130. *The Nitrosation of Methylaniline.*

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Recent studies on the diazotisation reaction (*J. Proc. Roy. Soc. N.S.W.*, 1932, **66**, 157) directed the authors' attention to the nitrosation of secondary amines as being probably analogous to the former reaction in its initial stages and yet avoiding the complications of unstable and reactive end-products. The volume changes occurring on heating reaction mixtures containing secondary amines, nitrous acid, and hydrochloric acid appeared at first to be of the same general character as those observed when aniline was used in place of the secondary amine (*loc. cit.*). However, the very marked characteristics of the volume–temperature curves obtained with methylaniline over a narrow range of carefully controlled conditions, especially in respect of acidity, seemed to merit a close investigation. Fig. 1 shows the type of curve obtained with 1 mol. of methylaniline hydrochloride, 1 mol. of sodium nitrite, and 0·5 mol. of hydrochloric acid in concentrated methyl-alcoholic solution, the experimental conditions being described on p. 511.

At a constant temperature of 8°, *i.e.*, a little below that at which the most marked irregularity in the expansion curve occurs, the reaction takes place at a rate convenient for observation; by carrying it out in a dilatometer, as before, the characteristic volume–time curves illustrated in Fig. 2 were obtained. There is a regular contraction during a more or less prolonged initiatory period, followed by a sudden expansion and an almost equally sudden contraction to a constant volume. The duration of the initiatory period was the longer the smaller the amount of acid added. The sudden expansion on the volume–time curves corresponds to the peak previously noted on the volume–temperature curves, and suggested that at this point an acceleration of the reaction had taken place with an evolution of heat so great that the temperature of the reaction mixture was no longer under the control of the cooling bath. That this was actually the case was proved by immersing a test-tube containing a similar reaction mixture in the bath and checking the temperature of the former against that of the latter: after the initiatory period, the temperature of the reaction mixture suddenly rose to over 1° higher than that of the bath. The volume–time curves show that the reaction was complete very soon after the rise in temperature.

In the preliminary investigations (*loc. cit.*), it was considered that the very great influence of the temperature factor on the initiation of the reaction, certainly in diazotisation, and probably in the nitrosation of secondary amines also, indicated an intramolecular change rather than a reaction between two or more molecules. This could be, conceivably, the transformation of the amine nitrite into a compound of the type $C_6H_5\cdot NR\cdot N(OH)_2$. The facts now brought forward, however, require another explanation, the most obvious being that given below.

Nitrous acid reacts with methylanilinium ions produced by the dissociation of methylaniline hydrochloride : $\mathrm{NMePhH_2^{\cdot} + NO{\cdot}OH \longrightarrow NMePh{\cdot}NO + H_2O + H^{\cdot}}$. The hydrogen ions so liberated combine with free methylaniline, when present, to give further methylanilinium ions. In the mixtures examined, free methylaniline was always present at the commencement of the experiment, the amount being smaller the greater the amount of acid added. Therefore, increase of acid causes more rapid conversion of all the free methylaniline into reactive methylanilinium ions. When no free methylaniline remains, hydrogen ions commence to accumulate in the solution and, it is assumed, catalyse the reaction and accelerate it cumulatively. This is a possible explanation of the development of heat and the subsequent rapid completion of the reaction.

It was hoped to obtain some information as to the correctness or otherwise of this hypothesis by following the reaction by electrical conductivity measurements. Until hydrogen ions are liberated, *i.e.*, until all the free methylaniline is used up, the conductivity would not be expected to vary greatly, but when they commence to accumulate, a sudden increase in conductivity would occur. Actually, conductivity measurements of a mixture of *N*/10-methyl-alcoholic solutions of methylaniline hydrochloride and sodium nitrite with the addition of a suitable amount of hydrochloric acid solution (0·3—0·6 mol.) show the expected behaviour (Fig. 3). The ease with which the sudden change in conductivity is observed enabled a series of determinations to be made of the duration of the initiatory period when different quantities of acid were added (see p. 512). The results seem to support the explanation put forward above. The application of similar methods of investigation to aniline and other typical amines is in progress.

FIG. 1.

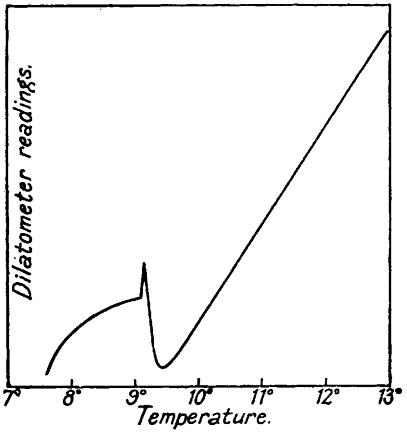
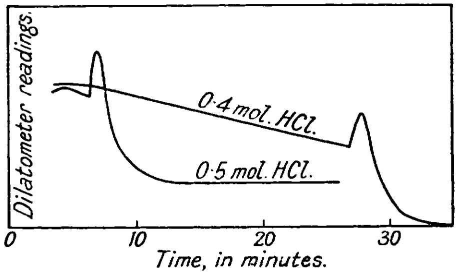


FIG. 2.



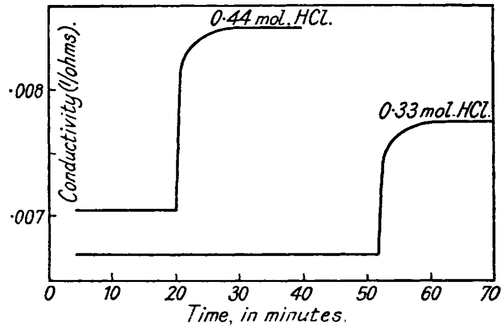


FIG. 3.

EXPERIMENTAL.

Volume–Temperature Curve (Fig. 1).—To a MeOH solution of purified NHMePh,HCl (1·458 g., 1 mol.) was added the requisite amount of conc. aq. HCl (0·5 mol.). The solution was cooled in an ice-bath and mixed with a solution of $\mathrm{NaNO_2}$ (0·700 g., 1 mol.) in MeOH, similarly cooled, the total vol. of MeOH used for the two solutions being 48 c.c. The mixture was then transferred to a dilatometer and the vol. observed over a range of slowly rising temperatures (7·6—15·5°) in the manner previously described (*loc. cit.*).

Volume–Time Curves (Fig. 2).—The mixtures were prepared as above, with 0·4 and 0·5 mol. of acid respectively, but were transferred to a dilatometer kept in a bath at 8° ± 0·05°. When 0·25 mol. of acid was used, no irregularity in the curve was detected over a period of 1·5 hr.

Conductivity Measurements (Fig. 3).—*N*/10-MeOH solutions of NHMePh,HCl and $NaNO_2$ (20 c.c. of each) and the requisite quantity of a MeOH solution of HCl were mixed at 21—22° The mixture was then transferred to a cell of about 40 c.c. capacity, fitted with a thermometer and having Pt electrodes 1 cm. sq. and about 3 cm. apart. The measurements were made at 22° ± 0·2°. A slight rise in temp., usually about 0·2°, was noted at the point at which the conductivity changed. In the curves the reciprocal of the obs. resistance in ohms is plotted against the time in mins.

Vol. of HCl soln., c.c.	0·9	1·2	1·4	1·6	1·8	1·9	2·0
Mols. of HCl ($NaNO_2$ = NHMePh,HCl = 1)	0·25	0·33	0·39	0·44	0·50	0·53	0·56
Duration of initial period, mins.	>75	52	31	20	11	7·5	4

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