105. *An Interpretation of the Sandmeyer Reaction. Part V. The Comparative Behaviour of Cuprous, Cupric, and Ferric Chlorides as Catalysts.*

By Herbert H. Hodgson and Douglas D. R. Sibbald.

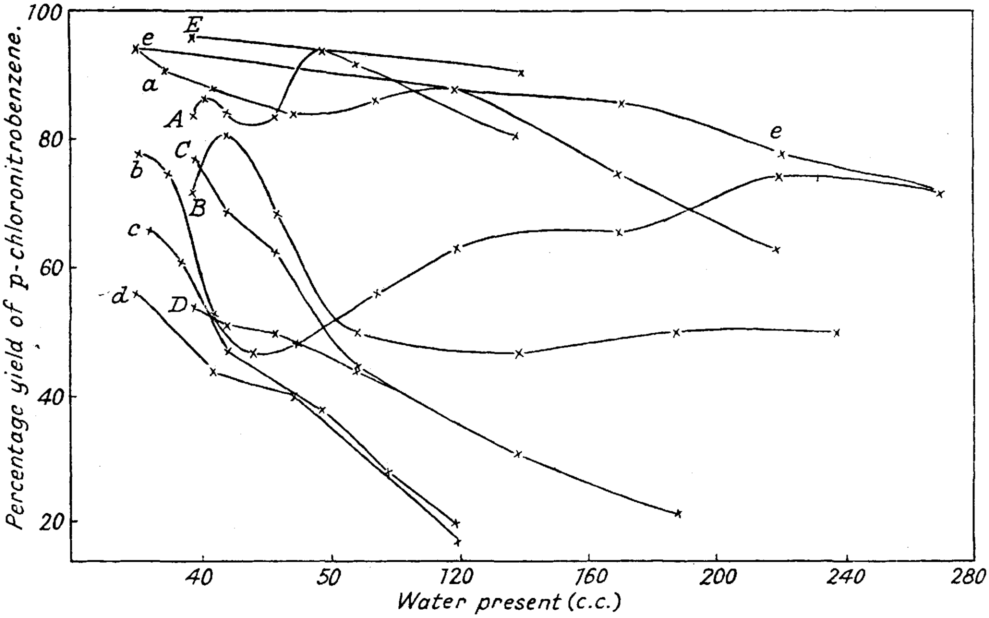
p-Nitrobenzenediazonium chloride has been decomposed over a range of hydrochloric acid concentrations with cuprous, cupric, and ferric chlorides as catalysts, and with cuprous and cupric chlorides together. With ferric chloride an almost proportional decrease in yield of *p*-chloronitrobenzene occurs on dilution, whereas cuprous chloride has one maximum at *ca.* 18·6% of acid and cupric chloride has maxima at 26·9% and 4%, the latter after the plot has crossed that for cuprous chloride. The curve for cuprous and cupric chloride in combination approximates to a straight line. These results are discussed from the standpoint of the complex-anion theory.

Hodgson, Birtwell, and Walker (J., 1942, 72) observed that cupric chloride catalysed the decomposition of *p*-nitrobenzenediazonium chloride in somewhat dilute hydrochloric acid solution, and this unexpected result led to the present comparative investigation of the catalytic effects of cuprous and cupric chloride over a wide dilution range. Ferric chloride was also included because of its efficiency in concentrated acid solution (cf. *idem*, this vol., p. 18). From the diagram, which shows the % yield according to the amount of water present, the plot for ferric chloride indicates an almost proportional decrease in yield with dilution, whereas that for cuprous chloride has a maximum at *ca.* 18·6% of acid (see Table I, *a*), and that for cupric chloride has maxima at 26·9% and 4% (see Table I, *b*), the latter after the plot has crossed that for cuprous chloride. When cuprous and cupric chlorides are used in combination (see Table II) the curve is approximately a straight line, the effect of the cuprous chloride being inappreciable at high dilutions; incidentally, the curve for the combination is tangential to the peaks of the cupric chloride curve.

The remarkable increase in activity of cupric chloride at 4% strength suggests the existence of a complex hydrated cupric chloride anion in which the chlorine is much more active than the bound water. This preferential activity of the chlorine may be due to its actual distance from the copper being greater than that of the bound water, as in the known examples of crystalline $K_2CuCl_4,2H_2O$ (cf. Harker, *Z. Krist.*, **1936**, **93**, 136; Chrobak, *ibid.*, **1934**, **88**, 30; Hendricks and Dickinson, *J. Amer. Chem. Soc.*, **1927**, **49**, 2149). The active amount of this complex would appear to be only slowly changed with increasing dilution.

EXPERIMENTAL.

General Procedure.—The *p*-nitroaniline was diazotised in concentrated hydrochloric acid by addition of solid sodium nitrite, and the mixture kept for 30 mins. Amounts of water and of metallic salts were then added as indicated in the tables, and the reaction carried out by 30 mins.' boiling under reflux. The *p*-chloronitrobenzene formed was removed by steam distillation, dried, and weighed. The mode of addition of the salts was as follows: cuprous chloride (4 g.) immediately after the addition of water; hydrated cupric chloride (6·9 g.) in aqueous solution whenever the amount of water to be added was sufficient for its dissolution; hydrated ferric chloride (10·8 g.) just prior to the addition of water.



	HCl. 50 c.c.	HCl. 25 c.c.		HCl. 50 c.c.	HCl. 25 c.c.
CuCl	A	a	Blank	D	d
$CuCl_2$	B	b	CuCl + $CuCl_2$	E	e
$FeCl_3$	C	c			

Note to Tables.—The added water is calculated on the anhydrous salt in all cases. The yield of *p*-chloronitrobenzene is given to the nearest 0·05 g. and to the nearest 0·5%. Greater accuracy would not alter the conclusions derived from the experimental data.

TABLE I.

Yield of *p*-chloronitrobenzene, expressed in g. and %, for the various salts and the blank.

Water added, g.	Water present, g.	Blank. g.	Blank. %.	CuCl, g.	CuCl, %.	$CuCl_2$, g.	$CuCl_2$, %.	$FeCl_3$, g.	$FeCl_3$, %.
(*a*) In these experiments *p*-nitroaniline (2·8 g.) was diazotised with sodium nitrite (2 g.) in hydrochloric acid (50 c.c., *d* 1·16).									
Nil	38·0	1·8	56	2·8	87·5	2·4	75	2·6	81
2·5	40·5	—	—	2·8	87·5	2·3	72	—	—
10·0	48·0	1·7	53	2·7	84·5	2·65	83	2·2	69
25·0	63·0	1·6	50	2·7	84·5	2·2	69	2·0	62·5
40·0	78·0	—	—	3·0	94·0	—	—	—	—
50·0	88·0	1·4	44	2·9	92·0	1·6	50	1·45	45
100·0	138·0	1·0	31	2·6	81·0	1·5	47	1·0	31
150·0	188·0	0·7	22	—	—	1·65	52	—	—
200·0	238·0	—	—	—	—	1·65	52	—	—
(*b*) Data as for (*a*), but with only 25 c.c. of hydrochloric acid (*d* 1·16).*									
Nil	1·9	1·8	56	3	94	2·5	78	—	—
4·3	23·3	—	—	—	—	—	—	2·1	66
10·0	—	—	—	2·9	91	2·4	75	—	—
14·3	38·3	—	—	—	—	—	—	1·95	61
25·0	44·0	1·4	44	2·8	87·5	1·7	53	—	—
29·3	48·3	—	—	—	—	1·5	47	1·5	47
50·0	69·0	1·3	41	2·7	84·5	1·55	48·5	—	—
54·3	73·3	—	—	—	—	—	—	1·2	38
75·0	94·3	—	—	2·75	86·0	1·8	56	0·9	28
100·0	119·3	0·55	17	2·8	87·5	2·0	62·5	0·65	20
150·0	169·0	—	—	2·4	75	2·1	66	—	—
200·0	219·0	—	—	2·0	62·5	2·4	75	—	—
250·0	269·0	—	—	—	—	2·3	72	—	—

* In this section water was added in portions of 10, 25, 50, 75, 100, etc., g., and to it has been added the water of crystallisation of the salts. This is particularly important when the volume of water is small.

TABLE II.

Cuprous and cupric chlorides in combination. Procedure as before, but with cuprous chloride (2·0 g.) and hydrated cupric chloride (3·45 g.).

With 50 c.c. of HCl (d 1·16).				With 25 c.c. of HCl (d 1·16).							
H_2O added, c.c.	Total H_2O present, g.	p-$Cl\cdot C_6H_4\cdot NO_2$ formed, g.	%	H_2O added, c.c.	Total H_2O present, g.	p-$Cl\cdot C_6H_4\cdot NO_2$ formed, g.	%	H_2O added, c.c.	Total H_2O present, g.	p-$Cl\cdot C_6H_4\cdot NO_2$ formed, g.	%
Nil	38·7	3·05	96	Nil	19·7	3·0	94	150	169·7	2·75	86
40	78·7	3·0	94	50	69·7	2·9	91	200	219·7	2·5	78
100	138·7	2·9	91	100	119·7	2·8	88	250	269·7	2·3	72

The authors are indebted to the Charles Brotherton Trust for a Research Scholarship to one of them (D.D.R.S.), and to Imperial Chemical Industries Ltd. (Dyestuffs Division) for the gift of p-nitroaniline.

TECHNICAL COLLEGE, HUDDERSFIELD.

[*Received, March* 1*st,* 1944.]