98. *The Decomposition of Diazo-compounds in Neutral Solution. Some Observations on the Diazo-coupling Reaction.*

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Aqueous solutions of diazotised amines, when maintained neutral by the presence of calcium carbonate, decompose to form bis- or mono-arylazophenols, aniline and *o*-toluidine giving the former, and *p*-toluidine, *o*-, *m*-, and *p*-nitroaniline, and α- and β-naphthylamine the latter. An aqueous solution of the equilibrium mixture $C_6H_5{\cdot}N{:}N{\cdot}OH \rightleftharpoons C_6H_5{\cdot}\overset{\oplus}{N}{\vdots}N\}\overset{\ominus}{OH}$ decomposes to form nearly equal parts of 2 : 4-bisbenzeneazo- and 4-benzeneazo-phenol. The results are held to indicate that undissociated benzenediazohydroxide and not benzenediazonium hydroxide is the coupling component.

When aniline is diazotised in hydrochloric acid, and the solution then rendered exactly neutral with calcium carbonate and filtered, the filtrate rapidly decomposes with formation of phenol, hydrochloric acid, and a small amount of tar. A somewhat similar result is obtained when sulphuric acid and barium carbonate are used; the neutralised solution then develops sulphuric acid with formation of phenol, and about 40% of 2 : 4-bisbenzeneazophenol. If, however, the neutralised solution is allowed to decompose in the presence of calcium carbonate, an almost quantitative yield of 2 : 4-bisbenzeneazophenol results. The same reactions were afforded by *o*- and *p*-toluidine, *viz.*, formation of the cresol, mineral acid, and tar when the neutralised solutions decomposed in the absence of calcium carbonate, but of 3 : 5-bis-*o*-tolueneazo-*o*-cresol and 3-*p*-tolueneazo-*p*-cresol when it was present. When, however, neutralised diazo-solutions from *o*- or *m*-nitroaniline or α-naphthylamine were allowed to decompose *per se*, a *p*-arylmonoazophenol resulted even in the presence of the free mineral acid developed, and an *o*-arylmonoazophenol or naphthol was obtained when *p*-nitroaniline or β-naphthylamine was so treated. In all these cases a certain amount of tar was also present, but when the decompositions took place in conjunction with calcium carbonate, clean products were obtained.

Previous work (Hirsch, *Ber.*, 1890, **23**, 3705) on the decomposition of benzenediazonium sulphate in acid solution has shown that a small quantity of 4-hydroxydiphenyl is also formed. Further, it is stated (Saunders, " The Aromatic Diazo-Compounds and their Technical Applications," 1936, p. 68) that the products of decomposition of diazo-salts in aqueous solution do not interfere with the reaction except in the naphthalene series, in which the naphthols which are formed remove the diazo-compound by coupling when they have reached a certain concentration; also (p. 69) that the decomposition is not affected by the amount of free mineral acid present. These statements are now found to require qualification.

The mechanism for the decomposition reactions suggested by the present experiments is that the aryldiazonium chloride (*a*) is involved in a solvolytic reaction with water (cf. Hammett, " Physical Organic Chemistry," McGraw-Hill Book Co., 1940, p. 167) in which the incipient solvation of the halide ion is the driving force of the reaction, and the diazonium ion is, in consequence, involved in a reversible reaction with water to give an equilibrium mixture of diazonium hydroxide (*b*) and diazo-hydroxide (*c*) (cf. Hammett, *op. cit.*, p. 295).

$$\underset{(a)}{\mathrm{R{\cdot}\overset{\oplus}{N}{\equiv}N{:}\}\overset{\ominus}{Cl}}} + \mathrm{H_2O} \rightleftharpoons \mathrm{R{\cdot}\overset{\oplus}{N}{\equiv}N{:}\}\overset{\ominus}{OH}}\ (b) \rightleftharpoons \underset{(c)}{\mathrm{R{\cdot}N{=}\overset{\delta+}{N}{-}\overset{\delta-}{OH}}}$$

$$+\overset{\oplus}{\mathrm{H}} + \overset{\ominus}{\mathrm{Cl}}$$

Subsequent decomposition of (*b*) into phenol then occurs, together with a small amount of more profound decomposition, affording the tar. When the hydrochloric acid is removed by means of calcium carbonate as rapidly as it is formed, the phenol resulting from the decomposition of (*b*) couples with the diazo-hydroxide (*c*) to give an azo-compound. To test the latter view, aniline was diazotised in hydrochloric acid solution by nitrous fumes to ensure that no metal was present (*e.g.*, sodium or potassium), since in the subsequent operations this would render the solution alkaline; the diazo-solution was then shaken with excess of silver oxide and filtered. The filtrate, which could now only contain the equilibrium mixture of (*b*) and (*c*), and in the ratio 3—4 : 6—7 (Hantzsch and Davidson, *Ber.*, 1898, **31**, 1612), rapidly decomposed and deposited a mixture of approximately equal parts of 2 : 4-bisbenzeneazo- and 4-benzeneazo-phenol (whereas Hantzsch, *ibid.*, p. 340, reports a little phenol and much tar). If phenol or α-naphthol is added to the filtrate from the silver oxide treatment, rapid and ultimately quantitative precipitation of 4-benzeneazo-phenol or -1-naphthol occurs, the rate of formation of the latter being somewhat greater than that of the former. The solution of the above equilibrium mixture is deep yellow, and, contrary to Hantzsch (*loc. cit.*), is only slightly alkaline, *viz.*, to methyl-orange and litmus, but not to phenolphthalein and brilliant-yellow. When this solution was treated with acetic acid in excess, a complex decomposition occurred and some phenol and diphenyl were isolated from the tar, a reaction in striking contrast to the clean decomposition of the solution alone.

We conclude from these experiments in neutral solution, where the equilibrium (*b*) $\rightleftharpoons$ (*c*) is uninfluenced by external acid or base, that the coupling takes place between the diazohydroxide (*c*) and the phenolic compounds, whether formed by the decomposition of the diazonium hydroxide (*b*) or by addition to the equilibrium mixture. This view is in harmony with that of Conant and Peterson (*J. Amer. Chem. Soc.*, 1930, **52**, 1220) and also with the reactions of diazonium and diazo-compounds which involve respectively the scission and the retention of nitrogen.

Of all the amines diazotised, only aniline and *o*- and *p*-toluidine failed to couple in the presence of the mineral acid developed when their diazo-solutions decomposed *per se*, and this acid amounted ultimately in the cases of both hydrochloric and sulphuric acid to *ca.* 60% of the theoretical amount expected if all the diazo-solution had been converted into phenol. The neutralised (calcium carbonate) solution of diazotised aniline or α-naphthylamine also failed to couple with phenol but did so with α-naphthol; whereas that from *p*-nitroaniline coupled at once with phenol.

EXPERIMENTAL.

General Procedure.—The amine (0·1 g.-mol.), dissolved in hydrochloric acid (24 c.c., *d* 1·16) and water (200 c.c.), was diazotised at 0° by addition of a solution of sodium nitrite (7 g.) in the minimum amount of water. The mixture was kept at 0° and neutralised with calcium carbonate (2—3 g.), filtered, and the clear solution stirred with calcium carbonate (6 g.). The mixture was allowed to decompose at room temperature during 3 days, being tested periodically to ensure that neutrality had been maintained; it was then heated at 70° for 4—5 hours for decomposition to become complete, as shown by addition of a drop to alkaline H-acid solution. The reaction mixture was then acidified with hydrochloric acid, filtered, and the precipitate of azo-compound washed with water and dried. The table gives the detailed results for eight representative amines.

Table of Decomposition Products.

Amine diazotised.	Weight taken, g.	Weight of azo-product, g.	Azo-product formed.
(1) Aniline	9·3	9·0	2 : 4-Bisbenzeneazophenol
(2) *o*-Toluidine	10·5	11·0	3 : 5-Bis-*o*-tolueneazo-*o*-cresol
(3) *p*-Toluidine	10·5	10·5	3-*p*-Tolueneazo-*p*-cresol
(4) *o*-Nitroaniline	13·8	14·0	2-Nitro-4-*o*-nitrobenzeneazophenol
(5) *m*-Nitroaniline	13·8	14·0	3-*Nitro*-4-m-*nitrobenzeneazophenol*
(6) *p*-Nitroaniline	13·8	13·1	4-*Nitro*-2-p-*nitrobenzeneazophenol*
(7) α-Naphthylamine	14·3	14·5	4-Naphthaleneazo-1-naphthol
(8) β-Naphthylamine	14·3	13·7	1-Naphthaleneazo-2-naphthol

Crystal description, analyses, and references. (1) Dark brown plates from ethyl alcohol, m. p. 124—125° (Ponzio, *Gazzetta*, 1913, **43**, i, 561, gives m. p. 123°) (Found: N, 18·7. Calc.: N, 18·6%). (2) Brown plates from cellosolve, m. p. 146° (Ponzio, *loc. cit.*, gives m. p. 146°) (Found: N, 16·2. Calc.: N, 16·3%). (3) Red plates from glacial acetic acid, m. p. 113° (Noelting and Kohn, *Ber.*, 1884, **17**, 304, give m. p. 112—113°) (Found: N, 12·4. Calc.: N, 12·4%). (4) Maroon needles from cellosolve, m. p. 190° (Hewitt and Mitchell, J., 1905, **87**, 226, give m. p. 186°) (Found: N, 19·6. Calc.: N, 19·5%). (5) Dark red plates from glacial acetic acid, m. p. 202° (Found: N, 19·4. $C_{12}H_8O_5N_4$ requires N, 19·4%). (6) Yellow micro-plates from alcohol, m. p. 168° (Found: N, 19·2. $C_{12}H_8O_5N_4$ requires N, 19·4%). (7) Very dark red micro-plates from glacial acetic acid (Found: N, 9·3. Calc.: N, 9·4%). (8) Maroon micro-plates from glacial acetic acid, m. p. 179° (Meldola and Hanes, J., 1894, **65**, 836, give m. p. 178—179°) (Found: N, 9·4. Calc.: N, 9·4%).

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