

50. *Decomposition Reactions of the Aromatic Diazo-compounds.*
Part X. Mechanism of the Sandmeyer Reaction.

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Decomposition reactions of the aromatic diazo-compounds are classified into three types: (I) Decompositions of diazonium kations, giving aryl kations. (II) Decompositions of covalent diazo-compounds, giving two neutral radicals. (III) Catalysed decompositions of diazonium kations, involving a single-electron transference and yielding neutral aryl radicals: $\text{ArN}_2^+ + e \longrightarrow \text{Ar}\cdot + \text{N}_2$.

The Sandmeyer and the Gattermann reaction are considered to be of Type III, and are represented as involving cyclical electron transfereces facilitated by the easy release of an electron from a cuprous kation or from metallic copper.

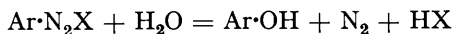
An examination of relative oxidation-reduction potentials affords an explanation of the *almost* unique character of cuprous salts, and of copper, and a discussion of the side reactions which occur in diazo-decompositions of this group further substantiates the view that transient neutral aryl radicals are involved.

The further possible extension of this theory of reaction catalysed by single-electron transference is indicated.

IN Parts I—IX (J., 1937, 133 to J., 1939, 1805) it was shown that many of the decomposition reactions of the aromatic diazo-compounds in non-aqueous solvents were of non-ionic type, and, in particular, that they were influenced by the presence of free metals. Extension of this work to include an experimental study of the complex salts of the diazo-compounds, especially those of copper, had been planned, with the object of elucidating the mechanism of the Sandmeyer and the Gattermann reaction, but the prosecution of this work has been delayed. In consequence of the recent publication, by Hodgson, Birtwell, and Walker (J., 1941, 771) of "An interpretation of the Sandmeyer reaction," however, it has been felt that tentative conclusions as to the mechanism of the Sandmeyer reaction, reached in consequence of the investigations mentioned above, should now be put forward, since they implement considerably the suggestions made hitherto, and may be of value in stimulating future experimental work.

Classification of Diazo-reactions.—The decomposition reactions of aromatic diazo-compounds in aqueous solution can be classified into three distinct groups:

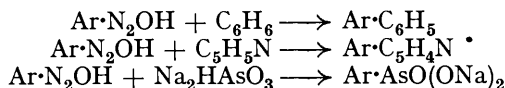
Type I. Decompositions in acid solution, leading to the formation of phenols:



This is undoubtedly a decomposition of a diazonium kation, $(\text{ArN}_2)^+$, since the rate of evolution of nitrogen

is independent of the nature of the radical X (Cain, *Ber.*, 1905, **38**, 2511; Cain and Nicoll, J., 1902, **81**, 1412; 1903, **83**, 206, 470; Moelwyn-Hughes and Johnson, *Trans. Faraday Soc.*, 1940, **36**, 948).

Type II. Non-ionic decompositions of aryl diazo-hydroxides, $\text{Ar}\cdot\text{N}:\text{N}\cdot\text{OH}$, which can exist in neutral and slightly alkaline solutions, e.g.,



(for discussion of mechanisms, see Grieve and Hey, J., 1934, 1799 *et seq.*; Haworth, Heilbron, and Hey, J., 1940, **349**, 358; Waters, J., 1937, 2014; Bart, *Annalen*, 1922, **429**, 55).

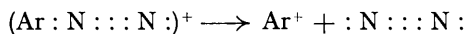
Type III. Reactions such as $\text{Ar}\cdot\text{N}_2\text{Hal} \longrightarrow \text{Ar}\cdot\text{Hal} + \text{N}_2$, which can occur in acid solution and usually need a special catalyst, such as a cuprous salt (Sandmeyer reaction) or metallic copper (Gattermann reaction). Reactions of this type occur under conditions in which diazonium cations and not covalent diazo-hydroxides must be involved, yet they have many characteristics in common with reactions of Type II (see below). *It is suggested that these reactions are non-ionic decompositions of diazonium kations, brought about by a single-electron transference from a catalyst.*

Mechanism of the Sandmeyer Reaction.—Hodgson, Birtwell, and Walker (*loc. cit.*) have recently given strong support for Hantzsch's view (Hantzsch and Blagden, *Ber.*, 1900, **33**, 2544) that Sandmeyer reactions are essentially decompositions of complex cuprous-diazonium salts, $(\text{ArN}_2, \text{Cu}_2)\text{X}_3$ (for empirical formulæ, see Lellmann and Remy, *Ber.*, 1886, **19**, 810; Hantzsch, *Ber.*, 1895, **28**, 1751), in which the halide anions, X, can be exchanged with others from the surrounding solution, but they 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, cadmium, mercury, arsenic, antimony, or bismuth: $(\text{ArN}_2)_2\text{ZnCl}_4$, $(\text{ArN}_2)_2\text{SbCl}_5$, etc. These double salts, amongst which one should include the sparingly soluble borofluorides, $\text{Ar}\cdot\text{N}_2\text{BF}_4$, decompose in the presence of water to give phenols, and yield appreciable percentages of aryl halides only when they are heated in the absence of water (Griess, *Annalen*, 1866, **137**, 52; Schwechten, *Ber.*, 1932, **65**, 1605), *i.e.*, in circumstances in which benzenediazonium halides can themselves give fairly high yields of aryl halides (Waters, J., 1937, 2007).

In view of the fact that cuprous salts will form addition complexes with covalent azo-compounds such as azomethane (Diels and Koll, *Annalen*, 1925, **443**, 262), it could be suggested that the cuprous diazonium halides are structurally different from all other metal diazonium halides, and that they contain a covalent azo-group, e.g., (I), which might decompose to give neutral aryl radicals, but the fact that metallic copper can be used instead of a cuprous salt greatly weakens the plausibility of this *ad hoc* suggestion.

The hypothesis that Sandmeyer reactions are oxidation and reduction processes involving the production of neutral radicals from diazonium kations does enable one to explain (a) the unique character of cuprous salts as catalysts, and (b) the course of the principal side reactions, without introducing any special structural formulæ for intermediate reaction complexes.

It is obvious that the diazonium kation, $\text{Ar}-\overset{+}{\text{N}}\equiv\text{N}:$, can only decompose *per se* to give nitrogen gas and an aryl kation, since both electrons of the $\text{Ar}-\text{N}$ link must be transferred to the nitrogen atom to give the stable N_2 molecule:

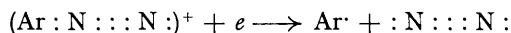


and there can be no reason for doubting that aryl kations will, like alkyl kations, e.g., CH_3^+ , react exceedingly rapidly with water molecules to give phenols:

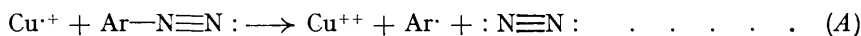


(compare the unimolecular hydrolysis of many alkyl halides; Hughes and Ingold, J., 1933, **1571**; **1935**, **244**, *et seq.*), even if other stable anions (e.g., Cl^-) are abundantly present in the solution.

To obtain a neutral aryl radical from a diazonium kation one must supply one additional electron:

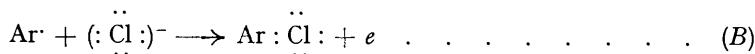


This can be provided by a *reducing agent* such as a cuprous kation,



and this electron transfer can easily occur within the complex kation of a cuprous-diazonium double salt. If a neutral aryl radical is formed in an (acid) aqueous solution containing halide anions in abundance,

then an aryl halide molecule can be formed by process (B), which entails an electron release, if there is available also an electron acceptor.

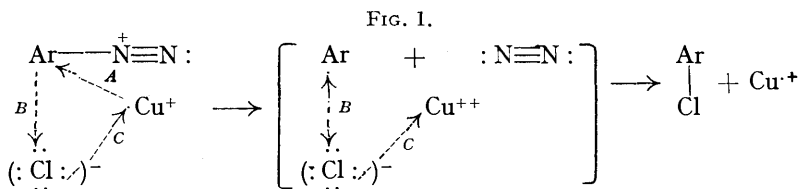


Some implications of the oxidising action of neutral aryl radicals in aqueous solution have already been discussed by the author (J., 1937, 2015) when proposing a mechanism for the Bart reaction. From the experimental evidence then advanced it would seem that a neutral aryl radical does not necessarily react immediately with the first water molecule which it encounters, and the fact that the electron affinity of chlorine (93 kg.-cals.) is less than the energy of fission of an O-H bond (110 kg.-cals.) may be adduced to support the view that reaction with halide anions (excepting fluoride) is more facile than reaction with water molecules.

In the Sandmeyer reaction the local halide anion concentration of the double salt is necessarily very high. Moreover, the electron released by process (B) can be accepted by the cupric kation formed in process (A) :



so that the whole cycle involving single-electron transference can take place within the immediate locus of the complex cuprous diazonium salt (Fig. 1). In this diagram broken arrows (--->) are used to indicate movements of single electrons. This interpretation of the mechanism of the Sandmeyer reaction differs from that of Hodgson and his colleagues (*loc. cit.*), who suggested that electron transfer takes place in reverse of phase (B) above, and postulated that there is an electron release at the significant carbon atom of the aryl group from a chlorine atom of a complex anion (Cu_2Cl_4).



The electron transferences postulated by Hodgson and his colleagues can, in fact, be represented adequately by Fig. 2 in which the (full) curved arrows represent movements of pairs of electrons, and, apart from the implicit view that the covalent (= coordinate) copper-to-chlorine links of the complex anion (Cu_2Cl_4)⁻² are concerned in this reaction process, this ionic mechanism gives no indication as to why cuprous double salts alone should decompose in this way. The author would suggest that the reaction mechanism of Hodgson *et al.* is cogent for the thermal decomposition of solid diazonium salts (see above) and that this should be classed as an ionic reaction of Type I.

The Unique Character of the Cuprous Diazonium Halides.—The single-electron transfer mechanism (Fig. 1) for the Sandmeyer reaction does explain the experimental fact that cuprous salts are almost unique in promoting reactions of Type III, since : (i) Metallic kations of constant valency, such as Na^+ , Zn^{++} , Al^{+++} , cannot act as electron sources; neither can kations in their highest state of oxidation, *e.g.*, Cu^{++} , Hg^{++} , Fe^{+++} , Sn^{IV} , Au^{+++} , Pt^{IV} . (ii) The oxidation potential for the release of an electron from the kations of other transition elements is far too high for the change to occur easily in acid media :

contrast $\text{Mn}^{++} \longrightarrow \text{Mn}^{+++}$	oxidation potential about + 1.5 volts
$\text{Ni}^{++} \longrightarrow \text{Ni}^{+++}$	„ „ very high
$\text{Co}^{++} \longrightarrow \text{Co}^{+++}$	„ „ + 1.8 volts
$\text{Fe}^{++} \longrightarrow \text{Fe}^{+++}$	„ „ + 0.75 volt
with $\text{Cu}^+ \longrightarrow \text{Cu}^{++}$	„ „ + 0.2

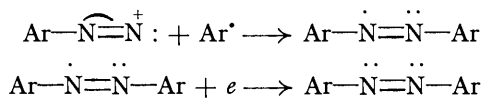
The stannous kation (oxidation potential *ca.* - 0.4 volt) is too powerful a reducing agent in acid solution, and converts diazonium kations into aryl hydrazines, whilst As^{+++} , Sb^{+++} , and Bi^{+++} are too feeble reducing agents in acid solution. In neutral solution As^{+++} and Sb^{+++} can be oxidised more easily : in these circumstances they do react with aromatic diazo-compounds, and undergo a valency change (Bart and Schmidt reactions; Type II : for mechanism compare Waters, J., 1937, 2014). (iii) Since silver, lead, mercurous, and thalious halides are insoluble in water and acids, these metals cannot be used for the preparation of aryl halides.

It is well known that the oxidation potential of a transition element can be altered by the formation of complex co-ordinated ions; *e.g.*, oxidation of bivalent nickel and cobalt cations is facilitated by their conversions into double cyanides. Hence, it is not surprising that nickel diazonium cyanides decompose to give excellent yields of aromatic nitriles (Korczynski, Mrozinski, and Vielan, *Compt. rend.*, 1920, **171**, 182; Korczynski and Fandrich, *ibid.*, 1926, **183**, 421), and cobalt salts can be used for the preparation of thiocyanates.

The oxidation potential for the initial phase (*A*) of the Sandmeyer reaction necessarily depends upon the nature of the aryl radical which accepts the extra electron, and from qualitative evidence it would appear that the presence of electrophilic substituents (NO_2 , Halogens) favours the attainment of high yields. Since the oxidation potential of a solution depends upon its acidity, and upon ionic concentrations, many avenues for exact study of reaction yields immediately suggest themselves.

Analogues of the Sandmeyer Reaction.—The oxidation potential of the iodide anion is not very much higher than that of the cuprous kation, and consequently it is not surprising that the reaction $\text{Ar}\cdot\text{N}_2\text{I} = \text{ArI} + \text{N}_2$ can be effected without the use of a copper salt. As Hodgson and his colleagues have pointed out, the fact that this decomposition is facilitated by the presence of iodine or of copper salts supports the hypothesis that oxidation (*a*) and reduction (*b*) processes are involved (Fig. 3). Other reactions in which oxidisable anions can replace the diazo-group in the absence of copper salts are the decomposition of diazonium perbromides, and the reactions of diazo-compounds with thiols, xanthates, and dithiocarbamates (see Saunders, "The Aromatic Diazo Compounds," 1936, p. 159). All these salts have oxidation potentials close to that of the cuprous ion.

The Side Reactions.—The fact that symmetrical diaryls are often formed in good yield when cuprous salts are added gradually to aqueous solutions of diazonium salts is in full accord with the mechanism of the Sandmeyer reaction suggested above, for in these circumstances the frequency of occurrence of phase (*C*) (reduction of the cupric ion) would be small, and aryl radicals produced by phase (*A*) would have the greatest chance of having a free life sufficiently prolonged for them to disperse throughout the solution, meet, and dimerise. In these circumstances, too, azo-compounds are produced (Hantzsch and Blagden, *loc. cit.*). These can be considered to result from reactions between aryl radicals and diazonium kations, though in this case the primary product is still a radical which, to attain stability, must acquire an additional electron from some other molecule :

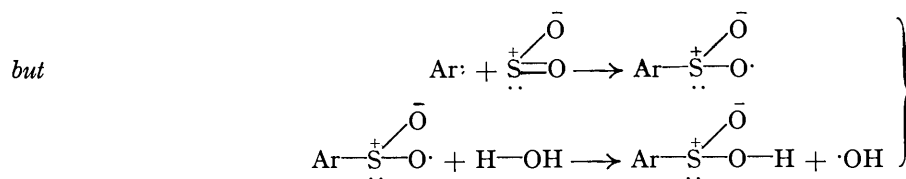
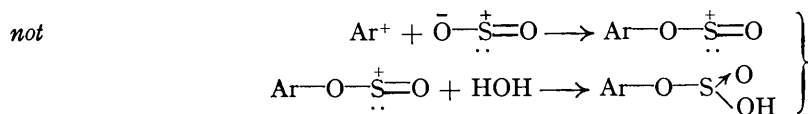


Though the production of diaryls and of azo-compounds necessitates the permanent oxidation of some of the cuprous salt, the stabilisation of the transient neutral radicals may in part be attained by more complicated chain reactions which lead to tar formation (compare Stephenson and Waters, *J.*, 1939, 1801). The fact that both diaryls and azo-compounds are regular by-products of Sandmeyer reactions does, however, lead one to infer that these reactions are not exclusively intramolecular decompositions of complex cuprous diazonium salts, but that there are produced aryl groups which have some degree of independent existence as "free radicals." Further discussion of this topic leads, however, to questions of radical stability in solution which have been discussed recently elsewhere (Waters, *Trans. Faraday Soc.*, 1941, **37**, 770).

The Gattermann Reaction.—Gattermann's reaction (*Ber.*, 1890, **23**, 1218), in which copper powder replaces the cuprous salt, must undoubtedly be a reaction of Type III, since in all details, even in regard to the nature of the by-products, it proceeds in a similar manner to Sandmeyer's reaction. Both Gattermann (Gattermann and Cantzler, *Ber.*, 1892, **25**, 1091) and Hantzsch and Blagden (*loc. cit.*) regard the copper powder as essentially a catalyst. However, the formation of a small quantity of a copper salt is usually noticed when this reaction is carried out, and hence the cyclic scheme of Fig. 1, in which electrons easily available at the surface of metallic copper play the same part as those obtainable from cuprous ions, may justifiably be put forward, particularly since the ionisation potential for the change $\text{Cu}^{0\cdot} \longrightarrow \text{Cu}^+ + e$ (− 0.13 volt; Nielsen and Brown, *J. Amer. Chem. Soc.*, 1928, **50**, 9) is very small indeed in acid solution, so that the reduction potentials for the initial stages (*A*) of the Sandmeyer and the Gattermann reaction would be almost identical.

Relevant evidence in favour of the transient existence of neutral radicals in reactions of the Gattermann type are (i) that diaryls and polyaryls are frequent by-products, and occasionally major products, as in Pschorr's syntheses of phenanthrene derivatives; (ii) that the reaction can be extended to include the introduction of groups such as NO_2 and SO_2H . It then takes a way characteristic of neutral aryl groups

and not of aryls kations : from the nitrite anion one gets nitro-compounds, not aryl nitrites, and from sulphur dioxide, sulphonic acids and not sulphites, *i.e.*,



(compare the addition of sulphites to styrene; Kharasch, May, and Mayo, *J. Org. Chem.*, 1938, 3, 175).

Though copper is by no means unique in giving up electrons to diazo-chlorides in acetone (Waters, J., 1939, 864), yet it seems as if copper were *almost* unique amongst metals for effecting the reaction $\text{Ar}\cdot\text{N}_2^+ + \text{M}\cdot \longrightarrow \text{Ar}\cdot + \text{N}_2 + \text{M}^+$ in aqueous acids. From an inspection of ionisation potentials it is evident why many metals, *e.g.*, iron, nickel, or platinum, cannot replace copper, but in other cases the inertness may be due to surface-film formation (*e.g.*, halides of silver and lead). That elementary mercury can play a similar part to copper in initiating the decomposition of diazonium salts has, however, been demonstrated by McClure and Lowy (*J. Amer. Chem. Soc.*, 1931, 53, 319). Their overall reaction, *viz.*, $\text{Ar}\cdot\text{N}_2\text{Cl} + \text{Hg} \longrightarrow \text{Ar}\cdot\text{HgCl} + \text{N}_2$, which is not quantitative, includes, naturally, chemical combination of the neutral aryl radical with the free mercury. The experimental fact that, whereas many metals will react with diazo-chlorides in acetone, ethyl acetate, or acetonitrile, yet only copper seems to be effective as a promoter of the non-ionic decomposition of the *syn*-diazocyanides (J., 1939, 1796) in a number of solvents, shows, however, that many problems concerning the critical potentials for initiating single-electron transferences remain to be solved.

Outside the sphere of the chemistry of the diazo-compounds, the facts that certain particular metals, and special salts, such as cuprous chloride and cobaltous chloride, can catalyse special reactions of Grignard reagents which are thought to involve free radicals (Gilman and Straley, *Rec. Trav. chim.*, 1936, 55, 821; Kharasch and Field, *J. Amer. Chem. Soc.*, 1941, 63, 2316), indicate that the theory which has been advanced above should not be regarded as a particular, *ad hoc*, hypothesis, but as a general reaction mechanism, capable of useful extension elsewhere. For instance, the discovery by Ullmann (*Ber.*, 1905, 38, 2211; 1907, 40, 2522; *Annalen*, 1907, 355, 316) that a trace (1 part in 10^6 or less) of copper will catalyse the condensation between certain aryl halides and phenols or amines is explicable as a chain reaction initiated by an electron transference: $\text{Ar}-\text{Br} + \text{Cu}^{0\cdot} \longrightarrow \text{Ar}\cdot + \text{Br}^- + \text{Cu}^+$. In this connection compare also Koelsch and Whitney (*J. Org. Chem.*, 1941, 6, 795).