

### S10. *The Kinetics and Mechanism of the Sandmeyer Reaction.*

By W. A. COWDREY and D. S. DAVIES.

The kinetics of the Sandmeyer reaction for replacing diazonium groups by halogen have been investigated. The reaction is of the first order with respect to both diazonium ion and dissolved cuprous chloride: the rate is, however, inversely proportional to the square of the total chloride-ion concentration. From these results it is inferred that the primary reaction involves collision between  $\text{ArN}_2^+$  and  $\text{CuCl}_2^-$  ions, and that the latter are converted into (unreactive)  $\text{CuCl}_4^-$  ions at higher chloride concentrations. The value of the equilibrium constant for the process  $\text{CuCl}_2^- + 2\text{Cl}^- \rightleftharpoons \text{CuCl}_4^-$ , inferred from the kinetics, is supported by measurement of the solubility of  $\text{CuCl}$  as a function of the chloride-ion concentration.

The rate of the Sandmeyer reaction of substituted diazonium compounds decreases in the order  $p\text{-NO}_2 > p\text{-Cl} > \text{H} > p\text{-CH}_3 > o\text{-CH}_3 > p\text{-OCH}_3$ .

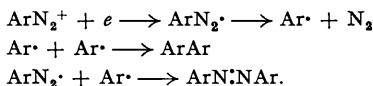
The symmetrical azo-compound is the major by-product: its yield increases with the  $\text{CuCl}_2^-$  concentration and in certain circumstances it is formed as a complex with cuprous chloride. Minor by-products include the hydrocarbon  $\text{ArH}$ , the phenol  $\text{ArOH}$ , in one case the diaryl  $\text{Ar}\cdot\text{Ar}$ , and an unidentified, water-soluble fraction.

The suggested mechanism, which involves only simple binary collisions, is (a) slow co-ordination of the terminal nitrogen atom of  $\text{ArN}_2^+$  to the copper in  $\text{CuCl}_2^-$ , giving  $[\text{ArN}_2\text{CuCl}_2]$ ; (b) decomposition of this to  $\text{ArCl}$  or (c) further fast addition to it of  $\text{ArN}_2^+$  to give  $[(\text{ArN}_2)_2\text{CuCl}_2]^+$ , which either (d) decomposes to  $\text{ArCl}$  or (e) reacts with  $\text{CuCl}_2^-$  to give  $\text{ArN:NAr}$ .

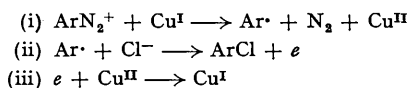
THE reaction between diazonium compounds and cuprous chloride, as is well known, yields mainly the aryl chloride. In addition, the products include the phenol, symmetrical azo-compound (Erdmann, *Annalen*, 1893, **272**, 141; Bogoslovskii, *J. Gen. Chem. Russia*, 1946, **16**, 193), and symmetrical diaryl (Ullmann and Frenzel, *Ber.*, 1905, **38**, 726).

Two mechanisms have been suggested. Hodgson (*J.*, 1941, 770; 1942, 376, 720; 1944, 18) has proposed that the main reaction consists of a simple nucleophilic displacement of  $\text{N}_2$  by a halide ion co-ordinated on to some other species, as in the ions  $\text{CuCl}_4^-$  and  $\text{FeCl}_4^-$ , and the

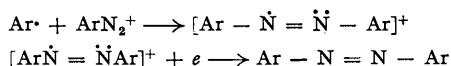
molecule HCl. The side reactions Hodgson ascribes to the reductive formation of aryl and diazo-radicals, which interact to give azo-compound or diaryl :



Unlike Hodgson, Waters (*J.*, 1942, 266) believes that the cuprous catalyst plays a special part in the Sandmeyer reaction by virtue of its reducing properties, giving rise to aryl radicals which then react with halide ions to produce the aryl halide. The electron liberated in this second step can then regenerate the catalyst :



Although the three processes are presumed to follow each other very rapidly [so that the actual cuprous ion oxidised in step (i) is regenerated in step (iii), and the radical need not become truly free], sufficient free aryl radicals liberate themselves to form diaryl by Hodgson's mechanism, and azo-compound by the sequence :



(the electron presumably being furnished by the cuprous catalyst).

Some work on the kinetics of the reaction was carried out by Waentig and Thomas (*Ber.*, 1913, 46, 3923), who reported that the reaction was first order with respect to diazonium concentration, accelerated (not systematically) by an increase in total cuprous chloride, and retarded by hydrogen chloride. Complexes of the formula  $\text{X}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}\cdot\text{Cu}_2\text{Cl}_2$  were isolated, and it was suggested that these substances formed rapidly and then decomposed slowly to the aryl chloride.

The present, more extensive, kinetic analysis proves to be inconsistent with the Waters and the Hodgson hypothesis : a new mechanism is proposed.

#### EXPERIMENTAL.

The detailed pattern of the kinetics was established in the case of diazotised *o*-toluidine, and the general outline confirmed in the other cases studied. As a preliminary, complete analyses of the products in typical experiments were carried out for this reaction. These established that the oil layer consisted only of *o*-chlorotoluene (determined by the intensity of the infra-red band at  $762\text{ cm}^{-1}$ ), 2 : 2'-azotoluene (determined colorimetrically and from the absorption at  $725\text{ cm}^{-1}$ ), toluene (infra-red band at  $735\text{ cm}^{-1}$ ), and cresol (bromine titration), the last two in small amounts. Together with the small amount of cresol which could be extracted from the aqueous layer, these yields amounted to only 85–94% of the total. The missing fraction (which had lost its nitrogen) was necessarily in the aqueous layer, but could not be isolated, although 10% of the missing carbon was found in the inorganic salts remaining after vacuum evaporation.

The yield of the chloro-compound rose at the expense of the azo-compound (the main by-product) (*a*) when the chloride-ion concentration in the medium was increased and (*b*) when the diazonium solution was added gradually to the cuprous chloride solution (normal preparative practice) instead of being all added simultaneously at the outset.

In the more extensive experiments, it was considered sufficient to measure the azo-yield colorimetrically (to determine the influence of conditions on the products) and to estimate the velocity of reaction from the nitrogen evolution. The reaction was carried out in a 2-l. flask fitted with a mercury seal stirrer and connected to a gas burette. Water at a constant temperature circulated round flask and burette. Diazonium solution and buffer were brought to the reaction temperature in the flask: a solution of cuprous chloride in hydrochloric acid was introduced into a closed side-bulb which was connected to the flask by a ground-glass joint and whose contents could be poured rapidly into the flask by rotating the side-arm in the joint. The reaction having thus been started, the change in gas volume (at atmospheric pressure) was recorded at intervals. Efficient agitation was essential: it was found sufficient to use a stirrer with two one-inch links rotated at 1500 r.p.m.

#### Results.

(*a*) *Kinetics*.—The reaction is of first-order initially: if *a* is the total volume of nitrogen evolved at the end of reaction and *x* the volume evolved after time *t*, a plot of  $\log(a - x)$  against *t* (see Fig. 1) is linear for a considerable proportion of the reaction period. That it is not so for the whole run is due to consumption of cuprous chloride in the side reaction

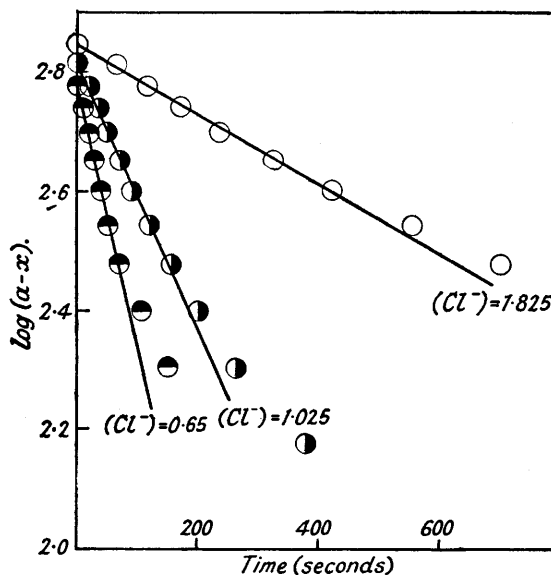


and if as little as 0.1 mol. of cuprous chloride is used per mol of diazonium compound, the nitrogen evolution stops before the diazonium ions are exhausted, and restarts when more cuprous chloride is added. Other side reactions (except phenol formation) also involve permanent catalyst oxidation. Rate constants, therefore, were determined from the initial slope of the first-order plots.

There was sometimes an induction period of a few seconds—possibly the time required for the establishment of the  $\text{CuCl}-\text{Cl}^-$  equilibrium.

To avoid changes in the ionic environment, the ionic strength was kept constant in most of the experiments at a value of 4.5 by the addition of ammonium sulphate. In addition, the acid concentration was adjusted so that the  $\text{HSO}_4^- \rightleftharpoons \text{SO}_4^{2-}$  equilibrium operated as a buffer and maintained the  $\text{OH}_3^+$  concentration in the range 0.01—0.03. Further experiments also showed that considerable changes in ionic strength and pH were without effect on the rate.

FIG. 1.



*Sandmeyer reaction of diazotised o-toluidine: typical reaction curves: a = final volume of nitrogen evolved; x = volume evolved at time t. In all cases  $[\text{CuCl}] = 0.025$ .*

The problem was further simplified when it was established that the addition of a second phase of chlorotoluene or mixed reaction products did not alter the velocity of reaction.

The variables which had most effect were diazonium, cuprous chloride, and chloride-ion concentrations. Table I and Figs. 2 and 3 show that the first-order rate constant is (i) unaffected by changing the initial diazonium concentration, (ii) almost linearly proportional to the total CuCl concentration, and (iii) almost proportional to the inverse square of the total chloride-ion concentration.

TABLE I.

*Effect of diazonium concentration on rate of reaction.*

	[CuCl <sub>dissolved</sub> ] = 0.025; [Cl <sup>-</sup> ] = 1.125.				
[ArN <sub>2</sub> <sup>+</sup> ] <sub>initial</sub>	0.022	0.033	0.044	0.066	
434.3k' (rate constant), sec. <sup>-1</sup>	2.0	1.8	1.9	1.8	±0.1

Figs. 4, 5, and 6 show that the azo-yield (i) decreases slightly on increasing the diazonium concentration, (ii) increases markedly with increase in the cuprous chloride concentration, and (iii) decreases as the chloride-ion concentration increases. In these figures, a minor correction has been applied to the chloride concentration to allow for the reaction of  $\text{Cl}^-$  with cuprous chloride.

The results can all be correlated in terms of the equations:

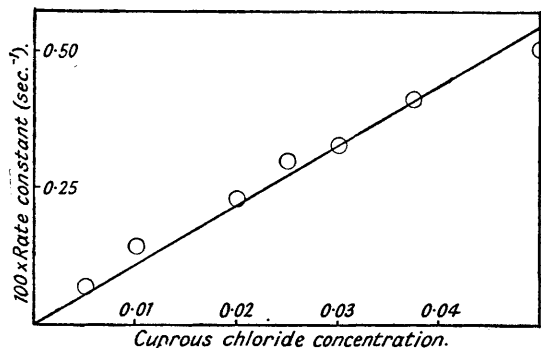
$$-\frac{d[\text{ArN}_2^+]}{dt} = \frac{k_1[\text{ArN}_2^+][\text{CuCl}_{\text{dissolved}}]}{1 + [\text{Cl}^-]^2/K} \quad \dots \quad (1)$$

$$\frac{dA}{dC} = \frac{2k_2[\text{CuCl}_{\text{dissolved}}]}{1 + [\text{Cl}^-]^2/K} \quad \dots \quad (2)$$

where  $C$  is the concentration of chloro-compound in moles/litre and  $A$  that of azo-compound in half-moles/litre at any time  $t$ .

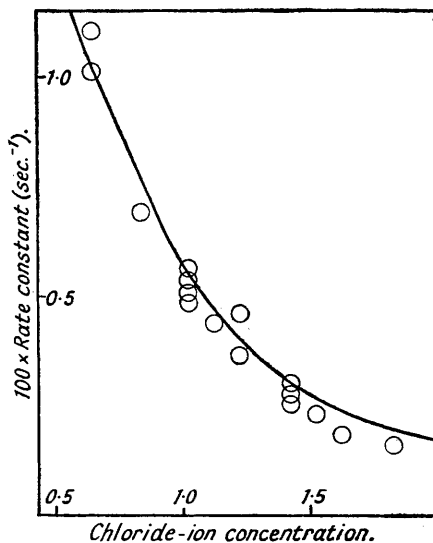
The full lines in Figs. 2—6 show the rates of nitrogen evolution and azo-yields calculated from these expressions (with  $k_1 = 3$ ,  $K = 0.1$ , and  $k_2 = 130$ ) in the following way.

FIG. 2.



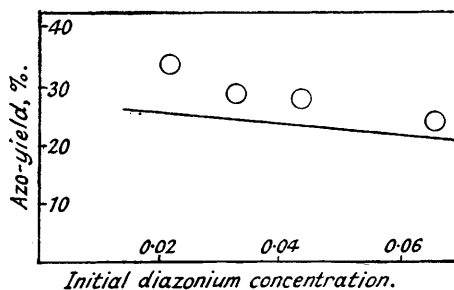
Effect of cuprous chloride concentration on rate of diazotised *o*-toluidine Sandmeyer reaction. The line shows the calculated values. In all experiments  $[\text{diazo}]_{\text{initial}} = 0.033$  and  $[\text{Cl}^-] = 1.425$ .

FIG. 3.



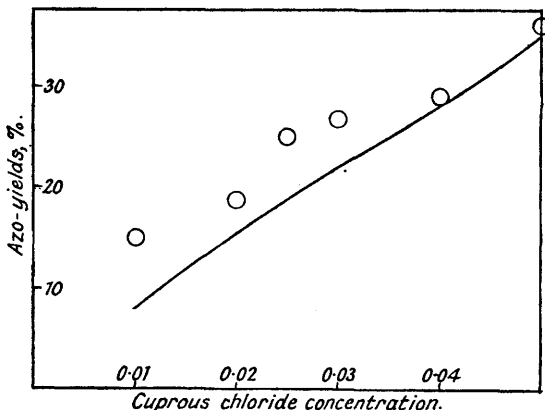
Effect of chloride-ion concentration on rate of Sandmeyer reaction of diazotised *o*-toluidine. The line shows the calculated values. In all cases  $[\text{diazo}]_{\text{initial}} = 0.033$  and  $[\text{CuCl}] = 0.025$ .

FIG. 4.



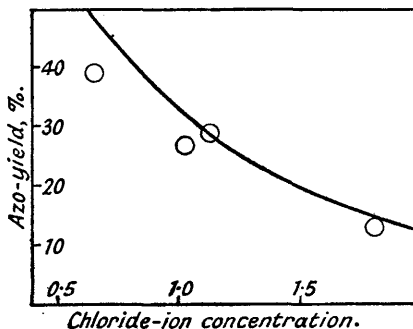
Effect of initial diazonium concentration on azo-yield in Sandmeyer reaction of diazotised *o*-toluidine. The line shows the calculated values. In all experiments  $[\text{CuCl}] = 0.025$  and  $[\text{Cl}^-] = 1.125$ .

FIG. 5.



Effect of cuprous chloride concentration on azo-yield in Sandmeyer reaction of diazotised o-toluidine. The line shows the calculated values. In all experiments  $[\text{diazo}]_{\text{initial}} = 0.033$  and  $[\text{Cl}^-] = 1.425$ .

FIG. 6.



Effect of chloride-ion concentration on azo-yield in Sandmeyer reaction of diazotized o-toluidine. The line shows the calculated values. In all cases  $[\text{diazo}]_{\text{initial}} = 0.033$  and  $[\text{CuCl}] = 0.025$ .

Since the azo-formation only involves the evolution of half the nitrogen, then, neglecting minor side reactions, we have

$$\frac{d[\text{N}_2 \text{ evolved}]}{dt} = \frac{-d[\text{ArN}_2^+]}{dt} \left\{ \left(1 + \frac{1}{2} \frac{dA}{dC}\right) / \left(1 + \frac{dA}{dC}\right) \right\} \dots \dots \dots (3)$$

so that, from equations (1) and (2), we have

$$\frac{d[\text{N}_2 \text{ evolved}]}{dt} = \frac{k_1[\text{ArN}_2^+][\text{CuCl}]}{1 + [\text{Cl}^-]^2/K} \left\{ \frac{1 + \frac{[\text{Cl}^-]^2}{K} + k_2[\text{CuCl}_{\text{dissolved}}]}{1 + \frac{[\text{Cl}^-]^2}{K} + 2k_2[\text{CuCl}_{\text{dissolved}}]} \right\} \dots \dots \dots (4)$$

the equation required to calculate the apparent rate constant for nitrogen evolution.

Assuming that the chloride-ion concentration is high and does not change, equation (2) can be integrated to:

$$\log \frac{B}{B-A} = \frac{2k_2C}{1 + [\text{Cl}^-]^2/K} \dots \dots \dots (5)$$

where  $B$  is the initial cuprous chloride concentration. It is also necessary that, minor side reactions being neglected,

$$C_{\text{final}} + A_{\text{final}} = [\text{diazo}]_{\text{initial}} \dots \dots \dots (6)$$

Graphical solution of the equation obtained by combining (5) and (6) gives values of  $A_{\text{final}}$  and  $C_{\text{final}}$  which can be used to determine the azo-yield  $[A_{\text{final}} / (A_{\text{final}} + C_{\text{final}})]$ .

The main limitation to this treatment is the assumption that cuprous chloride is consumed only in the reaction leading to azo-compound. Bearing in mind the fact that this is only approximately true, the agreement between predicted and observed azo-yields (Figs. 4—6) is not unreasonable. This is a more searching test of the equations (1) and (2) than the rate of nitrogen evolution: the azo-yield is a function of the whole course of reaction, while the rates quoted are a function only of the condition early in the reaction.

The apparent first-order rate constants ( $k'$ ) for nitrogen evolution in some other Sandmeyer reactions are shown in Table II. The same behaviour is observed when the  $\text{CuCl}$  and  $\text{Cl}^-$  concentrations are changed: the values of  $k_1$  calculated when  $K$  and  $k_2$  are given the same value as in the case of *o*-diazotoluene are also shown in the table. The use of the same values of  $K$  is justified later (see below): it may be observed that quite large changes in  $k_2$  (which governs the azo-yield) do not affect the nitrogen evolution rate markedly. The effect of substituents is very pronounced: the rate falls in the order  $p\text{-NO}_2 > p\text{-Cl} > \text{H} > p\text{-Me} > p\text{-MeO}$ , *i.e.*, the reaction is assisted by electron-attracting groups.

TABLE II.

Parent amine.	[CuCl].	[Cl <sup>-</sup> ].	434.3 $k'$	$k_1$ .	Parent amine.	[CuCl].	[Cl <sup>-</sup> ].	434.3 $k'$	$k_1$ .
<i>p</i> -Nitroaniline	Too fast to measure	—	—	>160	Aniline	0.01	1.5	7.9	41
Sulphanilamide					0.025	1.9	11.8	40	
Sulphanilic acid					0.01	1.9	4.1	34	
<i>p</i> -Chloroaniline	0.005	3.7	2.6	160	<i>p</i> -Toluidine	0.025	1.1	4.4	5.7
	0.01	3.7	5.4	170		0.025	1.5	2.5	5.5
<i>p</i> -Anisidine	0.025	1.5	0.17	0.38		0.025	1.9	1.4	4.8
	0.025	1.9	0.11	0.37					

Azo-compounds were isolated from among the products in these Sandmeyer reactions, and in one case (*p*-nitrobenzenediazonium) the diaryl was also obtained.

In two typical cases (diazotised aniline and *p*-toluidine) the rate constant was measured as a function of temperature between 0° and 20°. The results are shown in Table III: the apparent activation energies are respectively 6.0 and 7.5 kcal./mole. It would be difficult to measure the kinetics above 0° in the other cases: in the diazotised chloroaniline reaction the rate becomes too great to measure: in the cases of *o*-toluidine and anisidine the competing reaction of decomposition to phenol becomes serious.

Since  $[\text{Cl}^-]^2/K$  is greater than 20 at the chloride-ion concentrations studied in these experiments, the rate expression can be simplified to

$$\frac{d[\text{N}_2 \text{ evolved}]}{dt} = \frac{k_1 K [\text{ArN}_2^+][\text{CuCl}]}{[\text{Cl}^-]^2},$$

so that the apparent activation energy is the sum of the heat content changes represented by  $R \cdot d \ln k_1/d(1/T)$  and  $R \cdot d \ln K/d(1/T)$ . The physical significance of  $k_1$ ,  $K$ , and  $k_2$  will now be considered.

TABLE III.

	Temp.	[Cl <sup>-</sup> ].	[CuCl].	434.3 $k'$ (sec. <sup>-1</sup> ).	$E$ (kcal./mole).
Aniline	1°	1.9	0.01	4.1	6.0
	9.5	1.9	0.01	6.7	
	19	1.9	0.01	9.5	
<i>p</i> -Toluidine	0	1.5	0.025	2.5	7.3
	8	1.5	0.025	3.8	
	19	1.5	0.025	5.8	
	0	1.9	0.025	1.4	7.7
	8	1.9	0.025	2.0	
	19	1.9	0.025	3.4	

(b) *Nature of the Reactive CuCl Species.*—The negative catalysis by chloride ion appears to be the same in all the Sandmeyer reactions studied: it is therefore likely that the addition of chloride affects the ionic condition of the cuprous chloride rather than the diazonium ions. Qualitatively, it seems simplest to assume that the addition of  $\text{Cl}^-$  converts a catalytically active cuprochloride species into a more highly co-ordinated, catalytically less active (or inactive) substance. Quantitatively, it is possible to account for the inverse-square dependence of rate on chloride concentration by postulating that  $\text{CuCl}$  in a chloride solution exists as  $\text{CuCl}_2^-$  and  $\text{CuCl}_4^{2-}$ , the former alone being catalytically active. In such a case, ordinary equilibrium considerations lead to the equation

$$[\text{CuCl}_2^-] = \frac{[\text{CuCl}_{\text{dissolved}}]}{1 + [\text{Cl}^-]^2/K}$$

where  $K$  is the equilibrium constant  $[\text{CuCl}_2^-][\text{Cl}^-]^2/[\text{CuCl}_4^{2-}]$ . If now the reaction rate is of first order in both  $\text{CuCl}_2^-$  and  $\text{ArN}_2^+$ , the rate expression becomes

$$\frac{-d[\text{diazo}]}{dt} = \frac{k_1 [\text{ArN}_2^+][\text{CuCl}_{\text{dissolved}}]}{1 + [\text{Cl}^-]^2/K}$$

which is the same as equation (1) and enables  $K$  in this equation to be identified as the constant governing the  $\text{CuCl}_2^-/\text{CuCl}_4^{2-}$  equilibrium.

The assumptions (a) that  $\text{CuCl}_3^-$  is the reactive species, converted into  $\text{CuCl}_4^{2-}$  at high chloride concentrations, or (b) that  $\text{CuCl}_2^-$  is the catalyst, converted into  $\text{CuCl}_3^-$  as  $\text{Cl}^-$  is added, would lead to an inverse first-power dependence of rate on chloride concentration. It is quite possible, however, that a small proportion of the  $\text{CuCl}$  is present as  $\text{CuCl}_3^-$ , as long as  $\text{CuCl}_2^-$  and  $\text{CuCl}_4^{2-}$  are the principal forms.

It has been recognised for many years that cuprous chloride dissolves as  $\text{CuCl}_2^-$  at low chloride concentrations (cf. Noyes and Ming Chow, *J. Amer. Chem. Soc.*, 1918, **40**, 739; Bodländer and Störbeck, *Z. anorg. Chem.*, 1902, **31**, 1). A method was sought for elucidating the nature of the species involved, and determining the constants, in the equilibria between  $\text{CuCl}$  and  $\text{Cl}^-$  at high concentrations of the latter. At such high ionic strengths ( $> 2$ ) measurements of the total activity of the species in solution by freezing-point depression or similar methods would be difficult to interpret: the activity coefficients in question are not known and would be hard to measure. On the other hand, solubility measurements offer rather better possibilities. The total solubility  $s$  of cuprous chloride is equal to the sum of the concentrations of all the cuprochloride anions:

$$s = [\text{CuCl}_2^-] + [\text{CuCl}_3^=] + [\text{CuCl}_4^=]$$

If the solubility measurements are carried out at various chloride-ion concentrations but at constant total ionic strength, and the assumption made that the activity coefficient ratios  $f_{\text{CuCl}_2^-}/f_{\text{Cl}^-}$ ,  $f_{\text{CuCl}_3^=}/(f_{\text{Cl}^-})^2$ , and  $f_{\text{CuCl}_4^=}/(f_{\text{Cl}^-})^3$  are constant (but not necessarily unity) then

$$[\text{CuCl}_2^-] = a[\text{Cl}^-]; [\text{CuCl}_3^=] = b[\text{Cl}^-]^2; [\text{CuCl}_4^=] = c[\text{Cl}^-]^3$$

(where  $a$ ,  $b$ ,  $c$ , are constants) and

$$s = a[\text{Cl}^-] + b[\text{Cl}^-]^2 + c[\text{Cl}^-]^3. \quad \dots \quad (7)$$

The analytical deduction of  $a$ ,  $b$ , and  $c$  from an observed solubility-added chloride concentration curve is unfortunately impossible, since the value of  $[\text{Cl}^-]$  in equation (7) is not the added chloride concentration  $M$ , but

$$\begin{aligned} [\text{Cl}^-] &= M - [\text{CuCl}_2^-] - 2[\text{CuCl}_3^=] - 3[\text{CuCl}_4^=] \\ &= M - a[\text{Cl}^-] - 2b[\text{Cl}^-]^2 - 3c[\text{Cl}^-]^3. \quad \dots \quad (8) \end{aligned}$$

However, for assumed values of  $a$ ,  $b$ , and  $c$ , a curve relating  $s$  and  $M$  may be drawn from equations (7) and (8) by the method of successive approximations. Such curves may be compared with experimental  $s$ - $M$  plots, and the best values of  $a$ ,  $b$ , and  $c$  so chosen. The concentration equilibrium constants  $[\text{CuCl}_2^-][\text{Cl}^-]^2/[\text{CuCl}_4^=]$  (*i.e.*  $K$ ) and  $[\text{CuCl}_3^=][\text{Cl}^-]/[\text{CuCl}_4^=]$  are then given by  $a/c$  and  $b/c$  respectively. This was the method chosen.

Previous solubility determinations (Abel, *Z. anorg. Chem.*, 1901, **26**, 401; Bodländer and Störbeck, *loc. cit.*; Valetton and Frömel, *Z. anorg. Chem.*, 1924, **137**, 91; Brønsted, *Z. physikal. Chem.*, 1912, **80**, 206; Engel, *Comp. rend.*, 1895, **121**, 529; Kremann and Noss, *Monatsh.*, 1912, **33**, 1205) are surprisingly inconsistent. The most likely cause of error is solution through oxidation, and fresh determinations were undertaken under the Sandmeyer conditions (constant ionic strength and roughly constant pH) with special care to exclude air.

The chloride solution, with a small excess of solid cuprous chloride, was stirred at 5° in a vessel through which air-free nitrogen was passing. The solution was slowly cooled ( $\frac{1}{2}$  hour) to 0°, and a sample then withdrawn by suction through a sintered-glass filter, without opening the apparatus. The system was then further cooled to -2°, and then allowed to warm slowly to 0°, whereupon a further sample was withdrawn. The two samples were oxidised to the cupric state with hydrogen peroxide, the excess of the latter boiled off, and the copper analysed by precipitation and weighing as the salicylaldoxime complex.

The results are given in Table IV. Agreement between pairs of determinations was usually within 1%. Acidity had little effect.

TABLE IV.

(a)  $[\text{OH}_3^+] = 0.01-0.04$ ;  $\mu = 4.3$ .

$M$ (added chloride)...	0.2	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8
$s$ (mean) .....	0.0065	0.017	0.030	0.050	0.074	0.103	0.144	0.194	0.248

(b) Solution nearly neutral (no acid added);  $\mu = 4.5$ .

$M$ (added chloride) .....	0.2	1.0	1.8
$s$ (mean) .....	0.0072	0.079	0.264

It can readily be seen that gross errors would be caused by equating  $M$  and  $\text{Cl}^-$  at the higher end of the concentration range.

By the method outlined above, it was found that these values could best be interpreted by assuming that  $b = 0$ , and  $a/c = [\text{CuCl}_2^-][\text{Cl}^-]^2/[\text{CuCl}_4^=] = K$  was of the order 0.1 (with  $c = 0.17$ ). The fit, though not perfect (see Fig. 7) was better than that with  $a/c = 1$  or 0.01. The measurements can do no more than fix the order of magnitude of  $a/c$ . However, the fact that  $a/c$  ( $K$ ) is of the same order as the value inferred from the kinetics, lends probability to the hypothesis that  $\text{CuCl}_2^-$  is the active species. It also becomes possible to determine the activation energy corresponding to the bimolecular rate constant  $k_1$ . The temperature coefficient of  $K$  is determined by the heat of the reaction  $\text{CuCl}_2^- + 2\text{Cl}^- \rightarrow \text{CuCl}_4^=$ . This quantity can be determined as the difference between the heat of solution at constant ionic strength of  $\text{CuCl}$  in 0.2M- $\text{Cl}^-$  (where it dissolves almost entirely as  $\text{CuCl}_2^-$ ) and in 2.0M- $\text{Cl}^-$  (where it dissolves almost entirely as  $\text{CuCl}_4^=$ ), and has a value of  $0.9 \pm 0.75$  kcal./mole (determined by Mr. G. R. Nicholson of these laboratories).

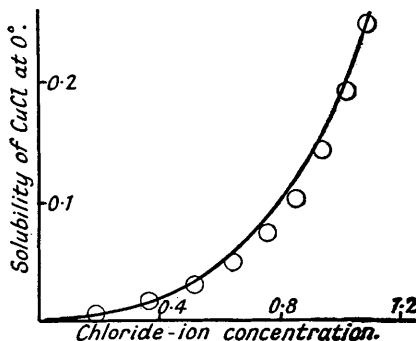
Hence, the true activation energy for the diazotised *p*-toluidine reaction is  $7.5 - 0.9 = 6.6 \pm 1$  kcal./mole. The non-exponential factor  $A$  therefore has the value  $10^{6 \pm 0.8}$  g.-mol.<sup>-1</sup> l. sec.<sup>-1</sup>.

(c) *Experiments involving Extreme Variation in the Conditions. Appearance of a Copper Azo-compound.*—It was observed earlier (p. S 49) that the yield of azo-compound was decreased by maintaining a very low stationary diazonium concentration throughout the reaction by running diazonium solution slowly into a cuprochloride solution. Fig. 4 shows that there is no decrease in azo-yield when the initial diazonium concentration is decreased from 0.07 to 0.02. It seemed important, therefore, to investigate this matter further. A diazonium solution was prepared and divided into two equal parts. A cuprous chloride solution with the same chloride concentration as the diazonium solution was buffered at  $[\text{OH}_3]^+ = 0.02$  and also divided into equal parts: the volume of this solution was considerably greater than that of the diazonium solution, so the change in  $[\text{CuCl}]$  on addition of the latter solution was not important.

To one portion of the cuprochloride solution, the diazonium solution was added gradually: to the other it was all added at once. The results of two such pairs of experiments with diazotised *o*-toluidine are given in Table V in the form of yields %.

It is confirmed, therefore, that the reduction of  $[\text{ArN}_2^+]$  to very low values considerably improves the yield of chlorotoluene at the expense of the azotoluene.

FIG. 7.



Variation of solubility of cuprous chloride with free chloride-ion concentration. The line is calculated with  $K = 0.1$ .

TABLE V.

$[\text{Cl}^-] = 1.6$ ;  $[\text{CuCl}]_{\text{final}} = 0.025$ .

Product.	Rapid addition.	Gradual addition.
Chlorotoluene .....	55.5, 54.5	64, 64
Azotoluene .....	20.2, 24.2	9.7, 9.7
Cresol .....	3.7, 1.3	1.9, 2.1
Toluene .....	ca. 4	ca. 4

In some of the experiments at high cuprous chloride concentration, the initial product was black and tarry, but, on being warmed to  $50^\circ$ , this lightened to give the usual red oil. The nature of this black material was further investigated. In a preparation in which the initial concentrations of diazotised *o*-toluidine,  $\text{CuCl}$ ,  $\text{Cl}^-$ , and  $\text{OH}_3^+$  were respectively 0.033, 0.1, 0.9, and 0.02, the black solid was filtered off. When moist, this did not dissolve rapidly in solvents, but when warmed with *cyclohexane* it dissolved to a red solution of azo-compound, leaving a light-coloured insoluble residue which was also insoluble in water and had the properties of cuprous chloride. The azo-yield of 53.7% corresponded with the observed deficit of 27% in the nitrogen evolution.

The black solid could also be decomposed by warming with 4*N*-hydrochloric acid; the azotoluene was extracted away with *cyclohexane* and determined: the aqueous layer became green on oxidation with hydrogen peroxide and gave a deep blue colour with ammonia; salicylaldoxime gave a precipitate, so this fraction undoubtedly contained copper. This was determined by weighing the salicylaldoxime precipitate. The azo: copper ratios (molar) thus obtained in analyses (a) of the moist black solid and (b) of a sample left in a vacuum desiccator at  $0^\circ$  for 12 hours to remove chlorotoluene were respectively 2.6 and 2.4. Elementary analysis of the dried compound gave C, 61.05; H, 5.45; N, 10.85%, which corresponds to a C : H : N ratio of 13.0 : 13.8 : 2 compared with 14 : 14 : 2 required by the azo-compound.

The actual value of the azo : copper ratio may not be significant, because the black solid may have contained free azotoluene (which could not be removed by solvents without decomposing the complex). The copper must have been combined, there being no other circumstance to make it separate from the solution. Cuprous chloride and azotoluene do not combine directly under these conditions, so that the copper-azo-compound must be an intermediate in the formation of the free azo-compound.

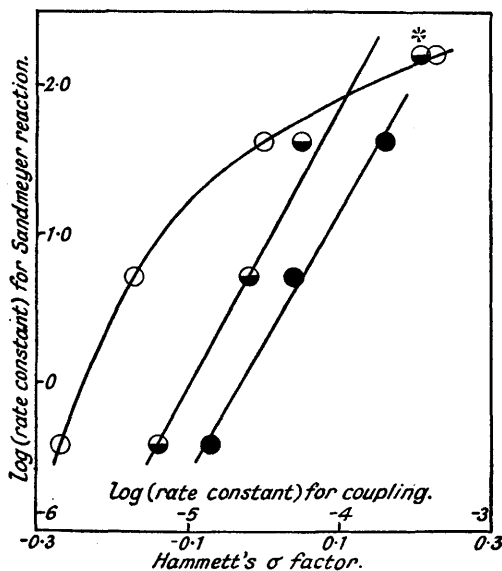
Copper azo-compounds are not found among the reaction products when the Sandmeyer reaction is carried out in very acid solution: presumably they are decomposed by acid. They are formed (at low acidities) in the Sandmeyer reactions of diazotised *p*-chloroaniline, aniline, *p*-toluidine, and *p*-anisidine. In none of these cases could the compound be crystallised or otherwise purified without decomposition.



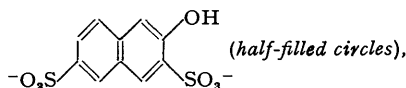
## DISCUSSION.

The experimental data given above may be summarised as follows. (1) The reaction is of first order with respect to each of the two species  $\text{ArN}_2^+$  and  $\text{CuCl}_2^-$ , the ion  $\text{CuCl}_4^{2-}$  (formed at higher chloride-ion concentrations) being catalytically inactive. (2) The ratio of the rates of production of azo-compound (the main by-product) and chloro-compound is proportional to the concentration of the ion  $\text{CuCl}_2^-$ . (3) Both activation energy (6.6 kcal./mole) and non-exponential  $A$  factor ( $10^8$ ) are low in a typical case (diazotised *p*-toluidine). (4) The azo-compound appears in the first instance co-ordinated to copper. (5) The effect of substituents on the reaction are such that the rate decreases in the sequence  $p\text{-NO}_2 > p\text{-Cl} > \text{H} > p\text{-Me} > p\text{-OMe}$ .

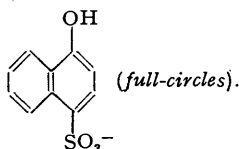
FIG. 8.



Relationship between Sandmeyer and coupling reactions. Sandmeyer rate constants plotted against (a) Hammett's  $\sigma$  factor (open circles), (b) rate of coupling of substituted diazo-compounds with



(c) rate of coupling of substituted diazo-compounds with



\* The coupling rate here plotted is for *p*-bromodiazobenzene: the Sandmeyer figure is for *p*-chlorodiazobenzene.

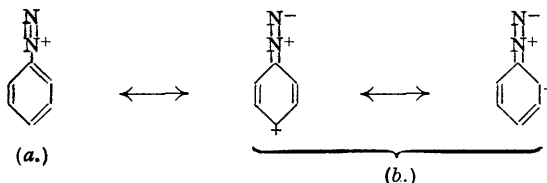
In connection with (5) it is noteworthy that the influence of substituents on the rate of the azo-coupling reaction (Conant and Peterson, *J. Amer. Chem. Soc.*, 1930, **52**, 1220) is very similar to that in the Sandmeyer reaction. Fig. 8 shows the logarithms of the two series of rate constants plotted against one another: the relationship is more nearly linear than that between the logarithm of the Sandmeyer rate constant and Hammett's  $\sigma$  factor. This suggests that the two reactions both involve the terminal nitrogen of the diazonium group: the effect of substituents on the electron availability at this point may well be different from the effect on the availability in the carboxylate group (which determines  $\sigma$ ).

The finding (1) implies that the rate-controlling step is either a collision between  $\text{ArN}_2^+$  and  $\text{CuCl}_2^-$  or the decomposition of a complex so formed [*e.g.*,  $\text{ArN}\equiv\text{N} \rightarrow \text{CuCl}_2$  (I)], present in small concentration, and in mobile equilibrium with the reactants. The latter seems the

less probable, since electron-attracting groups such as  $-\text{NO}_2$  should reduce the availability of electrons on the terminal nitrogen and displace the equilibrium away from the complex (I). In fact the nitro-group assists the reaction, and there seems no good reason why it should facilitate the decomposition of (I) sufficiently to over-compensate for the reduced concentration and thus drastically increase the overall rate.

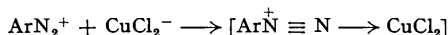
On the other hand, the withdrawal of electrons from the diazonium group would assist the approach of the negatively charged  $\text{CuCl}_2^-$  ion. A rate-determining collision between  $\text{ArN}_2^+$  and  $\text{CuCl}_2^-$  would therefore explain the substituent effect. Such a collision might occur in two ways: (i) The Cu might become co-ordinated on to the terminal nitrogen, and the complex subsequently undergo rapid reactions leading to the products; or (ii) the halogen might approach the nuclear carbon attached to the diazonium group, with direct displacement of nitrogen and formation of aryl chloride (as in the Hodgson mechanism). The scheme (ii) is unattractive since it affords no reason why  $\text{CuCl}_4^-$ , with its greater charge and larger number of Cl groups, should not be more reactive than  $\text{CuCl}_2^-$  and fails to explain the low  $A$  factor (see below); (i), on the other hand, is quite reasonable and can be made the basis for a complete mechanism explaining the kinetics of the appearance of azo- as well as chloro-compound.

The diazonium ion can probably be represented as a hybrid of the forms (a) and (b), so that the terminal nitrogen atom bears a small negative charge (despite the net positive charge on the ion). Introduction of a nitro-group will increase the predominance of structure (a) and reduce this negative charge. Interaction between  $\text{ArN}_2^+$  and a cuprochloride anion is therefore a reaction between negatively charged centres (though between oppositely charged ions) and as such may quite reasonably be the rate-controlling step.



In this connection, it is of interest that the  $A$  factor of the reaction (10<sup>6</sup>) is low. Bell (*J.*, 1943, 629) has drawn attention to a systematic connection between the magnitude of  $A$  and the ionic type of the reactants. An  $\text{A}^+-\text{B}^-$  reaction has a value for  $A$  of  $10^{13}$ — $10^{19}$ ; and  $\text{A}^+-\text{B}^+$  reaction a value of  $10^2$ — $10^7$ . The low value in the Sandmeyer reaction suggests that in this case it may be the charge on the reaction centres that determines  $A$ . It is also relevant that the  $A$  factor in the azo-coupling ( $\text{ArN}_2^+-\text{Ar}'\text{O}^-$ ) reaction, again formally of the  $\text{A}^+-\text{B}^-$  class, is only  $10^8$  (in calculating this value, allowance has been made in the activation energy for the heat of ionisation of the phenol).

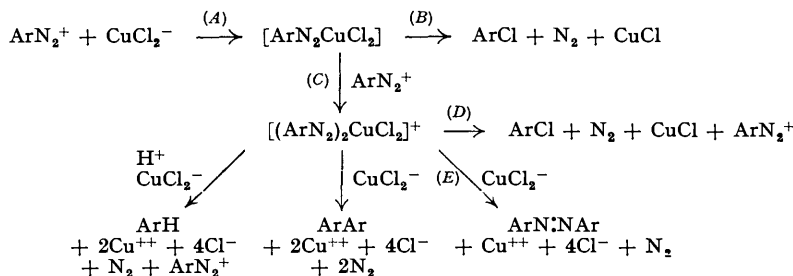
It is now necessary to consider the steps which follow the slow reaction



to give azo- and chloro-compound (and the other by-product). The stoichiometric equation for the formation of azo-compound is



so that at least four species (two diazo- and two cuprochloride ions) must be brought together, in a series of binary encounters, each leading to fairly stable complexes. The fact that  $d[\text{azo}]/d[\text{chloro}]$  is proportional to  $[\text{CuCl}_2^-]$  and independent of  $[\text{ArN}_2^+]$  at high  $\text{ArN}_2^+$  concentrations, but dependent on  $[\text{ArN}_2^+]$  at very low diazo-concentrations, appears to leave no alternative to the following scheme:



The detailed analysis of this mechanism can be made on the assumption that the concentrations  $x$  and  $y$  of the two complexes  $[\text{ArN}_2\text{CuCl}_2]$  and  $[(\text{ArN}_2)_2\text{CuCl}_2]^+$  only reach small stationary values, *i.e.*,  $dx/dt$  and  $dy/dt = 0$ , because the order of the reaction with respect to  $\text{ArN}_2^+$  does not tend towards zero when the initial  $\text{CuCl}$  concentration exceeds the initial  $\text{ArN}_2^+$  concentration, and similarly that the order with respect to  $\text{CuCl}$  does not fall when  $\text{ArN}_2^+$  is initially in excess. If there were considerable "storage" of the reactants in the form of the complexes, then the values of  $x$  and  $y$  (on which the rate depends) would become less and less dependent on the concentration of the reagent present in excess.

The usual kinetic analysis then yields the results that

$$-d[\text{ArN}_2^+]/dt = k_A[\text{ArN}_2^+][\text{CuCl}_2^-] \quad \text{[provided that the reverse reactions of processes (A) and (C) are slow]}$$

and  $d[\text{ArN}:\text{NAr}]/d[\text{ArCl}] = k_B[\text{CuCl}_2^-]/k_D$  [provided also that  $k_C[\text{ArN}_2^+] \gg k_B(1 + k_E[\text{CuCl}_2^-]/k_D)$ ]

This implies that stage (C) must be considerably faster than stage (B). This will only be true as long as  $[\text{ArN}_2^+]$  is sufficiently high. At very low values of  $[\text{ArN}_2^+]$  (as in gradual addition experiments),  $d[\text{ArN}:\text{NAr}]/d[\text{ArCl}]$  should tend towards  $k_C k_B[\text{CuCl}_2^-][\text{ArN}_2^+]/k_B(k_D + k_E[\text{CuCl}_2^-])$ , *i.e.*, the observed dependence of yield on diazonium concentration should appear.

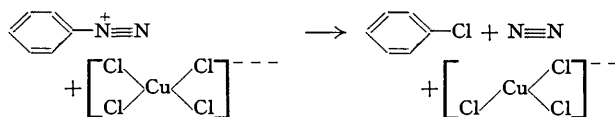
It is, incidentally, necessary to assume that the addition of the second diazonium ion on to the  $\text{CuCl}_2^-$  ion is faster than that of the first; if this were not so, then  $[\text{ArN}_2\text{CuCl}_2]$  would accumulate at the higher diazonium concentrations. The formation of  $[\text{ArN}_2\text{CuCl}_2]$ , though a reaction between oppositely charged species, is likely, as discussed on p. S 57, to involve similarly charged centres; the subsequent formation of  $[(\text{ArN}_2)_2\text{CuCl}_2]^+$  involves the terminal (negatively charged) nitrogen atom of diazonium ion and a  $\text{CuCl}_2^-$  group where the negative charge has already been neutralised by co-ordination of an  $\text{ArN}_2^+$ . The second reaction is therefore likely to be faster, and the assumption seems reasonable.

No attempt is made to define the precise course of the reaction between  $[(\text{ArN}_2)_2\text{CuCl}_2]^+$  and  $\text{CuCl}_2^-$  to give the azo-compound: it may possibly involve the incipient formation of an  $\text{Ar}^-$  ion, which immediately reacts with the other  $\text{ArN}_2^+$  ion attached to the copper.

The evidence for this "co-ordination" mechanism can be summarised as follows. The effect of chloride-ion concentration on the rate, coupled with the solubility measurements, shows that  $\text{CuCl}_2^-$  is the catalyst. That the rate-controlling step is the mutual approach of the  $\text{ArN}_2^+$  and  $\text{CuCl}_2^-$  ions is shown by the form of the kinetics and by the helpful effect of electron-attracting groups in the diazonium ion. The resultant  $(\text{ArN}_2\text{CuCl}_2)$  complex then can suffer three principal fates: it can decompose directly to  $\text{ArCl}$ , or it can combine with another  $\text{ArN}_2^+$  ion and then either decompose to  $\text{ArCl}$  or react with  $\text{CuCl}_2^-$  to give an azo-compound. This accords with the observed variation of azo-yield with diazonium, cuprous chloride, and chloride-ion concentrations, and permits a reasonable interpretation of the formation of a copper azo-compound.

Further, there is no conflict with Hodgson's evidence about yields of aryl bromide and chloride in mixed chloride-bromide solutions. It merely seems likely that  $\text{CuClBr}^-$ ,  $\text{CuBr}_2^-$ , and  $\text{CuCl}_2^-$  are the reactive species in such a system ( $\text{CuCl}_2\text{Br}_2^=$ ,  $\text{CuCl}_2\text{Br}_3^=$ , and  $\text{CuCl}_3\text{Br}^=$  would be fully co-ordinated and probably unreactive). The relative yields of chloride and bromide cannot be predicted, since nothing is known of the relative concentrations of the three active species, or of the relative reactivities of their halide ions.

*Discussion of Other Suggested Mechanisms.*—Hodgson (*loc. cit.*, 1941) suggests that the anionic cuprous complex attacks the nuclear carbon atom directly:



On this view, there is no reason why increased chloride-ion concentration should decrease the rate:  $\text{CuCl}_4^=$  should be as good a catalyst as  $\text{CuCl}_2^-$ , if not better. Further, it necessitates a completely separate formulation of the reactions leading to azo-compound and other by-products. The co-ordination mechanism is therefore to be preferred.

Nevertheless, it is true that diazotised *p*-nitroaniline is converted in good yield into *p*-chloronitrobenzene by cupric chloride, and also by other metallic chlorides. It is not at all unlikely that these reactions proceed by Hodgson's mechanism; there is no indication of any negative catalysis by  $(\text{Cl}^-)$ , nor is there any side reaction leading to azo-compound which demands explanation. It is noteworthy that the reaction of cupric chloride with diazotised *p*-nitroaniline

only proceeds at a reasonable rate at elevated temperatures (60—70°), whereas the corresponding reaction with cuprous chloride proceeds with considerable rapidity at 0°. (It may be noted that few diazonium compounds can survive decomposition to phenol at the temperature necessary for the cupric chloride reaction.) A reasonable hypothesis is that all complex metallic chloride anions can replace  $-\text{N}_2^+$  by  $-\text{Cl}$  by a direct nucleophilic attack on carbon; their reactivities, however, may vary. In the special case of cuprous chloride there is an alternative and much faster reaction in which the metal is first co-ordinated to the terminal nitrogen atom, resulting in a highly reactive complex. The metals in the other complex chloride ions either lack the requisite affinity for the diazo-nitrogen, or are unable to undergo the subsequent necessary rearrangement. It is possible to explain the specific ability of the

$\text{Ar}-\overset{+}{\text{N}}\equiv\text{N} \rightarrow \text{Cu} \begin{matrix} \text{Cl} \\ \diagup \\ \diagdown \\ \text{Cl} \end{matrix}$  complex to bend and thereby react in terms of the ability of the cuprous atom to donate electrons and become oxidised.

The Waters radical mechanism (which demands that the catalyst is a reducing agent and can therefore only apply to the cuprous chloride case) could lead to correct kinetics only if it is assumed that  $\text{CuCl}_2^-$  can liberate  $\text{Ar}\cdot$  radicals whereas  $\text{CuCl}_4^-$  cannot—a hypothesis which can only be sustained by assigning special properties to the  $(\text{ArN}_2, \text{CuCl}_2)$  complex.

The main objections to a *free*-radical mechanism for the Sandmeyer reaction with cuprous chloride are: (a) the absence of extensive reactions between  $\text{Ar}\cdot$  radicals and water molecules to yield large percentages of phenol  $\text{Ar}\cdot\text{OH}$  and/or hydrocarbon  $\text{Ar}\cdot\text{H}$ ; (b) the absence of *unsymmetrical* diaryls produced by the process  $\text{Ar}\cdot + \text{Ar}\cdot\text{Cl} \rightarrow \text{Ar}\cdot\text{C}_6\text{H}_4\text{Cl} + \text{H}\cdot$ ; (c) the fact that an increase in diazonium concentration, which would increase the probability of interaction between  $\text{Ar}\cdot$  and  $\text{ArN}_2^+$ , does not increase the yield of azo-compound over most of the  $[\text{ArN}_2^+]$  range. Again, the cyanide Sandmeyer reaction leads to identical yields whether diazonium chloride or sulphate is used; this necessitates the assumption that in a solution containing more  $\text{Cl}^-$  than  $\text{CN}^-$  the radical always reacts with  $\text{CN}^-$ , although in other circumstances a reaction with  $\text{Cl}^-$  must be postulated.

Waters, however (*loc. cit.*, p. 266, and private communication), postulates that in general his whole cycle of single-electron transfers takes place within the immediate locus of the complex cuprous-diazonium salt, and that only a small fraction of the aryl radicals become "free" enough to take part in side reactions. This, unfortunately, reduces to an attempt to define in detail the electron transfers occurring in the transition state, a matter on which the experimental evidence at present available can give no help, beyond indicating the true molecular formula of the complex itself.

The authors wish to thank Sir Cyril Hinshelwood, F.R.S., and Dr. W. A. Waters for valuable comments and suggestions.

IMPERIAL CHEMICAL INDUSTRIES, LTD., RESEARCH LABORATORIES,  
HEXAGON HOUSE, MANCHESTER, 9.

[Received, June 29th, 1948.]