173. *The Free-radical Reactions of the Aromatic Diazo-compounds: A Reply to Hodgson's Criticisms.*

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It is shown that Hodgson's criticisms (this vol., p. 348), which involve the application of our theory of free-radical reactions to experimental conditions which it was not intended to embrace, are not valid, and that the views put forward by him do not provide a satisfactory theoretical interpretation of the known experimental facts.

The experimental conditions under which reactions in solution are likely to involve the formation and transient existence of free radicals were clearly specified by us more than ten years ago (*Chem. Reviews*, 1937, **21**, 169). Within this field a satisfactory theory of homolytic reactions has been developed and confirmed by a large body of experimental evidence. In recent publications (this vol., p. 348; *J. Soc. Dyers Col.*, 1948, **64**, 99) Hodgson has applied a free-radical concept to experimental conditions which our own theory was never intended to embrace, and has unjustifiably inferred that it is unnecessary to postulate that free radicals are concerned in any of the reactions of diazo-compounds in solution.

Contrary to the impression now given by Hodgson, which is implicit in the title of his paper,* the free-radical theory was never intended to include the ordinary reactions of diazonium salts in aqueous solution or the typical coupling reactions which take place in alkaline solution, but was confined primarily, and in the first place wholly, to reactions in non-ionising solvents. The initial evidence which led to the suggestion that free uncharged aryl radicals could be produced from *some* of the decomposition reactions of the aromatic diazo-compounds was the discovery (Grieve and Hey, *J.*, 1934, 1797; Hey, *ibid*, p. 1966) that the normal " laws of aromatic substitution " were not obeyed when (i) un-ionised diazoaryl hydroxides, (ii) nitrosoacylarylamines (aryldiazoacetates), and (iii) arylazotriphenylmethanes decomposed in aromatic solvents, C_6H_5R. Unsymmetrical diaryls were thereby formed in a manner which showed that the substituting reagent did not *consistently* have either kationoid (*e.g.*, NO_2^+) or anionoid (*e.g.*, OH^-) character, but gave rise to a complex mixture of products from which, in the earlier examples studied, the *ortho-* and *para*-isomers were isolated whatever the nature of the group R. In later studies substitution was found to take place *at all three positions* with respect to CO_2Et (Hey, *J.*, 1934, 1966), and Cl and Br (France, Heilbron, and Hey, *J.*, 1938, 1364), and in similar reactions with pyridine numerous examples were later recorded of the simultaneous occurrence of substitution at the α-, β-, and γ-positions (Haworth, Heilbron, and Hey, *J.*, 1940, 349, and subsequent papers). It is often supposed that free aryl radicals are typically *para*-substituting reagents, but this is not rigorously true; it merely happens that because *para*-substituted diaryls, being more symmetrical, are less soluble and more highly crystalline than their isomers, they can be isolated more easily from tarry reaction mixtures. As far as we are aware, the quantitative examination of the total product from such a homolytic reaction in the liquid phase has not yet been attempted, and Table I gives the best conclusions which can be drawn from available experimental evidence.

Table I.

Reactants.	Yields of isomers, %. ortho.	meta.	para.	Total yield, isolated, %.
$Ph{\cdot}C_6H_4{\cdot} + PhCl$	32	20	48	38
$Ph{\cdot}C_6H_4{\cdot} + PhBr$	33	15	52	35

(From France, Heilbron, and Hey, *loc. cit.*)

Further evidence of the absence of consistent kationoid or anionoid characteristics of reactions involving decompositions of diazo-compounds in non-ionising media is afforded by the fact that phenyl groups from (i) diazobenzene hydroxide and (ii) diazobenzene acetate will combine equally well with electronegative elements, such as chlorine from carbon tetrachloride or sulphur from carbon disulphide, and with electropositive elements, such as hydrogen from hexane or ether, or metallic elements such as mercury or antimony (Waters, *J.*, 1937, 2007, 2014; 1939, 864; Grieve and Hey, *J.*, 1938, 108).

The views now put forward by Hodgson indicate that he regards the formation of a symmetrical diaryl Ar·Ar as an inevitable consequence of the occurrence of the free aryl radical Ar in

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* " 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."

solution, thus repeating the error made by Wieland (*Ber.*, 1922, **55**, 1816), but the whole theory of the reactions of free aryl radicals *in solution*, whether derived from diazo-compounds or from other sources, shows consistently that dimerisation is not a characteristic property of the aryl radical under these conditions (cf. Waters, *Trans. Faraday Soc.*, 1941, **37**, 770).

The experimental evidence which has accumulated since the publication of our joint review in 1937 has substantiated our hypotheses by the discovery of several new reactions which cannot be brought about by solutions of diazonium *salts* in ionising media. These are (*a*) combination with free elements, *e.g.*, As, Sb, Hg, Se, Te (a property which is exhibited by both the fragments of decomposing covalent diazo-compounds), and (*b*) the initiation of addition polymerisation of olefins, $R\cdot CH\colon CH_2$. These reactions have been noted regularly whenever uncharged alkyl or aryl radicals have been generated by other means, *e.g.*, from the thermal or photochemical decompositions of (i) lead or mercury alkyls, (ii) aldehydes or ketones, (iii) diacyl peroxides, and (iv) azo-compounds. It follows, therefore, that any theory which attempts to explain arylation reactions which can only be brought about in solution in non-aqueous (and usually non-ionising) media such as benzene, nitrobenzene, and pyridine, by schemes involving diazonium kations overlooks a great volume of experimental evidence which clearly shows that the differences between the chemical reactivities of the ionised, water-soluble, diazonium salts and the covalent diazoacetates and diazohydroxides are quite as great as are the differences in their physical properties. For this reason we again insist that one single reaction mechanism cannot explain satisfactorily all the decomposition reactions of the diazo-compounds. The two reaction mechanisms are just as necessary in this branch of aromatic chemistry as they are for the interpretations of the reactions of the aliphatic azo- and diazo-compounds from which the production of free uncharged hydrocarbon radicals has been abundantly proved.

While we admit that bimolecular (or more complex) reactions not involving " free " ions or radicals may occur between molecules of aromatic diazo-compounds and other substances, we must point out that the crucial experimental evidence for the existence of *free* aryl radicals is provided by the demonstration that the decomposition of diazobenzene acetate (nitrosoacetanilide) is a slow first-order process which is independent of the polar nature of the solvent in which it is carried out (Grieve and Hey, *J.*, 1934, 1797; Butterworth and Hey, *J.*, 1938, 116). These results, together with the kinetic studies of Pray (*J. Physical Chem.*, 1926, **30**, 1417, 1477) and of Waring and Abrams (*J. Amer. Chem. Soc.*, 1941, **63**, 2757) and the recent studies on the decomposition of benzoyl peroxide in various solvents carried out by Nozaki and Bartlett (*J. Amer. Chem. Soc.*, 1946, **68**, 1686), show that all these reactions are fundamentally identical in type and all yield free radicals by homolytic fission. On this point Hodgson has expressed the view that the free-radical hypothesis is based on a fallacy in that it implies the simultaneous fission of two bonds of greatly unequal strength, as in *A*, and that therefore a mechanism based on the decomposition of the diazonium ion, as in *B*, is to be preferred.

$$(A.)\quad \mathrm{Ar}-\vdots-\mathrm{N{=}N}-\vdots-\mathrm{X} \qquad\qquad [\mathrm{Ar}-\underset{\cdot}{\vdots}-\mathrm{N{\equiv}N}]^+\quad (B.)$$

A clear-out decision between these two processes is provided by the figures given in Tables II and III. A comparison of the decomposition of some *p*-substituted diazoacetates and of the corresponding diazonium ions clearly shows that, whereas in the former case the reaction rate is essentially independent of the substitutent at the *para*-position, in the latter case the substituent profoundly affects the speed of the reaction. On the other hand, the rates of decomposition of a series of nitroso-acylanilides $[C_6H_5\cdot N(NO)\cdot CO\cdot R' \rightleftarrows C_6H_5\cdot N\colon N\cdot O\cdot CO\cdot R']$ show with equal clarity that the speed of the reaction is very much influenced by the nature of the acyl group, whereas in the decomposition of diazonium salts it has long been known that the rate of evolution of nitrogen is essentially independent of the anion. These results indicate conclusively that the decomposition of the diazobenzene acetates does not proceed through the diazonium ion, and that the mechanisms of the two processes must be fundamentally different. The question of the simultaneous fission

TABLE II.

R.	Decomp. of p-$R\cdot C_6H_4\cdot N\colon N\cdot OAc$, $k\,.\,10^3$ at 20°.*	Decomp. of $[p$-$R\cdot C_6H_4\cdot N_2]^+\cdot$, $k\,.\,10^3$ at 50°.†
H	4·57	27·0
Me	4·99	1·8
Cl	4·11	0·15
Br	4·23	0·23

* Grieve and Hey, *J.*, 1935, 689.
† From Euler (" International Critical Tables ").

TABLE III.

R'.	Decomp. of $C_6H_5{\cdot}N{:}NO{\cdot}R'$, $k \,.\, 10^4$.
$H{\cdot}CO$	1·23 at 45°
$CH_3{\cdot}CO$	1·67 at 25°
$C_2H_5{\cdot}CO$	4·44 at 25°
n-$C_3H_7{\cdot}CO$	Explodes at 25°

(Preliminary unpublished results by Dr. G. H. Williams.)

of two bonds does not arise, the reactions involved being similar to the analogous decompositions of arylazotriphenylmethanes and of diacyl peroxides. Evidence for the transient existence of the second radical X• is often quite clear. Thus carbon dioxide is evolved when diazobenzene acetate decomposes in carbon tetrachloride, and the reaction mixture attacks metals such as mercury, which are quite inert to acetic acid or even to hydrochloric acid (Waters, *J.*, 1937, 113).

Both of us have, since 1937, considered that the distinctive features of the homolytic and the heterolytic decompositions of organic molecules were sufficiently distinct for an attempt to be made at the elucidation of the mechanisms concerned in border-line cases, in which either, or both, free radicals or ions might be involved (for the basis of classification see Waters, *J.*, 1942, 266), but these later extensions into less well defined territory do not influence in any way the validity of the original hypothesis. Proceeding on this basis we have considered (*a*) whether there can occur, in approximately neutral aqueous solution, any homolytic reactions involving un-ionised diazohydroxides, $Ar{-}N{=}N{-}OH$, and also (*b*) whether the chemistry of the diazo-compounds affords any examples of catalysed one-electron-transfer reactions analogous to those whereby free neutral hydroxyl is formed in aqueous solution. Two recent papers by one of us (Waters, *J.*, 1942, 266; 1946, 1154) have considered these possibilities, and relevant experimental work is in hand. With regard to (*a*) our attention has been drawn by Dr. Z. E. Jolles to his isolation of benzene, anisole, phenetole, toluene, and naphthalene from decompositions of alkaline diazotised solutions of aniline, *o*- and *p*-anisidine, *p*-phenetidine, *m*- and *p*-toluidine, and α- and β-naphthylamine, and also to the production of diaryl derivatives as regular components of the resultant resins (cf. *Gazzetta*, 1931, **61**, 403; *Atti R. Accad. Lincei*, 1932, **15**, 292, 395). This work vitiates Hodgson's suggestion that the claim to have identified benzene as a minor product from the decomposition of diazobenzene hydroxide (*J.*, 1937, 2016) is unfounded and that instead nitrobenzene had been formed by an ionic reaction in which free nitrite anions were concerned. The product identified as benzene was separated from the reaction mixture by a procedure which should have minimised contamination with any substance of higher boiling point. In this connection reference should be made to the fact that as long ago as 1925 Gellisen and Hermans (*Ber.*, 1925, **58**, 984) recognised the dual character of the reactions of certain diazo-compounds with water, and quoted examples of the replacement of the diazo-group by hydrogen without the use of any added reducing agent. The evidence for the occurrence of homolysis of an un-ionised diazoaryl hydroxide in aqueous solution is of necessity inconclusive, since as soon as any reaction has taken place there is regularly formed a water-insoluble tarry product which may then extract the diazohydroxide and thereafter allow it to decompose homolytically in the non-aqueous phase (cf. the mechanism proposed for the Hey–Gomberg reaction, *J.*, 1938, 108).

With regard to (*b*), which was indicated in the paper which dealt with the Sandmeyer reaction, we can see no inherent difference between the proven reaction (i) and either (ii) or (iii) :

$$\text{(i)}\quad Fe^{++} + HO{-}OH \longrightarrow Fe^{+++} + (HO{:})^{-} + {\cdot}OH$$
$$\text{(ii)}\quad Ph{-}N{=}N{-}OH + Fe(CN)_6^{=\,=} \longrightarrow Fe(CN)_6^{=\,-} + (HO{:})^{-} + N_2 + Ph{\cdot}$$
$$\text{(iii)}\quad PhN_2^{+} + Cu^{+} \longrightarrow Ph{\cdot} + N_2 + Cu^{++}$$

and are prepared to agree with Hodgson that (iii) may occur within a diazonium–cuprous halide, so that the phenyl radical attacks vicinal chloride anions and never truly becomes " free ". In just the same way it has been suggested that (i) occurs within the solvate shell of a ferrous ion, *e.g.* :

$$(Fe^{++}, HO{-}H) + HO{-}OH \longrightarrow (Fe^{+++}, \overset{-}{O}H) + H_2O + {\cdot}OH$$

Here again the crucial experiments which show that more than one mechanism may well be involved are the many observations which indicate that the decompositions of different complex diazonium halides are differently affected by the dilution of the solution (cf. Hodgson, *Chem. Reviews*, 1947, **40**, 251). In the case of the ferrocyanide reaction (ii) the anomalous product is formed in best yield when the pH of the solution is controlled to such a value that an un-ionised diazohydroxide can be formed (W. A. Waters, unpublished observations).

Further investigation of these border-line cases is desirable, but whatever the outcome we feel that we are fully justified in maintaining that the decomposition reactions of the aromatic diazo-compounds can take either homolytic or heterolytic courses according to circumstances, and that occasionally both processes may occur simultaneously. We further maintain that since the factors which facilitate, or inhibit, the elimination of nitrogen from a substituted kation $[R-C_6H_4-N_2]^+$ or covalent molecule $R-C_6H_4-N=N-X$ are differently affected by the nuclear substituent R, any one complete generalisation drawn from experiments made with a few diazo-compounds only is likely to be invalid.

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