

**235.** *Studies in the Diazotisation and Nitrosation of Amines. Part IV. A General Interpretation of the Reaction.*

By J. CAMPBELL EARL and NOEL G. HILLS.

From an examination of the experimental evidence it is concluded that the primary reaction between nitrous acid and amines is an addition of the amine to undissociated nitrous acid acting as a nitroso-compound. Previous workers have interpreted experimental results they have obtained as indicating that the reaction, in some cases, is one of the third order. An attempt is made to explain this apparent contradiction.

In the earlier papers of this series a considerable amount of experimental evidence has been accumulated on the matter of the action of nitrous acid on amines. This is now supplemented and an attempt is made to provide a general interpretation of the reaction which is in accord with all the experimental data.

In the discussion which follows, special attention is directed to five observations of particular interest.

(1) Methylamine nitrite in 0.05N-aqueous solution is stable at 25° (Taylor, J., 1928, 1099). The addition of nitrous acid brings about its decomposition, but the rate of decomposition is retarded if sulphuric acid is present at the same time.

(2) Aniline nitrite, although it dissolves in water to an initially clear solution, decomposes rapidly, the solution becoming cloudy almost immediately owing to the precipitation of diazoaminobenzene (Earl and Hall, *J. and Proc. Roy. Soc. N.S.W.*, 1932, 66, 454).

(3) Methanol solutions of secondary amine nitrites with limited additions of hydrochloric acid show remarkable and definite conductivity changes on standing. The conductivity remains constant for a time inversely proportional to the amount of acid added and then rises rapidly to another constant value (Earl and Hall, J., 1933, 510; Earl and Hills, J., 1938, 1954).

The above observations are now supplemented by further experimental evidence, given below.

(4) The effect of adding hydrochloric or sulphuric acid to 0.15N-solutions of dimethylamine nitrite at 5° has been studied. It is found that the decomposition of the nitrite is accelerated by the acid, but there is an optimum ratio of acid to nitrite at which the decomposition takes place most rapidly. The following table summarises the observations :

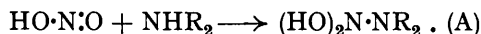
Mol. of acid per mol. of nitrite .....	0.1	0.3	0.5	0.7	1.0
HCl; % nitrite remaining after 3 hours .....	98.0	94.7	92.7	94.7	98.7
H <sub>2</sub> SO <sub>4</sub> ; % nitrite remaining after 5 hours .....	96.0	—	90.7	93.3	97.3

(5) It has been possible to follow the conductivity changes during the nitrosation of methylaniline in aqueous solution by choosing an appropriate dilution (M/100) so that the nitrosoamine remained in solution at the end of the reaction. The temperature was kept low (5°) to diminish the reaction velocity. The conductivity-time curves (Fig. 1) show an initial fall in conductivity, followed by a rise which is more or less pronounced according to the amount of hydrochloric acid present at the commencement of the reaction and is not observed when no acid has been added.

*General Discussion.*—Taylor (*loc. cit.*) followed the decomposition of methylamine nitrite in the presence of nitrous acid by determining the amount of methylamine which could be liberated from time to time by the addition of alkali. The velocity constant

corresponded to a reaction of the third order and the conclusion reached after a careful discussion of the experimental results was that the reaction involved methylammonium and nitrite ions and undissociated nitrous acid. For the decomposition of ammonium nitrite a similar conclusion was reached by Abel, Schmid, and Schafranik (*Z. physikal. Chem.*, Bodenstein Festband, 1931, 510), using entirely different methods. Nevertheless, it is difficult to picture a mechanism involving the postulated reactants.

In a study on the aliphatic amine nitrites, Adamson and Kenner (J., 1934, 839) suggested that amines react with undissociated nitrous acid in the same way as with nitroso-compounds and with carbonyl compounds. They considered that the reaction involves free amine, undissociated nitrous acid and protons. The experimental evidence which has been presented in this series of papers supports the explanation offered by Adamson and Kenner, rather than the more generally accepted view that the reaction is between substituted ammonium ions and nitrous acid (cf. Reilly and Drumm, J., 1935, 871). At this stage we prefer to consider the primary reactions as a simple addition in accordance with the equation

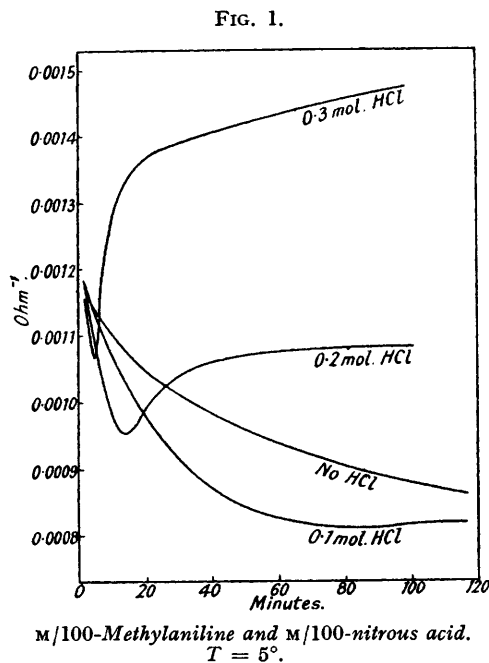


without taking account of the possible intervention of protons. That is, it may be regarded as analogous to the first stage of the reaction of a primary amine with a nitroso-compound to form an azo-compound.

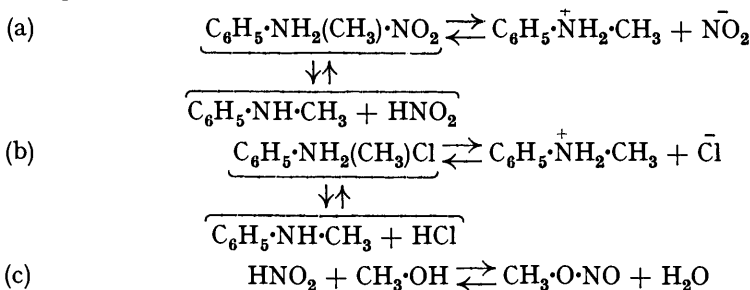
The supposition that free amine and nitrous acid are the essential reactants is quite in accord with Taylor's observation of the stability of 0.05N-solution of methylamine nitrite. For such a solution it can be calculated by the formula  $X = \sqrt{K_w/K_a K_b}$  ( $X$  = degree of hydrolysis;  $K_w$ , the ionic product of water;  $K_a$  and  $K_b$  the dissociation constants of methylamine and nitrous acid respectively) that only 0.000235 of the dissolved salt is hydrolysed to free base and nitrous acid. The actual concentration of each of the two reactants would therefore be 0.000012N. The concentration of undissociated nitrous acid would be further lowered by the electrolytic dissociation of part of it into  $\text{H}^+$  and  $\text{NO}_2^-$  ions. In these circumstances it is understandable that the reaction would proceed too slowly to be measured. Addition of nitrous acid increases the concentration of that reagent and consequently accelerates the reaction. The addition of a strong acid has two effects: (a) the liberation of free nitrous acid from the methylamine nitrite, (b) salt formation with the amine. Naturally a point is reached at which the increase in concentration of nitrous acid does not compensate for the diminution of the available free amine, so that there is an optimum addition of acid as shown in the experiments (*v.s.*).

On the other hand, in a dilute solution of aniline nitrite, calculation shows that 0.201 is hydrolysed to free amine and nitrous acid, giving for a 0.05N-solution a working concentration of 0.01N-nitrous acid and amine. Under these conditions it is reasonable to expect that the reaction represented by equation (A) would proceed readily and the instability of an aqueous solution of aniline nitrite is explained.

A comparison of the conductivity changes observable when methylaniline is nitrosated in methanol and in water also leads to an interpretation of the reaction in the sense of equation (A). It is true that the behaviour of the methanol reaction-mixture can be explained plausibly as involving methylanilinium ions and nitrous acid (Earl and Hall, *loc. cit.*); but an equally plausible explanation which has the advantage of fitting in with



the other evidence, can be given. In the reaction mixture the following systems are operating :



In view of the known ease of esterification of nitrous acid, it may be assumed that very little free nitrous acid is present in the reaction mixture. In the early stages of the reaction the reactants are furnished from system (a) alone, that is, the reaction proceeds as it does when no hydrochloric acid is present. The later stages of the reaction call upon the systems (b) and (c). The hydrogen-ion concentration necessarily increases, because hydrochloric acid is liberated, and in the presence of increased hydrogen-ion concentration the system (c) becomes more labile and liberates nitrous acid more easily. Therefore the reaction proceeds rapidly to a conclusion.

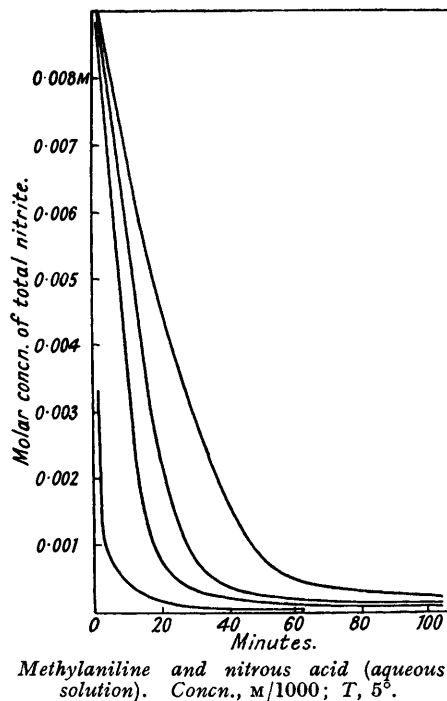
With an aqueous reaction mixture system (c) does not come into consideration. There is no increase in the availability of nitrous acid as the hydrogen-ion concentration increases. In consequence the final rise in conductivity is more gradual, especially when the initial concentration of acid is low.

It must be noted that the conductivity-time curves do not give any indication as to the velocity with which the reaction is proceeding at any particular instant. Measurement of the rate of disappearance of the nitrite shows this quite clearly. Methanol solutions of both *p*-toluidine nitrite and *N*-methyl-*p*-toluidine nitrite showed a regular disappearance of nitrite at second-order rate in the absence of acids (Earl and Laurence, this vol., p. 419).

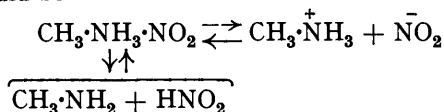
Methylaniline nitrite in aqueous solution disappears at a regular rate in the presence of acids, although the reaction was accelerated by increasing the proportion of acid (Fig. 2). It can be seen by comparison with the conductivity-time curves that the time at which the rate of disappearance of nitrite commences to decrease corresponds approximately with that of minimum conductivity and that when the reaction is complete no further conductivity changes occur, but no other connection between the two series of curves can be traced.

From the evidence given, it may be reasonably concluded that the fundamental reaction of diazotisation and nitrosation is that represented by equation A. A possible inner mechanism of the reaction was suggested by Adamson and Kenner (*loc. cit.*), but there is at present little direct experimental evidence to support it. It does appear, however, that their conclusion that the reaction involves free amine and undissociated nitrous acid is justified by the evidence discussed in this paper.

FIG. 2.



Taylor's interpretation of his observations on methylamine nitrite showed that the decomposition with excess of nitrous acid is a reaction of the third order. Since then, he has expressed some doubt as to the exact significance of his interpretation (Sidgwick's "Organic Chemistry of Nitrogen," 1937 edn., p. 24). The system present in a solution of methylamine nitrite would be



As has been pointed out, the actual concentrations of free amine and nitrous acid would be very small, but the addition of nitrous acid to the system would enable the reaction to proceed. The net effect of withdrawing free amine from the system by reaction with the added nitrous acid would be a simultaneous decrease in the concentrations of nitrous acid, methylammonium and nitrite ions, giving the appearance of a third-order reaction, although the actual reactants might be nitrous acid and free amine.

In continuation of the above work, further experiments are in progress on the effect of adding materials of low dielectric constant to an aqueous reaction mixture. Under these conditions the electrolytic dissociation of substances present will be depressed, but hydrolysis is not likely to be affected in the same degree.

The grant of a Commonwealth scholarship to one of the authors (N. G. H.) is gratefully acknowledged.

THE UNIVERSITY, SYDNEY.

[Received, April 25th, 1939.]

---