

142. *An Interpretation of the Sandmeyer Reaction. Part VI. The Influence of the Chloride Ion on the Decompositions of Neutral p-Nitrobenzenediazonium Chloride and of p-Nitrobenzenediazonium Cobaltinitrite.*

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Evidence is submitted that the chlorine anion plays little or no part in the conversion, by heating, of neutral *p*-nitrobenzenediazonium chloride into *p*-chloronitrobenzene, and that in the absence of copper salts it does not interfere with the decomposition of neutral *p*-nitrobenzenediazonium cobaltinitrite to *p*-dinitrobenzene. Cupric chloride in neutral solution decomposes *p*-nitrobenzenediazonium chloride to give an 85% yield of *p*-chloronitrobenzene.

Most of the decompositions of diazonium salts by metallic chlorides hitherto reported have been studied in acid solutions (cf. Blumberger, *Rec. Trav. chim.*, 1930, **49**, 257, 267; Hodgson, Birtwell, and Walker, *J.*, 1941, 770; 1942, 720; Hodgson and Sibbald, *J.*, 1944, 395), and found to vary greatly in the presence of hydrochloric acid either with sodium chloride or with the addition of various catalysts: in particular, when the acid concentration altered from 29 to 6%, the yield of *p*-chloronitrobenzene altered from 56 to 17%. Sodium chloride was present in all these experiments, and in the case of the 56% yield the solution was saturated with it, so that it appeared of interest to ascertain whether metallic chlorides, *i.e.*, the chlorine anion, took part in the decomposition or whether the *p*-chloronitrobenzene formed was mainly due to un-ionised hydrogen chloride (cf. Hodgson *et al.*, *J.*, 1942, 720). For this purpose, the acid solution of *p*-nitrobenzenediazonium chloride was exactly neutralised with the appropriate base, and the corresponding metallic chlorides added in equivalent amounts to secure exactly parallel sets of decompositions. Except in the cases of calcium and zinc chlorides, it is not possible to ensure complete neutrality throughout the decomposition on account of the hydrochloric acid formed by the decomposing diazonium chloride, but in the above two cases this may be overcome by having present an excess of calcium carbonate or zinc oxide, respectively. Comparison of the figures obtained with and without filtering off the excess base shows that the acid formed is without significant effect upon the yield and consequently may be ignored in the other experiments where its presence is unavoidable.

From Table I it is seen that in neutral decompositions the addition of relatively large amounts of metallic chlorides causes no significant rise in the yield of chloro-compound above that obtained when no salts are added. There is, however, one exception, *viz.*, that when cupric chloride is added to the solution neutralised with calcium carbonate the yield rises to 85%, this remarkable result being obtained with about one-third of the equivalent amount of chlorine present in solution, and it would appear to indicate the presence of the complex hydrated cupric chloride anion held to exist in the experiments in acid solution (Hodgson and Sibbald, *loc. cit.*). The results are claimed to show that the chloride ion plays little if any part in the substitution of chlorine for the diazo-group, since the only cases of appreciable substitution are those in which there is the possibility of the existence of covalent (or partly polarised) chlorine, *viz.*, with hydrogen, cupric, and calcium chlorides.

The behaviour of zinc chloride, which unexpectedly did not follow that of calcium chloride, is probably due to the same cause as that which differentiates it from cuprous or cupric salts in the decomposition of its complex salts with diazonium compounds, *viz.*, that bound, anionoid, and therefore reactive, water is further from the zinc than the polarised chlorine atoms (*i.e.*, the reverse of the case of crystalline $K_2CuCl_4 \cdot 2H_2O$). Support for this view is to be found in Hodgson and Foster's observation (J., 1942, 581) that decomposition of the zinc diazonium complexes in phenol results in *ca.* 50% chlorine substitution.

p-Nitrobenzenediazonium cobaltinitrite has been shown (Hodgson and Marsden, J., 1944, 22) to undergo replacement of the diazo- by the nitro-group when treated with sodium nitrite, copper sulphate, and cuprous oxide. When this decomposition is carried out in the presence of sodium chloride and copper sulphate in neutral solution, the product formed is pure *p*-chloronitrobenzene, showing that the cupric chloride has been more effective than the cobaltinitrite, or alternatively that polarised chlorine is more reactive than the polarised nitro-group in the cobalt complex. When the cobaltinitrite is decomposed by sodium nitrite and sodium chloride in the absence of copper, the product is entirely *p*-dinitrobenzene, showing that the fully ionised chlorine is without effect on the decomposition, which arises *via* the polarised nitro-group in the complex and is in accord with the results obtained with metallic chlorides mentioned above. Decompositions with sodium nitrite and sodium chloride in conjunction with copper sulphate give mixtures of *p*-chloronitro- and *p*-dinitrobenzene. The m. p.'s of mixtures of these two compounds are not very precise but extend over a short range; nevertheless, they seem to indicate that, except for a very slight depression near pure *p*-chloronitrobenzene, the composition-m. p. curve is a straight line connecting the m. p.'s of the pure substances. The approximate compositions in Table II are calculated on this assumption.

EXPERIMENTAL.

Decomposition of p-Nitrobenzenediazonium Chloride in Neutral Aqueous Solution in the Presence of Various Metallic Chlorides.—Procedure. *p*-Nitroaniline (2.8 g.) was dissolved in hydrochloric acid (10 c.c., *d* 1.18) and water (10 c.c.) by warming, the solution poured with stirring into water (80 c.c.), cooled to 0° to cause deposition of a fine suspension of *p*-nitroaniline, and diazotised by the rapid addition of sodium nitrite (2.0 g.) dissolved in the minimum of water. The solution was neutralised with the appropriate base, and the salts then added on the following plan: that since 27 g. of sodium chloride is the approximate amount for saturation, the other salts are added in equivalent amounts with the exception of crystalline cupric chloride. After filtration, the filtrate was refluxed for 30 minutes, then steam-distilled, and the volatile *p*-chloronitrobenzene weighed. Two experiments were carried out in which the excess base was not removed.

TABLE I.

Metallic base.	Metallic salt added, and wt. (g.).	Yield of $p\text{-C}_6\text{H}_4\text{Cl}\cdot\text{NO}_2$ formed :	
		g.	%.
Nil	Nil	0.9	28
CaCO ₃ (excess retained)	Nil	0.2	6
CaCO ₃ (excess removed)	Nil	0.2	6
ZnO (excess retained)	Nil	0.15	5
ZnO (excess removed)	Nil	0.15	5
CaCO ₃ (excess removed)	CaCl ₂ 26.5	0.4	12
ZnO (excess removed)	ZnCl ₂ ·2H ₂ O 39.6	0.2	6
NaHCO ₃ (neutral to litmus)	NaCl 27.0	0.1	3
K ₂ CO ₃ (neutral to litmus)	KCl 34.3	0.2	6
CaCO ₃ (excess removed)	CuCl ₂ ·2H ₂ O 6.9	2.7	85

Decomposition of p-Nitrobenzenediazonium Cobaltinitrite in the Presence of Various Salts in Neutral Solution.—Procedure. The cobaltinitrite was prepared in the dry solid state by Hodgson and Marsden's method (*loc. cit.*), and a portion (3 g.) added gradually in finely powdered form to water (20 c.c.) in which cuprous oxide (1.2 g.) was suspended, and various salts were dissolved as indicated, the whole being stirred at room temperature. After the decompositions were complete and evolution of nitrogen had ceased, the mixtures were steam-distilled. The results are given in Table II.

TABLE II.

Dissolved salts.	M. p. of steam-volatile product.
NaNO ₂ (3 g.); CuSO ₄ ·5H ₂ O (3 g.)	171.2° (pure <i>p</i> -dinitrobenzene)
NaNO ₂ (3 g.); CuSO ₄ ·5H ₂ O (3 g.); NaCl (2.6 g.)	90° (<i>ca.</i> 15% <i>p</i> -dinitro- and 85% <i>p</i> -chloronitrobenzene)
CuSO ₄ ·5H ₂ O (3 g.); NaCl (2.6 g.)	84° (pure <i>p</i> -chloronitrobenzene)
NaNO ₂ (3 g.)	171.2° (pure <i>p</i> -dinitrobenzene)
NaNO ₂ (3 g.); NaCl (2.6 g.)	171.2° (pure <i>p</i> -dinitrobenzene)
NaCl (2.6 g.)	85.5° (<i>ca.</i> 5% <i>p</i> -dinitro- and 95% <i>p</i> -chloronitrobenzene)

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