53. *Studies in the Diazotisation and Nitrosation of Amines. Part V. The Effect of lowering the Dielectric Constant of the Reaction Mixture.*

By J. Campbell Earl and Noël G. Hills.

An investigation has been made of the reaction between nitrous acid and some aliphatic amines in aqueous solutions of which the dielectric values were lowered by the presence of dioxan. The reaction, under certain conditions, appeared to be bimolecular, like that between nitrous acid and the aromatic amines in water or methanol. The behaviour of the reaction mixtures with regard to electrical conductance resembled that, described in earlier papers of this series, of reaction mixtures containing nitrous acid and aromatic amines.

The reaction between nitrous acid and amines, both aliphatic and aromatic, probably takes place in two principal stages: first, formation of an unstable complex by addition of the amine to nitrous acid, and then elimination of water from the complex with formation of an *N*-nitrosoamine, or some other product, which may or may not undergo further change. As a rule, the first of these stages is apparently much the slower of the two and therefore determines the order of the reaction. It is with this stage that the present investigation is concerned.

Fig. 1.

Dimethylamine and nitrous acid (1 : 1) *with* 0·5 *mol. of* HCl *in dioxan–water solutions.*

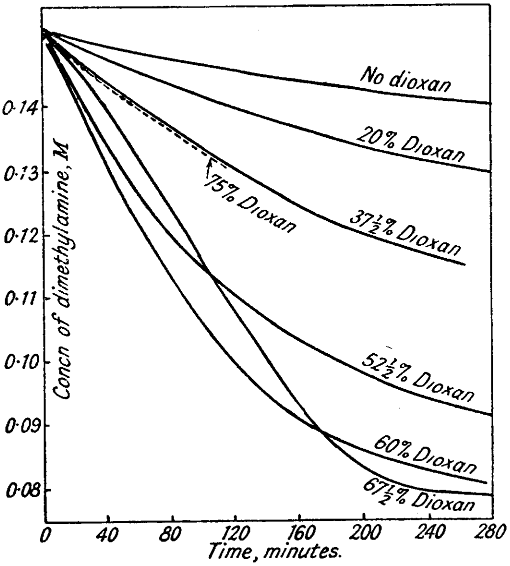
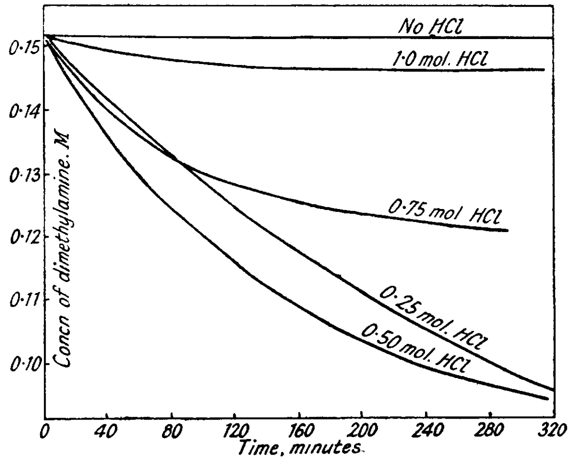


Fig. 2.

Dimethylamine and nitrous acid in 47½% *dioxan :* HCl *varied* ; T = 50°.



The condition of an amine nitrite in solution is represented by the scheme

$$\begin{array}{c} \text{NHRR}' + \overset{+}{\text{H}} + \overset{-}{\text{NO}}_2 \rightleftharpoons \overset{+}{\text{N}}\text{H}_2\text{RR}'\,\overset{-}{\text{NO}}_2 \rightleftharpoons \overset{+}{\text{N}}\text{H}_2\text{RR}' + \overset{-}{\text{NO}}_2 \\ \upharpoonleft\!\downharpoonright \\ \text{NO·OH} \end{array}$$

If the electrolytic dissociation of an amine nitrite can be suppressed, its hydrolysis into free amine and free nitrous acid will be favoured. As Kraus and Fuoss (*J. Amer. Chem. Soc.*, 1933, **55**, 21) had shown that tetra*iso*amylammonium nitrate is only feebly ionised in dioxan solution, it was decided to use water–dioxan mixtures in order to determine whether an aliphatic amine nitrite in such solvents would behave similarly to an aromatic amine nitrite in water, owing to its decreased electrolytic dissociation.

The aliphatic amines selected were dimethylamine and dibenzylamine, the latter being strictly aliphatic in respect to its imino-group. These were used with an equimolecular proportion of nitrous acid, and, as a rule, with less than this proportion of hydrochloric acid. The proportion of dioxan in the solvent was varied in different experiments, but never exceeded 75%, since this was the maximum consistent with the various solubilities at the lowest temperature used. In the experiments illustrated in Fig. 1 the concentration of the hydrochloric acid was half that of each of the other two reactants, this proportion having been found to produce the maximum rate of reaction in water (Earl and Hills, J., 1939, 1089 *). The results show that the velocity of the reaction increases with increasing dioxan content in the solvent up to about 53%; beyond this, the accelerating effect is less in evidence in the earlier part of the reaction, but develops later, the reaction appearing to be self-catalysed.

The experiments illustrated in Fig. 2 show that, in 47·5% dioxan solution, as in aqueous solution, reaction is fastest with 0·5 mol. of hydrochloric acid, being negligible with no acid and very slow with 1·0 mol.

When the reaction with dimethylamine is followed conductimetrically in dioxan–water solutions, the same effects are observed as for methylaniline in aqueous solution (Earl and Hills, *loc. cit.*), *viz.*, an initial fall in conductivity ascribable to the disappearance of ammonium and nitrite ions, and then a more or less sudden increase in conductivity, due no doubt partly to the production of hydrogen ion from the amine hydrochloride, attacked at this stage by nitrous acid, and partly to formation of nitric acid by atmospheric oxidation of nitrous acid. That it is not solely this oxidation that is responsible for the increase in conductivity, however, is apparent from the results of experiments with pairs of identical reaction mixtures, such that in one member of each pair the reaction was followed by determining the amount of amine left at different stages, and in the other by determining the electrical conductivity from time to time. After the point at which the conductivity began to increase, the amine still continued to disappear, although more slowly than before. This effect is more pronounced with the weaker base, dibenzylamine (see Fig. 3).

FIG. 3.

Dibenzylamine nitrite (0·1M) *with* 0·03M-HCl *in* 60% *dioxan, T* = 10°.

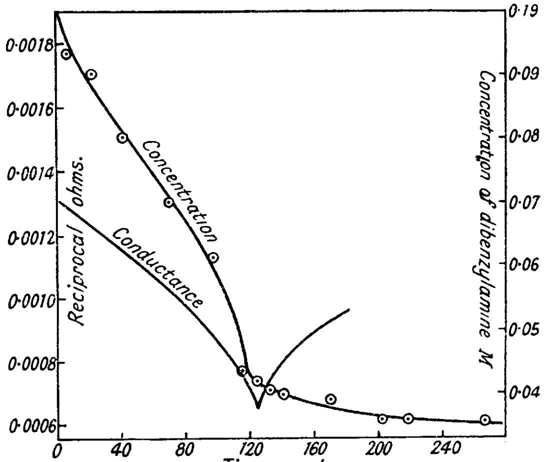
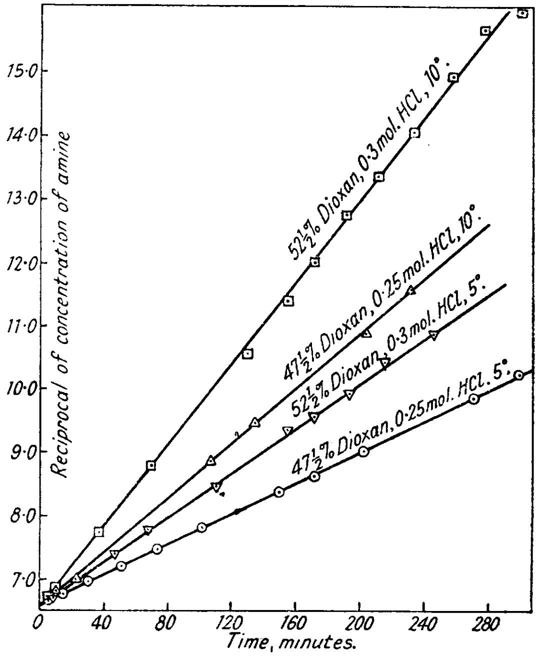


FIG. 4.

Dimethylamine and nitrous acid (*each* 0·152M) *in dioxan–water solution.*



The effects of different concentrations of hydrochloric acid upon the course of the reaction with dibenzylamine were also followed by conductivity measurements. The curves thus obtained were all similar to that shown in Fig. 3 and resemble more closely the methylaniline conductivity curves (Earl and Hills, *loc. cit.*) than do those for dimethylamine, but, like the dimethylamine curves for the reaction in the presence of much dioxan (cf. Fig. 1), they indicate an initial retardation.

Experiments were made to determine the order of the reaction with dimethylamine in a solvent containing rather less dioxan than would produce the maximum velocity at the temperature of the experiment. The results are shown in Fig. 4, in which the reciprocal of the amine concentration is plotted against time. There was no evidence of any irregularity such as self-catalysis. At both 5° and 10° with 47½% and with 52½% of dioxan there was evidence of a second-order reaction, as proved by the straight-line graph, provided that there was present 0·25—0·30 mol. of hydrochloric acid per mol. of amine, or nitrous acid,

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* In Fig. 2 in this paper, the molecular proportions of hydrochloric acid to amine nitrite used to obtain the curves are not shown. For the curves from left to right they are 0·80, 0·20, 0·15, 0·10. The initial concentration of the nitrite should be M/100, not M/1000 as stated.

at the beginning of the experiment. More dilute solutions (*ca.* 0·075M-amine and nitrous acid) also indicated reactions of this order, but variation of the proportion of hydrochloric acid had an entirely different effect. With a higher proportion, the reaction appeared to be termolecular at first and somewhat indeterminate later; but when the proportion was diminished to 0·15 mol. per mol. of amine or nitrous acid, the reaction seemed to become unimolecular, as shown by a straight-line relationship between time and the logarithm of the amine concentration. Velocity constants are not given, since the initial concentrations of the amine and nitrous acid in the forms in which they react are conjectural, being dependent upon the equilibria existing in the reaction mixtures.

The results described therefore justify the views put forward for the mechanism, although certain features, *viz.*, the acceleration of the reaction during its earlier stage, and the change in the order of the reaction with dimethylamine brought about by altering the proportion of hydrochloric acid, require further work before they can be explained.

EXPERIMENTAL.

In experiments in which the rate of disappearance of dimethylamine was measured, the calculated amounts of the base and of hydrochloric acid, both in aqueous solution, were added to such a volume of the requisite dioxan–water mixture that, when the reaction was started by adding an aqueous solution of sodium nitrite equivalent to the base, the reaction mixture should be 0·150M with respect to the base and the nitrite. For conductivity measurements the reagents were made of 0·200M concentration. There was, however, a small contraction due to the mixing of the dioxan and water, the maximum effect being in mixtures containing 52½% of dioxan, so that the initial concentrations of amine and nitrite in the two sets of experiments were 0·152M and 0·203M, respectively. On account of the sparing solubility of dibenzylamine, mixtures in which it was used were made up to be 0·10M with respect to amine and nitrite.

In order to follow the change in concentration of both amines, samples were taken with a pipette (with suitable precautions on account of the toxicity of dioxan) and run into excess of sodium hydroxide solution. The amine was then distilled into standard acid and titrated in the usual manner, the methyl-red–methylene-blue achromatic indicator being used. The presence of dioxan appeared not to affect the titration in any way. Dibenzylamine proved more difficult than dimethylamine to determine exactly by this method.

The conductance of the reaction mixtures was measured in a cell of the ordinary Arrhenius type, in a Wheatstone bridge circuit suitably matched with transformers to a valve-oscillator similar to that described by Grinnell Jones and Josephs (*J. Amer. Chem. Soc.*, 1928, **50**, 1049), used as the source of alternating current.

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