

367. *Studies in the Diazotisation and Nitrosation of Amines. Part I.
The Use of Dilatometric and Conductimetric Methods.*

By J. CAMPBELL EARL and NOEL G. HILLS.

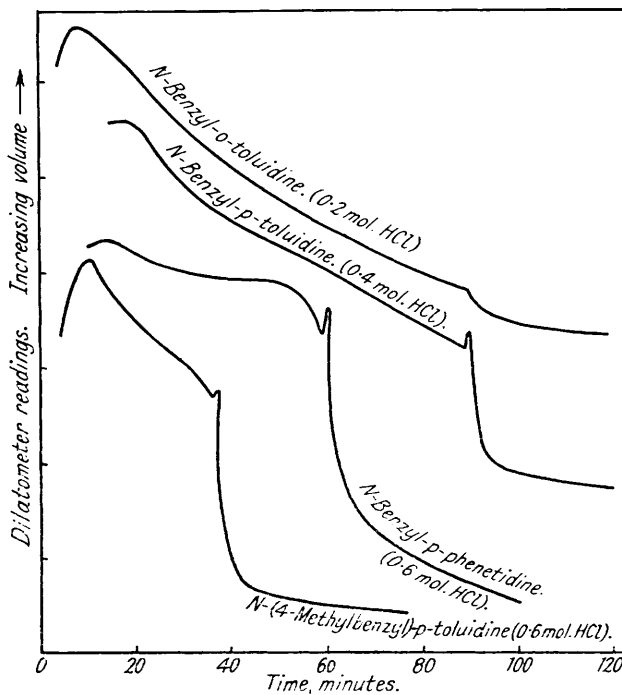
The customary methods of chemical kinetics when applied to the reaction between nitrous acid and amines lead to results which are not entirely satisfactory from the point of view of a general interpretation of the reaction. In methanol solutions containing aromatic amines and nitrous acid, definite changes in volume and in electrical conductivity accompany the chemical reaction. From these changes it is apparent that the reaction is not a simple one.

UNDER controlled conditions, primary and secondary aromatic amines react with nitrous acid in methanol solution in the presence of hydrochloric acid at such a rate that the changes taking place can be followed dilatometrically or conductimetrically (Earl and Hall, J., 1933, 510; Earl and Hills, *J. Proc. Roy. Soc. N. S. W.*, 1936, 70, 322). With methylaniline and aniline, the amines already investigated in this way, the reactions involved are complex: the forms of both the volume-time and the conductivity-time curves are very characteristic, more so with the secondary than with the primary amine.

Before using these observations in a general interpretation of the mechanism of the nitrous acid-amine reaction, it is obviously necessary to apply the methods to a wider range of amines. Moreover, the methods themselves require further study to determine whether they are subject to interference by occurrences in the reaction mixture, unconnected with the reaction being studied. For example, it is probable that there is little free nitrous acid at any time in the reaction mixture in view of the known readiness with which methyl nitrite is formed, so that the formation and decomposition of methyl nitrite might be a factor in the changes of conductivity and volume observed. The present paper describes an extension of the earlier experimental work on the lines indicated.

Secondary amines in general give the more definite results. The dilatometric method applied to *N*-benzyl-*p*-phenetidine, *o*-toluidine, and *p*-toluidine and to *N*-4-methylbenzyl-*p*-toluidine gives curves for the volume-time change (Fig. 1) very similar to those previously

FIG. 1.

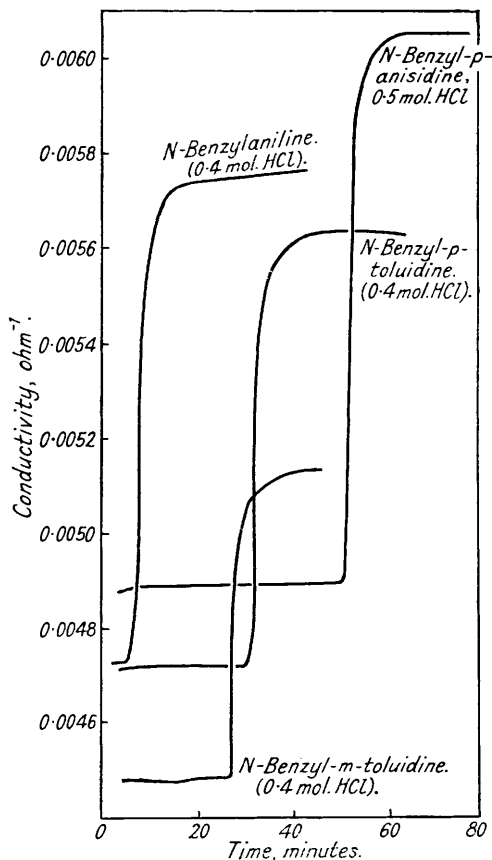


Dilatometer curves for secondary amines.

obtained for methylaniline. The conductivity changes were followed for a much wider range of secondary amines, *viz.*, ethylaniline, *N*-methyl-*o*-anisidine, *N*-methyl-*p*-toluidine, the *N*-benzyl derivatives of aniline, *m*- and *p*-toluidines, *p*-anisidine, and *p*-phenetidine, and finally *N*-4-methylbenzyl-*p*-toluidine. All these show an almost constant conductivity for a preliminary period, followed by a very abrupt rise to another constant value. A selection of typical curves of this series is given in Fig. 2. With a further group of secondary amines, *N*-benzyl-*o*-toluidine, *m*-xylylidine, and *o*-phenetidine, the rise in conductivity after the initial period is not so abrupt (Fig. 3).

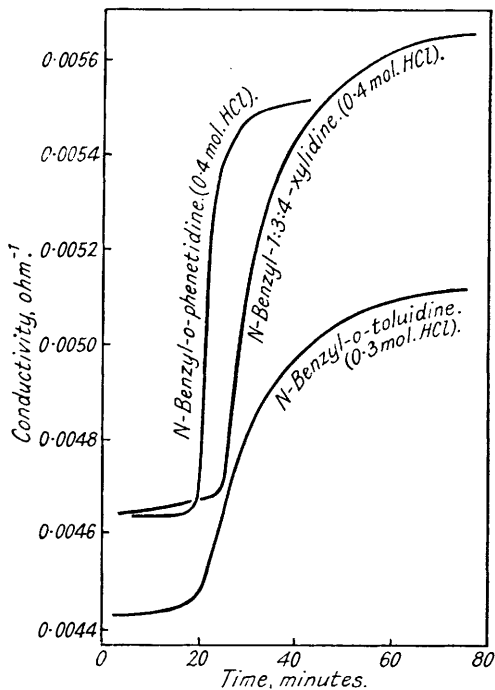
The conductivity measurements were made with $N/22.5$ -solutions of the amines, but for the dilatometer experiments, $N/5.6$ -solutions were used. Solid sodium chloride separated during the latter experiments and this may have had some effect on the curves. For conductivity measurements, the precipitation of sodium chloride would of course introduce serious complications. Some experiments were made, therefore, with amyl nitrite instead of sodium nitrite, volume-time and conductivity-time curves being obtained for methylaniline and *N*-benzyl-*p*-phenetidine under comparable temperature and

FIG. 2.



Conductivity curves for secondary amines.

FIG. 3.

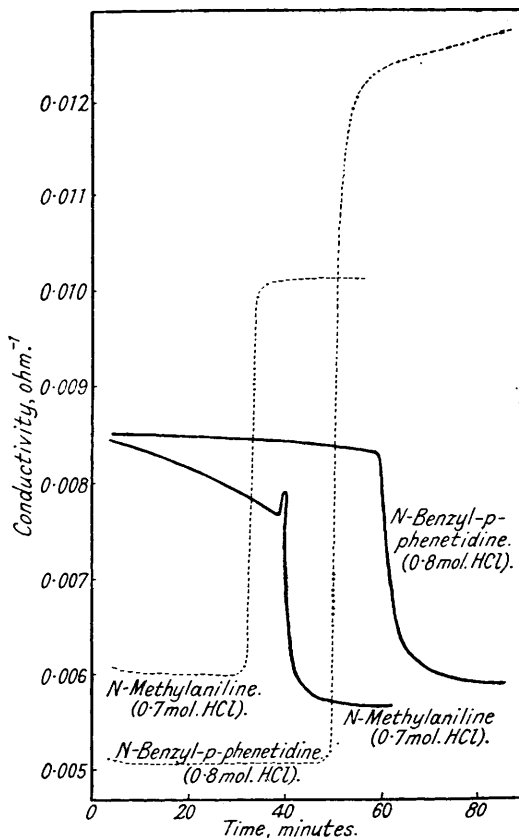


Conductivity curves for secondary amines.

concentration conditions (Fig. 4). It is apparent that precipitation of sodium chloride during the dilatometer experiments does not greatly change the character of the volume-time curves, and also that conductivity changes of the same kind take place in both concentrated and dilute solutions.

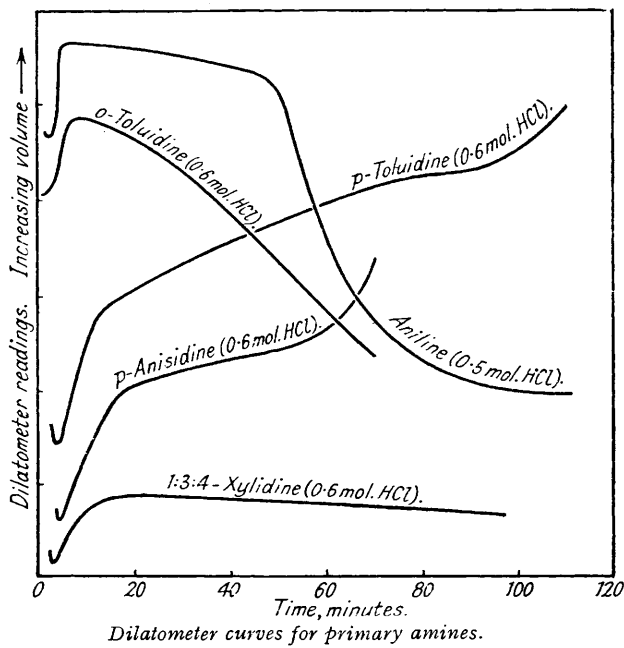
Primary amines with nitrous acid give products which readily take part in further reactions, so that the volume and conductivity changes are subject to the simultaneous influence of many factors. The volume-time curves for reaction mixtures containing primary amines are, in general, not very characteristic (Fig. 5). The conductivity-time curves are of more interest. Measurements were made with aniline, *o*-, *m*-, and *p*-toluidines, *o*- and *p*-anisidines, *p*-xylylidine, *m*-4-xylylidine and α -naphthylamine. A comparison of the curves (Fig. 6) shows that in all cases there is a preliminary period of almost constant or falling conductivity, followed by a rapid rise until the evolution of nitrogen commences. The initial fall is very pronounced with α -naphthylamine. With some of the amines there is a remarkable irregularity in the rising part of the curve which requires interpretation.

FIG. 4.



Dilatometer curves ——— } for secondary amines using amyl nitrite.
 Conductivity " }

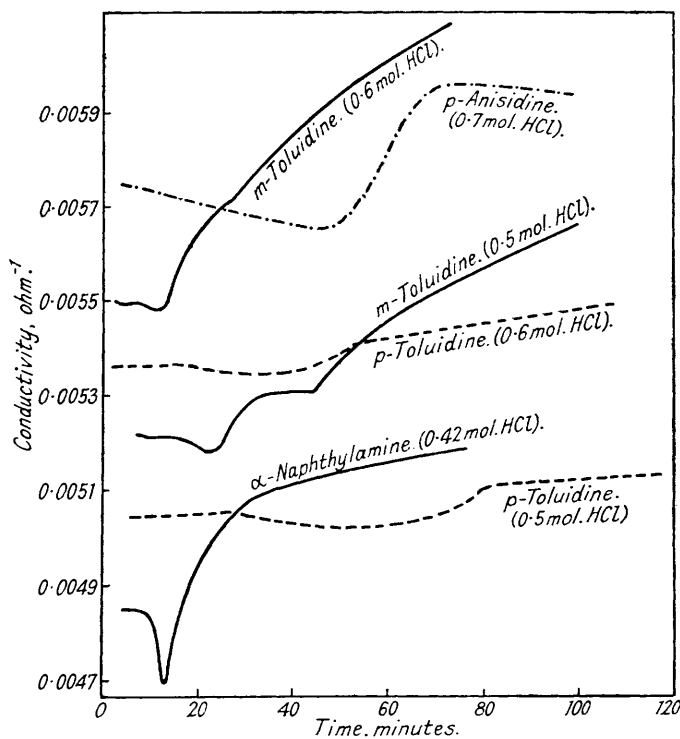
FIG. 5.



Dilatometer curves for primary amines.

At this stage it is not intended to draw many conclusions from the observations recorded, because they are only part of a general attack on the problem and must be correlated with evidence obtained by different methods of approach. However, the conductivity curves for both primary and secondary amines are consistent with the formation of a complex in the early stages, followed by a later decomposition with the liberation of hydrogen ions. The early part of the reaction may therefore find an

FIG. 6.



Conductivity curves for primary amines.

explanation from a closer study of the aromatic amine nitrites in amplification of the preliminary work on aniline nitrite (Earl and Hall, *J. Proc. Roy. Soc. N.S.W.*, 1932, **66**, 453; J., 1937, 1129). Work on these lines is now proceeding. That the later rise in conductivity is actually due to an increase in hydrogen-ion concentration may be confirmed by following the changes by a suitable potentiometric method. This also is being done.

EXPERIMENTAL.

Volume-time Curves (Figs. 1, 4, 5).—(a) *With sodium nitrite as the source of nitrous acid.* To 20 ml. of a 0.4M-solution of the amine hydrochloride in methanol, the requisite amount of approximately 3.5N-hydrochloric acid in methanol was added, and the volume made up 25 ml. with methanol. This solution was mixed at 5° with 20 ml. of a 0.4M-solution of sodium nitrite in methanol, and the mixture was at once transferred to a dilatometer similar to that previously described (*J. Proc. Roy. Soc. N.S.W.*, 1932, **66**, 157).

(b) *With amyl nitrite.* The requisite amount of hydrochloric acid in methanol was added to 20 ml. of a 0.4M-solution of the amine in methanol, and the volume made up to 44 ml. After being cooled to 5°, the solution was mixed with 0.936 g. of amyl nitrite and transferred to the dilatometer.

Conductivity-time Curves (Figs. 2, 3, 4, 6).—The cell used was the one described previously (J., 1933, 510). When sodium nitrite was used as the source of nitrous acid, the reaction mixtures were prepared in the same way as those for the volume-time experiments, but all

solutions were of one-quarter the concentration, and the determinations were carried out at 25°.

When amyl nitrite was used, the concentrations of the reactants were the same as for the corresponding volume-time experiments. The determinations in this case were made at 5°.

The authors thank the Carnegie Corporation of New York for a scholarship which enabled one of them (N. G. H.) to take part in the work.

THE UNIVERSITY, SYDNEY, N.S.W.

[Received, October 3rd, 1938.]
