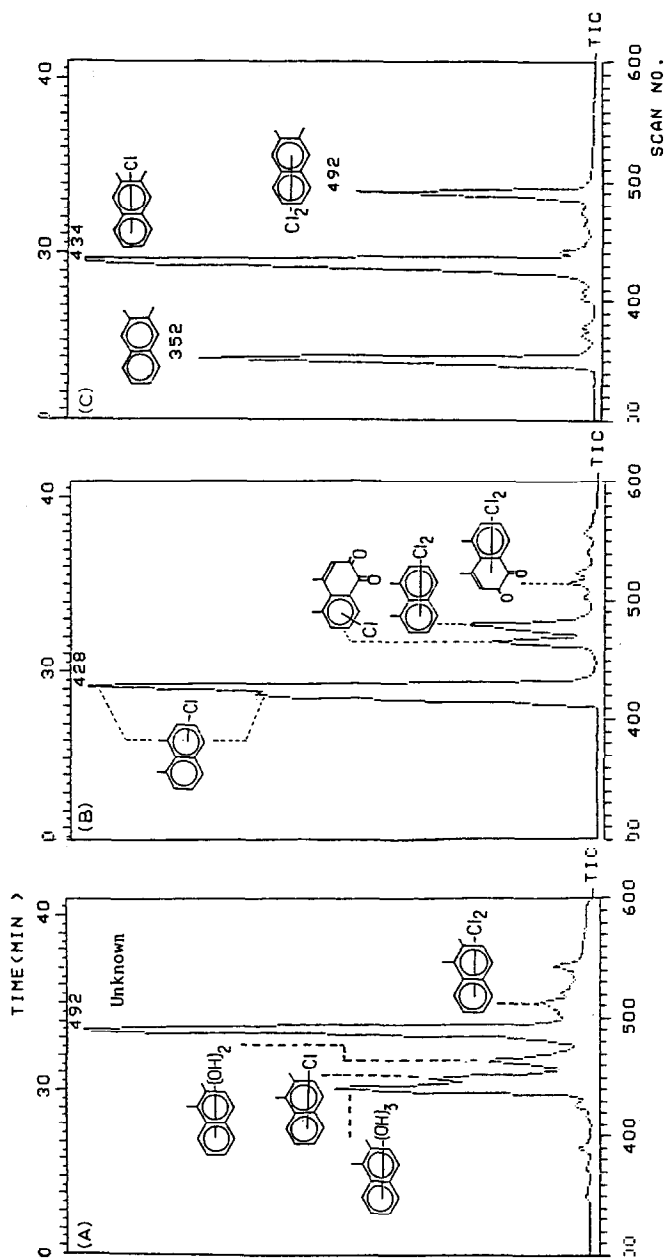


Fig. 4. Mass chromatograms (total ion current) of diethyl ether extracts of 1,2- (A), 1,8- (B) and 2,3-dimethylnaphthalene (C) solutions (3.2 mmol/l) after treatment with hypochlorite (20 equiv. of chlorine per mol of compound) at room temperature for 2 h. Other details as in Fig. 3.

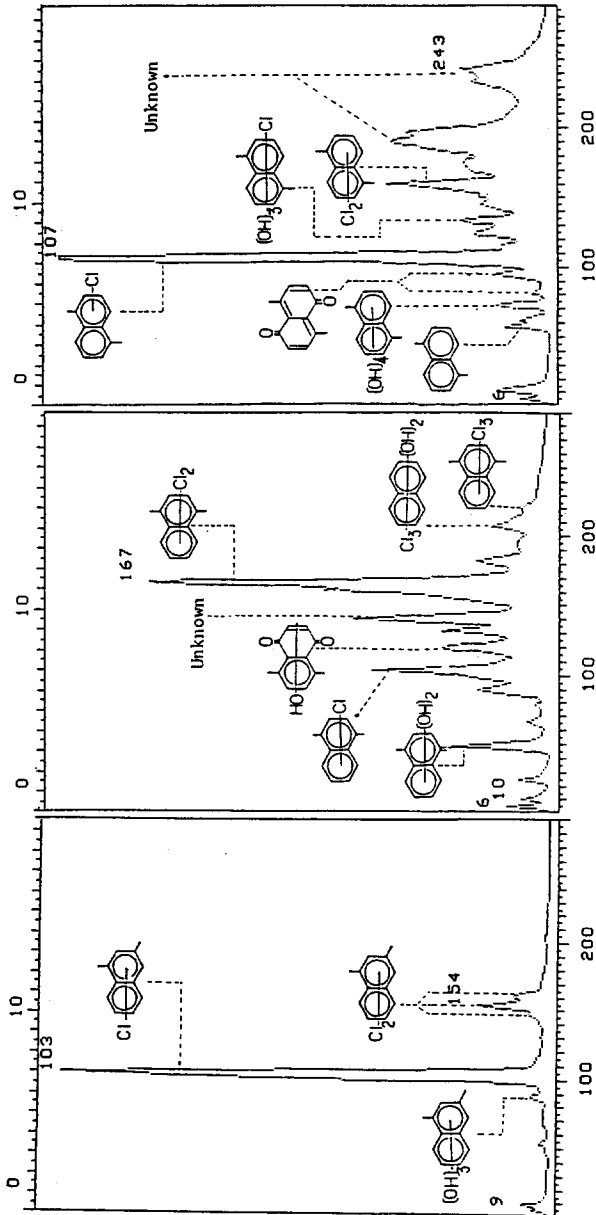


Fig. 5. Mass chromatograms (total ion current) of diethyl ether extracts of 1,3- (A), 1,4- (B) and 1,5-dimethylnaphthalene (C) solutions (3.2 mmol/l) after treatment with hypochlorite (20 equiv. of chlorine per mol of compound) at room temperature for 2 h. The GC column temperature was programmed from 120 to 240°C at 5°C/min. For other GC-MS conditions, see Experimental.

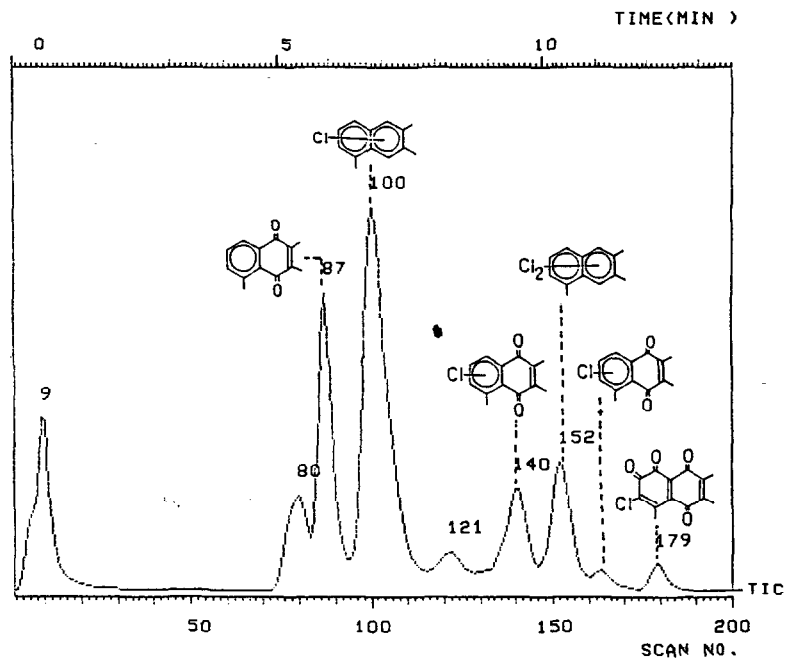


Fig. 6. Mass chromatogram (total ion current) of a diethyl ether extract of 2,3,5-trimethylnaphthalene solution (0.294 mmol/l) after treatment with hypochlorite (20 equiv. of chlorine per mol of compound) at room temperature for 2 h. The GC column temperature was programmed from 140 to 240°C at 5°C/min. For other GC-MS conditions, see Experimental.

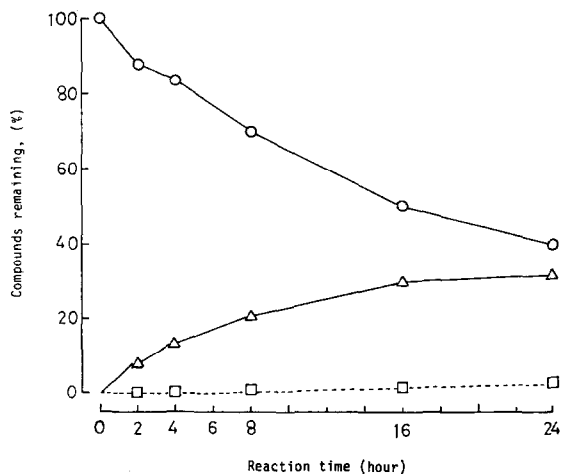


Fig. 7. Time course of the reaction of naphthalene (0.39 mmol/l) with an excess of hypochlorite at room temperature. The yields are derived from GC peak areas, relative to the area of starting material. ○—○, Starting material; △—△, monochloronaphthalenes; □—□, dichloronaphthalenes. Each point represents the average of three experiments.

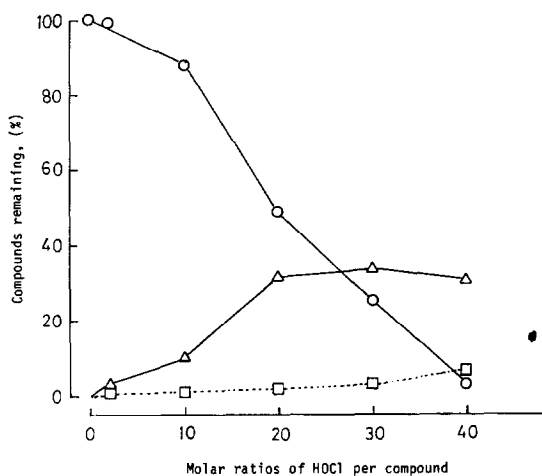


Fig. 8. Residual amounts of reaction products in aqueous naphthalene solutions (0.39 mmol/l) after treatment with hypochlorite (various equivalents of chlorine per mol of compound) at room temperature for 16 h. Other details as in Fig. 7.

and 2,3-dimethylnaphthalenes, and low reactivity for the 1-ethyl-, 1,4-, 1,5- and 2,6-dimethylnaphthalenes.

The distribution of the chlorinated products can be explained in terms of the electrophilic substitution by chlorine. Methyl substituents are activating and *o*-/*p*-directing; if they are *m*-substituted, *e.g.*, 1,3-dimethyl- and 2,3,5-trimethylnaphthalene, the activating effect is enhanced, whereas if they are *p*-substituted, *e.g.*, 1,4-, 1,5- and 2,6-dimethylnaphthalenes, the effect is weakened.

Fig. 9 shows the results of GC determinations of diethyl ether extracts from naphthalene solutions after treatment with an excess of hypochlorite at various pH values for 16 h. Dichlorinated compounds were detected at high concentrations in acidic solution, but large amounts of monochloro-substituted compounds were obtained under neutral conditions. These chlorinated compounds were hardly detected when naphthalene was treated with an excess of hypochlorite at pH 10. This can be explained in terms of the concentrations of undissociated hypochlorous acid in the chlorinated water. Therefore, the effect of pH on the reaction of naphthalene with hypochlorite in water is correlated with the titration curve of hypochlorous acid as shown in Fig. 9.

A summary of the GC determinations of the diethyl ether extracts from the other methylnaphthalene solutions after treatment with an excess of hypochlorite at various pH values for 1 h is shown in Table III. The effect of pH described above was also observed in these reactions.

In order to confirm whether similar reactions take place under conditions present in water treatment, different initial concentrations of naphthalene were treated with an excess of hypochlorite at pH 5, 7 and 9 for 16 h. The results of GC determinations of the diethyl ether extracts from the chlorinated naphthalene solutions are shown in Fig. 10. It was observed that the reactions of naphthalene with hypochlorite in water proceed more rapidly with increasing initial concentrations of

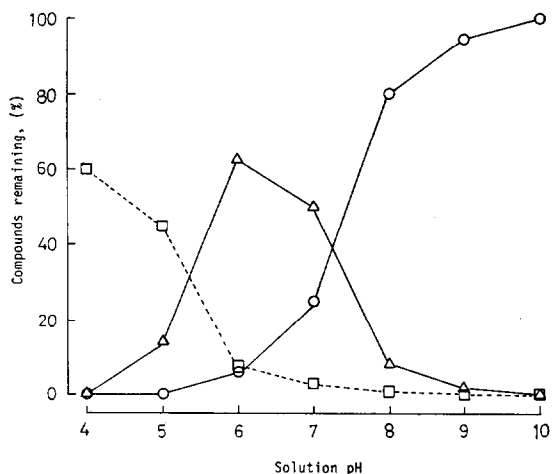


Fig. 9. Residual amounts of reaction products in aqueous naphthalene solutions (0.39 mmol/l) after treatment with an excess of hypochlorite at various pH values and room temperature for 16 h. Other details as in Fig. 7.

both compounds and with decreasing pH. However, no chlorinated compounds were detectable when 5 ppm of naphthalene were treated with hypochlorite under alkaline conditions. In contrast, the monochlorinated compound was detected in higher concentrations after treatment of even lower concentrations of naphthalene with an excess of hypochlorite under neutral and acidic conditions.

It was worth stressing the relationship between the results reported here and the customary chemical treatment of waste water. Industrial wastes 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, naph-

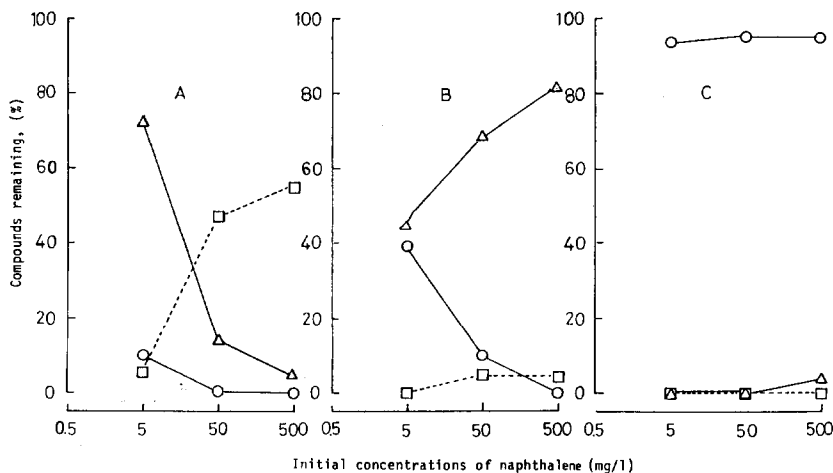


Fig. 10. Effect of the initial concentrations of compounds on the residual amounts of reaction products of aqueous naphthalene solutions after treatment with an excess of hypochlorite (20 equiv. of chlorine per mol of compound) at pH 5 (A), 7 (B) and 9 (C) for 16 h. Other details as in Fig. 7.

TABLE II
 CHLORINATION PRODUCTS OF METHYLNAPHTHALENES IN WATER AFTER TREATMENT WITH AN EXCESS OF HYPOCHLORITE AT 20°C FOR 1 h

Each compound (5 mg) dissolved in 1 ml of methanol was shaken with 100 ml of water (pH 7) containing 25 mg of chlorine. After adjusting to pH 2, the reaction mixture was extracted with diethyl ether (3 × 20 ml) for GC analysis.

Compound	Residual amounts of products (%) [*]				Total
	Original	Cl ₁ deriv.	Cl ₂ deriv.	Other	
Naphthalene	79.3	1.5	N.D.**	N.D.	80.80 ± 3.73***
1-Methylnaphthalene	38.5	31.8	N.D.	N.D.	70.30 ± 2.29
2-Methylnaphthalene	12.2	60.3	N.D.	N.D.	72.50 ± 2.29
1-Ethyl-naphthalene	70.8	11.1	N.D.	N.D.	81.90 ± 5.12
2-Ethyl-naphthalene	44.5	45.4	N.D.	N.D.	89.90 ± 1.98
1,2-Dimethylnaphthalene	7.6	61.2	N.D.	18.5	87.30 ± 2.04
1,3-Dimethylnaphthalene	N.D.	68.0	N.D.	2.1	70.10 ± 2.59
1,4-Dimethylnaphthalene	52.0	25.3	N.D.	N.D.	77.30 ± 5.80
1,5-Dimethylnaphthalene	70.9	5.0	N.D.	N.D.	75.90 ± 1.82
1,8-Dimethylnaphthalene	36.6	35.3	N.D.	N.D.	71.90 ± 3.85
2,3-Dimethylnaphthalene	28.5	40.1	1.1	N.D.	68.70 ± 5.01
2,6-Dimethylnaphthalene	55.1	15.5	N.D.	N.D.	70.60 ± 3.67
2,3,5-Trimethylnaphthalene	5.0	53.0	N.D.	11.4	69.40 ± 5.24

^{*} Yields derived from GC peak areas, relative to the area of the starting material.

^{**} Not detected by GC analysis.

^{***} Average and standard deviation for three samples.

TABLE III
 CHLORINATION PRODUCTS OF METHYLNAPHTHALENES IN WATER AFTER TREATMENT WITH AN EXCESS OF HYPOCHLORITE AT
 ROOM TEMPERATURE FOR 1 h, AS A FUNCTION OF pH
 Procedure and details as in Table II.

Compound	pH	Residual amount of product (%)				Total
		Original	Cl ₁ -deriv.	Cl ₂ -deriv.	Other	
Naphthalene	5	65.0	19.0	Trace	N.D.	84.00 ± 1.50
	7	88.0	2.0	N.D.	N.D.	90.0 ± 3.00
	9	79.6	N.D.	N.D.	N.D.	79.60 ± 0.96
2-Methylnaphthalene	5	4.4	90.5	N.D.	N.D.	94.90 ± 3.31
	7	32.3	60.0	N.D.	N.D.	92.30 ± 4.35
	9	94.8	3.7	N.D.	N.D.	99.40 ± 1.91
1,4-Dimethylnaphthalene	5	28.3	65.5	N.D.	N.D.	93.80 ± 1.42
	7	78.6	17.7	N.D.	N.D.	96.30 ± 2.31
	9	100	N.D.	N.D.	N.D.	100 ± 5.00
2,3-Dimethylnaphthalene	5	14.5	59.9	3.3	N.D.	77.70 ± 1.21
	7	66.1	34.5	0.4	N.D.	91.00 ± 1.00
	9	72.2	13.4	N.D.	N.D.	85.70 ± 2.04
2,3,5-Trimethylnaphthalene	5	N.D.	66.9	5.0	8.6	80.50 ± 2.23
	7	36.5	48.3	Trace	2.2	87.00 ± 1.05
	9	77.0	2.0	N.D.	N.D.	79.00 ± 2.17

thalene and methylnaphthalenes are common components in such waste water³⁶, unpurified water³⁴, and coal-tar coatings of water-supply systems^{23,24} and this has led to the suggestion that chlorinated naphthalenes could be generated during the chlorine treatment of such waters and in the water-supply system. This suggestion was clearly supported by an earlier report³⁷ in which several chlorinated naphthalenes and other polynuclear aromatic hydrocarbons were found to be present in drinking water.

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