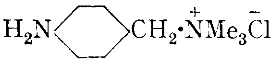
197. *The Mechanism of Diazotisation.*

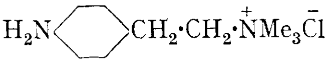
By J. Reilly and P. J. Drumm.

The generally accepted view of the mechanism of diazotisation of aromatic amines is that first advanced by Hantzsch and Schümann (*Ber.*, 1899, **32**, 1691), according to whom interaction takes place between arylammonium ions $Ar\dot{N}H_3$, resulting from the ionisation of the amine salt, and undissociated nitrous acid. It follows that (1) amines of different basicities should, in the absence of excess of mineral acid, diazotise at different rates, the order of which should coincide with the order of the basicities; (2) the rate of diazotisation of an amine should not be appreciably altered by the presence of a greater amount of acid than that necessary for the prevention of hydrolysis of the amine salt.

The present work was undertaken, at the suggestion of Professor Robinson, to test the correctness of the above view. Three amines were chosen in which a strongly positive pole $\overset{+}{N}Me_3$ was attached to the nucleus (I) or separated from it by one (II) or two (III) methylene groups. In (I) the positive pole $\overset{+}{N}Me_3$ will induce a drift of the unshared salt-forming electrons of the amino-nitrogen atom in its direction, thereby reducing the tendency of the nitrogen atom to attract positive ions ($\dot{H}$) and so leading to a depression of the basic character of the amino-group. In (II) and still more in (III) the attraction of these electrons by the positive pole will be decreased by the insertion of the neutral methylene group or groups, the result being a strengthening of the basicity of the amino-group. The order of basicity of these amines will be, therefore, (III) > (II) > (I) and, according to the mechanism of Hantzsch and Schümann, the rate of diazotisation of (III) should be greatest and that of (I) least.


(I.)


(II.)


(III.)

The results in the following table (column 2) are in agreement with this view, and further support for the Hantzsch–Schümann theory is the fact that the rate of diazotisation of any particular amine is practically the same whether two or four molecules excess of hydrochloric acid are present.

Temp. 1°. k = Velocity constant $= 1/t.\ x/a(a - x)$.

Amine.	$RNH_3Cl + HNO_2$.	$RNH_3Cl + HCl + HNO_2$.	$RNH_3Cl + 2HCl + HNO_2$.	$RNH_3Cl + 4HCl + HNO_2$.
	k.	*k*.	*k*.	*k*.
(I)	0·012	0·033	0·040	0·041
(II)	0·022	0·036	0·038	0·039
(III)	0·027	0·038	0·039	0·038

A further conclusion to be drawn from these results, and those obtained by Hantzsch and Schümann (*loc. cit.*) for other aniline bases, is that the ions of the bases, in the presence of excess of mineral acid, are converted at approximately the same rate into diazonium ions.

On account of the very rapid formation of diazonium salts in concentrated solution, the rate of reaction was measured in *N*/1000-solution, where it is so retarded as to be capable of more accurate measurement. Further, as the formation of diazonium salt proceeds somewhat irregularly at the commencement, the speed of the reaction is best calculated after a certain interval.

Hantzsch and Schümann (*loc. cit.*) measured rates of diazotisation indirectly by estimation of the free nitrous acid from time to time with starch–iodide. This method proved unsuitable in the present instance, and the rates were calculated by direct measurement of the amount of diazonium salt present at various intervals of time: the diazonium solution was coupled with an alkaline solution of Schaeffer's acid, and the solution of the resulting azo-dye was matched in a colorimeter with one similarly and simultaneously prepared from a completely diazotised solution of the amine.

For the preparation of p-*aminobenzyltrimethylammonium chloride hydrochloride* (as II), *p*-nitrobenzyl chloride was condensed with dimethylamine, the product reduced and acetylated, the *acetyl* derivative converted into the quaternary chloride, and the acetyl group split off by heating with hydrochloric acid. β-*p*-Aminophenylethyltrimethylammonium chloride (III) was prepared from β-phenylethyldimethylamine, the quaternary picrate of which was nitrated, giving, as Goss, Hanhart, and Ingold (J., 1927, 257) have shown, 70% of the *p*-nitro-compound; this was smoothly reduced by stannous chloride, and the amine (III) isolated as the *hydrochloride*.

The diazonium salts obtained from the above amines show pronounced stability, that from (I) being the most stable and that from (III) the least stable.

EXPERIMENTAL.

p-Aminophenyltrimethylammonium chloride hydrochloride (as I), prepared from *p*-aminodimethylaniline according to Pinnow and Koch (*Ber.*, 1897, **30**, 2861), crystallised from methyl alcohol in colourless, slightly hygroscopic prisms, m. p. 219° (decomp.), freely soluble in water, moderately soluble in hot methyl alcohol, and insoluble in absolute ethyl alcohol.

p-*Aminobenzyltrimethylammonium Chloride Hydrochloride* (as II).—*p*-Nitrobenzyldimethylamine was obtained by Stedman's method (J., 1927, 1905) as a yellow oil, b. p. 150°/20 mm., with a pronounced ammoniacal odour. The *picrate* separated from alcohol in clusters of yellow prisms, m. p. 151° (Found: N, 16·9. $C_{15}H_{15}O_9N_5$ requires N, 17·1%). Reduction with stannous chloride at 100° gave a 60% yield (compare Stedman) of *p*-aminobenzyldimethylamine as a colourless viscous oil of pronounced basic odour, b. p. 136—137°/20 mm., readily soluble in water. The *azo*-β-*naphthol* derivative was obtained from alcohol in reddish needles, m. p. 129·5° (Found: N, 13·6. $C_{19}H_{19}ON_3$ requires N, 13·8%). The preceding base in benzene solution was acetylated with a similar solution of acetic anhydride (1·25 mols.), and the oil left after removal of the solvent was treated with sodium hydroxide solution. Chloroform then extracted a solid which, after repeated crystallisation from benzene–light petroleum (b. p. 40—60°), gave colourless blades, m. p. 103°, of p-*acetamidobenzyldimethylamine* (Found: N, 14·3. $C_{11}H_{16}ON_2$ requires N, 14·6%). This was boiled in benzene solution with methyl iodide (1 mol.) and the precipitated salt was washed with hot benzene, dried, and extracted with hot water, from which, on cooling, p-*acetamidobenzyltrimethylammonium iodide* separated in colourless cubes, m. p. 232° (Found: N, 8·3; I, 37·8. $C_{18}H_{19}ON_2I$ requires N, 8·4; I, 38·0%). A hot aqueous solution of the iodide was digested with freshly prepared, moist silver chloride (1 mol.), and the filtered solution strongly acidified with hydrochloric acid and evaporated to dryness on the water-bath. The semi-solid residue on trituration with absolute ethyl alcohol gave p-*aminobenzyltrimethylammonium chloride hydrochloride*, which crystallised from boiling anhydrous methyl alcohol in colourless prisms, shrinking to a clear, amber-coloured, glassy liquid at 194—196° and melting and decomposing at 270° (Found: N, 11·7; Cl, 29·7. $C_{10}H_{17}N_2Cl,HCl$ requires N, 11·8; Cl, 29·9%). This salt is moderately readily soluble in hot methyl alcohol, practically insoluble in absolute ethyl alcohol, and is extremely hygroscopic.

β-p-*Aminophenylethyltrimethylammonium Chloride Hydrochloride* (as III).—When β-phenylethyldimethylamine (Decker and Becker, *Ber.*, 1912, **45**, 2406) was treated in benzene solution with methyl iodide (1 mol.), the quaternary iodide separated almost immediately; it was obtained from hot water in colourless plates, m. p. 231° (Found: I, 43·7. Calc. for $C_{11}H_{18}NI$: I, 43·6%). The picrate, prepared from sodium picrate and the iodide in hot aqueous solution, crystallised from alcohol in clusters of yellow prisms, m. p. 131° (Found: N, 14·4. Calc. for $C_{17}H_{20}O_7N_4$: N, 14·3%). It (12 g.) was nitrated in nitric acid (90 g., *d* 1·5) at — 5° according to Goss, Hanhart, and Ingold (*loc. cit.*). The nitric acid solution was mixed with ice and rendered faintly alkaline with sodium hydroxide solution; on cooling, the nitro-picrates separated. Three crystallisations from boiling alcohol gave β-*p*-nitrophenylethyltrimethylammonium picrate in short yellow prisms, m. p. 145—146°. This compound (11 g.) in concentrated hydrochloric acid (200 c.c.) was shaken with benzene to remove picric acid, and then reduced with stannous chloride (25 g.) at 100° during 1 hour. The solution was concentrated and kept and the tin double salt (11 g.) was separated and dissolved in water, tin removed as sulphide, and the filtrate evaporated to dryness on the water-bath. The residue crystallised from boiling methyl alcohol in colourless, very hygroscopic prisms, m. p. 283° (decomp.) (Found: N, 11·0;

Cl, 28·4. $C_{11}H_{19}N_2Cl,HCl$ requires N, 11·1; Cl, 28·2%), of β-p-*aminophenylethyltrimethylammonium chloride hydrochloride*, moderately soluble in boiling methyl alcohol and almost insoluble in absolute ethyl alcohol.

We wish to express our gratitude to Professor R. Robinson, F.R.S., for his kind interest in the work. Miss Hanorah O'Sullivan, M.Sc., has independently confirmed our experimental figures; for this we wish to thank her.

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