9. *An Interpretation of the Sandmeyer Reaction. Part IV. Catalysed Decomposition of Diazonium Kations by Anionoid Complexes with Special Reference to those of Cobalt and Ferric Iron.*

By Herbert H. Hodgson, Stanley Birtwell, and John Walker.

The catalysed decompositions described in Part III (J., 1942, 720) have now been conducted for both diazotised *m*- and *p*-nitroaniline in hydrochloric acid solution of *d* 1·16. At this acid concentration, ferric chloride and cupric chloride are practically as efficient as cuprous chloride. Cobalt chloride in the blue complex anionoid condition appreciably catalyses the reaction, whereas in the pink kationoid state it has lost its catalytic influence. These experiments provide additional evidence for the anionoid mechanism suggested in Part I (J., 1941, 770).

In Part III (*loc. cit.*) replacement of the diazonium group in *p*-nitrobenzenediazonium chloride by chlorine was effected by anionoid complexes in two concentrations of hydrochloric acid, and the alteration in water content affected the yields of *p*-chloronitrobenzene. Since increase in hydrogen chloride concentration resulted in increased replacement by chlorine, it follows that this must be ascribed to the increase in concentration of the anionoid complex in the stronger acid, the simultaneous reaction by anionoid water with production of *p*-nitrophenol showing a corresponding decrease. It appeared of interest, therefore, to carry out the reactions in concentrated hydrochloric acid (*d* 1·16), for which purpose solutions of *m*- and *p*-nitroaniline were diazotised by addition of solid sodium nitrite, and the resulting diazonium salt solutions decomposed, while just boiling, by the addition of metallic chlorides whose metals are prone to form complex halogeno-anions, *viz.*, those of aluminium, antimony chromium, cobalt, copper (cuprous and cupric), iron (ferric), mercury(ic), nickel, tin (stannic), zinc. On addition of the sodium nitrite, sodium chloride was precipitated, so that all the solutions were saturated thereby, and all the decompositions were thus carried out under practically the same conditions, except for the small differences in boiling points of the various solutions. Under the more concentrated conditions, the yield of *p*-chloronitrobenzene by hydrochloric acid alone became 54·4% against 41% under the more dilute conditions of Part III (*loc. cit.*, Table III), indicating that it is the chlorine of the un-ionised hydrogen chloride which is the active agent in the replacement and not the chlorine ion (cf. Part I, J., 1941, 770). This result is in substantial agreement with the earlier views of Hantzsch (*Ber.*, 1900, **33**, 2534) and the deductions of Waters (J., 1939, 868) on the activity of un-ionised hydrogen chloride in the decomposition of benzenediazonium chloride in very concentrated aqueous solution, or in concentrated hydrochloric acid, where the yield of chlorobenzene falls off very rapidly as the solution is diluted.

A noteworthy feature of the decompositions of diazotised *p*-nitroaniline is the efficiency of ferric and cupric chlorides as catalysts, a 77·6% yield of *p*-chloronitrobenzene (previously 63%) being obtained, *i.e.*, the same as that with cuprous chloride under like conditions. On the other hand, aluminium chloride only slightly increased the yield over the blank, and calcium, chromium, mercuric, and zinc chlorides had no effect upon it. In marked contrast, antimony trichloride reduced the yield to 37·1% (blank, 54·4%), a similar effect having already been observed under more dilute conditions (41% to 32%), and it would appear that antimony chloride activates anionoid water preferentially to chlorine.

The experiments with cobalt chloride have an interesting bearing on its ionic state. When anhydrous, or in solutions of high chloride-ion concentration, it is blue, owing, it is generally supposed, to the $[CoCl_4]^{--}$ anion, and such solutions afford a 70·9% yield of chloro-compound, whereas the more aqueous pink solution, containing $Co(H_2O)_6Cl_2$, gives a yield of only about 10%, *i.e.*, the same as that in hydrochloric acid at the same dilution with no cobalt present. Also, when *p*-nitroaniline is diazotised by Hodgson and Walker's method (J., 1933, 1620) in concentrated sulphuric–glacial acetic acid solution, and then decomposed by the blue solution of cobalt chloride in concentrated hydrochloric acid, the yield is decreased to that of the blank (40·5%), showing that the dissociation of the complex ion in the composite solution had inhibited its efficiency for replacement of the diazonium group by chlorine. These experiments with cobalt chloride support the interpretation given for the previous results with cupric chloride, and with copper sulphate and sodium bromide (Part III), that the decomposition is due to the complex $[CuCl_4]^{---}$ or $[CuBr_4]^{---}$ anion. In this connection, it is of interest that anhydrous cupric bromide is black, this colour being ascribed to $Cu[CuBr_4]$, and that the addition of sodium bromide to copper sulphate in the experiments referred to in Part III (*loc. cit.*) produced a colour change from blue to green-brown, due probably to the formation of the $[CuBr_4]^{--}$ anion; in like manner, cupric chloride is held to be $Cu[CuCl_4]$ (cf. Emeléus and Anderson, "Modern Aspects of Inorganic Chemistry," 1938, p. 144).

The great efficiency of ferric chloride in concentrated hydrochloric acid solution must also be ascribed to the formation of a complex anion, and there is considerable evidence for the existence of $HFeCl_4$ (cf. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XIV, p. 75).

The experiments with *m*-nitroaniline usually gave somewhat lower yields of *m*-chloronitrobenzene, but in every case in the same order of efficiency as those with *p*-nitroaniline (see table). In these reactions also, ferric and curpric chlorides proved to be as efficient as cuprous chloride, and the decreased yields were to be anticipated in view of the lower positivity of the significant carbon atom to which the diazonium group is attached (cf. Part I, *loc. cit.*).

EXPERIMENTAL.

General Procedure.—*m*- or *p*-Nitroaniline (2·6 g.) was dissolved in hot hydrochloric acid (*d* 1·6, 50 c.c.), and the solution cooled to room temperature, treated with finely powdered sodium nitrite (2 g.), and kept for 30 mins., diazotisation then being complete. The metallic salt was then added, and the mixture gently boiled for 30 mins. under reflux, the vapours being led into water to collect any chloronitrobenzene carried over. The reaction mixture was then steam-distilled, the distillate kept at 0° to ensure that all the chloronitrobenzene had separated, aud the latter then removed, dried, and weighed. The second product of the decomposition reaction was in all cases identified qualitatively as the corresponding nitrophenol.

For the cobalt experiments with nitrosyl sulphate diazotisations, *p*-nitroaniline (2·6 g.), dissolved in glacial acetic acid (30 c.c.), was added to a solution of sodium nitrite (2 g.) in sulphuric acid (10 c.c., *d* 1·84), the mixture kept for 1 hour, and then poured into a solution of hydrated cobalt chloride (6 g.) in hydrochloric acid (100 c.c., *d* 1·16), which was then boiled for 30 mins. and worked up as above. The *p*-nitrophenol in the flask, after removal of *p*-chloronitrobenzene by steam, was estimated by conversion into 4-chloro-2 : 6-dibromophenol, and then found to account for *p*-nitroaniline not converted into *p*-chloronitrobenzene : 3·3 g. of dibromo-compound = 1·5 g. of *p*-nitroaniline; 1·2 g. of *p*-chloronitrobenzene = 1·05 g. of *p*-nitroaniline; total = 2·55 g. (cf. 2·6 g. initially taken).

Yields of *m*- and *p*- chloronitrobenzenes from the decompositions of diazotised *m*- and *p*-nitroanilines in boiling hydrochloric acid (50 c.c., *d* 1·16) with additions of metallic chlorides as given below.

Addition.	*p*-$C_6H_4Cl{\cdot}NO_2$, g.	%	*m*-$C_6H_4Cl{\cdot}NO_2$, g.	%
HCl (*d* 1·16) : blank	1·6	54·4	1·4	47·3
$AlCl_3$, hydrated (10·7 g.)	1·8	60·7	1·6	54·4
$SbCl_3$ (9 g.)	1·1	37·1	0·9	31·6
$CaCl_2$, anhyd. (4 g., and 20 g.)	1·6	54·4	1·4	47·3
$CrCl_3$	1·6	54·4	—	—
$CoCl_2$, hydrated (6·0 g.)	2·1	70·9	1·8	60·7
$CoCl_2$, hydrated (6·0 g.), solution diluted with water until pink	0·3	10·2	—	—
Blank of above, without $CoCl_2$	0·3	10·2	—	—
Cu_2Cl_2 (4·0 g.)	2·3	77·6	2·0	67·5
$CuCl_2$, hydrated (6·9 g.)	2·3	77·6	2·0	67·5
$FeCl_3$, anhyd. (6·5 g.)	2·3	77·6	2·0	67·5
$HgCl_2$ (10·0 g.)	1·6	54·4	—	—
$NiCl_2$, hydrated (6·0 g.)	1·8	60·7	—	—
$SnCl_4$, hydrated (14·0 g.)	1·8	60·7	—	—
$ZnCl_2$, anhyd. (5·5 g.)	1·6	54·4	1·4	47·3

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TECHNICAL COLLEGE, HUDDERSFIELD.

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