111. p-*Aminodimethylaniline. Part I. The Properties of its Diazonium Compounds.*

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The diazotisation of *p*-aminodimethylaniline proceeds normally under the usual conditions. The solutions of the diazonium compound are very stable, but show anomalous behaviour towards copper bronze. Although the stability of the weakly acid solutions and their rate of reaction with amines or phenols vary greatly with the p_H value, the yield of azo-compound depends mainly on the substance coupled.

The literature contains several incidental references to the diazotisation of *p*-aminodimethylaniline in aqueous solution (Heidlberg, *Ber.*, 1887, **20**, 150; Hantzsch and Witz, *Ber.*, 1902, **35**, 896; Aitken and Reade, J., 1926, 1896) and to the coupling of the diazotised solution (Nölting, *Ber.*, 1885, **18**, 1144; D.R.-PP. 77169, 81376; Friedl., **3**, 1008; **4**, 799; Höchster Farb., D.R.-P. 87585), but in no case is the efficiency of the process indicated. Diazotisation by means of amyl nitrite in alcoholic solution was stated by Stollé (*Ber.*, 1912, **45**, 2681; cf. Saunders, " The Aromatic Diazo-Compounds and their Technical Applications," 1936, 19) to require careful attention to detail.

Aromatic compounds containing a nuclear dimethylamino-group readily react with nitrous acid, the products depending upon the other substituents present and upon the experimental conditions; this effect is particularly well marked in the case of the *p*-substituted dimethylanilines (compare *inter alia*, Reade *et al.*, J., 1926, 1896; 1929, 2863; 1935, 53; Hodgson *et al.*, J., 1930, 277; 1932, 1812, 2976). The various possibilities, *e.g.*, nuclear nitration, nitrosoamine formation, might all occur in the case of *p*-aminodimethylaniline in addition to the normal diazotisation. Although the free amino-group should favour nuclear nitration in a neutral or weakly acid solution, yet the positively charged NH_3^+ group, which is present in more strongly acid solutions and is actually involved in the diazotisation process (Hantzsch and Schümann, *Ber.*, 1899, **32**, 1691), would reduce this tendency and might even favour nitrosoamine formation (compare Hodgson, *J. Soc. Dyers Col.*, 1930, **46**, 183). The positively charged $NHMe_2^+$ group, present in acid solution, might also tend to inhibit diazotisation, although the inhibiting effect would probably be much less than that of the positive charge on the diazonium group in *p*-aminobenzenediazonium salts, which is such as to make direct diazotisation of

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* This common and useful convention has its dangers, in that the suggested sharp division of a reaction into the steps *mesomeric state* ⟶ *single structure* ⟶ *product* is in general quite illusory.

the amino-group extremely difficult (Griess, *Ber.*, 1884, **17**, 697; Nietzski, *ibid.*, p. 1350; Schoutissen, *J. Amer. Chem. Soc.*, 1933, **55**, 4535).

Diazotisation of *p*-aminodimethylaniline with nitrous acid occurs quantitatively, although very slowly, below 5°. The solutions so prepared are very stable towards boiling 40% sulphuric acid, evolution of nitrogen not being complete in 2 hours. Addition of copper bronze, however, causes a rapid evolution of nitrogen in the cold, and a quantitative study showed that the volume of gas liberated corresponded to almost complete diazotisation, and was unaffected by use of excess of nitrous acid; in this decomposition dimethylaniline was formed instead of the expected *p*-chlorodimethylaniline. It is probable that under these conditions the diazonium compound is reduced by means of the copper.

Diazotisation of the base in hydrochloric acid solution, with subsequent addition of a 10% cuprous chloride solution, gave *p*-chlorodimethylaniline at temperatures above 80° (compare Heidlberg, *loc. cit.*), the yield being 80%. Addition of an excess of potassium iodide to a similarly diazotised solution in hydrochloric acid leads to precipitation of *p*-iododimethylaniline on warming, but the reaction proceeds very slowly. In carrying out the diazotisation under diverse conditions no evidence was obtained for the formation of nitrosoamines or of nuclear-substituted nitro- or nitroso-compounds. It is thus evident that the diazotisation of *p*-aminodimethylaniline in hydrochloric acid solutions, although slow at low temperatures, as expected, is otherwise normal and requires no special conditions. Diazotisation of the amino-group apparently forestalls any of the substitution reactions usually found in the *p*-substituted dimethylanilines and the diazonium compound formed is unaffected by excess of the reagent whether this be nitrous acid (as formed under ordinary conditions) or nitrogen trioxide in ether, acetone or hydrochloric acid (compare Stollé, *loc. cit.*).

When *p*-aminodimethylaniline was diazotised and coupled either with dimethylaniline in weakly acid solution (Nölting, *loc. cit.*) or with pyrogallol in alkaline solution (Friedl., **4**, 799), a very poor yield of azo-compound was obtained; much nitrogen was evolved and, in the latter case, some dimethylaniline was formed. These results indicate that the diazonium solution decomposes at a rate comparable with that of the coupling process. Hantzsch (*loc. cit.*) noted the formation of a resinous decomposition product on adding alkali to the diazo-solution, and Stollé (*loc. cit.*) found that the diazonium chloride decomposed on warming in aqueous solution.

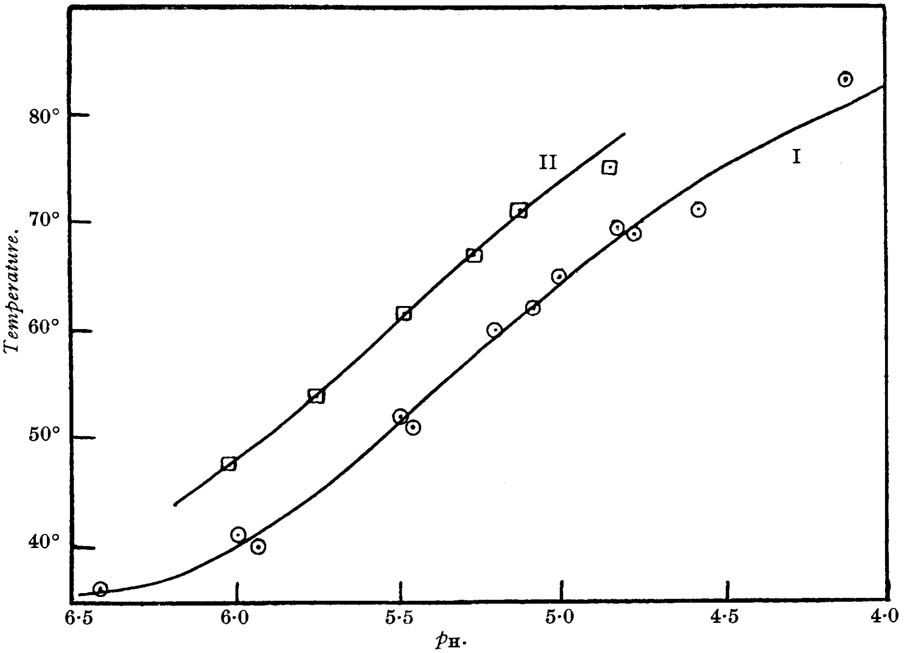
In acid solution, *p*-dimethylaminobenzenediazonium chloride should be analogous to the very stable diazonium chlorides derived from the *p*-chloro-, -bromo-, -iodo-, and -nitro-anilines (compare Snow, *Ind. Eng. Chem.*, 1932, **24**, 1420) in view of the positive charge on the $NHMe_2^+$ group (compare also Reilly and Drumm, J., 1935, 871). Unlike *p*-aminodimethylaniline, the monomethyl compound cannot be diazotised (Hantzsch, *loc. cit.*; see also Saunders, *op. cit.*, p. 63).

The above considerations of stability of diazonium salt solutions can only be applied to solutions lying on the acid side of p_H 3·5. In the region between p_H 3.5—7, these solutions in general consist of mixtures of diazonium and diazo-hydroxides and become increasingly unstable as the neutral point is approached (see Saunders, *op. cit.*, p. 72). Qualitative experiments show that changes in p_H have a marked influence on the stability of *p*-dimethylaminobenzenediazonium chloride: a solution in dilute hydrochloric acid is rendered much less stable by addition of salts such as sodium acetate, and alkali hydroxides cause immediate and rapid decomposition in the cold.

The stability of diazo-compounds in weakly acid solutions has received but little attention, and is complicated by the difficulty of obtaining an accurate measure of the stability. Titration of the diazo-compound which remains unchanged after a given period of time (Marriott, *J. Soc. Dyers Col.*, 1936, **52**, 172) is of little value if it has any tendency to couple with the phenol produced in the decomposition, and methods based on measurement of evolved nitrogen are not accurate, for a diazo-group is never completely eliminated as nitrogen in the decomposition (Oddo and Indovina, *Gazzetta*, 1935, **65**, 1037). A method was therefore devised by which the stability of diazotised *p*-aminodimethylaniline was evaluated by observing the temperature at which an opalescence appeared ("incipient decomposition temperature") in the previously clear diazo-solution in the presence of standard buffer solutions, whose p_H values between the limits 4·0—6·5 had been previously determined by means of hydrogen and calomel electrodes (see p. 618). Although the method is not capable of great accuracy, owing partly to personal error in observing the appearance of the opalescence, the results nevertheless give a measure of stability from which certain deductions may be made. The decomposition points, which vary between 36° and 83° and have an accuracy within a few degrees, probably represent the temperature at which the decomposition proceeds fast enough for the reaction products just to become visible. Hence, the success of the method is due to the high temperature coefficient of the decomposition, a rise of a few degrees greatly increasing the speed of reaction.

When the incipient decomposition temperature for each buffer solution was plotted against the p_H values, the points lay on a fairly smooth curve (see figure), clearly showing the decrease in stability with the increase in p_H value (compare Marriott, *loc. cit.*). A similar curve, parallel to the first but representing higher temperatures, was obtained by repeating the determinations with solutions in which the concentration of diazo-compound was halved; in these solutions, at a given p_H value, a higher temperature was necessary for the decomposition products to become visible. The curves bear a resemblance to that constructed for diazotised *p*-nitroaniline from Marriott's results (Saunders, *op. cit.*, p. 72). In each case there is a fall from high stability at p_H 3·5 to a very low stability at p_H 7·0.

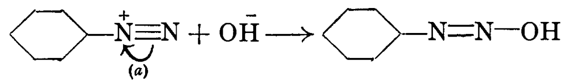
Stability–p_H curves for diazotised p-*aminodimethylaniline.*



I. *Original solution : 5 g. of base/200 c.c.*
II. *Original solution : 2·5 g. of base/200 c.c.*

The stability curves, in general, indicate that the concentration of diazo-hydroxide must be the factor governing the rate of decomposition, because an increase in the p_H value, which decreases the stability, at the same time increases the extent to which the diazonium salt is converted into the un-ionised diazo-hydroxide (compare Hantzsch, *Ber.*, 1898, **31**, 1612; 1900, **33**, 2147). In this conversion the change from quadricovalent positive nitrogen to tercovalent neutral nitrogen involves an appropriation by the positive nitrogen of one of the covalent pairs of electrons (I; process *a*) :

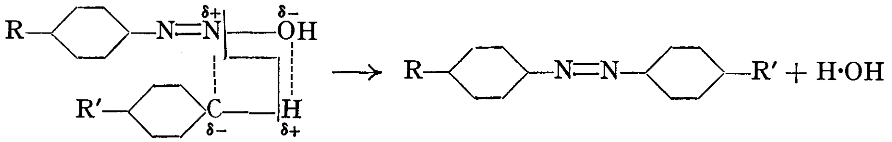
(I.)



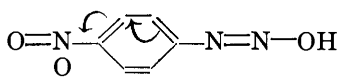
The tendency for this appropriation would be increased by a *p*-nitro- but diminished by a *p*-dimethylamino-group; consequently at a given p_{H} value the concentration of un-ionised diazo-hydroxide in a solution of diazotised *p*-aminodimethylaniline is lower than that in a solution of diazotised *p*-nitroaniline. This difference accounts for the relatively high stability of the former between p_{H} 4 and p_{H} 5 as compared with the rapid fall in stability of the latter over the range of p_{H} 3·5—7·0. At the same time, the nitro-group has a certain stabilising effect on the diazo-hydroxide, since at p_{H} 7 the stability of diazotised *p*-nitroaniline is higher than that of diazotised aniline. Diazotised *p*-aminodimethylaniline decomposes rapidly in alkaline solution even at low temperatures, whereas under the same conditions diazotised *p*-nitroaniline forms a highly stable *iso*diazotate. Diazotised aniline is unstable in alkaline solution owing to the formation of the unstable normal diazotate.

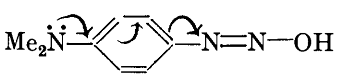
Decomposition of diazotised *p*-aminodimethylaniline in alkaline and weakly acid solutions affords nitrogen, a diazo-resin, and some dimethylaniline. The resin is similar in its properties to those described by Oddo and Indovina (*loc. cit.*) and must be formed in a similar manner, *i.e.*, mainly by the coupling of unchanged diazo-compound with the phenolic product of decomposition. The formation of dimethylaniline (see p. **619**) conforms with the general behaviour of diazo-compounds in these circumstances (Jolles, *Atti R. Accad. Lincei*, 1932, **15**, 292).

The coupling reaction with diazotised amines proceeds normally under those conditions in which the formation of un-ionised diazo-compounds is possible (Goldschmidt, *Ber.*, 1895, **28**, 2020; Schoutissen, *loc. cit.*; *Rec. Trav. chim.*, 1935, **54**, 381; Pelagatti and Ricci, *Ann. Chim. appl.*, 1935, **25**, 603), the diazonium ion showing little or no tendency to take part in such reactions (compare, however, Wistar and Bartlett, *J. Amer. Chem. Soc.*, 1941, **63**, 413). The reaction may be represented by the following mechanism :



It may thus be considered as dependent on the tendency for the development of a positive charge on the nitrogen atom farthest from the nucleus (compare Hanser and Breslow, *ibid.*, p. 418). Although a powerful electron-attracting group (*e.g.*, NO_2) will assist in the formation of the positive charge (see II), a *p*-substituted dimethylamino-group, with its strong

(II.)




(III.)

tautomeric effect, will diminish the tendency for positive-charge formation (see III). The tendency for diazotised *p*-aminodimethylaniline to take part in coupling reactions should therefore be comparatively decreased, and good yields of azo-compounds will only be obtained when the amine or phenol employed contains highly activated coupling positions, *e.g.*, α-naphthylamine and resorcinol. When coupling takes place in weakly acid solutions, the p_{H} value would not be expected appreciably to influence the yield of azo-compound, for, in a diazo-solution, the p_{H} value determines only the concentration of the diazo-hydroxide and has no bearing on either its coupling power or its stability. It is evident, however, that a low p_{H} value should have the effect of increasing the time necessary for the completion of the " coupling-decomposition " process, owing to the relatively small amount of un-ionised diazo-hydroxide present in the solution, and the rate of coupling of diazotised amines has been shown to be a simple function of the hydrogen-ion concentration (Conant and Peterson, *J. Amer. Chem. Soc.*, 1930, **52**, 1220; Blumberger, *Rec. Trav. chim.*, 1930, **49**, 280). Moreover, it is the free amine and not its salt which couples (Goldschmidt and Merz, *Ber.*, 1897, **30**, 670) and the concentration of this also depends on the p_{H} value.

Change of temperature in the coupling reaction should influence both the rate of coupling and the rate of decomposition. The stability of diazotised *p*-aminodimethylaniline in weakly acid solution is, however, so sensitive to temperature change that it is advisable to keep the temperature low in the coupling reactions.

The results of a number of experiments substantially verified the above conclusions. In nearly all cases the coupling reaction was exceedingly slow and was accompanied by a steady decomposition. On raising the p_H value, the rate of coupling and the rate of decomposition both increased, without influence on the yield of azo-compound. Increase of temperature was sometimes found necessary to complete the slower couplings but the yield was not noticeably affected. The yields of aminoazo-compounds obtained under the best conditions are, when arranged in descending order, in close agreement with the usual order of coupling reactivity of the amines concerned :

Amine.	Yield of azo-compound, %.	Colour of azo-compound.	Amine.	Yield of azo-compound, %.	Colour of azo-compound.
m-Phenylenediamine	94	Brick-red	γ-Acid	40	Purple-brown
α-Naphthylamine	91	Dull red	Anthranilic acid	37	Brown
β-Naphthylamine	84	Dark red	Sulphanilic acid	19	Yellow
Naphthionic acid	44	Purple-brown	Dimethylaniline	<20	Orange

The coupling of diazotised *p*-aminodimethylaniline with phenols was expected to show certain differences from the process considered above. Amines couple with diazo-solutions in the region p_H 3·5—7, whereas phenols normally couple over the range p_H 5·0—9·0 (Saunders, *op. cit.*, p. 104), *i.e.*, in the region where diazotised *p*-aminodimethylaniline has its lowest stability. On the other hand, phenols are usually more reactive than amines. As in the experiments on the coupling of amines, good yields of azo-compound were expected only from phenols having highly activated coupling positions. In the coupling of phenols, considerations of p_H value are of some importance. It is well known that the rate of coupling is decreased by excess of alkali, owing to a decrease in the amount of hydrolysis of the metal diazotate and phenoxide, but since the stability of diazotised *p*-aminodimethylaniline decreases with increasing alkalinity, it follows that its coupling with phenols should be carried out in solutions of a p_H value just high enough to give a conveniently rapid rate of reaction, but not necessarily in the alkaline region as is generally recommended. The temperature should also be kept as low as possible, since, with diazotised *p*-aminodimethylaniline, temperature change has a somewhat greater effect on the rate of decomposition than on the rate of coupling, as shown by the following data obtained with pyrogallol :

Temp.	−15°	−10°	+25°
Yield of azo-compound, %	56	54	42

The yields of hydroxyazo-compounds obtained under the best conditions are summarised below, and the sequence may be compared with that obtained by Meyer, Irschich, and Schlosser (*Ber.*, 1914, **47**, 1753).

Phenol.	Yield of azo-compound, %.	Colour of azo-compound.	Phenol.	Yield of azo-compound, %.	Colour of azo-compound.
α-Naphthol	97	Dark brown	γ-Acid	70	Dull red
Resorcinol	96	Purple brown	Pyrogallol	56	Yellow-brown
β-Naphthol	87	Blue-black	Salicylic acid	12	Brown
β-Naphthol-6-sulphonic acid	76	Crimson			

In the coupling with β-naphthol the yield could be increased to 93% by raising the p_H value by means of sodium acetate only, as in the coupling of amines. Many phenols, however, are too soluble in acid solution for this method to be applicable; *e.g.*, β-naphthol-6-sulphonic acid will not couple in sodium acetate solution. In the case of γ-acid (7-amino-1-naphthol-3-sulphonic acid), the solution had to be made alkaline quickly, since the coupling position is governed by the amino-group in acid solution and not by the hydroxy-group.

In the coupling of diazotised *p*-aminodimethylaniline with amines and phenols there was only one case, that of dimethylaniline, where any resinous substance was detected;

on the other hand, diazotised α-naphthylamine gives a large amount of diazo-resin when its coupling with salicylic acid is attempted (Frankland, J., 1880, **37**, 746). This fact is evidently related to the lower coupling reactivity of the *p*-hydroxydimethylaniline than of the naphthol formed in the decomposition of the respective diazo-solutions.

EXPERIMENTAL.

Diazotisation of p-*Aminodimethylaniline.*—The base, prepared by the method of Jacobs and Heidelberger (*J. Biol. Chem.*, 1915, **21**, 114) but extracted with purified benzene instead of with ether, was diazotised with the requisite amount of sodium nitrite in hydrochloric acid solution at room temperature. The amount of diazonium compound could not be determined by measuring the nitrogen evolved on boiling with 40% sulphuric acid owing to the very slow rate of decomposition. In presence of copper bronze, however, the decomposition is sufficiently accelerated to enable this procedure to be followed, provided that the reaction is performed in a neutral atmosphere, since a mixture of copper bronze and hydrochloric acid readily absorbs oxygen. Under these conditions, a 2% solution of *p*-aminodimethylaniline in hydrochloric acid (2N, 4N, or 8N), when treated with the requisite amount of sodium nitrite, or even with 50% excess, consistently yielded 90—95% of the theoretical volume of nitrogen. Similar results were obtained in comparative experiments with *p*-toluidine and *p*-anisidine.

Action of Copper Bronze on Diazotised p-*Aminodimethylaniline.*—*p*-Aminodimethylaniline (4 g.), in hydrochloric acid (15 c.c.) and water (15 c.c.), was diazotised with sodium nitrite (2·1 g.) in water (15 c.c.). Copper bronze (10 g.) was added and, when the evolution of nitrogen had ceased, the mixture was made alkaline and steam-distilled. Evaporation of the dried ethereal extract of the distillate yielded dimethylaniline (1·6 g., 45%), identified by conversion into *p*-nitrosodimethylaniline, m. p. and mixed m. p. 85°.

p-Aminodimethylaniline, diazotised as described above, behaved normally with cuprous chloride and potassium iodide, yielding *p*-chlorodimethylaniline, m. p. 33·5° (80%) (Heidlberg, *loc. cit.*) and *p*-iododimethylaniline, m. p. 80° (33%), respectively.

Action of Nitrogen Trioxide on p-*Aminodimethylaniline.*—Nitrogen trioxide was led into a solution of the base (2 g.) in ether (50 c.c.) at 0°; the solution became dark green and then brown, a brown plastic mass finally separating. The latter could not be recrystallised but its properties corresponded to those of *p*-dimethylaminobenzenediazonium nitrite, for it exploded on heating and was soluble in alcohol, water, and acids. The aqueous solution decomposed on warming, with evolution of nitrogen. A similar reaction occurred in acetone solution, the diazonium compound separating on addition of ether.

When nitrogen trioxide was passed into a solution of *p*-aminodimethylaniline in concentrated hydrochloric acid at 0° *p*-dimethylaminobenzenediazonium chloride was produced.

Qualitative Examination of the Stability of Diazotised p-*Aminodimethylaniline.*—The base (8 g.) in hydrochloric acid (30 c.c.) and water (30 c.c.) was diazotised with sodium nitrite (4·1 g.) in water (20 c.c.), and the solution diluted with water to 200 c.c. Using 5 c.c. for each test, a comparison was made of the effect of 10 c.c. of 4N-solutions of various salts and bases on the stability of the solution. The results were as follows :

Added salt.	p_H Range of solution.	Observation.
NH_4Cl or $AgNO_3$	3·5	No decomp. apparent at 100°
Na_2HPO_4, $(NH_4)_2C_2O_4$, NaOAc, $Pb(OAc)_2$, or $CaCO_3$ (solid)	3·5—7·0	Considerable decomp. at 50°, with formation of N_2, NMe_2Ph, and a dark resinous substance
$Pb(OH)_2$ (solid), $(NH_4)_2CO_3$, NH_4OH, Na_2CO_3, or NaOH	7·0	Decomp. rapid at 20°

The Relation between p_H *Value and Stability.*—(a) *Preparation of solutions.* *p*-Aminodimethylaniline (5 g.) in hydrochloric acid (80 c.c.) and water (80 c.c.) was diazotised with sodium nitrite (2·5 g.) in water, and the solution diluted to 200 c.c. Buffer solutions were prepared as follows : 5 c.c. of the above solution were diluted to 50 c.c. with a mixture of water and supersaturated sodium acetate solution (125 g. of anhydrous A.R. salt in 200 c.c. of solution). By varying the composition of the mixture in each case solutions of different p_H value were obtained; these all contained the same concentration of diazo-compound, and were of a uniform golden-yellow colour. A second series of solutions was prepared by treating 2·5 g. of the base exactly as described above.

(b) *Measurement of* p_H *values.* A hydrogen electrode vessel containing the solution was combined with a normal calomel electrode by a saturated potassium chloride bridge solution, and the E.M.F. of the complete cell measured. The results were reproducible and were in excellent agreement with those obtained by using a quinhydrone electrode, although the hydrogen electrode was rather more reliable at the higher p_H value.

(c) *Determination of stability.* The diazo-solution (5 c.c.), contained in a boiling-tube (2·5 cm. × 15 cm.) provided with a thermometer and a glass stirrer, was partly immersed in water (20 c.c.) contained in a larger boiling-tube (4 cm. × 16 cm.) and was held in position by a cork ring separating the two tubes. The apparatus was supported on a wire gauze in front of a hole cut in a cardboard screen, behind which was an opal electric light bulb so arranged that light shone directly through the diazo-solution. As it was essential that these solutions should be perfectly clear, they were in all cases filtered just before use. The apparatus was heated by a Bunsen burner, and the temperature noted at which a sudden opalescence appeared in the solution: the mean of 6 readings was taken as the "incipient decomposition" temperature. The values obtained were almost independent of the rate of heating, so long as a steady increase was maintained in the region immediately below the temperature of change. The results are given below.

E.M.F. of cell (volt).	p_H.	Mean decomp. temp.	E.M.F. of cell (volt).	p_H.	Mean decomp. temp.	E.M.F. of cell (volt).	p_H.	Mean decomp. temp.
Solution I: 5 g. of base/200 c.c.								
0·689	6·95	*	0·603	5·47	51°	0·564	4·79	69°
0·657	6·43	36°	0·588	5·21	60	0·552	4·59	71
0·643	6·00	41	0·581	5·09	62	0·526	4·14	83
0·630	5·93	40	0·577	5·02	65	0·359	1·26	†
0·605	5·50	52	0·567	4·84	69·5			
Solution II: 2·5 g. of base/200 c.c.								
0·635	6·02	47	0·605	5·50	61·5	0·584	5·14	71
0·620	5·77	54	0·593	5·29	67	0·568	4·86	75

* = Unstable at room temperature. † = No change at 100°.

Action of Alkali on Diazotised p-*Aminodimethylaniline.*—*p*-Aminodimethylaniline (5 g.) in hydrochloric acid (10 c.c.) was diazotised with sodium nitrite (2·5 g.) in water (15 c.c.). On addition of excess of 4N-sodium hydroxide there was a copious evolution of nitrogen. Steam-distillation of the mixture yielded a small quantity of dimethylaniline, identified by conversion into *p*-nitrosodimethylaniline. The solid resin remaining in the flask was soluble in benzene, from which it was precipitated as a brown powder by addition of light petroleum (b. p. 80—100°). The resin, which dissolves in acids to give an intensely red solution, is insoluble in alkalis. It therefore may contain an *o*-hydroxyazo-compound, possibly 3-*p*-dimethylaminobenzeneazo-4-hydroxydimethylaniline or the corresponding bisazo-compound.

The Coupling of Diazotised p-*Aminodimethylaniline.*—The diazo-solutions used in the coupling experiments were prepared by the following standardised procedure. *p*-Aminodimethylaniline (1 g.) in a mixture of hydrochloric acid (2 c.c.) and water (10 c.c.) was diazotised with sodium nitrite (0·51 g.) in water (5 c.c.) at 5—10°, any excess of nitrous acid being removed by addition of urea.

(a) *With amines.* To the above solution was added the molar equivalent of the amine in water, alcohol, etc., as given below. Sodium acetate (5 g.) in water (20 c.c.) was then added, and the mixture kept for 2—3 days at room temperature. After filtration, the solution was kept at 40° to ensure that the reaction was completed. The total yields and colours of the azo-compounds are summarised in the table on p. 617, and additional individual data are: *p*-phenylenediamine hydrochloride (1·33 g.) in water (20 c.c.), the mixture was basified before filtration; α- and β-naphthylamines (1·06 g.) in alcohol (5 c.c.), followed by water (60 c.c.); naphthionic acid (1·65 g.) and γ-acid (1·76 g.) in aqueous sodium hydroxide, followed by acetic acid, the mixtures being neutralised before filtration; anthranilic acid (1·01 g.) and sulphanilic acid (1·27 g.) each in water (10 c.c.); dimethylaniline (0·9 g.) in acetic acid (15 c.c.)—the small yield of dye was contaminated with tar, probably derived from decomposition products, the coupling tendency being very low.

(b) *With phenols.* To the above diazotised solution was added the molar equivalent of the phenol in alcohol or 50% aqueous alcohol, and 4N-sodium hydroxide solution was gradually added at − 10° until the neutral point was reached, whereupon the reaction was found to be complete. The yields and colours of the resulting azo-compounds are given in the table on

p. 617. With Schäfer's acid, sodium chloride was added to complete the separation; an aqueous solution of the dye is crimson, changed to orange-red by addition of acid or alkali. With salicylic acid, dilution of the solution before neutralisation caused no appreciable difference in yield.

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UNIVERSITY COLLEGE, SWANSEA. [*Received, January* 16*th*, 1941.]

NOTE.

The Cure of Bumping in Mercury–Glass Diffusion Pumps. By N. K. ADAM and E. W. BALSON.

THE violent and sometimes dangerous bumping which often occurs, when the mercury and glass are clean, may be quickly cured by allowing a few hundred c.c. of hydrogen sulphide to pass through the pump at atmospheric pressure and room temperature. Two pumps, which bumped badly before this simple treatment, boiled perfectly smoothly for a long time afterwards; and the vacuum was unimpaired.—UNIVERSITY COLLEGE, SOUTHAMPTON. [*Received, May* 31*st*, 1941.]