85. *The Decomposition Reactions of the Aromatic Diazo-compounds in Aqueous Solution explained on Simple Electronic Theory, and without Recourse to the Current Free-radical Hypothesis.*

By Herbert H. Hodgson.

One electronic mechanism only is shown to be sufficient to explain: *s*-azo-compound formation in acid, neutral, or alkaline media; the Gomberg and similar reactions in which *s*-diaryls are not formed and in which invariability of *op*-substitution occurs; the conversion of 2 : 2′-tetrazodiphenyl into dibenzopyridazine (diphenylazone) and carbazole; the reactions of diazobenzene hydroxide in faintly alkaline solution with carbon disulphide, *cyclo*hexane, and without added solvent; and numerous oxidations by diazo-compounds. The alternative free-radical hypothesis with its inherent difficulties is discussed and found to be entirely unnecessary, if not invalid, for the interpretation of the decompositions of aromatic diazo-compounds in aqueous solution.

A MECHANISM for the formation of symmetrical azo-compounds in acid solution with cuprous hydroxide as a reducing agent was first proposed by Hodgson, Leigh, and G. Turner (hereinafter referred to as H. *et al.*) (*J.*, 1942, 744) and supported by considerable experimental evidence. It postulated two stages, *viz.*, (1) formation of an aryl from a diazo-radical which in turn was formed from a diazonium ion by acceptance of an electron from the reducing agent, $\mathrm{Ar{\cdot}\overset{+}{N}{\equiv}N{:}} + \mathrm{e} \longrightarrow \mathrm{Ar{\cdot}\ddot{N}{=}\ddot{N}^*} \longrightarrow \mathrm{Ar^*} + \mathrm{N_2}$; (2) union of the aryl with another diazo-radical, $\mathrm{Ar\,\ddot{N}{=}\ddot{N}^*} + \mathrm{{}^*Ar} \longrightarrow \mathrm{Ar{-}\ddot{N}{=}\ddot{N}{-}Ar}$. (Dots represent electrons, an asterisk the single electron of a radical, and a dash a covalent link.) This mechanism has recently been adversely criticised by Saunders and Waters (hereinafter styled S. & W.) (*J.*, 1946, 1154), who regard it as improbable on the ground that the driving force in the homolysis of covalent diazo-compounds is the elimination of molecular, stable, nitrogen gas which leads to the simultaneous production of two neutral radicals. From the outset, therefore, S. & W. ignore the fact that ionic diazonium, not covalent diazo-compounds were concerned in the experiments of H. *et al.*

S. & W.'s mechanism is also two-staged, *viz.*, (1) production of the free aryl radicals by fission of two single links in a covalent diazo-compound, (2) union of the aryl radical with a dissociated diazo-kation (admitted therefore by S. & W. to exist in alkaline solution) which is first converted into a diazo-radical by the reducing agent, *i.e.*, by the H. *et al.* mechanism. S. & W.'s statement, that the mechanism of H. *et al.* is entirely different from their own, thus applies to stage (1) only, and raises the whole question of whether all the decomposition reactions of diazo-compounds in aqueous solution can be explained on simple electronic theory, or, alternatively, whether the hypothesis of free aryl radicals as advanced by Hey *et al.* (*J.*, 1934, 1799 *et seq.*) and Waters *et al.* (*J.*, 1937, 2007 *et seq.*) should be invoked (cf. *Ann. Reports*, 1937, **34**, 282; 1940, **37**, 250). This alternative will now be submitted to examination, in the course of which the validity of the free-radical hypothesis will be challenged and, in any event, its necessity denied (cf. also Kenner, *Nature*, 1945, **156**. 369).

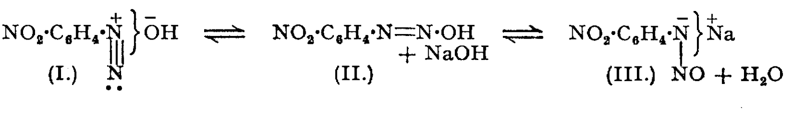
S. & W.'s Hypothesis for the Formation of s-*Azo-compounds.*—S. & W. appear to postulate the free existence of radicals prior to subsequent reaction, and their origin to be the homolysis of undissociated diazo-hydroxide into two radicals with elimination of nitrogen, without the intervention either of a catalyst or of a reducing agent. In fact, the homolysis of $\mathrm{R{-}\vdots{-}\ddot{N}{=}\ddot{N}{-}\vdots{-}OH}$ into R*, *OH, and $\mathrm{N_2}$ does not involve electron acceptance of any kind. Two insuperable difficulties arise with this conception which its authors, although referring to them (cf. Hey, *J.*, 1934, 1801), do not attempt to explain, *viz.*, the non-formation of diaryl and of a phenol by the union of R* with *R and of R* with *OH, respectively. When, however, an aqueous solution of benzenediazonium chloride or sulphate is allowed to decompose spontaneously in the presence of calcium carbonate to maintain neutrality, the product is almost entirely a mixture of benzene-azo-, -bisazo-, and -trisazo-phenol (Hodgson and Marsden, *J.*, 1943, 379), and its origin is easily explained on simple electronic theory (*loc. cit.*). Similarly, when nitrosoacetanilide reacts with water the product is *p*-hydroxyazobenzene (Grieve and Hey, *J.*, 1934, 1797). These experiments would apparently afford far more evidence of free radicals than those quoted by S. & W. (*loc. cit.*) or by Hey for the Gomberg reactions (*loc. cit.*), where the absence of diphenyl or of phenol, under conditions which favour the formation of both, is surely proof that free phenyl and hydroxyl radicals do not exist prior to the actual reaction, but are involved, if at all, during the intermediate phase which precedes the final separation of the resultants. From Waters's own viewpoint (*J.*, 1937, 2015) that " neutral radicals are extremely reactive entities which interact with practically the first molecule they encounter ", the formation of diphenyl and of phenol with subsequent coupling to azophenol would certainly occur if covalent diazobenzene hydroxide decomposed in aqueous medium into C_6H_5* and *OH in the manner envisaged by S. & W. Apparently, however, S. & W. are content to believe that free phenyl and hydroxyl radicals can co-exist without any mutual effect on each other, but with truly remarkable activities towards any other substance that may be present: *e.g.*, in the Gomberg reaction the assumed free aryl radicals preferentially attack relatively unreactive molecules rather than combine with each other, and we have the extraordinary result that diazotised aniline will only form diphenyl if benzene be also present. This non-formation of symmetrical diaryls was also observed by Hodgson and Marsden (*J.*, 1940, 208), who employed stabilised diazonium salts for a great variety of Gomberg reactions in different media. In this connection, Waters (*J.*, 1937, 2014) cites the occurrence of diphenyl formation in the Bart reaction (see later) as to be expected if free aryl radicals are present during the course of the reaction.

Another weakness of the covalent homolysis theory is its comparative failure to account for the activity of the second radical as compared with that of the aryl radical. To the author, this predominant reactivity of the supposed aryl radical in diazo-decompositions is in itself evidence that only a diazonium ion is involved.

Finally, it must be emphasised that the arguments of S. & W. are all based on reactions of covalent diazo-compounds *in alkaline or neutral solution*, and that the experiments of H. *et al.* and the deductions therefrom are dismissed in six lines as improbable, notwithstanding the fact that the former were all conducted in strong acid solution and therefore under conditions where the diazonium ion would greatly predominate. This condition would also obtain in neutral solution owing to the relatively greater stability of the diazonium ion because of the resonance energy.

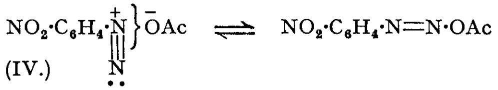
At this stage it is convenient to examine the main experimental evidence on which S. & W.'s hypothesis is based, especially as they state " that while previously the homolysis of undissociated diazo-compound into two free radicals with liberation of nitrogen was regarded as occurring regularly in non-dissociating solvents, there are now indications " that many diazo-compounds can be converted, in part at least, into free radicals in aqueous solution ".

The Reactions of Sodium Benzenediazoate (*the Gomberg Reaction*).—The author (*J. Soc. Dyers and Col.*, 1946, **62**, 199) has recently reviewed the work in this subject. At that time he accepted the free-radical mechanism, but contended that the origin of the free radicals was *via* the decomposition of diazonium kations and not by the fission of covalent diazo-compounds. Later consideration of the facts, including his own experimental work, has convinced him that the Gomberg reaction can be simply explained without any need for the existence of free radicals. Since nitrogen has to be evolved as $:\mathrm{N}\equiv\mathrm{N}:$ before reaction occurs, it would appear more realistic to have it already in a triple-bonded condition and with only one link to be ruptured such as the diazonium ion provides, rather than with two links to sever such as the covalent diazo-compounds entail, *viz.*, $\mathrm{R}-\vdots-\ddot{\mathrm{N}}=\ddot{\mathrm{N}}-\vdots-\mathrm{X}$. Moreover, this viewpoint brings the Gomberg reaction into line with all the other reactions in which nitrogen is evolved, *e.g.*, replacement of nitrogen by hydrogen, hydroxyl, halogen, etc. Since the union of aryl nuclei in the Gomberg and similar reactions is stated to take place in acid media (cf. Hirsch, *Ber.*, 1890, **23**, 3705; 1892, **25**, 1196; Hodgson and Marsden, *J.*, 1940, 208; Elks, Haworth, and Hey, *J.*, 1940, 1284), neutral (Gomberg and Bachmann, *J. Amer. Chem. Soc.*, 1924, **46**, 2339; Gomberg and Pernert, *ibid.*, 1926, **48**, 1372) or alkaline media (previous references), it surely follows that the diazonium ion, which may be present exclusively in acid, and at all events will predominate in acid and neutral media (*loc. cit.*) while certainly existent in alkaline media to a variable extent, should be regarded as the necessary and sufficient reagent. In this connection, Hirsch (*loc. cit.*) in his preparation of hydroxydiphenyls by the interaction of diazotised aniline with phenol had to make the medium sufficiently acidic to prevent coupling, thereby indicating the diazonium ion as the active reagent. The improvement in the yields of diaryl from diazotised nitroanilines when sodium hydroxide is replaced by sodium acetate (cf. Hodgson and Marsden, *J.*, 1940, 208; Hodgson and Foster, *J.*, 1942, 581) is due to the repression (probably complete) of the unreactive nitrosoamine (III) present in the equilibrium system



$$\underset{\text{(I.)}}{\left.\mathrm{NO_2{\cdot}C_6H_4{\cdot}}\overset{+}{\mathrm{N}}\underset{\ddot{\mathrm{N}}}{\vert\vert\vert}\right\}\overset{-}{\mathrm{O}}\mathrm{H}} \rightleftharpoons \underset{\text{(II.)}}{\mathrm{NO_2{\cdot}C_6H_4{\cdot}N{=}N{\cdot}OH} + \mathrm{NaOH}} \rightleftharpoons \underset{\text{(III.)}}{\left.\mathrm{NO_2{\cdot}C_6H_4{\cdot}}\overset{-}{\mathrm{N}}\underset{\mathrm{NO}}{\vert}\right\}\overset{+}{\mathrm{Na}}} + \mathrm{H_2O}$$

by the production of the simpler system (IV), which then behaves like the analogous very reactive system cited for diazotised 4-nitro-1-naphthylamine (Hodgson, Nicholson, and



$$\mathrm{NO_2{\cdot}C_6H_4{\cdot}\underset{\underset{\cdot\cdot}{N}}{\overset{+}{N}}\!\!\equiv\}\overset{-}{O}Ac \rightleftharpoons NO_2{\cdot}C_6H_4{\cdot}N{=}N{\cdot}OAc}$$

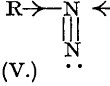
(IV.)

G. Turner, *J.*, 1944, 15). Kühling's observation (*Ber.*, 1895, **28**, 41; 1896, **29**, 165; cf. also Kliegl and Huber, *ibid.*, 1920, **53**, 1641) of the reactivity of an aqueous solution of the sodium salt of diazotised *p*-nitroaniline with toluene, is of course due to the presence of the *p*-nitrobenzenediazonium hydroxide (I) in the equilibrium system above; the fact of its existence has been confirmed by reaction with potassium iodide to form *p*-iodonitrobenzene. The non-reactivity of solid potassium *syn*-diazoate with benzene (Gomberg and Pernert, *loc. cit.*), and the similar non-reactivity of sodium *p*-nitrobenzene-*anti*-diazoate [the nitrosoamine (III) above] with 1-chloro-2 : 4-dinitrobenzene in boiling benzene (Hodgson and Marsden, *J.*, 1945, 207) must be ascribed to the absence of diazonium salt.

The decrease in yield when other bases are diazotised which do not contain nitro-groups is probably due to the shift in the equilibrium system in favour of the coupling but non-decomposing diazoate, with consequent diminution in quantity of the reactive diazonium acetate. Gomberg's observation that nitro- and chloro-anilines react better in neutral than in alkaline solution is due to the diminution or even suppression of nitrosoamine formation which alkalis promote, with consequent enhancement of the quantity of the reactive diazonium salt; with aniline and the toluidines, alkali will tend to stabilise the diazo–diazonium equilibrium and reduce phenol formation to a minimum.

Some Anomalies of the Free-radical Hypothesis.—Grieve and Hey (*J.*, 1934, 1797) first pointed out that no attention appeared to have been paid to the invariability of the *p*- and/or *o*-substitution irrespective of any directing group present, and they concluded that the substituting agent must be amphoteric in type, *i.e.*, capable of functioning alternatively as if it were a kationoid or an anionoid reagent as occasion demands, and that a mechanism involving the formation and transient existence of free phenyl radicals will provide the requisite interpretation. The paper cited deals only with the phenyl radical, which may be regarded as amphoteric, but in the decompositions with the stabilised diazonium salts of the nitroanilines (Hodgson and Marsden, *J.*, 1940, 208), where the nitrophenyl radicals, if formed, could hardly be regarded as amphoteric or at the best very feebly so, substitution still occurred in the *p*-position with nitrobenzene, and the largest yield recorded (69%) of *pp'*-dinitrodiphenyl was obtained for the reaction of the diazonium salt from *p*-nitroaniline, in which a radical with a strong kationoid bias would be attacking a kationoid *p*-position. Moreover, Grieve and Hey give no reason why these powerful free radicals should not attack the relatively inert *m*-positions in preference to a hostile (kationoid) *p*-position. This problem admits of ready solution when the free-radical hypothesis is discarded for a polar one, since only from this viewpoint can the absence of *s*-diaryls be interpreted; in addition, the invariability of *op*-substitution must also be explained by it.

The Polar Theory.—On this hypothesis, the kationoid diazonium ion (stabilised in Hodgson and Marsden's experiments, *J.*, 1940, 208) attacks the anionoid reactant (say benzene) at an anionoid carbon atom (VII), thereby causing its covalent hydrogen to become kationoid and so attracting the anion (usually hydroxyl or acetate) of the diazonium salt. Complete ionisation of the hydrogen with consequent release of the electron enables elimination of nitrogen with consequent formation of diaryl and HX (usually water or acetic acid). *In this reaction free-radical formation never occurs and so the absence of* s-*diaryl is explained.* Azo-formation, which can also occur partially, *e.g.*, with diphenyl, or completely with phenol or naphthol in alkaline, neutral, or slightly acid media, depends on the anionoid character of the significant carbon atom of the second component, which, when sufficiently great, will enable attack by the diazonium ion in resonance structure (VI), so that scission of nitrogen is prevented and an azo-link is established (VIII). For ordinary cases of coupling, therefore, the main driving force is

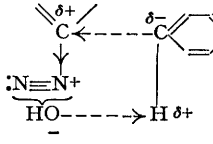


$$\mathrm{R\!\rightarrow\!\overset{+}{N}\!\equiv\!\underset{\cdot\cdot}{N}}$$

(V.)

$$\mathrm{\longleftrightarrow R{-}\ddot{N}{=}\ddot{N}^{+}}$$

(VI.)



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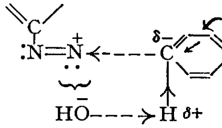
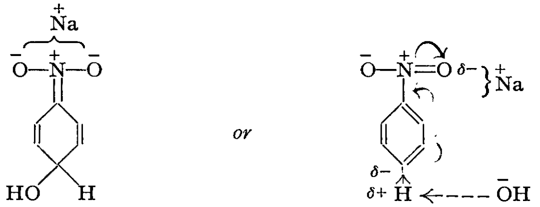


(VIII.)

the formation of water (or the feebly ionised acetic acid), but for a weakly anionoid molecule like benzene, this driving force has to be augmented by that due to elimination of nitrogen [hence attack by the diazonium ion in resonance form (V)]. Both reactions can occur simultaneously, however, to varying extents depending on the anionoid character of the second reactant. In Hirsch's experiments (*loc. cit.*) the anionoid character of the *o*- and *p*-positions in phenol was so reduced by making the reaction medium acidic, with consequent repression of the ionisation of the hydroxyl group, that coupling was prevented [*i.e.*, attack by the diazonium ion in resonance form (VI)] and so diphenyl formation occurred [*i.e.*, attack in resonance form (V) with simultaneous formation of water and molecular nitrogen as driving force]. Moreover, this mechanism is in accord with the kinetic studies of Wistar and Bartlett (*J. Amer. Chem. Soc.*, 1941, **62**, 413), who attribute coupling to the diazonium ion whether in acid or in alkaline solution, nor is it inconsistent with the modified coupling hypothesis of Hodgson (*J. Soc. Dyers and Col.*, 1942, **58**, 228), who postulated the highly polarised diazo-component, $\mathrm{R{-}N{=}\overset{\delta+}{N}{-}\overset{\delta-}{X}}$, as the active reagent in ordinary coupling reactions. On this latter viewpoint, coupling depends on the anionoid character of the second component being sufficiently strong to react with the polarised covalent diazo-compound (hydroxide, chloride, sulphate, etc.). If this is impossible, as in benzene, then the diazonium ion in resonance form (V) is necessary to provide the extra driving force by scission of molecular nitrogen. Both reactions can occur simultaneously, however, depending on the anionoid character of the second reactant.

In any event the assumption of free radicals is entirely unnecessary to explain the kinetic results, and if the diazonium ion is responsible for coupling, as claimed by Wistar and Bartlett (*loc. cit.*), surely it must be the active reagent for the case of decreased anionoid character afforded by the Gomberg reaction.

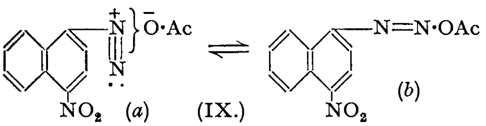
The Anomalous p-*Reactivity of Nitro-hydrocarbons.*—This unexpected reactivity seems to have been one of the main factors which inspired the adoption of a free-radical theory for the Gomberg reaction by Grieve and Hey (*loc. cit.*). It can, however, be attributed to solvent action at the nitro-group, whereby the kationoid character of the *op*-positions is reversed to anionoid. Since *m*-dinitrobenzene and *s*-trinitrobenzene form stable salts with sodium or potassium hydroxide in methyl alcohol, which in the latter case are very stable (cf. Sidgwick, " Organic Chemistry of Nitrogen ", 1937, p. 260), incipient salt formation can reasonably be assumed for nitrobenzene, and either a quinonoid formulation be adopted (cf. Meisenheimer, *Annalen*, 1902, **323**, 205), or, alternatively, the hydroxyl anion can be assumed to be attracted to the partly ionised hydrogen, with similar structures for the corresponding *o*-quinonoid forms.



The diazonium ion will then join with the hydroxyl ion in a two-point attack at the $\geqslant\overset{\delta-}{\mathrm{C}}{-}\overset{\delta+}{\mathrm{H}}$ bond, whereby diphenyl formation will occur. The overwhelming predominant activity of the *p*-position and the absence of *m*-reactivity are thus accounted for, since of the incipient *o*- and *p*-quinonoid structures brought into being by the salt formation, the latter is the more stable (cf. Veselý and Jakeš, *Bull. Soc. chim.*, 1923, **33**, 955, for the relative stabilities of the *p*- and *o*-quinonoid structures). In the more intimate interaction which the sodium acetate–glacial acetic acid medium provides, possibly by hydrogen bonding with the nitro-group, or salt formation, or both, the anionoid activity is developed as above to such an extent that the yield of diaryl increases about sevenfold.

In the case of *o*-nitrotoluene, Grieve and Hey (*loc. cit.*) found that substitution occurred more readily at the *op*-positions with respect to the nitro-group than at the corresponding positions with respect to the methyl group, a fact which illustrates the present argument that the greater tendency to produce ionic quinonoid structures exhibited by the nitro-group over the methyl group has resulted in the greater reactivity at the *op*-positions to the nitro-group.

A Partial Analogy with the Gomberg Reaction.—Analogy is to be found in many respects during the gradual decomposition of 4-nitronaphthalene-1-diazonium chloride (or sulphate) by sodium acetate in aqueous solution, and incidentally in a homogeneous medium (Hodgson, Nicholson, and G. Turner, *J.*, 1944, 15). The decomposition takes several hours to complete, but can be arrested at any time by addition of hydrochloric acid. The precipitated reaction products consist mainly of 4 : 4′-dinitronaphthalene-1′ : 2-azo-1-naphthol, 4 : 4′-dinitro-1 : 1′-azonaphthalene, and 4 : 4′-dinitro-1 : 1′-dinaphthyl, and their formation corresponds with the setting up of the equilibrium (IX, *a*) ⇌ (IX, *b*), after which the following simultaneous reactions occur : (1) Decomposition of (IX, *a*) by anionoid water or by hydroxyl ions in the normal manner to form 4-nitro-1-naphthol, which will then couple with (IX, *b*) to form the azo-dye. Decomposition of (IX, *a*) by an oxidation–reduction process, probably facilitated by the equilibrium disturbance necessitated by reaction (1), whereby radicals (X) and (XI) result on the one hand, and irresolvable oxidation products on the other, which are very soluble in acetone. Union of (X) and (XI) affords the azo-compound, while union of two (XI) radicals gives the dinaphthyl. The mechanism of this reaction thus fits in with the scheme adopted by the author for all diazo-decompositions. The outstanding difference from the Gomberg reaction is the formation of *s*-dinaphthyl, and here apparently the 4-nitronaphthyl radical (XII) when formed is sufficiently stabilised by the nitro-group to have a free existence and so enabled to combine with another like radical.



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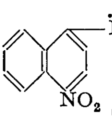

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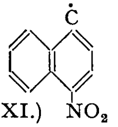

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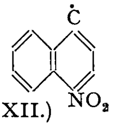
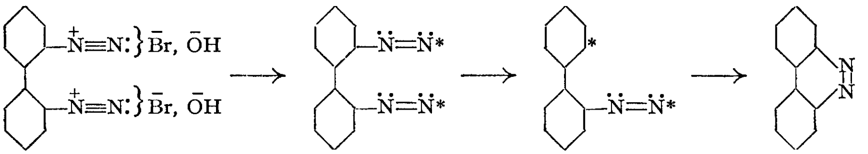


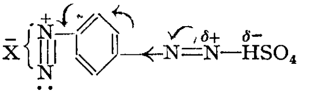
(XII.)

The Closure of the Dibenzopyridazine (*Diphenylazone*) *Ring*.—This reaction takes place either by the action of cuprous bromide (Dobbie, Fox, and Gauge, *J.*, 1911, **99**, 1615) in acid solution, or by that of alkaline sodium arsenite (Sandin and Cairns, *J. Amer. Chem. Soc.*, 1936, **58**, 2019) on tetrazotised 2 : 2′-diaminodiphenyl. The same explanation as that given by H. *et al.* (*loc. cit.*) for the formation of *s*-azo-derivatives in acid solution can hold for both cases, *viz.*, the initial formation of a bisdiazonium compound (XIII), with subsequent transfer of two electrons from the reducing agent to form the di-radical (XIV), partial elimination of nitrogen (XV), and consequent closure of the ring to give dibenzopyridazine (XVI). This simple electronic explanation applies to both cases and avoids the difficulty of S. & W., who, while postulating homolytic fission in the alkaline case, have to resort to heterolytic fission and special pleading for the acid case.



(XIII.) (XIV.) (XV.) (XVI.)

Incidentally, it is of interest that where both a diazonium and a covalent diazo-group can exist together as in tetrazotised *p*-phenylenediamine in concentrated sulphuric–phosphoric acid solution (Schoutissen, *J. Amer. Chem. Soc.*, 1933, **55**, 4541) (XVII), the diazo-group can couple in the strong acid solution, *i.e.*, retain its nitrogen, while the diazonium group will subsequently give the usual reactions of diazonium salts, *i.e.*, it will readily part with its nitrogen. Here, then, is the clue to an explanation of the difference in the decompositions of nitrosoacylaryl- and nitrosoacylalphyl-amines, since the aryl will be more in the diazonium condition than the alphyl compound owing to the inductive (+ *I*) effect of the alkyl group in the alphyl compound diminishing the positive character of the diazonium group and hence producing a



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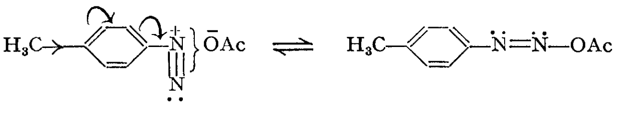
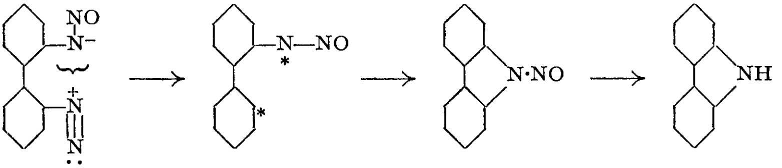


shift in the diazo–diazonium equilibrium in favour of the diazoacetate : In consequence, the Gomberg reaction will have less driving power than in the case of the nitrosoacylarylamines.

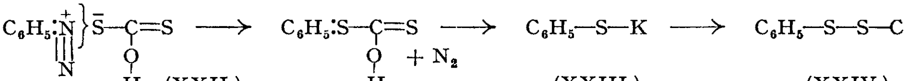
Carbazole Formation in the Acid Dibenzopyridazine Reaction.—The appreciable yield of carbazole obtained in this reaction is not dealt with by S. & W., but whereas an explanation appears to be well-nigh impossible on the free-radical hypothesis, it readily follows from the author's viewpoint, *viz.*, that on tetrazotisation one diazonium group may readily pass into the nitrosoamine form under the influence of the other (cf. the partial analogy in Schoutissen's reaction, where one diazonium group passes into the diazo-form), with initial salt formation (XVIII), whence passage of an electron from the nitrosoamine to the diazonium group causes elimination of nitrogen (XIX), and ring closure (XX) with subsequent hydrolysis produces carbazole (XXI), the yield of which is improved by rise of temperature. An analogous reaction in which strongly positive diazonium groups are concerned is the formation of 4 : 8 : 4′ : 8′-tetranitro-1 : 1′-dinaphthylamine by the action of cuprous hydroxide on 4 : 8-dinitronaphthalene-1-diazonium sulphate (Hodgson and Crook, *J.*, 1937, 571). It will be recalled that Schoutissen (*J. Amer. Chem. Soc.*, 1933, **55**, 4541) found that a diazonium group was as effective in its electron-attracting influence as two nitro-groups.



(XVIII.) (XIX.) (XX.) (XXI.)

The tendency to carbazole formation when tetrazotised 2 : 2′-diaminodiphenyl is decomposed, and the electronic situation necessitated, may well account for the difficulty in carrying out the ordinary Sandmeyer reaction. Incidentally, the main product of the reaction between the above tetrazo-compound and potassium iodide is carbazole (Mascarelli, *Gazzetta*, 1908, **38**, ii, 619), the di-iododiphenyl being formed in small amount only.

The Decompositions of Benzenediazo-hydroxide in (a) *Carbon Disulphide,* (b) cyclo*Hexane, and* (c) *without Added Solvent* (cf. Waters, *J.*, 1937, 2014).—(*a*) In accord with Leuckardt's classical work (*J. pr. Chem.*, 1890, **41**, 170; Hartley and Smiles, *J.*, 1926, 1824), the reaction can proceed normally *via* a diazonium xanthate (XXII), which by elimination of nitrogen and subsequent hydrolysis gives the mercaptate (XXIII) with subsequent oxidation to the disulphide (XXIV), without recourse to the hypothesis of free radicals :

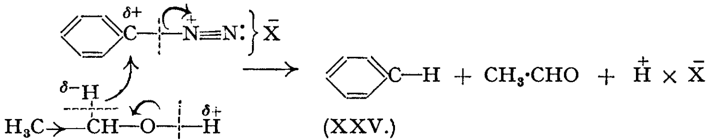


$$C_6H_5{:}\underset{\substack{|||\\ N\\ \cdot\cdot}}{\overset{+}{N}}\}\bar{S}-\underset{\substack{|\\ O\\ |\\ H}}{C}=S \longrightarrow C_6H_5{:}S-\underset{\substack{|\\ O\\ |\\ H}}{C}=S + N_2 \longrightarrow C_6H_5-S-K \longrightarrow C_6H_5-S-S-C_6H_5$$

(XXII.) (XXIII.) (XXIV.)

(*b*) This reaction, which yields benzene, is analogous to the corresponding reduction by ethyl alcohol, where the anionoid CH_2 group in (XXV) supplies the hydrogen as in the attached scheme, since *cyclo*hexane is a ring of anionoid CH_2 groups.

(*c*) In the general scheme put forward by Waters (*J.*, 1942, 266) the homolysis of undissociated diazo-compounds into two free radicals with liberation of nitrogen was regarded as occurring regularly only in non-dissociating solvents (cf. Grieve and Hey, *J.*, 1938, 109), but he stated (*J.*, 1946, 1155) that the production of a trace of benzene in decomposition (*c*) showed that radical formation in aqueous solution and subsequent decomposition as Ar* + H_2O ⟶ Ar–H +*OH *is not quite impossible.* This decomposition has been reinvestigated by the author with Dr. E. R. Ward, and nitrobenzene obtained in small yield. We have not been able to detect the trace of benzene mentioned, because nitrobenzene itself gives a positive test by the iodic acid method (Masson and Race, *J.*, 1937, 1718), and *m*-dinitrobenzene on further nitration; in addition, we have obtained aniline by reduction. Consequently, we believe that the trace of benzene recorded was actually nitrobenzene.

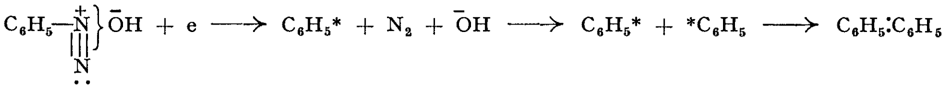


(XXV.)

In the same paper (*loc. cit.*) the Bart reaction is cited as occurring spontaneously without recourse to any copper derivative as catalyst, the presence of the reducing agent which brings about the reaction being apparently overlooked.

The Reactions of Benzenediazonium Chloride with Solvents and Metals in Absence of Water.—Since Waters (*J.*, 1937, 2010) states that Sir Robert Robinson pointed out that the reactions previously discussed by Waters (*J.*, 1937, 113, 200) could all be considered as typical interactions between covalent diazobenzene chloride and another reagent, any apparent analogy with reactions in aqueous solution should, in the author's opinion, not be unduly stressed.

The Oxidising Reactions of Diazobenzene Hydroxide.—The first example quoted (*J.*, 1937, 2015) is the oxidation of leuco-methylene-blue by *benzenediazonium sulphate*, which, apart from the irony of the situation, indicates a much simpler mechanism than that of free radicals since it is the readiness to be an electron acceptor which gives to the diazonium ion its oxidising properties. All the oxidations (cited in the paper) of diazo-compounds in aqueous solution are due to electron acceptance by diazonium ions, and the fact that diphenyl derivatives are also regular by-products (cf. Schmidt, *Annalen*, 1920, **421**, 159; Bart, *ibid.*, 1922, **429**, 55) emphasises an ordinary electronic mechanism for the oxidation :

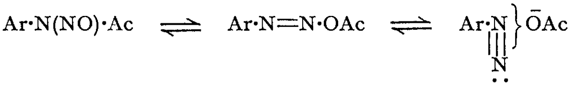


$$C_6H_5{-}\underset{\underset{\ddot{N}}{|||}}{\overset{+}{N}}\Big\}\bar{O}H + e \longrightarrow C_6H_5{*} + N_2 + \bar{O}H \longrightarrow C_6H_5{*} + {*}C_6H_5 \longrightarrow C_6H_5{:}C_6H_5$$

Conclusion.—(1) The source of the free radicals in Hey and Waters's hypothesis is given as the undissociated diazo-hydroxide, the amount of which is regarded as considerable, especially near neutrality, in striking contrast to the views of Conant and Tishler ("The Chemistry of Organic Compounds", Macmillan, 1939, p. 382), who consider that the free diazo-hydroxide is only present in very small amount at any time.

(2) The positivity of the carbon atom to which the diazonium group is attached is a determining factor in diazo-decompositions in sulphuric acid with cuprous hydroxide (cf. Hodgson, Leigh, and G. Turner, *loc. cit.*; Hodgson, Birtwell, and Walker, *J.*, 1941, 770). Gradations of positivity are well exemplified as follows : formation of symmetrical azo-compounds (minimum positivity), of dinaphthyls (medium), and replacement by hydrogen (maximum). This viewpoint is much simpler than any which the hypothesis of free radicals could provide.

(3) The formation of diaryl compounds from nitrosoacylarylamines is due to the presence of diazonium salt in the equilibrium scheme :



$$Ar{\cdot}N(NO){\cdot}Ac \rightleftharpoons Ar{\cdot}N{=}N{\cdot}OAc \rightleftharpoons Ar{\cdot}\underset{\underset{\ddot{N}}{|||}}{N}\Big\}\bar{O}Ac$$

and there is no evidence to show that the solid nitrosoacylarylamine is not such an equilibrium mixture; on the contrary, the reactions investigated by Hey *et al.* indicate the existence of such a mixture.

(4) S. & W. exclude the reduction of diazotised α- and β-naphthylamine with alkaline sulphite (Lange, D.R.-P., 78,225) because there is no *a priori* evidence (*e.g.*, the isolation of diaryls or of azo-diaryls) that free radicals are concerned. It must be pointed out that the patent refers to reaction in acetic acid solution, and that the mechanism involved has already been adequately discussed on the same lines as heretofore (cf. Hodgson, Nicholson, and G. Turner, *J.*, 1944, 15), and for cases where dinaphthyl formation occurs alongside that of *s*-azo-compounds.

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