154. *An Interpretation of the Sandmeyer Reaction. Part III. Further Evidence in favour of a Mechanism involving Anionoid Halogen.*

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Catalysed decompositions of diazonium kations are produced by anionoid complexes; the efficiency of complexes with metals other than cuprous copper appears to be dependent on the degree of positivity of the kation. This point of view, expressed in Part I, is emphasised by further experimental data.

Our recent interpretation of the Sandmeyer reaction (J., 1941, 770), based on work commenced in 1931, indicated a mechanism whereby stable halogen ions were rendered exceedingly reactive by labile combination with cuprous salts to form anionoid complexes, the catalytic function of the cuprous salt being to destabilise the halogen octet. This interpretation was subsequently extended to explain the similar catalytic action of cupric salts, and it provides a rational explanation for all halogen replacements of the diazonium group whether in aqueous or other media, or in the dry state. The decomposition of diazo-perbromides can only be explained by such an anionoid mechanism.

Discussion of Waters' Complex Cuprous-Kation Theory (this vol., p. 266).—Waters' suggested mechanism, which is almost identical with that for the reduction of a diazonium compound to a diaryl, is based on his statement that we have " not been able to suggest why the *cuprous* double salts decompose in a way which is so very different from the double salts which diazonium halides readily form with the halides of other metals, such as zinc," *i.e.*, " the unique character (p. 267) of cuprous salts as catalysts " for the Sandmeyer reaction. The term " unique " is modified by Waters to " *almost* unique " in the summary and on p. 270.

We must reaffirm emphatically that, far from being unable to suggest why cuprous salts were *almost* unique as Sandmeyer catalysts, we held the belief (implicit in the very first paragraph of our paper, *loc. cit.*) that there was no justification for such a point of view as that now advanced by Waters, and in support thereof we quoted examples in both the benzene and the naphthalene series where cupric salts act as efficiently (or nearly so) as cuprous salts, *i.e.*, examples for which the Waters explanation can have no validity whatever (cf. Waters, *loc. cit.*, p. 268). Moreover, Waters does not mention these reactions (Hodgson *et al.*, p. 772), although it is obvious that if cupric salts can behave under identical circumstances like cuprous salts, his whole argument for an oxidation–reduction mechanism involving a complex kation of a cuprous–diazonium double salt becomes invalid (cf. also, the antithesis to his claim, p. 267, for avoiding special structural formulæ for intermediate reaction complexes). In like manner, Sandmeyer's own statement that cupric salts were without the same action as cuprous salts was based on insufficient evidence.

We have previously pointed out (*loc. cit.*, p. 772) that the Sandmeyer reaction appears to be dependent on the degree of positivity of the diazonium ion, which, when of sufficient magnitude, enables the more ephemeral cupric halogen complexes to react like their more abundant cuprous analogues. This dependence is now further illustrated by the data for decompositions by cupric salts (see Table IV), which indicate that when the significant carbon has only a relatively small positive charge (as in diazotised aniline or *p*-toluidine), the yield of chloro-compound is only small, but with increase of positivity, as in *p*-chlorobenzenediazonium chloride, and still more so in *p* nitrobenzenediazonium chloride, due to the $(-I)$ inductive effects of the chloro- and the nitro-group respectively, yields as ample as those with cuprous chloride are obtained. Incidentally, but important for the argument, no diaryl formation was observed in the decompositions with cupric salts, the usual by-product being the corresponding phenol. Waters implicitly concedes this point, since he depicts (*loc. cit.*, p. 268, Fig. I) the positive centres of a complex kation of a cuprous–diazonium double salt as attracting each other, an attraction which could only result in electron release to the significant carbon of the aryl group when this is at a higher positive potential than the cuprous copper. We submit that attraction is far more likely to occur between the reactive anionoid centre of a complex anion (such as is generally acknowledged to be formed when cuprous salts dissolve in mineral acids) and the positive significant carbon, than between positive centres in a complex structure such as that depicted by Waters.

Halogen Replacements by Metallic Complexes other than those of Copper.—P. H. Groggins ("Unit Processes in Organic Syntheses," McGraw-Hill Book Co., New York and London, 1938, p. 199) states: "Copper is *not* the only metal that can *advantageously* be employed for the replacement of the diazo-group by halogen. When the precaution is taken to ensure a maximum concentration of chloride ions, saturated solutions of calcium chloride, zinc chloride, and zinc-ammonio chloride *often* give equally good results." Recent work also, by ourselves with C. K. Foster (this vol., p. 581), has shown that many complex double salts of diazonium compounds with zinc chloride of general formula $(ArN_2)_2ZnCl_4$ are decomposed *in solution* in molten phenol by a mechanism identical with that of the Sandmeyer reaction in water, to give up to 50% yields of chloro-compound, the anionoid phenol playing a rôle identical with that of anionoid water.

When the double salts of diazonium chlorides with lead tetrachloride are heated with alcohol, the diazo-group is replaced by chlorine (Chattaway, J., 1924, **125**, 1981), the reaction being analogous to the decomposition of the perbromides and indicating the function of the metal to be that of host for the formation of the reactive complex anion.

The Dual Rôle of Cuprous Compounds.—We consider that it is more rational to postulate distinct mechanisms, (1) for halogen substitution and (2) for diaryl formation, than a single mechanism such as that proposed by Waters for both. Hodgson and Walker found (J., 1932, 1620) that when the amount of water was reduced, *i.e.*, the concentration of the complex cuprous anion increased, diaryl formation could be prevented altogether in the decomposition of *o*- and *p*-nitrobenzenediazonium chlorides by cuprous chloride in hydrochloric acid solution. The Waters mechanism does not explain the complete absence of diaryl formation in such cases, which is due not to the high concentration of chlorine ions, since this may be very moderate, but to conditions which favour the maximum production of a complex anion. Likewise, when the water content was increased (cf. Hodgson *et al.*, *loc. cit.*, p. 776), the formation of diaryl (2) was also increased but was accompanied by that of nitrophenol, indicating that anionoid water now competed with the cuprous reducing agent for the diazonium salt.

The Waters mechanism, moreover, differs only in elaboration from that already proposed by Groggins (*op. cit.*, p. 199), who also introduces hydroxyl anions as competitors with the kationoid complex. We submit that it is more reasonable to assume competition for the diazonium kation between a complex cuprous anion and anionoid water (since there are no hydroxyl ions present in such strong acid solutions, in a realistic sense of the term), than to assume a competing cuprous kation. The fact that by reducing the amount of anionoid copper complex by dilution of the solution with water, the yield of halogen compound is decreased, whereas that of phenol is increased, supports our explanation.

Decompositions by Copper Sulphate, with and without other Oxidising Agents.—Reactions between nitroaryldiazonium sulphates, copper sulphate, and sodium chloride or bromide in sulphuric acid solution to give chloro- or bromo-aryls in 90—100% yields were discovered by Hodgson (*J. Soc. Dyers and Col.*, 1926, **42**, 365). Benzenediazonium sulphate itself has now been found to give a 38% yield of bromobenzene under similar conditions. To eliminate any chance of cuprous salt formation (cf. Waters, *loc. cit.*), a number of reactions have been carried out with *p*-nitrobenzenediazonium sulphate, copper sulphate, and sodium bromide, in the presence of ammonium persulphate and also of ferric chloride. Although the yields of halogeno-aryl were not much affected (see Table I), nevertheless in the ferric chloride experiment a mixture of about equal parts of 4-chloro- and 4-bromo-nitrobenzene resulted. When hydrogen peroxide was used as the supplementary oxidising agent, the yield of 4-bromonitrobenzene was reduced, and the reaction included the initial formation of a yellow precipitate (probably of a perbromide), which, on heating, decomposed with evolution of bromine and separation of 4-bromonitrobenzene. The last experiment might suggest that when oxidising agents are present, bromine replacement occurs *via* intermediate formation of a perbromide, but in the decompositions with sodium bromide and copper sulphate alone, the by-product was always the corresponding phenol, which was never found to have been brominated. Further, a mixture of copper sulphate, sodium bromide, and phenol, in the presence of dilute sulphuric acid, gave no precipitate of tribromophenol, even when heated under reflux on the water-bath for an hour and subsequently kept for 24 hours. Initial formation of perbromide does not therefore take place in the copper sulphate and sodium bromide experiments, and the mechanism of decomposition of the diazonium salt is *via* a cupric-copper anionoid complex as originally suggested by Hodgson *et al.* (*loc. cit.*, p. 772).

Decompositions by Ferric Chloride and Cupric Chloride in Hydrochloric Acid Solution.—Experiments in which dilute sulphuric acid solutions of *p*-nitrobenzenediazonium sulphate were decomposed in the presence of ferric chloride alone, and also with copper sulphate and sodium chloride, gave results (see Table II) which indicated clearly the catalytic influence of the copper salt and of the chloride-ion concentration. In the decompositions of *p*-nitrobenzenediazonium chloride (see Table III), it is of interest that a 41% yield of 4-chloronitrobenzene was obtained in concentrated hydrochloric acid alone, and that in this acid only minor variations were produced by additions of antimony trichloride, stannic chloride, and aluminium chloride. Ferric chloride and cupric chloride, however, increased the yield to 63% and 73% respectively. The catalytic influence of these salts is thus clearly demonstrated, and in the case of cupric chloride an efficiency almost equal to that of cuprous chloride was obtained with the nitro-compounds.

Conclusions.—The experimental evidence proves : (1) Cuprous salts do *not* possess the unique (or almost unique) character claimed for them first by Sandmeyer and recently by Waters. (2) In cases where the diazonium kation possesses sufficient positivity, cupric salts can function with efficiencies comparable with those of cuprous salts. (3) Metals other than copper can form anionoid complexes with halogens which decompose in like manner to the copper salts. (4) The Sandmeyer reaction is an oxidation–reduction process involving an electrophilic diazonium kation and a nucleophilic (anionoid) halogen which is part of a cuprous copper complex. (5) There are no fundamental differences in the mechanism of formation of halogen compounds during the decompositions of complex salts of diazonium chlorides with cuprous chloride, cupric chloride, zinc chloride or any other chloride, including hydrogen chloride, in aqueous or other media; such differences as do occur, *e.g.*, in the distribution of yield, are due to differences in stability and concentration of the complex anion, whereby the competing action of anionoid water can become negligible (cuprous salts) or predominant (zinc salts). (6) All the reactions studied can be interpreted by the simple anionoid mechanism already proposed (Hodgson *et al.*, J., 1941, 770; this vol., p. 376).

EXPERIMENTAL.

The Effect of Oxidising Agents on the Replacement of the Diazo-group by Bromine by Means of Sodium Bromide and Copper Sulphate.—Finely powdered *p*-nitroaniline (11 g.) was added to a solution of sodium nitrite (5·6 g.) in sulphuric acid (40 c.c., *d* 1·84) at 30—40° and, after dissolution, the mixture was cooled and poured on ice. The solution of diazonium salt was filtered, made up to 280 c.c., and divided into four equal portions, each being therefore equivalent to 1/50 g.-mol. of diazotised *p*-nitroaniline. Four solutions were then made up of crystallised copper sulphate (5 g.) and sodium bromide (5 g.) in water (25 c.c.), to which different oxidising agents were added, followed by the diazo-solution (Table I). The four mixtures were refluxed on the water-bath for 15 minutes, decomposition then being complete (decomposition began at *ca.* 80°). The 4-bromonitrobenzene was isolated by steam-distillation.

TABLE I.

Oxidising agent.	Yield of halogen compound, g.	Yield of halogen compound, %.	M. p. of steam-volatile compounds.
None	2·5	63	125—126°
Ammonium persulphate (2·5 g.)	2·5	63	,,
20 Vol. Hydrogen peroxide (20 c.c.)	1·7	43	,,
Ferric chloride (3·5 g.)	2·6	74	102 *

* This m. p. corresponds to a mixture of equal parts of 4-chloro- and 4-bromo-nitrobenzene. See Table II (Hodgson *et al.*, *loc. cit.*, p. 775).

Aniline (18·6 g.), dissolved in sulphuric acid (20 c.c., *d* 1·84) and water (200 c.c.), was diazotised below 10° by a solution of sodium nitrite (14 g.) in water (50 c.c.). The mixture was poured into a solution at 80° of crystallised copper sulphate (100 g.) and sodium bromide (100 g.) in water (400 c.c.), heated on the boiling water-bath for 30 minutes, and steam-distilled; bromobenzene (12 g., 38% yield) passed over.

Decomposition of Diazotised p-*Nitroaniline by Ferric Chloride, alone and with Additions.*—*p*-Nitroaniline (1/50 g.-mol.) was diazotised by the nitrosylsulphuric acid method above, and the solution decomposed under the same conditions as those given above.

TABLE II.

Decomposition reagent.	Yield of 4-chloronitrobenzene, g.	Yield of 4-chloronitrobenzene, %.	M. p. of steam-distilled product.
Ferric chloride (7 g.) in water (25 c.c.)	0·5	16	80—83°
Ferric chloride (3·5 g.), crystallised copper sulphate (5 g.), and sodium chloride (5 g.) in water (25 c.c.)	2·0	64	,,
Ferric chloride (3·5 g.) and crystallised copper sulphate (5 g.) in water (25 c.c.)	1·9	60	,,

Replacement of the Diazo-group by Chlorine.—A solution of *p*-nitroaniline (22 g.) in hydrochloric acid (50 c.c., *d* 1·16) and water (75 c.c.), while still warm enough to prevent crystallisation, was diazotised by stirring into a mixture of aqueous sodium nitrite and ice (250 g.). The filtered solution was made up to 400 c.c. and divided into 8 portions of 50 c.c., which each contained 1/50 g.-mol. of diazonium salt. These portions were added to solutions of 1/25 g.-mol. of various salts dissolved in (*a*) water (25 c.c.) or (*b*) hydrochloric acid (50 c.c., *d* 1·16). The temperature during the addition was maintained at *ca.* 80° and the mixtures were subsequently heated under reflux on the water-bath at 90—95° for 45—60 minutes. The 4-chloronitrobenzene formed was isolated by steam-distillation.

TABLE III.

Addition for (*a*), 1/25 g.-mol. in water (25 c.c.).	Yield of 4-chloro-1-nitrobenzene, g.	%	Addition for (*b*), 1/25 g.-mol. in HCl (50 c.c., *d* 1·16).	Yield of 4-chloro-1-nitrobenzene, g.	%
None (solution boiled)	0·3	9·5	HCl only (solution heated)	1·3	41
Zinc chloride (5·5 g.)	0·3	9·5	Zinc chloride (5·5 g.)	1·3	41
			Antimony trichloride (9 g.)	1·0	32
Hydrated stannic chloride (14·0 g.)......	0·4	13	Hydrated stannic chloride(14·0 g.) ...	1·3	41
Hydrated aluminium chloride (10·7 g.)	0·45	14·5	Hydrated aluminium chloride (10·7 g.)	1·5	48
Ferric chloride (anhydrous) (6·5 g.) ...	1·1	35	Ferric chloride (anhydrous) (6·5 g.) ...	2·0	63
Hydrated cupric chloride (6·9 g.)	2·5	80	Hydrated cupric chloride (6·9 g.)	2·3	73

The temperatures at which these reactions were carried out were necessary for the decompositions to be rapid and complete, but when the solutions were kept at room temperature during long periods, as good and sometimes better yields were obtained; *e.g.*, the cupric chloride experiment of Table III, when carried out at room temperature for 96 hours before removal of the product, gave 2·5 g. (80% yield), and with a mixture of crystallised copper sulphate (10 g.) and sodium chloride (5 g.) instead of cupric chloride, 2·7 g. of 4-chloro-1-nitrobenzene (86% yield) were obtained.

Decompositions of Various Diazonium Salts by Cupric Chloride, and by Copper Sulphate and Sodium Chloride.—In the following experiments, the amines were diazotised in hydrochloric acid, the concentration being 1/25 g.-mol. in acid (12·5 c.c., *d* 1·16) and water (77·5 c.c.). The diazonium solutions were then stirred into the decomposition solutions, which contained two equivalents of copper (2/25 g.-mol.) in water (50 c.c.).

TABLE IV (All the data are calculated to the nearest 1%).

Amine diazotised.	G.-mol. taken.	Decomposed by crystallised copper sulphate (20 g.) and sodium chloride (10 g.) in water (50 c.c.). Yield of chloro-compound, g.	%	Decomposed by hydrated cupric chloride (13·8 g.) in water (50 c.c.). Yield of chloro-compound, g.	%
Aniline	0·2	3·9	17	3·8	17
p-Toluidine	0·2	4·2	17	4·2	17
p-Chloroaniline	0·04	4·0	68	3·6	61
m-Nitroaniline	0·04	5·1	81	5·0	80
p-Nitroaniline	0·04	5·6	89	5·6	89
o-Nitroaniline	0·04	5·1	81	5·0	80
2 : 4-Dinitroaniline	0·04	6·3	81	6·2	80

Remarks.—The larger amounts of aniline and *p*-toluidine were taken to ensure greater accuracy in estimating the yields of chloro-compound, and the diazonium solutions were decomposed by a solution of (1) copper sulphate (100 g.) and sodium chloride (50 g.), and (2) hydrated cupric chloride (69 g.), in water (250 c.c.).

The 2 : 4-dinitroaniline (6·7 g.) was diazotised by the special method described by Saunders ("The Aromatic Diazo-Compounds and Their Technical Applications," London, 1936, p. 10), in 60 c.c. of sulphuric acid, and the solution diluted to 175 c.c. before decomposition by cupric chloride. No increase in yield was obtained by saturating the diazonium solution with sodium chloride before the addition of the cupric chloride solution.

The authors thank I.C.I. (Dyestuffs) Ltd. for various gifts.

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[*Received, June* 27*th*, 1942.]