CLXVIII.—*Studies in the Reactivity of Aromatic Hydroxyl Groups. Part I.*

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THIS work has been undertaken with a view to investigate the influences affecting the reactivity of hydroxyl groups in aromatic compounds. Many investigations with the same general object have been carried out, and those most closely connected with the work now described are the determinations of velocity coefficient by Panoff (*A.*, 1903, ii, 357) for the reaction between acetic anhydride and various phenols in benzene solution at 100°, and by Bernoulli and Goar (*Helv. Chim. Acta*, 1926, **9**, 730) for the reaction between benzoyl chloride, or substituted benzoyl chlorides, and a number of phenols.

In the present case the reaction between phenols and acetyl bromide in ethyl acetate solution at 0° is used, and the half-periods of the reactions are obtained from a time–titration curve. The reciprocals of these half-periods are the comparative figures quoted.

A previous attempt on similar lines, using ether as solvent, failed owing to the ether unexpectedly taking part in the reaction (Bassett and Taylor, J., 1929, 1568).

The half-periods obtained for the compounds studied (in minutes) were as follows : Phenol, 14·5 (1) ; *o*-cresol, 25·25 (0·574) ; *m*-cresol, 8·5 (1·71) ; *p*-cresol, 6·17 (2·35) ; thymol, 31 (0·468) ; carvacrol, 20 (0·725). The reciprocals of these figures, against phenol as unity, are given in parentheses. Panoff, and Bernoulli and Goar (*locc. cit.*), obtained similar results in the reactions which they studied, except that they found *m*-cresol to react slightly more rapidly then *p*-cresol. In all cases they found ortho-substituted phenols to react slowly.

The figures obtained in the present work do not depend upon the particular high concentrations chosen, since the ratio for phenol and thymol was found to be unchanged at half the concentration, although for some phenols the more dilute solution gives an inconveniently slow reaction.

While changes in the concentration of the phenol affect the rate of the reaction, material changes in the proportion of acetyl bromide (*e.g.*, 0·75, 1, 1·25 equivs. per equiv. of phenol) have no effect. This suggests that the reaction measured is not the simple bimolecular one, but that there is a preliminary rapid addition of the two reactants, followed by a slower unimolecular breakdown, which is the reaction actually measured. The point may be of importance, especially in connexion with the " ortho effect."

The effect of adding a little water to the reacting mixture is interesting. The titrations fell as though no water were present, but before reaching the lowest point they began to rise again, finally reaching a point nearly equal to the initial titration. It is evident, therefore, that when only a little water is present the formation of phenyl acetate proceeds almost to completion and is followed by a slower hydrolysis. This preferential reaction of acetyl bromide with phenol instead of with water is curious, since in the absence of phenol the reaction with water is very rapid. It may perhaps be connected with the above suggestion as to the rapid formation of an addition compound of phenol and acetyl bromide as the first stage in the reaction. Such a course for the reaction had already been inferred from the work done with ethereal solutions (*loc. cit.*). It is proposed to carry out these determinations on a larger number of phenols, selected with a view to throw light on the problems involved.

EXPERIMENTAL.

The ethyl acetate was treated with acetyl chloride to remove final traces of alcohol, washed with sodium carbonate and water, dried, and distilled. The acetyl bromide was of A.R. quality, and was found to be of about 94% purity, the remainder being acetic acid and hydrogen bromide. For the purpose of calculating equivalents, it was treated as the pure substance, since it was shown that comparatively large variations in the amount of acetyl bromide had no effect on the half-period of the reaction. The phenols used were carefully purified and dried.

A determination was carried out by dissolving in ethyl acetate a weight of the phenol equivalent to 1 c.c. of acetyl bromide and making up the solution to 8 c.c. To this solution 1 c.c. of acetyl bromide was added after both had been brought to 0°. The mixture was well shaken and quantities of 1 c.c. were withdrawn at suitable intervals (commencing at 1 min. from the time of mixing), added to about 100 c.c. of water, and titrated with *N*/5-sodium hydroxide. The reaction was carried out in a small stoppered flask which was maintained at 0° throughout with crushed ice. The small quantities of liquid used permitted of very efficient cooling, and the 1 c.c. of the mixture withdrawn for each titration dissolved quickly and almost completely in about 100 c.c. of water, thus permitting practically instantaneous quenching of the reaction. Frequent shaking of the flask was necessary in order to secure uniform results. The infinity reading was usually taken on the following day, and was shown to be unchanged in the course of a further 24 hours. It was found most satisfactory to derive the zero titration from that taken at one minute, and a typical example is given. The half-periods quoted are the means of two or three concordant determinations.

Carvacrol.

Titrations of 1 c.c. of the reaction mixture at stated intervals with 0·1945*N*-sodium hydroxide.

t (mins.)	1	4	7	10	16	26	∞
C.c.	15·3	14·5	13·95	13·35	12·55	11·55	8·65

Zero titration derived from curve = 15·6 c.c.

Half value = 12·125 c.c. Half-period = 20 mins.

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