CCCXXXVI.—*The Mechanism of the Bromination of Phenol in Aqueous Solution.*

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It has been shown by Dinwiddie and Kastle (*Amer. Chem. J.*, 1911, **46**, 502) that when phenol is brominated in aqueous solution only tribromophenol and tribromophenol bromide are formed, whereas on bromination in non-hydrolytic solvents such as chloroform, carbon tetrachloride, carbon disulphide, etc., substitution takes place with the formation of a dibromophenol, probably 2:4-dibromophenol. They suggest that the peculiar behaviour of phenol in aqueous solution is due to its existence in solution in the quinonoid form, the reaction taking place according to the following scheme.

In order to test this suggestion, the action of bromine on phenol in carbon tetrachloride solution was investigated. Standard solutions of phenol and of bromine in carbon tetrachloride were prepared. Known volumes of each solution were mixed, and after standing, an aqueous solution of potassium iodide was added, and the whole quickly shaken. The liberated iodine was then estimated by titration with standard sodium thiosulphate solution.

It was thus found that although phenol be left with excess of bromine in carbon tetrachloride solution during several hours, much less bromine reacts than is necessary to form the tribromoderivative. If to such a mixture water be added, the colour of the bromine becomes less intense; tribromophenol is immediately formed in the aqueous layer, and redissolves in the carbon tetrachloride.

A known volume of the phenol solution was mixed with a known excess of the bromine solution, and at certain definite intervals aliquot portions of the mixture were removed and titrated. On plotting the time against the amount of bromine reacted, a continuous curve was obtained, many days, however, elapsing before the tribromophenol stage was reached. Hence the statement of Dinwiddie and Kastle (*loc. cit.*) concerning the formation of dibromophenol expressed only a part of the truth. The velocity of the reaction also varied regularly with the concentrations of the reacting substances.

To phenol (20 grams) in carbon tetrachloride (200 c.c.), the requisite quantity of bromine solution to form monobromophenol was slowly added (34.1 grams of bromine in 200 c.c. of carbon tetrachloride) in order to test whether the product would consist mainly of a mixture of phenol and tribromophenol, or of monobromophenol. After a few minutes, when the colour of the bromine had almost disappeared, the carbon tetrachloride was evaporated, and a theoretical yield of a mixture of *o*- and *p*-monobromophenol was obtained. On similar treatment with twice the quantity of bromine, a theoretical yield of 2:4-dibromophenol was obtained, the reaction in this case taking many hours to complete. The above compounds were also prepared by treating phenol solution with excess of the bromine solution, and adding an aqueous solution of potassium iodide at the necessary time, calculated on the results of previous titrations. This method, however, proved to be less satisfactory than the former.

The degree of moisture of the solutions was also found to have an effect on the velocity of the reaction. When the moist solutions were dried with calcium chloride, the reaction was found to be retarded, and on further dehydration with zinc chloride or phosphoric oxide, the bromination was retarded still more.

2812 THE MECHANISM OF THE BROMINATION OF PHENOL, ETC.

From these observations and experiments, theoretical conclusions can be drawn bearing on the mechanism of the bromination of phenol. If the reaction takes place by direct substitution, there is no reason why bromination should not be effected as readily in non-hydrolytic solvents as in water. Also the accelerating effect of a trace of water is inexplicable on this theory. The different characters of the reactions in water and carbon tetrachloride are illustrated by the difference in velocity and in products of incomplete bromination. However, these facts and several others are explained on the assumption that the slow reaction between dry phenol and dry bromine in an inert solvent is one of direct substitution, whereas the rapid bromination of phenol in aqueous solution is due to the action of hypobromous acid, formed by the interaction of bromine and water. The hypobromous acid probably reacts with the phenol by addition, with subsequent elimination of water.

The removal of the hypobromous acid from the system during bromination in aqueous solution causes the reaction

to proceed to completion from left to right, hydrobromic acid being formed as a by-product. The water in the reaction cycle is constant in amount and therefore acts as a pseudo-catalyst. This explains the accelerative action of a trace of water in the bromination in carbon tetrachloride solution.

In order to test the above suggestion, the action of hypobromous acid on phenol was investigated. A very dilute solution of hypobromous acid was made from bromine water and zinc oxide. On treatment with a little phenol a slight white precipitate was obtained, and potassium iodide-starch paper proved that the hypobromous acid had reacted. A large volume of the suspension having been extracted with a little carbon tetrachloride, the precipitate was proved to be tribromophenol.

The behaviour of hypobromous acid towards phenol is evidence in favour of the mechanism suggested, which is further supported by the fact that bromination is retarded by conditions hindering the formation of hypobromous acid from bromine and water. One such condition would be bromination in the presence of a large

excess of hydrobromic acid, or indeed in any strongly acid solution. Pope and Wood (T., 1912, **101**, 1823) describe the bromination of phenol in concentrated hydrobromic acid solution, and state that the bromine is absorbed very slowly by the phenol. They recommend this method for the preparation of dibromophenol. Dinwiddie and Kastle (*loc. cit.*) mention the retarding effect of glacial acetic acid, and Hewitt, Kenner, and Silk (T., 1904, **85**, 1225) show that concentrated sulphuric acid mixed with the glacial acetic acid retards the bromination still more.

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