

**256. Decomposition Reactions of the Aromatic Diazo-compounds. Part XI.  
The Mechanism of Formation of Azo-compounds, Polyaryls, and Aryl Sulphides.**

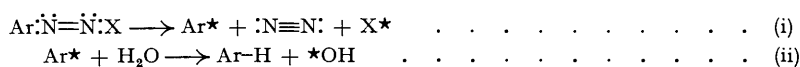
By K. H. SAUNDERS and WILLIAM A. WATERS.

The appearance of azo-compounds and polyaryls among the products of decomposition of diazo-compounds in aqueous solution near the neutral point in the presence of a mild reducing agent, and the conversion of 2 : 2'-tetrazodiphenyl into diphenylazone, indicate that in part diazo-compounds can undergo decomposition of Type II (Waters, *J.*, 1942, 266) in aqueous solution, giving free aryl radicals which may, among other reactions, either (a) react with diazo-kations with single electron transfer from the reducing agent giving a symmetrical azo-compound, or (b) attack undecomposed covalent diazo-compounds giving a diazodiaryl compound which, by a similar decomposition in the tar phase, eventually yields polyaryls, or combines as in (a) to form an arylazo-diaryl. There is also evidence to suggest that diazo-sulphides undergo homolysis in aqueous media to produce radicals.

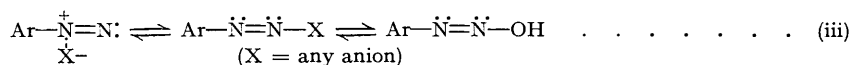
THERE are a number of decomposition reactions of the aromatic diazo-compounds for the mechanism of which no satisfactory hypotheses have yet been advanced. Among these may be mentioned (1) the production of symmetrical azo-compounds by the reduction of benzenoid diazo-compounds free from negative substituents [in especially high yield from diazotised  $\psi$ -cumidine and *as.-m*-xylidine in the presence of ammoniacal cuprous oxide (Vorländer and Meyer, *Annalen*, 1901, **320**, 122)]; (2) formation of both azobenzene and benzeneazo-diphenyl from benzenediazonium salts in the presence of potassium ferrocyanide (Griess, *Ber.*, 1876, **9**, 132; Locher, *ibid.*, 1888, **21**, 911); (3) formation of diphenyl sulphide together with benzeneazodiphenyl from benzenediazonium salts by interaction with sodium cupro-thiosulphate (Börnstein, *Ber.*, 1901, **34**, 3968) and (4) the closure of the diphenylazone ring by the action of cuprous bromide (Dobbie, Fox, and Gauge, *J.*, 1911, **99**, 1615) or sodium arsenite (Sandin and Cairns, *J. Amer. Chem. Soc.*, 1936, **58**, 2019) on tetrazotised 2 : 2'-diaminodiphenyl.

In the general scheme previously put forward by one of us (Waters, *loc. cit.*), the homolysis of undissociated diazo-compounds into two free radicals with liberation of nitrogen was regarded as occurring regularly only in non-dissociating solvents (compare Grieve and Hey, *J.*, 1938, 109), though the production of a trace of benzene

from a faintly alkaline solution of diazobenzene hydroxide (Waters, *J.*, 1937, 2016) showed that radical formation in aqueous solution (i), and subsequent decomposition as in (ii), is not quite impossible : \*



However, the fact that diaryls, sometimes mixed with symmetrical azo-compounds, can be formed in good yield by the action of ammoniacal cuprous oxide on negatively-substituted aromatic diazo-compounds, indicates that many diazo-compounds can be converted, in part at least, into free radicals in aqueous solution. The source of these radicals must be the undissociated diazo-hydroxide molecules, which at any time comprise

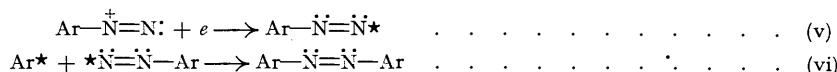


only a part of the diazo-compound present, though near the neutral point the equilibrium will tend to favour the diazo-hydroxide form, the actual percentage present being dependent both on the pH of the solution and on the nature of the aryl group concerned.

Shortly after decomposition commences in one of the above mixtures there is thus present, distributed at random through the solution, a certain amount of diazo-hydroxide which has broken up into free radicals, as in (i), which besides reacting with water molecules [as in (ii)], might combine with dissociated diazo-kations, the reducing agent supplying the necessary electron to produce a symmetrical azo-compound by the reaction

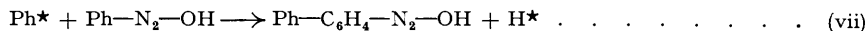


Whether ammoniacal cuprous oxide will convert a given diazo-compound into an azo-compound, or into a diaryl, is therefore determined by the amount of the undissociated diazo-hydroxide present under the given conditions, and upon the mean life of the free aryl radical. If the amount of undissociated hydroxide is large, many free aryl radicals are formed and hence the yield of diaryl will be high. This corresponds with the fact that negative substituents drive the equilibrium (iii) to the right. The formation of  $\alpha\alpha'$ - and  $\beta\beta'$ -azonaphthalene by reduction of  $\alpha$ - and  $\beta$ -diazonaphthalenes, for example, with alkaline sulphite (Lange, D.R.-P. 78,225; "Friedländer," 4, 1016) should perhaps be excluded from this discussion, because there is no *a priori* evidence (*e.g.*, the isolation also of diaryls or of azo-diaryls) that free radicals are concerned. The formation of *s*-azo-nitronaphthalenes in strongly acid solution with cuprous oxide as a reducing agent has been ascribed to the union of free aryl radicals with free diazo-radicals (Hodgson, *J.*, 1942, 744), the latter being formed by the prior acceptance of an electron by a diazonium ion :

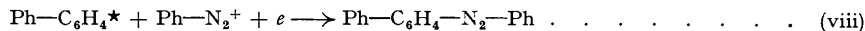


a mechanism entirely different from that [equation (iv)] contemplated here, and one which we regard as improbable, since the driving force in the homolysis of the covalent diazo-compounds is the elimination of molecular, stable, nitrogen gas which leads to the *simultaneous* production of *two* neutral radicals.

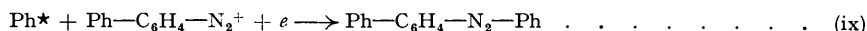
In reactions (2) and (3) some of the free phenyl radicals must concurrently attack the undissociated benzene-diazo-hydroxide :



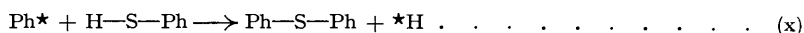
The molecule of diazodiphenyl hydroxide thus formed then can decompose into a diphenyl radical,  $\text{Ph-C}_6\text{H}_4^*$ , which by combination with a diazobenzene kation, as in (iv), yields an arylazo-diaryl under the influence of the reducing agent :



Alternatively, however, benzeneazodiphenyl may be produced by combination of a phenyl radical with dissociated diazodiphenyl hydroxide (as in ix) :



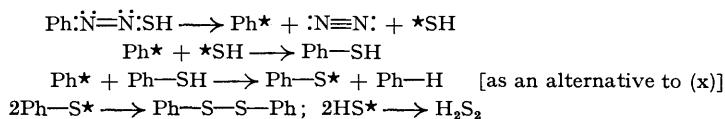
In reduction by potassium ferrocyanide, the azobenzene is produced by (iv), while a third compound, an oil of unknown constitution, is also mentioned by Griess (*loc. cit.*) and provides further evidence of that multiplicity of products which often characterises free radical reactions. In Börnstein's reaction (3) the diphenyl sulphide may arise from a similar union of phenyl radicals with thiophenol (x).



Graebe and Mann's account (*Ber.*, 1882, 15, 1683) of the production of diphenyl sulphide, diphenyl disulphide, and sulphur from benzenediazonium salts and hydrogen sulphide, or ammonium sulphide, supplies evidence

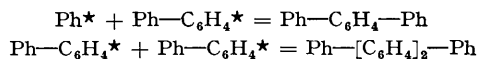
\* Dots represent electrons, an asterisk the single electron of a free radical, and a dash a covalent link.

for the formation of free radicals by the homolysis of diazobenzene hydrogen sulphide, a substance well-known for its instability (Griess, *Annalen*, 1866, **137**, 74). The following reactions can then all occur :

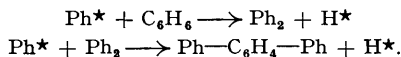


The oxidation of the hydrogen sulphide to  $\text{H}_2\text{S}_2$  and thence to sulphur is strongly diagnostic of a Type II reaction (cf. Waters, *J.*, 1937, 2015; 1942, 266).

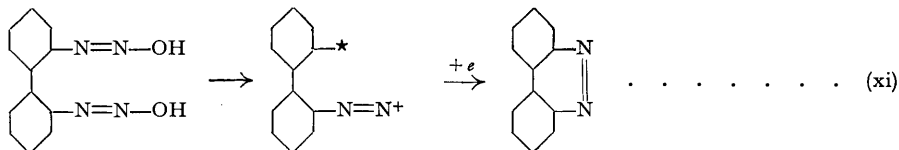
The formation of "dialzo-resins" is also to be explained on these lines, for when the aromatic reaction products separate from the aqueous phase they will, like the non-aqueous phase in the Gomberg reaction (Grieve and Hey, *loc. cit.*), then extract free radicals, or their precursors, from the solution, thereby building up by subsequent homolytic reactions the chain-molecules which form the deeply-coloured, nitrogen-containing resins so often observed. Indeed, Angeli and Jolles (*Gazzetta*, 1931, **61**, 403) have already suggested that the dialzo-resins are related, in their mode of formation, to benzeneazodiphenyl. Further, the non-aqueous phase is the probable site of formation of polyphenyls which, it may be noted, can be produced by the reduction of benzenediazonium salts in alcohol with copper (cf. Gerngross, Schashnow, and Jonas, *Ber.*, 1924, **57**, 747). The polyphenyls, which are obtained in poor yield, can be built up from free phenyl and diphenyl radicals formed by homolysis of diazobenzene hydroxide and of diazodiphenyl hydroxide :



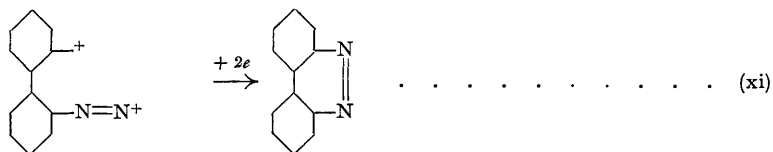
and alternatively, or concurrently, by reactions such as :



The formation of diphenylazone can best be explained by the following scheme, which is analogous to reaction (iv).



It is possible that in the acid solution of Dobbie, Fox, and Gauge's experiment an aryl kation is first formed by a heterolytic fission of Type I (Waters, *loc. cit.*) and that ring closure then takes place by the simultaneous transfer of two electrons from the reducing agent :



An aryl kation would, however, tend to combine at once with an anion from the solution, and as it is difficult to replace the diazo-groups in 2 : 2'-tetrazodiphenyl by chlorine or bromine in aqueous solution the free radical mechanism (x) with a single electron-transfer from the cuprous salt is more probable.

This discussion leaves out of account the yet unsolved question as to how different reducing agents affect the free radical reactions, so that from the same diazo-compound different end-products may result, though probably the solubility of the electron-donor and its oxidation-reduction potential are the key factors; insoluble donors promote reaction in a non-aqueous phase, while soluble donors promote reaction in solution.