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Chlorine Dioxide Oxidation of Aromatic Hydrocarbons Commonly Found in Water

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With the advance of analytical instrumentation more and more organic compounds are being found in trace amounts in drinking water supplies (REPORT TO CONGRESS, 1975) and it is known that some of these compounds are formed during water treatment procedures used for disinfecting the raw water (BELLAR et al. 1974, ROOK 1976). There has been concern recently regarding the formation of chloroform and other halogenated organics by the reaction of chlorine with organic compounds present in raw water supplies (STEVENS et al. 1976). Alternative disinfection agents such as chlorine dioxide and ozone have been suggested and are used in some water treatment facilities. In order to assess the relative safety of chlorine dioxide as a disinfectant, it is important to know the chemical fate of the organic contaminants in the presence of aqueous chlorine dioxide.

Only a few studies of the reactions of chlorine dioxide with organic compounds have been reported in spite of its use in water disinfection and in the pulp and paper industry. Reactions of chlorine dioxide with oleic acid and triolein (LEOPOLD and MUTTON 1959, LINDGREN and SVAHN 1966), tertiary aliphatic amines (ROSENBLATT et al. 1963) and cyclohexene (LINDGREN and SVAHN 1965) have been investigated. A general review of the reactions of organic compounds with chlorine dioxide has been reported (GORDON et al. 1972). From earlier reports (FEUSS 1964), and from our own experience in chlorine dioxide preparation, it is highly probable that these workers used chlorine dioxide contaminated with chlorine.

This paper reports reactions of naphthalene and 1- and 2-methylnaphthalene in aqueous solutions of chlorine dioxide essentially free from chlorine (TAYMAZ and WILLIAMS 1979). These compounds have been reported to occur frequently in waters in the United States (JUNK and STANLEY 1975) and are common contaminants of industrial waste waters (SITTING 1974).

EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer, Model 457, infrared spectrometer using CCl_4 as solvent. Nuclear

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magnetic resonance spectra were determined using a Bruker, Model VP-80, spectrometer. Samples were dissolved in $CDCl_3$ and the internal standard was TMS. Gas-liquid chromatographic analyses were conducted on a Perkin-Elmer, Model 910, gas chromatograph equipped with a flame ionization detector and with helium as the carrier gas at a flow rate of 40 mL/min. The 1.8 m x 2 mm i.d. coiled glass column was packed with 3% OV-101 on Chromosorb 750, 80-100 mesh. The oven was programmed from 80 - 250°C at 5°C/min. The injector and detector temperatures were 240 and 270°C, respectively.

Gas chromatographic-mass spectrometric analyses were performed on a Finnigan, Model 4000, automated gas chromatograph-mass spectrometer. The 1.8 m x 2 mm i.d. coiled glass column was packed with 3% OV-17 on Chromosorb 750, 80-100 mesh. The carrier gas was helium at a flow rate of 20 mL/min. The mass spectrometer conditions were: electron impactionization energy 70 eV, temperature source 290°, separator 240°.

A thin layer chromatography plates were purchased from Analtech, Inc. and chloroform was used as the developing solvent. Naphthalene, 1- and 2-methylnaphthalene were purchased from BDH Chemicals; 1- and 2-Naphthoic acid and sodium chlorate from Fisher Scientific Company; 1-Chloronaphthalene and phthalic acid from CSI Chemicals; 1-Naphthaldehyde from Eastman Organic Chemicals and 2-chloro- and 1,4-Dichloronaphthalene from RFR Corporation. 1-Hydroxymethylnaphthalene was synthesized by $NaBH_4$ reduction of 1-naphthaldehyde. 2-Methyl-1,4-naphthoquinone was synthesized by the chromic acid oxidation of 2-methylnaphthalene. Chloro-derivatives of 1- and 2-methylnaphthalene were prepared according to the literature (HINTERHOFER and EICHBERGER 1977).

Generation of Chlorine Dioxide

Chlorine dioxide was prepared from sodium chlorate and oxalic acid (HUSBAND et al. 1955) using a sodium hydroxide wash-bottle to remove chlorine (BUGAENKO and ROSHCHEKTAEV 1967).

The chlorine dioxide concentration of the aqueous solutions was determined spectrophotometrically using acid chrome violet K and volumetrically using ferrous ammonium sulfate (TAYMAZ and WILLIAMS 1979).

Reaction of Naphthalene with Chlorine Dioxide

Naphthalene (30 mg; 0.23 mmol or 3 mg; 0.023 mmol) was stirred in aqueous chlorine dioxide solution (100 mL; 4 g/L; 5.97 mmol) for 3.5 days in the dark at room temperature in a stoppered flask. At the end of this time, nitrogen was bubbled through the solution to remove excess chlorine dioxide. The mixture was then extracted with diethyl ether (3 x 35 mL), the ether extracts combined and dried (Na_2SO_4) and evaporated to dryness using a rotary evaporator. The products were separated by thin layer chromatography, the bands visualized by UV, removed and extracted with MeOH and then subjected to GC/MS analysis. A portion of the separated products was treated with diazomethane solution and analyzed by GC and GC/MS. Identification of the products was by comparison of the retention time and spectral data with authentic standards.

Reaction of Methylnaphthalenes with Chlorine Dioxide

1-Methyl and 2-methylnaphthalene (30 mg; 0.21 mmol or 3 mg; 0.021 mmol) were treated with ClO_2 solution (100 mL; 4 g/L) under the same reaction conditions as for naphthalene and isolation and identification of the products were carried out similarly.

RESULTS AND DISCUSSION

It can be seen from Tables 1 and 2 that in dilute aqueous solutions chlorine dioxide reacts with naphthalene and methylnaphthalenes to produce chlorinated derivatives and oxidation products.

The reaction products from naphthalene (30 mg, Table 2 were separated by preparative thin layer chromatography into two main bands, visualized by UV irradiation, at R_f 0.80 and 0.02. GC and GC/MS analysis of the extract from the first band (R_f 0.80) showed the presence of naphthalene (85%) and a monochloronaphthalene (1.5%, Table 1, 1-2). Authentic 1- and 2-chloronaphthalenes had similar retention times and identical mass spectra and therefore no definite identification could be made with the trace amount isolated.

The extract from the second band (R_f 0.02) represented ca. 11% of the starting material. GC and GC/MS analysis of this extract could not detect any products amenable to GC analysis either before or after derivitization with diazomethane. Its ready solubility in sodium hydroxide and its low R_f on thin layer chromatography suggested the presence of phenolic or hydroxyl groups. The infrared spectrum showed the presence of -OH (3200-3600 cm^{-1}) and C = 0 (1680 cm^{-1}) peaks and the mixture gave a pink colour with alkaline ethanol, indicative of polyhydroxy naphthoquinones (PATAI 1974). ^{13}C-nmr spectrometry of the crude reaction mixture also indicated the presence of hydroxyl substituted aromatic carbons (peaks at 159 and 162 ppm) (STOTHERS 1972). It was therefore concluded that the majority of the oxidation products were polyhydroxyquinones or polyhydroxynaphthalenes. Reaction of chlorine dioxide with ten fold less naphthalene (3 mg, Table 2) under the same conditions as before gave complete reaction of the naphthalene with the formation of 1,4-dichloronaphthalene (1.2%) and phthalic acid (2.6%) (Table I, 1-3) and the complex mixture of polyhydroxylated naphthols/ naphthoquinones.

TABLE 1

COMPOUNDS IDENTIFIED FROM THE OXIDATION OF NAPHTHALENE, 1- AND 2-METHYLNAPHTHALENE WITH CHLORINE DIOXIDE

Name	Retention Time[a]	Compound Number
Naphthalene	1.0	1
Monochloronaphthalene	3.2	2
1,4-Dichloronaphthalene	3.5	3
Phthalic acid[b]	1.5	4
2-Methylnaphthalene	2.2	5
1-Chloro-2-methylnaphthalene	3.7	6
3-Chloro-2-methylnaphthalene	4.3	7
1,3-Dichloro-2-methylnaphthalene	5.8	8
2-Hydroxymethylnaphthalene	6.0	9
2-Naphthaldehyde	5.0	10
2-Naphthoic acid[b]	6.4	11
2-Methyl-1,4-naphthoquinone	5.1	12
1-Methylnaphthalene	2.4	13
4-Chloro-1-methylnaphthalene	3.8	14
2-Chloro-1-methylnaphthalene	4.2	15
2,4-Dichloro-1-methylnaphthalene	5.3	16
1-Hydroxymethylnaphthalene	6.0	17
1-Naphthaldehyde	5.0	18
1-Naphthoic acid[b]	6.1	19

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[a] Retention times relative to naphthalene (2.2 mins.).

[b] Identified as methyl esters.

TABLE 2

SUMMARY OF AQUEOUS CHLORINE DIOXIDE OXIDATION OF NAPHTHALENE, 1- AND 2-METHYLNAPHTHALENE[a,b]

Starting Material	Amount of Starting Material (mg)	Products Identified[c]
Naphthalene	3	3, 4
"	30	1, 2
2-Methylnaphthalene	3	4, 6
"	30	5 - 12
1-Methylnaphthalene	3	4, 14
"	30	13 - 19

[a] See Table 1 for product identification.

[b] The amount of chlorine dioxide was 400 mg for each reaction.

[c] Retention times and mass spectra were identical with those of authentic standards.

This is in contrast to the results reported earlier (SCHMIDT and BRAUNSDORF 1922) which indicated napthalene as unreactive toward chlorine dioxide. Other oxidizing agents have been reported to oxidize naphthalene under rather drastic conditions. Potassium permanganate oxidation produced phthalonic acid (GARDNER and NAYLOR 1943), whereas peracetic acid oxidation gave o-carboxycinnamic acid (AUGUSTINE 1969). Oxidation with hydrogen peroxide under UV irradiation was reported to give 1- and 2-naphthol (BOYLAND and SIMS 1953).

The reaction products from 2-methylnaphthalene (30 mg, Table 2) were separated by TLC and analysed by GC/MS. Analysis of the TLC extract (R_f 0.83) showed 2-methylnaphthalene (40%) and <1% of other identifiable products. The chlorinated derivatives, 1-chloro, 3-chloro-, and 1,3-dichloro-2-methylnaphthalene, and simple oxidation products, 2-naphthoic acid and 2-methyl- 1,4-naphthoquinone were identified by comparison of retention time and mass spectra with authentic compounds. 2-Naphthaldehyde and 2-hydroxymethylnaphthalene were identified as such since they had the same mass spectra but different retention times to authentic 1-naphthaldehyde and 1-hydroxymethylnaphthalene.

The majority of the products (R_f 0.03) were polyhydroxylated methylnaphthalenes or quinones as evidenced by ^{13}C-nmr, ir and their colour reaction with alkaline ethanol. When the reaction was repeated with a lesser amount of 2-methylnaphthalene (3 mg, Table 2) the only identifiable products were 1-chloro-2-methylnaphthalene and phthalic acid.

Similar treatment of 1-methylnaphthalene gave reaction products corresponding to those from 2-methylnaphthalene. Low levels of 1-methylnaphthalene (3 mg, Table 2) gave phthalic acid and 4-chloro-1-methylnaphthalene. Higher levels of 1-methylnaphthalene (30 mg, Table 2) gave a complex mixture of products (37.5%) and unreacted 1-methylnaphthalene (60%). 2-Chloro-, 4-chloro-, and 2,4-dichloro-1-methylnaphthalene, 1-hydroxymethylnaphthalene, 1-naphthaldehyde and 1-naphthoic acid (Table 1, 13-19), which were present in trace amounts (<1%) were identified by comparison of retention times and mass spectra with those of authentic standards.

The products are consistent with those reported by other workers investigating the oxidation of 1-methyl- and 2-methylnaphthalenes. The products from dilute nitric acid oxidation were 1- and 2-naphthoic acids, respectively (NOLLER 1965). Chromium trioxide-acetic acid oxidation of 2-methylnaphthalene gave 2-methyl-1, 4-naphthoquinone, and 1-methylnaphthalene produced 5-methyl-1,4-naphthoquinone (NOLLER 1965). Production of quinonoid compounds when ClO_2 is reacted with polynuclear aromatic compounds such as acenaphthene, anthracene, carbazole, chrysene and phenanthrene has been reported (THIELEMANN 1972).

Based on the recovery of unreacted starting material in the 30 mg reactions the order of reactivity with aqueous chlorine dioxide was 2-methyl >1-methyl > naphthalene. The solubilities in water of these compounds were very low so that the 30 mg reactions were mainly heterogeneous while the 3 mg reactions were mainly homogeneous reactions. It has been reported that the products from the reaction of chlorine with naphthalene differ between heterogeneous and homogeneous reaction conditions (SMITH et al. 1977). This appears to be true for the chlorinated products in these chlorine dioxide reactions but the complexity of the reaction products makes interpretation difficult.

The initial chlorine dioxide solutions contained no detectable chlorine (TAYMAZ and WILLIAMS 1979), with a lower detection limit of 0.1 mg chlorine/L. However, the presence of trace amounts of chlorine in the chlorine dioxide solutions cannot be excluded. Whether the low levels of chlorinated products found in our reactions are due to chlorine present as a contaminant or formed from decomposition of the chlorine dioxide or chlorite ion cannot be decided. Despite the previous reports that chlorine dioxide did not react with naphthalene, we have shown that chlorine dioxide does react with naphthalenes under aqueous conditions. The extention of this work to the identification of reaction products under conditions used in water treatment plants needs to be carried out.

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