152. *An Interpretation of the Sandmeyer Reaction. Part VIII. The Decomposition of Diazonium Salts by Cupric Chloride in Neutral and Acid Solution.*

By Herbert H. Hodgson.

Cupric chloride is an effective catalyst for the replacement of the diazo-nitrogen of strongly positive diazonium kations by chlorine in both weakly acid and neutral solutions, but much less efficient for weak kations; it is superior to cuprous chloride under the above conditions. The negative (—*I*) inductive effect of the methoxyl group strongly influences the decomposition of diazotised *o*- and *p*-anisidine. The results are held to support the complex anion theory.

In Part VI of this series (Hodgson and Sibbald, *J.*, 1945, 545) it was recorded that a neutral solution of *p*-nitrobenzenediazonium chloride when treated with hydrated cupric chloride afforded an 85% yield of *p*-chloronitrobenzene, a result which appeared to indicate that substitution of the diazonium group by chlorine had occurred *via* the mechanism of a complex hydrated cupric chloride anion (cf. Harker, *Z. Krist.*, 1936, **93**, 136; Chrobak, *ibid.*, 1934, **88**, 20; Hendricks and Dickinson, *J. Amer. Chem. Soc.*, 1927, **49**, 2149). A similar mechanism had been suggested previously for the parallel experiment in hydrochloric acid solution (Hodgson and Sibbald, Part V, *J.*, 1944, 393). It consequently appeared of interest to examine whether this reaction of cupric chloride was a general one for aryl diazonium chlorides, and the table below contains the data of a representative set of such reactions, all carried out under identical conditions.

From the table it will be seen that for amines which give highly positive diazonium kations, such as the nitroanilines and *p*-chloroaniline, cupric chloride is an effective catalyst for the replacement of the diazonium group by chlorine under both acidic and neutral conditions. For amines, however, whose diazonium kations are much less positive, such as those from aniline, the three toluidines, and α- and β-naphthylamine, cupric chloride is practically ineffective. Benzidine gives a slightly improved yield compared with the last named amines, but in 3 : 3′-dichlorobenzidine, where the chlorine atoms greatly increase the positivity of the diazonium kation by the negative (—*I*) effect, the amount of replacement by chlorine is considerably improved. Anthranilic acid, however, gives mainly salicylic acid both in acid and neutral decompositions. At the slight acidities of the acid reactions, the catalytic power of the cupric chloride is generally somewhat inferior to that in neutral solutions. In solutions of the less positive diazonium kations the main reaction is phenol formation, and the phenol in neutral solution tends to couple with undecomposed diazo-compound, a reaction which is very pronounced in the benzidine decompositions. When the neutral decompositions were carried out with calcium carbonate also present, little or no steam-volatile product was obtained, owing to azo-dye formation.

With *m*- and *p*-nitrobenzenediazonium chlorides, cuprous chloride gives smaller yields than cupric chloride under both acid and neutral conditions, thereby confirming the result of Part V (*loc. cit.*).

Neutral solutions of *o*- and *p*-nitrobenzenediazonium chlorides saturated with sodium chloride gave no chloronitrobenzene and *m*-nitrobenzenediazonium chloride gave only 6% of *m*-chloronitrobenzene, whereas when hydrochloric acid was present small yields of the chloronitro-compounds were obtained in all three reactions (cf. Hodgson and Birtwell, Part I, *J.*, 1941, 770, who postulate un-ionised hydrogen chloride as the main active reagent and not the chloride ion; cf. also Hodgson and Sibbald, Part VI, *loc. cit.*).

In the decompositions of diazotised *o*- and *p*-anisidines there is a surprisingly large replacement of the diazonium group by chlorine, indicating that the negative (—*I*) inductive effect of the methoxyl group is predominant and has appreciably increased the positivity of the diazonium group.

Previous work by Contardi (*Ann. Chim. Appl.*, 1923, **7**, 13) in fairly strong acid solution had shown that the substitution of the amino-group by chlorine (or bromine), particularly in amines with strong electro-negative substituents ortho or para to the amino-group, was readily attained by allowing cupric chloride (or bromide) to react with the respective diazonium salt [cf. Hodgson, *J. Soc. Dyers and Col.*, 1926, **42**, 365, who found that a mixture of copper sulphate and sodium chloride (or bromide) was also effective]. Contardi believed that the replacement proceeded through an undefined complex salt to which Hodgson and Birtwell (*loc. cit.*) (cf. also Hodgson and Sibbald, *J.*, 1945, 819) gave a more precise form.

Experimental.

General Procedure.—A solution of the amine (g.-mol./50) in a mixture of hydrochloric acid (10 c.c., *d* 1·18) and water (30 c.c.), was diazotised by the addition at 0° (floating ice) of sodium nitrite (2 g.) dissolved in a little water; *o*- and *p*-nitroanilines, however, were diazotised as usual. Excess of nitrous acid was removed by urea, and the solution either (*a*) filtered and treated with hydrated cupric chloride (7 g.), or (*b*) neutralised with calcium carbonate, filtered, and then treated with the cupric chloride (7 g.). It was then diluted so that the total volume of water used was 100 c.c., saturated with sodium chloride, kept at room temperature for 30 minutes, and finally heated gradually to the boil before steam distillation, which was carried out at such a dilution that solid salt was always present. The steam distillate containing the volatile chloro-compound was treated with sodium hydroxide (10 g.) if the phenolic product also formed was steam-volatile, and again steam distilled. Solid products were weighed and identified; liquid products were extracted with ether, the extract dried, the ether removed, and the residue weighed and identified.

Table of Decomposition Data.

Amine diazotised.	Chloro-compound obtained.	Yield (%). (*a*) Acid.	Yield (%). (*b*) Neutral.	Blank. (*a*).	Blank. (*b*).	Other data.
Aniline	Chlorobenzene	18	18	9	9	
o-Toluidine	*o*-Chlorotoluene	15	15	15	1·5	(*b*) 56% *o*-Cresol.
m-Toluidine	*m*-Chlorotoluene	7	7	—	—	(*b*) 54% *m*-Cresol.
p-Toluidine	*p*-Chlorotoluene	22	15	—	—	(*b*) 34% *p*-Cresol.
o-Anisidine	*o*-Chloroanisole	70	75	—	—	Very little hydroxy-compound.
p-Anisidine	*p*-Chloroanisole	67	77	—	—	,, ,, ,,
o-Nitroaniline	*o*-Chloronitrobenzene	85	85	13	0	Practically no *o*-nitrophenol formed.
m-Nitroaniline (cupric chloride)	*m*-Chloronitrobenzene	86	77	13	6	
m-Nitroaniline (cuprous chloride)	*m*-Chloronitrobenzene	75	48	—	—	
p-Nitroaniline (cupric chloride)	*p*-Chloronitrobenzene	75	85	3·5	0	
p-Nitroaniline (cuprous chloride)	*p*-Chloronitrobenzene	60	44	—	—	
Anthranilic acid	*o*-Chlorobenzoic acid with	24	27	—	—	
	salicylic acid	56	63	—	—	Determined as *p*-nitrobenzene-azosalicylic acid.
p-Chloroaniline	*p*-Dichlorobenzene	30	67	—	—	
α-Naphthylamine	α-Chloronaphthalene	18	22	—	—	
β-Naphthylamine	β-Chloronaphthalene	24	28	—	—	
Benzidine	4 : 4′-Dichlorodiphenyl	22	17	—	—	
3 : 3′-Dichlorobenzidine	3 : 3′ : 4 : 4′-Tetrachlorodiphenyl	48	41	—	—	

The author is indebted to Imperial Chemical Industries Limited (Dyestuffs Division) for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD.

[*Received, February 23rd*, 1946.]