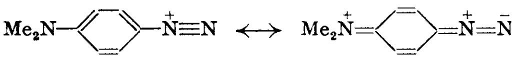
369. p-*Aminodimethylaniline. Part IV.* The Effect of Substituents on the Stability and Mode of Decomposition of the Diazonium Compounds.*

By John H. Gorvin.

The stability of diazotised *p*-aminodimethylaniline and certain of its derivatives is discussed in terms of resonance in the diazonium ion. The decomposition of weakly acidic or neutral solutions of these compounds seems to proceed extensively through the un-ionised diazo-form since appreciable amounts of the simple deamination products are obtained.

Although the high stability of diazotised *p*-aminodimethylaniline in strongly acid solution may be partly conditioned by the electron-attracting $^{+}NHMe_2$ group (Ayling, Gorvin, and Hinkel, Part I, *J.*, 1941, 613), considerations of basic strength make it probable that the stability prevailing even at pH 3·5 is due to the high resonance energy of the univalent ion (I) (cf. De Jonge and Dijkstra, *Rec. Trav. chim.*, 1948, **67**, 328; Mills, *J.*, 1944, 349). In the diazonium–diazo-equilibrium this ion will predominate in the acid range (cf. Hantzsch, *Ber.*, 1930, **63**, 1279); corresponding stabilisation of the diazoate ion will be impeded by the NMe_2 group with consequent high instability in the alkaline region (cf. Part I). In the present work interest centred on the trend of stability over the pH range 3·5—7·0 as influenced by *o*-substituents; for this study the "incipient-decomposition" method (Part I) proved adequate. The compounds selected for comparison with *p*-aminodimethylaniline were its *o*-chloro-, *m*-nitro-, and 2-chloro-3-nitro-derivatives (Ayling, Gorvin, and Hinkel, *J.*, 1942, 755; 1946, 530). The tests showed that whereas the sharp fall from high stability at pH 3·5 to low stability at pH 7·0 shown by the parent substance is reproduced by its *m*-nitro-derivative, diazotised solutions of the two *o*-chloro-bases were relatively unstable at the lower pH and showed comparatively little change in stability over the range. The curves obtained for the *o*-substituted compounds (see Fig.) more nearly approached that of diazotised aniline (Saunders, "The Aromatic Diazo-compounds and their Technical Applications," Arnold, 1949, p. 99) than those of *p*-aminodimethylaniline and 4-amino-*NN*-dimethyl-3-nitroaniline. Now the shape of these curves is determined by (*a*) the stability at pH 3·5, and (*b*) the amount of un-ionised diazo-compound present at a given pH (cf. Part I). On the hypothesis that the stability of diazotised *p*-aminodimethylaniline is caused by resonance of type (1), steric hindrance of the mesomerism of the dimethylamino-group by an *o*-substituent (cf. Hughes, *Quart. Reviews*, 1948, **2**, 107) will decrease (*a*) and increase (*b*). The shapes of the curves obtained are consistent with the hypothesis.



. . . . . (1)

Published information on the mode of decomposition over the pH range 3·5—7·0 is scanty. If the same mechanism predominated as in strongly acid solutions (pH <3·5) in which only the diazonium ion is involved (see Saunders, *op. cit.*, p. 62) stability would decrease only slightly. It is possible that diazotised aniline decomposes almost entirely in this way (Moelwyn-Hughes and Johnson, *Trans. Faraday Soc.*, 1940, **36**, 948; Hodgson and Marsden, *J.*, 1943, 379; *J. Soc. Dyers Col.*, 1944, **60**, 16; 1945, **61**, 20) though the occurrence of benzene in the reaction product (Jolles, *Atti R. Accad. Lincei*, 1932, **15**, 292; Hey and Waters, *J.*, 1948, 882) suggests that homolysis of un-ionised diazohydroxide may also participate. Compounds showing a sharp fall in stability must decompose by a mechanism different from, and additional to, that occurring in strong acid. For diazotised *p*-nitroaniline Hodgson and Norris (*J.*, 1949, 87) describe such a mechanism, but it is improbable that this could fully account for the case of diazotised *p*-aminodimethylaniline since the hydrolysis involved would be impeded by the *p*-dimethylamino group. In Part I it was stated that the rate of decomposition is determined by the concentration of un-ionised diazohydroxide. The possibility of homolysis was not then discussed but it was reported that the diazo-resin produced in the decomposition was accompanied by dimethylaniline; the formation of this can adequately be explained only by a free-radical decomposition mechanism (Gorvin, Thesis, Univ. of Wales, 1938, p. 18). It is

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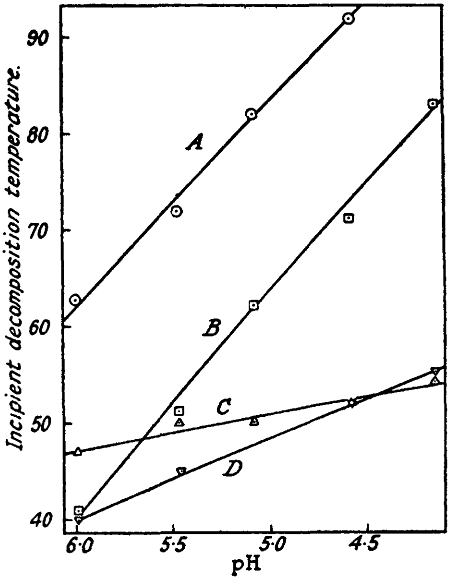
* Part III, *J.*, 1946, 530.

generally true that the odour of dimethylaniline is a characteristic of all solutions of the diazotised base in weakly acid or alkaline conditions, and the corresponding odour of *o*- or *m*-chlorodimethylaniline is similarly noticeable with the chloro-substituted compounds. In Table I are recorded the steam-volatile products obtained from a series of diazonium chlorides after decomposition in presence of calcium carbonate; the simple " deamination product " was found in every instance.

Although a few cases have been recorded of spontaneous reductive elimination of the diazo-group in dilute sulphuric acid solution (cf. Gelissen and Hermans, *Ber.*, 1925, **58**, 986) the phenomenon has been observed in neutral or alkaline solution only by Jolles (*loc. cit.*), by Waters (*J.*, 1937, 2015), and under special conditions by Gomberg and Pernert (*J. Amer. Chem. Soc.*, 1926, **48**, 1372). Hodgson (*J.*, 1948, 348, 556 ; cf. Hey and Waters, *ibid.*, p. 884) has questioned its occurrence. It seems to proceed by homolysis of the diazohydroxide (Saunders and Waters, *J.*, 1946, 1154) with subsequent reaction of the resulting phenyl or substituted phenyl radical with another organic molecule (Merz and Waters, *J.*, 1949, 2427). According to Hey (*Ann. Reports*, 1940, **37**, 278 ; cf. Waters, *J.*, 1937, 113 ; Haworth and Hey, *J.*, 1940, 364 ; Heilbron, Hey, and Lambert, *ibid.*, p. 1280), of the two possible mechanisms (2) and (3) for the latter reaction the process (2) seems to occur preferentially when R'H is an aliphatic compound, and process (3)

Stability-pH curves.



A. Diazotised 4-*amino*-NN-*dimethyl*-3-*nitroaniline.*
B. Diazotised 4-*aminodimethylaniline.*
C. Diazotised 4-*amino*-2-*chlorodimethylaniline.*
D. Diazotised 4-*amino*-2-*chloro*-NN-*dimethyl*-3-*nitroaniline.*

TABLE I.

Reductive elimination of diazo-groups by decomposition in neutral solution.

Dimethylaniline derivative.		
diazotised.	in product.	Yield (%).
p-Amino-	Dimethylaniline	9·5
4-Amino-2-chloro-	*o*-Chloro-	2·4
,, 3-chloro-	*m*- ,,	29
,, 3-nitro-	*m*-Nitro-	24
,, 3-chloro-2-nitro-	3-Chloro-2-nitro-	10
,, 2-chloro-3-nitro-	2-Chloro-3-nitro-	13
,, 2-chloro-5-nitro-	2-Chloro-5-nitro-	33
,, 2 : 5-dinitro-	2 : 5-Dinitro-	6·5

$$R\cdot + R'H \longrightarrow RH + \cdot R' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$R\cdot + R''H \longrightarrow RR'' + \cdot H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

when R″H is aromatic, though there is no sharp division between the two types. It is therefore possible that the products recorded in Table I are formed predominantly by reaction between the free radical and the *N*-methyl groups of adjacent molecules (process 2). This hypothesis is supported by the increased yield of deamination product obtained when ether was added as a source of aliphatic hydrogen (cf. Hanby and Waters, *J.*, 1939, 1793) to diazo-compounds decomposing in acetate buffer (Table II). The acetic acid present in these solutions, like the water itself (Merz and Waters, *loc. cit.*), does not appear to act as a source of hydrogen atoms. This observation is not inconsistent with a possible location of the homolysis in the non-aqueous phase, *i.e.*, the diazo-resin, which will be largely built up by process (3) according to the scheme of Saunders and Waters (*loc. cit.*) and only to a minor extent by azo-coupling either with the phenol (Part I; cf. Oddo and Indovina, *Gazzetta*, 1935, **65**, 1037, 1054) or with the deamination product. The radical •R′ produced by loss of hydrogen from the *N*-methyl group can react in its turn by process (2) or (3), thus increasing the complexity of the diazo-resin. Further evidence in favour of this interpretation is provided by the failure of the coupling reaction between diazotised 4-amino-3-chlorodimethylaniline and dimethylaniline in acetate buffer (Part V, succeeding paper). In this case the dimethylaniline acts as an additional source of hydrogen atoms, and the resulting yield of *m*-chlorodimethylaniline is increased from 29% (Table II) to >40%.

TABLE II.

Reductive elimination of the diazo-group in acetate solution.

Dimethylaniline derivative		Yields (%),	
diazotised.	in product.	acetate.	acetate saturated with ether.
4-Amino-3-chloro-	*m*-Chloro-	29	—
,, 3-nitro-	*m*-Nitro-	27	52
,, 2-chloro-5-nitro-	2-Chloro-5-nitro-	18	38

The yields recorded in Tables I and II are obviously dependent on three variables : (*a*) the extent of fission of the un-ionised compound, (*b*) the fate of the free radical formed, and (*c*) the degree to which the dimethylaniline produced undergoes azo-coupling or further reaction with free radicals. Substituents in the benzene ring reduce the number of free positions at which process (3) may occur, which may partly account for the high yields of *m*-chloro- and *m*-nitrodimethylaniline; the possibility remains however that the *m*-group in the free radical may to some extent impede process (3) by steric hindrance to the advantage of (2). The comparatively low yield of dimethylaniline on the other hand is produced from the unsubstituted compound by process (2) under conditions where opportunities for process (3), from the point of view either of the free radical or of the resultant base, are maximal. Azo-coupling can have caused little reduction in the yields. Diazotised *p*-aminodimethylaniline (Part I) and its *m*-derivatives (Part V) couple very poorly with dimethylaniline : *o*-substituted dimethylanilines do not couple readily with diazo-compounds (Friedländer, *Monatsh.*, 1898, **19**, 627). Dimethylaniline tends to separate from a neutral solution and commingle with any diazo-resin present; it can then act as a solvent for free radicals or for un-ionised diazohydroxide (Grieve and Hey, *J.*, 1938, 108) and provide a medium for free-radical reactions while remaining largely protected from the coupling reagent.

Since in weakly acid solutions decomposition of the diazonium ion and of the diazohydroxide proceed simultaneously it may be suggested that (*a*) with unstabilised ions, *e.g.*, benzenediazonium, the ionic decomposition predominates, and (*b*) with very stable ions decomposition proceeds largely through un-ionised forms, *e.g.*, by hydrolysis (cf. diazotised *p*-nitroaniline) or by a free-radical mechanism. It would be expected that, in diazotised *p*-aminodimethylaniline, inhibition of the mesomerism of the NMe_2 group would favour the ionic process at the expense of the homolysis. Comparison of the yields of dimethylaniline and of *o*- and *m*-chlorodimethylaniline (Table I) suggests that such is the case. The yields of *m*-substituted deamination products are also reduced by an *o*-substituent with one exception, that of 2-chloro-*NN*-dimethyl-5-nitroaniline. Under the conditions of Table II, however, the yield of this compound is significantly less than that of *m*-nitrodimethylaniline.

Diazotised 4-amino-*NN*-dimethyl-3-nitroaniline subjected to the Sandmeyer procedure yields deamination product in addition to 4-chloro-*NN*-dimethyl-3-nitroaniline. This, however, is probably caused by reduction by the cuprous ion (cf. Hodgson, Leigh, and Turner, *J.*, 1942, 744; Hodgson and Mahadevan, *J.*, 1947, 173). The Sandmeyer reaction, like diazocoupling, is retarded by positive substituents such as dimethylamino (Cowdrey and Davies, *J.*, 1949, S 48), but as diazotised *p*-aminodimethylaniline behaves normally under the same conditions (Part I) the nitro-group may, as in the coupling process (Part V), be exerting a steric effect tending to impede the normal reaction to the advantage of the side-reaction.

EXPERIMENTAL.

Materials.—The bases were prepared as described in Parts II and III, except that 4-amino-*NN*-dimethyl-3-nitro- and -2 : 5-dinitro-aniline were prepared according to Hodgson and Crook (*J.*, 1932, 2976; 1934, 873). These bases were recrystallised to constant m. p. before use, the latter from carbon tetrachloride in brown-orange rhombic plates, m. p. 80°, a polymorphic modification (Hodgson and Crook, *loc. cit.*, report black needles, m. p. 100°). Although a carbon tetrachloride solution could be induced to yield black needles, the form of low m. p. was unusually persistent; the highest m. p. obtained for a sample consisting largely of black crystals was 87°.

Relation between pH *and Stability.*—The bases 4-amino-*NN*-dimethyl-3-nitro- (3·33 g.), 4-amino-2-chloro-*NN*-dimethyl-3-nitro- (3·96 g.) and 4-amino-2-chloro-*NN*-dimethyl-aniline (3·14 g.) were each diazotised with sodium nitrite (1·3 g.). The solutions were made up to 100 c.c. so that each contained 40 c.c. of hydrochloric acid (*d* 1·2). Buffer solutions were prepared according to the procedure described in Part I (p. 618), each of these containing the same molar concentration of diazo-compound as Solution I. The methods used for the determination of pH and decomposition temperature for each solution were those adopted for diazotised *p*-aminodimethylaniline. The results are given below and may be compared with previous figures reproduced from Part I.

		Mean decomp. temps.			
		Substituent in *p*-NH$_2$·C$_6$H$_4$·NMe$_2$.			
E.M.F. of cell (v.).	pH.	3-NO$_2$.	2-Cl-3-NO$_2$.	2-Cl.	None.
0·689	6·95	—	*	*	*
0·643	6·00	63°	40°	47°	41°
0·603	5·47	72	45	50	51
0·581	5·09	82	—	50	62
0·552	4·59	92	52	52	71
0·526	4·14	†	55	54	83
0·359	1·26	†	‡	‡	†

* = Unstable at room temperature. † = No change apparent at 100°.
‡ Decomp. apparent at 100° after several mins.

It should be pointed out that the method used in obtaining these results employs a standard condition of stability, namely, incipient decomposition, which does not necessarily represent the same absolute stability for two different diazo-compounds. Thus, although the shapes of the curves for diazotised *p*-aminodimethylaniline and its *o*-chloro-derivative may be compared, it cannot be assumed that their point of intersection corresponds to two solutions of identical stability.

Decomposition of Diazonium Solutions in Presence of Calcium Carbonate (*cf. Table* I).—The amine (1 g.) in water (10 c.c.) and hydrochloric acid (4 c.c.; *d* 1·2) was diazotised with a slight excess of sodium nitrite, urea being subsequently added. The solution was diluted to 200 c.c. and left at room temperature for 7 days in presence of precipitated calcium carbonate (15 g.); it was then steam-distilled. The volatile decomposition product was recovered from the distillate by ether-extraction, and the solvent removed. In the case of amines giving a crystalline deamination product the residue was dissolved in hydrochloric acid (20%), and the filtered solution neutralised with aqueous ammonia. The crystalline dimethylaniline derivative, weighed as such, was identified in each case by mixed m. p. determination with the authentic substance (Part III), after recrystallisation if necessary. The m. p.s did not indicate the presence of more than traces of other steam-volatile decomposition products. In the decompositions of diazotised *p*-aminodimethylaniline and its *o*- and *m*-chloro-derivatives, the oily residue from the ether-extraction was weighed and dissolved in a suitable solvent with a slight excess of picric acid and the solution allowed to crystallise (dry benzene was used for dimethylaniline picrate, ethanol for the other two). From the weight of picrate (similarly identified by mixed m. p. determination with the authentic substance) the yield of deamination product was calculated.

The decompositions were repeated, in some instances using the requisite amount of sodium nitrite without addition of urea; the yields appeared to be quite reproducible. When *p*-aminodimethylaniline was diazotised by the standard procedure and the solution immediately steam-distilled over calcium carbonate, the decomposition proceeded rapidly and dimethylaniline commenced to distil at once. The reaction appeared complete after 2½ hours. The yield of dimethylaniline (9·6%, estimated as picrate) was substantially the same as that obtained by slow decomposition in the cold.

Decompositions of Diazonium Solutions in Acetate Buffer (*cf. Table* II).—From the amine to be studied, two similar diazo-solutions (A and B) were prepared by the standard procedure (each from 0·5 g. of base); the solutions were each treated with sodium acetate (5·0 g.; anhydrous) and diluted to 100 c.c. Solution A was set aside to decompose. Solution B was thoroughly shaken with ether, separated from the ethereal layer, and set aside to decompose in a loosely stoppered flask; the ethereal extract yielded only traces of tar on evaporation. After 10 days solutions A and B were separately extracted with ether; the solvent was removed and the residues steam-distilled. In addition to steam-volatile material the ether had now extracted resinous decomposition products which remained in the distillation flask. The steam-volatile product was extracted from the distillate and worked up by the standard procedure. This experiment serves to eliminate any possibility that the deamination product might be formed in the diazotisation rather than during the subsequent decomposition. The yields obtained from the two bases studied, as well as from diazotised 4-amino-3-chlorodimethylaniline decomposing in the absence of ether are set out in Table II.

*Reaction of Diazotised 4-Amino-*NN*-dimethyl-3-nitroaniline with Cuprous Chloride.*—The base (2 g.) in hydrochloric acid (8 c.c.; *d* 1·2) and water (20 c.c.) was treated at room temperature with sodium nitrite (1·0 g., 25% excess) followed by urea (a somewhat intractable foam is produced in this diazotisation). The solution was added to cuprous chloride (4 g.) in hydrochloric acid (30 c.c.) at *ca.* 60°, heated to 100°, and steam-distilled. The distillate, a mixture, represented *ca.* 70% of the original base. By crystallisation from methanol it was partly separated into 4-chloro-*NN*-dimethyl-3-nitroaniline (at least 40%) and *m*-nitrodimethylaniline (at least 20%). The chloro-compound was identified by comparison with an authentic specimen, m. p. 82°, prepared from *p*-chlorodimethylaniline (Part I) by the method of Pinnow (*Ber.*, 1898, **31**, 2986; cf. Clemo and Smith, *J.*, 1928, 2420).

The author is very grateful to Dr. L. E. Hinkel and Mr. E. E. Ayling for their interest and encouragement. Thanks are also offered to Imperial Chemical Industries Limited, Dyestuffs Division, for a grant.

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[*Received, January 9th,* 1951.]