

THE PRODUCTION OF BROMOPHENOLS RESULTING FROM THE CHLORINATION OF WATERS CONTAINING BROMIDE ION AND PHENOL

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Abstract—The formation of 2,4,6-tribromophenol is shown to result from the chlorination of water containing phenol and bromide ion at pH 7.4. Direct bromination with hypobromous acid is compared with bromination by hypochlorous acid and bromide ion. Under conditions where HOCl is not limiting, a higher yield of bromine substitution products can be expected from bromination by HOCl + Br⁻ than by direct bromination by HOBr.

INTRODUCTION

Much attention has been given to the formation of chlorinated organics, both volatile and non-volatile, during the treatment of natural waters with chlorine (Bellar *et al.*, 1974; Carlson *et al.*, 1975; Glaze & Henderson, 1975; Jolley, 1975; Symons *et al.*, 1975; Glaze *et al.*, 1976; Jolley *et al.*, 1976; Kopperman *et al.*, 1976; Rook, 1976).

The formation of volatile brominated organics (bromoforms and mixed haloforms) has also been recognized (Rook, 1974; Kissinger & Fritz, 1976; Symons *et al.*, 1975) and attributed to the action of chlorine on the bromide ion present in these waters (Rook, 1974; Morris, 1976):



Although bromide levels are generally low, 0.2 ppm (Bowen, 1966), 0.1 ppm (Simmons and Sweetman, 1977) levels as high as 2.2 ppm have been reported (Houghton, 1946). Recent droughts in California have demonstrated that salt water, containing 65 ppm Br⁻, can enter into drinking water sources, enhancing natural bromide levels (Rasmussen, 1977). Wastewaters from the photographic industry may be a source of bromide, as well as anti-knock additives in gasoline (Rook, 1975).

Brominated phenols, indoles and anisoles formed from precursors during BrCl disinfection of wastewater effluent, have been identified in fish by Kuehl *et al.* (1978). In separate experiments he has shown that some of these brominated compounds readily bioaccumulate.

Chlorinated phenols have often been detected in treated wastewaters (Burttschell *et al.*, 1959; Morris, 1975; Murphy *et al.*, 1975; Rockwell & Larson, 1978). It is possible that brominated phenols could be formed during the chlorination process if bromide is present in the chlorinating water. This study investigates chlorine-induced bromination using phenol as a model compound.

MATERIALS AND METHODS

Reagents

The water used was acid-distilled to remove ammonia. Aqueous phenol was prepared from redistilled analytical grade liquified phenol. The phenol concentration during all reactions was 1 ppm. Hypochlorous acid was generated by bubbling chlorine gas through water. Hypobromous acid was produced by adding elemental bromine to water. The reagents were standardized according to Standard Methods (1976). Potassium bromide was used as the source of the bromide ion. The phosphate buffer (pH 7.4) was made according to Standard Methods (1976).

Apparatus

A Model 700 F & M Laboratory Gas Chromatograph was used with a carrier gas of 95% argon, 5% methane, at a flow rate of approximately 60 ml/min. An electron capture detector with a tritium source (maximum temperature 225°C) was used because of its high sensitivity for halogenated compounds.

Column I: 6 mm i.d. × 2 M glass column packed with 4% Ultraphase SE 30 + 6% OV 210 on 80/100 Chromosorb W.

Column II: 6 mm i.d. × 2 M glass column packed with 3% OV 1 on 80/100 Chromosorb W.

Procedure

Silylated Erlenmeyer flasks (25 ml) were used for most reactions. Larger volumes were required for a mass spectrometry analysis. Buffered phenol solution (pH 7.4) and various concentrations of HOBr or HOCl and KBr were added to a flask, the solution mixed, and the reaction timing begun. The ratios of HOBr:phenol or HOCl:KBr:phenol were calculated on a molar basis. The reactions were stopped after 1 h contact time by the addition of excess sodium thiosulfate to destroy the HOCl and/or HOBr in the solution. The reaction products were concentrated using XAD-4 resin (Rohm & Haas), derivatized with bis-trimethylsilyl acetamide (BSA), and analyzed by electron capture GC as described by Prater *et al.* (1979).

Standard 2,4,6-tribromophenol solutions were made up in 20 ml water buffered at pH 7.4 and carried through the same concentration and derivatization steps as the reaction volumes. The average recovery for these "water" standards, compared to standards of 2,4,6-tribromophenol made up directly in pyridine and derivatized with BSA, was 97%. Standard curves of these water standards were prepared daily. Peak heights of the trimethylsilyl derivatives of

Table 1. Bromination of phenol by hypobromous acid

HOBr:phenol	2,4,6-tribromophenol (ppm)
10:1	1.5
8:1	2.0
4:1	1.0
2:1	0.2
1:1	0.1

2,4,6-tribromophenol were utilized for quantitation. Linear regressions of these standard curves gave correlation coefficient values, $r \geq 0.987$.

RESULTS AND DISCUSSION

Direct bromination with HOBr was tested at four ratios of HOBr:phenol (HOBr as measured is actually total free bromine, i.e. HOBr + OBr⁻; $pK_a = 8.7$). The main product in all cases was 2,4,6-tribromophenol. In some cases small amounts of 2,4- and 2,6-dibromophenol, close to the limit of detection, were found. Table 1 shows the resulting concentrations of 2,4,6-tribromophenol. The amount of the 2,4,6-tribromophenol product decreased as the HOBr:phenol ratio was increased from 8:1 to 10:1. This may result from a further bromination product (e.g. pentabromophenol, which would not appear on the chromatogram under the conditions used), or may be due to ring cleavage (Moye & Sternhell, 1966).

Chlorine-induced bromination, with equimolar amounts of hypochlorous acid (actually total free chlorine, i.e. HOCl + OCl⁻, $pK_a = 7.5$) and KBr added, produced 2,4,6-tribromophenol. Table 2 shows that the amount of 2,4,6-tribromophenol increased with increasing HOCl and KBr. No other products were found, indicating that the reaction HOCl + Br⁻ → HOBr + Cl⁻ is much faster than the stepwise chlorination of phenol.

The identity of the 2,4,6-tribromophenol product produced by HOCl and KBr was first established by comparison of its retention time on two chromatographic columns, with the retention times of a 2,4,6-tribromophenol standard. Confirmation was provided by gas chromatography-mass spectrometry (AEI MS 30) on a "scaled up" reaction of HOCl:KBr:phenol (10:10:1).

Comparing Tables 1 and 2 shows that the extent of reaction at pH 7.4 is less where the oxidation of Br⁻ to HOBr must precede the bromination of phenol. (Since the pK_a of HOCl is 7.5, the [HOCl] ≈ [OCl⁻] at pH 7.4. At a lower pH the reaction HOCl + Br⁻ → HOBr + Cl⁻ would be expected to

Table 2. Chlorine-induced bromination of phenol by equimolar concentrations of HOCl and KBr

HOCl:KBr:phenol	2,4,6-tribromophenol (ppm)
10:10:1	2.1
8:8:1	1.9
4:4:1	0.7
2:2:1	0.02

Table 3. Chlorine-induced bromination of phenol with excess HOCl

HOCl:KBr:phenol	2,4,6-tribromophenol (ppm)
5:10:1	0.6
10:5:1	1.8
5:5:1	0.8
10:1:1	0.3
5:1:1	0.2

proceed more rapidly.) Additional reactions were conducted with an excess of HOCl and one reaction with HOCl:KBr:phenol of 5:10:1 (Table 3). This last reaction shows the limiting effect of the HOCl concentration. The 2,4,6-tribromophenol produced is approximately that of the reaction 5:5:1. An excess of HOCl as expected increases the production of 2,4,6-tribromophenol. Indeed, the 2,4,6-tribromophenol is in excess of that found by the corresponding bromination with hypobromous acid. For example, with a tenfold excess of HOCl and equimolar concentrations of bromide and phenol, 0.3 ppm of 2,4,6-tribromophenol was produced, as compared to 0.1 ppm produced by direct bromination with equimolar concentrations of HOBr and phenol solution. This would be explained by some fraction of the HOBr participating in oxidation reactions with the phenol. The resulting bromide, while excess HOCl is present, can again be oxidized to HOBr. This "recycling" of the Br⁻ will be especially significant during the disinfection of natural waters, where the primary source of "chlorine demand" is for oxidation reactions (Jolley, 1973).

Where the hypochlorous acid was 5 to 10 times in excess of the Br⁻, chlorine substitution appears to have occurred. This is indicated by comparison of the reaction of HOCl:phenol (10:1), included as a control, with the above reactions. Figure 1 shows the products of the HOCl:phenol (10:1) reaction and the HOCl:KBr:phenol (5:1:1 and 10:1:1) reactions. The HOCl:phenol reaction produced two peaks (retention times [R.T.]: 2.2 and 3.2 min). These peaks are assumed to represent chlorinated phenols. These peaks also appear in the two HOCl:KBr:phenol reactions, indicating that there is enough excess HOCl to produce chlorinated products. A new peak (R.T.: 4.5 min) is also present. This peak and the two "chlorination" peaks (R.T.: 2.2 and 3.2 min) increased from the 5:1:1 to 10:1:1 (HOCl:KBr:phenol) reactions (the chromatograms shown are for different final volumes of concentrated products). The position of the peak (R.T.: 4.5 min), which is after the chlorination peaks (R.T.: 2.2 and 3.2 min), after the dibromophenol peaks (R.T.: 2.8 min), and before the 2,4,6-tribromophenol (R.T.: 6.2 min), suggests a mixed bromochlorophenol, possibly a dibromochlorophenol.

CONCLUSIONS

This study suggests that chlorination, bromination and mixed halogenation products could be expected

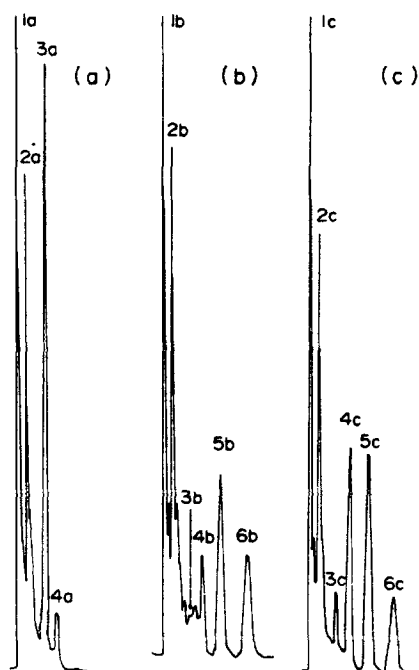


Fig. 1. (A) Gas chromatogram of products from the reaction of HOCl and phenol (10:1). (1a) and (2a) solvent peaks. (3a) chlorinated product (retention time 2.2 min), (4a) chlorinated product (retention time 3.2 min). (B) Gas chromatogram of products from the reaction of HOCl, KBr, and phenol (5:1:1). (1b) and (2b) solvent peaks, (3b) chlorinated product (retention time 2.2 min), (4b) chlorinated product (retention time 3.2 min), (5b) is suggested to be a bromochlorophenol (retention time 4.5 min), (6b) 2,4,6 tribromophenol peak (retention time 6.2 min). (C) Gas chromatogram of products from the reaction of HOCl, KBr, and phenol (10:1:1). Identity of peaks 1c-6c the same as described above for 1b-6b. Column: 4% SE-30 and 6% OV 210, isothermal at 181°C.

upon chlorination of waters containing bromide ion. The extent of formation of the chlorinated organics during water treatment can also be affected by the presence of ammonia in the water. This is attributed to the rapid formation of chloramines, which do not react to the same extent as does HOCl (Jolley, 1975). Morris (1976) has found that the reaction of HOCl with Br^- is faster than the reaction of HOCl with NH_3 when the pH is below 7.8 and $[\text{Br}^-] = [\text{NH}_3]$. In waste water effluent HOBr, chloramines, and bromamines, singly or in combination, may be formed, depending on the pH and concentration of NH_3 and Br^- (Inman & Johnson, 1978). Phenol can serve as a useful model compound to test if bromination occurs during the chlorination of wastewaters containing high concentrations of bromide and ammonia.

Chlorination in the presence of bromide ion will likely produce largely brominated products where $[\text{Br}^-]$ approaches the free chlorine dose or mixed halogenation products where the $[\text{Br}^-]$ is small. A high yield of bromine substitution is the result of recycling of bromide while HOCl remains until a stable reaction product results. Bromide ion concen-

tration should not be ignored as a water quality parameter.

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