

214. *An Interpretation of the Sandmeyer Reaction. Part VII. The Formation of Complex Salts between Aryl Diazonium Chlorides and Ferric Chloride of General Formula, $R \cdot \overset{+}{N}_2 \} FeCl_4^-$, and the Decomposition of *p*-Nitrobenzenediazonium Chloride by Ferrous Salts.*

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Complex salts of aryl diazonium chlorides with ferric chloride of general formula $R \cdot \overset{+}{N}_2 \} FeCl_4^-$ have been made from eight amines; they decompose with hot concentrated hydrochloric acid to give chloro-aryls. With ethanol, *p*-nitrobenzenediazonium ferrichloride rapidly decomposes to give *p*-chloronitrobenzene analogously to aryl diazonium perbromides, but some nitrobenzene is also obtained. Hydrobromic acid displaces chlorine from the ferrichloride to form the corresponding ferribromide. Decompositions of the ferrichloride and ferribromide with concentrated hydrobromic acid and concentrated hydrochloric acid respectively follow the same course as the analogous cuprous halide reactions described in Part I. Ferrous chloride and ferrous sulphate decompose concentrated hydrochloric acid solutions of *p*-nitrobenzenediazonium chloride to give over 80% yields of *p*-chloronitrobenzene.

ALTHOUGH it is generally agreed that an unstable intermediate product is formed in the solution during the usual Sandmeyer reaction with cuprous chloride or bromide (cf. Saunders, "The Aromatic Diazo Compounds," E. Arnold and Co., London, 1936, p. 155), only a few examples of double compounds of cuprous salts with diazonium halides exist (cf. Lellmann and Remy, *Ber.*, 1886, **19**, 810; Hantzsch, *Ber.*, 1895, **28**, 1751; Neumann, *Monatsh.*, 1894, **15**, 492), and Sandmeyer himself was unable to isolate any kind of intermediate complex (*Ber.*, 1884, **17**, 2650). Nevertheless, the present series of investigations in this field have been based on the existence, however ephemeral, of intermediate complex anions and, while none have hitherto been actually isolated, ocular demonstration of their existence was given in Part IV (*J.*, 1944, **18**) in the case of complex cobalt anions of the type $(R \cdot \overset{+}{N}_2)_2 \} CoCl_4^-$, and it was then suggested that the efficiency of ferric chloride as a catalyst in concentrated hydrochloric acid was due to the formation of complex salts of the type $R \cdot \overset{+}{N}_2 \} FeCl_4^-$. Incidentally, Schmidt and Maier (*J. pr. Chem.*, 1931, **133**, 153) have previously obtained double salts of *p*-diethylaminobenzediazonium chlorides with mercurous, ferric, zinc, and cadmium chlorides.

In the present experiments these ferrichlorides having the above general formula were found capable of isolation with the greatest ease, owing to their sparing solubility in concentrated hydrochloric acid, and eight examples of them are recorded in Table I. These ferri-complexes decompose when heated with concentrated hydrochloric acid similarly to the original solutions of diazonium chlorides when these are treated with ferric chloride (Part V, *J.*, 1944, 393), and so furnish strong evidence of intermediate compound formation preceding decomposition in concentrated hydrochloric acid. When the ferrichloride is treated with concentrated hydro-

bromic acid the chlorine is replaced by bromine and the ferribromide, $R \cdot N_2^+ \} FeBr_4^-$, has been isolated; it decomposes in hydrobromic acid solution giving excellent yields of RBr .

When the ferrichloride from diazotised *p*-nitroaniline was decomposed by boiling hydrobromic acid a mixture was obtained of *p*-bromonitrobenzene (93%) and *p*-chloronitrobenzene (7%) (cf. Part I, J., 1941, 770, for analogous decompositions of diazonium salts with cuprous chloride and cuprous bromide in hydrobromic and hydrochloric acids respectively), while the corresponding ferribromide when decomposed by boiling hydrochloric acid gave a mixture of *p*-bromonitrobenzene (50%) and *p*-chloronitrobenzene (50%). As well as substantiating the theory advanced in Part I (*loc. cit.*) the data, quoted below, indicate that in the competitive introduction of chlorine and bromine where the bromo-complex is being decomposed by hydrochloric acid, ferric iron is more favourable to the introduction of bromine than is cuprous copper since the latter provides a mixture of *p*-monitrobenzene (36%) and *p*-chloronitrobenzene (64%).

p-Nitrobenzenediazonium ferrichloride is very rapidly decomposed by ethanol and, while *p*-chloronitrobenzene is the main product, some nitrobenzene is also formed due to the usual reduction of diazonium salts by ethanol. In the analogous case of the zinc chloride double salts (cf. Hodgson and Foster, J., 1942, 581) nitrobenzene was the main product (*ca.* 66%) of decomposition with ethanol.

Ferrous chloride and ferrous sulphate also decompose very efficiently concentrated hydrochloric acid solutions of *p*-nitrobenzenediazonium chloride giving *p*-chloronitrobenzene in about 81% yield; but whereas the yield only falls slightly (*ca.* 6%) even at great dilutions, the difference between the two yields when the ferrous salt is present and absent rises appreciably with dilution, thereby proving that the mechanism of decomposition involves the presence of a complex anion containing iron and chlorine. An attempt to isolate this afforded a solid whose composition we were unable to determine but which contained iron, chlorine, and nitroso group, the presence of the last being shown by indications of the formation of *p*-nitrosanitrobenzene when the solid was decomposed and steam distilled.

EXPERIMENTAL.

Preparation of the $R \cdot N_2^+ \} FeCl_4^-$ Complexes.—The arylamine (0.02 g.-mol.) or diamine (0.01 g.-mol.) was heated with hydrochloric acid (30 c.c., *d* 1.18) and the solution cooled rapidly to below 0° to form a fine suspension of the hydrochloride to which finely powdered sodium nitrate (1.5 g.) was cautiously added. This may be effected without the evolution of brown fumes by working at a sufficiently low temperature during the addition. The solution of the diazonium salt was filtered through sintered glass to remove residual solid matter and treated with finely powdered hydrated ferric chloride (5.4 g.) which was stirred in gradually with external cooling. The complex separated immediately as a yellow crystalline product and stirring was continued to allow any excess ferric chloride to dissolve, after which the solid was removed by filtration as before, washed with cold hydrochloric acid (*d* 1.18) to remove ferric chloride, and dried under reduced pressure over sodium hydroxide.

General Properties.—The complexes are yellow or orange crystalline solids, readily soluble in water but only sparingly soluble in concentrated hydrochloric acid; all the solutions in which the complexes are stable in the cold and several, *e.g.*, that from benzidine, whose complex may be recrystallised from such media, only decompose on prolonged heating. The dry solids may, in many cases, be kept for considerable periods without change (*e.g.*, the compound from *p*-nitroaniline was kept for over twelve months and retained unimpaired its coupling power with alkaline β -naphthol), but those from aniline and the naphthylamines remained stable for only a few days, decomposing slowly to give the chloro-derivatives.

Method of Analysis.—(a) *Iron content.* The complexes were dissolved in water, decomposed by heating, and the iron precipitated as ferric hydroxide with ammonia and estimated in the usual way as Fe_2O_3 , all organic matter being removed by ignition.

TABLE I.
Analytical data.

Amine.	Yield of $RN_2^+ \} FeCl_4^-$, %.	Iron, %, in the complex.	
		Found.	Calc.
Aniline	73	18.4	18.45
<i>m</i> -Nitro-aniline	63	16.2	16.1
<i>p</i> -Nitro-aniline	76	16.15	16.05
<i>p</i> -Toluidine	76	17.75	17.6
α -Naphthylamine	66	15.8	15.8
β -Naphthylamine	49	15.5	15.8
Benzidine	74	18.6	18.5
4 : 4'-Diaminodiphenyl disulphide	78	17.0	16.7

(b) *The diazonium ion content.* The complex from *p*-nitroaniline was dissolved in water and coupled with alkaline β -naphthol and the *p*-nitrobenzeneazo- β -naphthol weighed (Found : 1.067 g. complex gave 0.90 g. of dye. Calc. : 0.92 g.). Since the analyses for iron were in accord with the presumed general formula in the case of all the complexes studied, the above estimation was carried out for the above complex alone.

Preparation of p-Nitrobenzenediazonium Ferribromide.—The ferric chloride complex from *p*-nitroaniline was added in the solid state to excess hydrobromic acid (*d* 1.7) and, after stirring the suspension for 15 mins., the red-brown crystalline product was separated off and dried under reduced pressure over sodium hydroxide (Found : Fe, 10.9. $NO_2 \cdot C_6H_4 \cdot N_2^+ \} FeBr_4^-$ requires Fe, 10.7%).

Decompositions of p-Nitrobenzenediazonium Ferrichloride.—(a) *In hydrochloric acid.* The complex (4 g.) was refluxed for 30 mins. with hydrochloric acid (15 c.c., *d* 1.18) and the mixture steam distilled; yield of *p*-chloronitrobenzene, 1.5 g., 82%.

(b) *In absolute ethanol.* The complex (4.5 g.) was boiled under reflux for 15 minutes with ethanol (30 c.c.). A rapid decomposition accompanied by the formation of acetaldehyde took place at the start of the reaction. The greater part of the alcohol was removed by distillation, and the products, volatile in steam, collected. The solid matter was

contaminated with a small quantity of nitrobenzene which was removed as far as possible by pressing in filter paper (yield of *p*-chloronitrobenzene, 1.5 g., ca 74%).

(c) *In glacial acetic acid.* The complex was refluxed with glacial acetic acid (20 c.c.) for 30 mins. and on steam distillation gave *p*-chloronitrobenzene (0.5 g., 32% yield). The liquid remaining from the steam distillation was made alkaline, filtered, rendered just acid and extracted with ether; from the ether extract *p*-nitrophenol (0.6 g., 55% yield) was obtained; 87% of the complex is thus accounted for in this decomposition.

(d) *In hydrobromic acid.* The complex (3.5 g.) was refluxed with hydrobromic acid (16 c.c., *d* 1.7) and water (18 c.c.) for 30 mins. (The water was added to reduce the acid to the same molarity as the hydrochloric acid used in the next experiment.) The halogenonitrobenzene, m. p. 123.3°, removed by steam distillation, amounted to 1.9 g. From the data of Hodgson and Birtwell (*J.*, 1941, 775) this product is a mixture of *p*-bromonitrobenzene (93%) and *p*-chloronitrobenzene (7%), the yields being 88% and 8% respectively and the total replacement, 96%.

Decompositions of p-Nitrobenzenediazonium Ferribromide.—(a) *In hydrochloric acid.* The complex (5.3 g.) was refluxed with hydrochloric acid (17 c.c., *d* 1.18) for 30 mins. and the volatile products obtained as in (d) above, giving 1.6 g., m. p. 102°, and corresponding to *p*-bromonitrobenzene (50%) and *p*-chloronitrobenzene (50%) (Hodgson and Birtwell, *loc. cit.*); the yields were 40% and 51% respectively and the total replacement, 91%.

(b) *In hydrobromic acid.* The complex (5.3 g.) was refluxed with hydrobromic acid (16 c.c., *d* 1.7) for 30 mins. and on steam distillation yielded *p*-bromonitrobenzene (1.9 g., 94%).

Decompositions of p-Nitrobenzenediazonium Chloride with Ferrous Salts. Procedure.—*p*-Nitroaniline (2.8 g.) was diazotised in hydrochloric acid (50 c.c., *d* 1.18) by the addition of solid sodium nitrite (2 g.) as described above, after which the ferrous salt was added with varied amounts of water and the mixture refluxed for 30 mins. The *p*-chloronitrobenzene formed was removed by steam distillation, dried and weighed. The results obtained are shown in Table II together with the blanks (water alone) found by Hodgson and Sibbald (*J.*, 1944, 394).

TABLE II.

Yields of *p*-chloronitrobenzene, expressed in g. and %.

(a) With hydrated ferrous chloride (8 g.).					(b) With hydrated ferrous sulphate (11 g.).				
Water added,			Blank,	Difference due	Water added,			Blank,	Difference due
g.	G.	%.	%.	to salt, %.	g.	G.	%.	%.	to salt, %.
Nil	2.6	81	56	25	Nil	2.6	81	56	25
25	2.5	78	50	28	50	2.5	78	44	34
50	2.4	75	44	31	100	2.4	75	31	44
100	2.4	75	31	44					
150	2.3	72	22	50					

In carrying out the above experiments it was observed that, when ferrous chloride was added in the cold, an immediate evolution of nitrogen occurred and a brick-red solid was deposited which when steam distilled gave *p*-chloronitrobenzene; the last portions of the latter in the condenser were pronouncedly green, suggesting the presence of a nitroso-compound, e.g., *p*-nitrosobenzene. Evidence for the latter was further obtained by the red colour given with a hot mixture of aniline and glacial acetic (azo-compound formation). Reduction of this green product with zinc and hydrochloric acid gave a solution which when filtered and boiled with ferric chloride had a perceptible odour of *p*-benzoquinone and whose steam distillate liberated iodine from potassium iodide.

When the above experiments were carried out after excess nitrous acid had been destroyed by urea, the decomposition appeared to be even more violent and a complex salt of ferrous iron appeared impossible to isolate under either set of conditions.

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