The Chlorination of Benzoic Acid in Aqueous System by Use of Oxidizing Acids.

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Benzoic acid is chlorinated in aqueous solution by means of sodium chlorate or potassium permanganate and hydrochloric acid. The oxidant in this reaction must have a redox potential above that of chlorine. Free chlorine is ineffectual. The presence of high chloride-ion concentration resulted in the greatest yield in the shortest time. It has been established experimentally that chlorinated quinones, formed during the reaction, result from oxidation of the benzoic acid before halogenation.

Two analogous chlorinations have been investigated, namely, Otto's original reaction (*Annalen*, 1862, **122**, 142) and one in which potassium permanganate was used in place of the potassium or sodium chlorate. The reactions were carried out with vigorous stirring at approximately 80°. The oxidant was added dropwise in aqueous solution during 70 min.

A 30% yield of *m*-chlorobenzoic acid was obtained from benzoic acid by using sodium chlorate, and a 50% yield by using potassium permanganate. Yields of crude product, which contained chlorinated quinones, were consistently 75—80%. The purification of this material was difficult. The method adopted involved hydrolysis of the quinone side-products with sodium hydroxide to a water-soluble compound which could be washed out after acidification. Recrystallization then gave the pure product.

The success of potassium permanganate and hydrochloric acid in the chlorination of benzoic acid, which does not appear to have been recorded, demonstrates that sodium chlorate and a chloride in acid media are not specific reagents for chlorination in Otto's reaction. In the majority of reactions, hydrochloric acid furnished both the chloride and the hydrogen ion; 20%-HCl was the best concentration. Less concentrated hydrochloric acid gives lower yields of *m*-chlorobenzoic acid, and much more slowly. The rate is markedly increased by concentrated hydrochloric acid but its use is impracticable because of the gross loss of hydrogen chloride gas at the reaction temperature. On replacement of hydrochloric acid by chlorine gas in combination with the equivalent amounts of sodium chlorate or potassium permanganate in sulphuric acid, little or no chlorination occurred. Use of hydrochloric acid and molecular chlorine was likewise unsuccessful. It appears that chlorination is effected only when chlorine is liberated *in situ*.

Attempts to chlorinate the various monochlorobenzoic acids resulted in 98% recovery of the *p*-chloro-, 93% recovery of the *m*-chloro-, and partial chlorination of the *o*-chloro-isomer, and no quinone-like by-products. A similar result was obtained with 3 : 4-dichloro-benzoic acid. It is therefore concluded that the chloranil and other chlorinated by-products must be formed from the benzoic acid and not from the chloro-acids.

Oxidation of a 1 : 1 mixture of benzoic and *m*-chlorobenzoic acid with potassium permanganate and sulphuric acid showed that 75% of the *m*-chlorobenzoic acid could be recovered but only 25% of the benzoic acid, the products being carbon dioxide and chlorine. Sultanor [*J. Gen. Chem.* (*U.S.S.R.*), 1946, **16**, 1835] has demonstrated the relatively high thermal stability of the chlorobenzoic acid. By greatly prolonging the reaction time in the halogenation of benzoic acid by these reagents there is further chlorination : a reaction time of several days, and use of increased amounts of sodium chlorate and hydrochloric acid, re-sulted in the formation of (unidentified) dichlorobenzoic acids. Separation either as barium salts or by chromatography (Marvel and Rands, *J. Amer. Chem. Soc.*, 1950, **72**, 2642) failed.

From the evidence it would appear that the chloranil is formed by decarboxylation of benzoic acid and chlorination of the resulting benzoquinone. Analysis of the gaseous products of chlorination of benzoic acid revealed considerable quantities of carbon monoxide, but there are several possible sources for this.

EXPERIMENTAL

Preparation of m-*Chlorobenzoic Acid.*—(*a*) Potassium permanganate (9 g.) in water (200 ml.) or (*b*) sodium chlorate (3·7 g.) in water (100 ml.) was added during 60—75 min. to benzoic acid (12·2 g.) and 5·5N-hydrochloric acid (200 ml.) stirred under reflux at 80—90°. After a further 30 minutes' stirring the mixture was cooled and the pale orange product collected, washed, and dried (12 g.; m. p. 125—140°). This was dissolved in the minimum amount of 10% sodium hydroxide solution, and the solution was filtered, diluted, and acidified with 20% sulphuric acid. The precipitate was collected and most of the pink colour (chloranilic acid) was washed out with water. Recrystallisation from aqueous alcohol (charcoal) and then benzene gave *m*-chlorobenzoic acid (7·5 g.), m. p. and mixed m. p. 157—158° (Found : C, 53·3; H, 3·3. Calc. for $C_7H_5O_2Cl$: C, 53·7; H, 3·2%).

Oxidation of a 1 : 1 *Mixture* (*by wt.*) *of* m-*Chlorobenzoic Acid and Benzoic Acid.*—The finely ground mixture (5 g.) was refluxed with potassium permanganate (15 g.) and 25% sulphuric acid (150 ml.) overnight, then extracted with ether, and the ether evaporated to give 2·52 g. of mixed acids (Found : equiv., 147, 146. Calc. for 75% $C_7H_5O_2Cl$ + 25% $C_7H_6O_2$: equiv., 147·9).

Prolonged Chlorination of Benzoic Acid.—In a 3-l. round-bottomed flask fitted with a reflux condenser are placed benzoic acid (20 g.) and concentrated hydrochloric acid (1200 ml.). A solution of sodium chloride (53 g.) in water (300 ml.) is added in 10-ml. quantities at 10-min. intervals, and the mixture refluxed for 6—7 days. The clear supernatant liquid is decanted from the dark orange oil. Upon cooling, about 20 g. of dichlorobenzoic acid are obtained, a further 9 g. (total yield 92%) being obtained from the oil by the procedure used in the removal of chloranil from *m*-chlorobenzoic acid (Found : equiv., 190, 198. Calc. for $C_7H_4O_2Cl_2$: equiv., 191).

Test for Carbon Monoxide evolved in the Chlorination.—The apparatus is that used in the preparation of *m*-chlorobenzoic acid but instead of the reflux condenser is a tube leading consecutively into two gas wash-bottles containing arsenious oxide (10 g.) and sodium hydroxide (21 g.) dissolved in water (200 ml.), two drying towers containing phosphoric oxide, a U-tube containing iodine pentoxide heated to 150° by an oil-bath, and a 250-ml. suction flask containing a solution of starch and potassium iodide. A water aspirator is attached to the last container and gentle suction is maintained. The reaction flask is heated to 80—90°, and air drawn through the system for 45 min. as a test for the iodine pentoxide which is first purified by Vandaveer and Gregg's method (*Ind. Eng. Chem. Anal.*, 1929, **1**, 129). Potassium permanganate is then added and, *ca.* 20 min. after the first addition, a blue colour appears in the starch solution, indicating the presence of carbon monoxide. Its presence was also proved by running the gases through fresh blood instead of iodine pentoxide and the starch–iodide indicator, and application of the hæmoglobin test.

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