89. *Studies in the Diazotisation and Nitrosation of Amines. Part II. Changes in Hydrogen-ion Concentration during the Reaction.*

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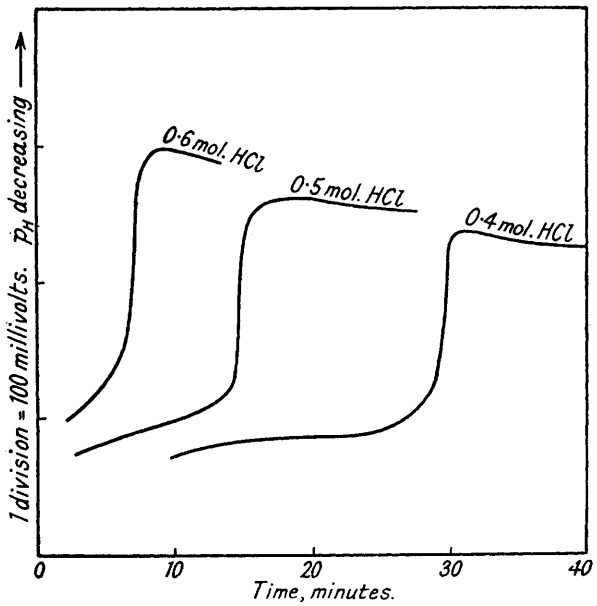
The changes in p_H have been followed during the reaction in methanol solution between nitrous acid and the following amines: aniline, methylaniline, *N*-benzyl-*o*- and -*p*-toluidine. The resulting curves are compared with those previously obtained for changes of conductivity during the same reactions.

In Part I (J., 1938, 1954) the occurrence of definite and characteristic changes in electrical conductivity during the reaction between nitrous acid and amines in methanol solution was discussed. As a logical outcome of the results obtained it was decided to examine also the changes in the hydrogen-ion concentration in the reaction mixture to determine how far these influenced the electrical conductivity. For this purpose a glass electrode was used.

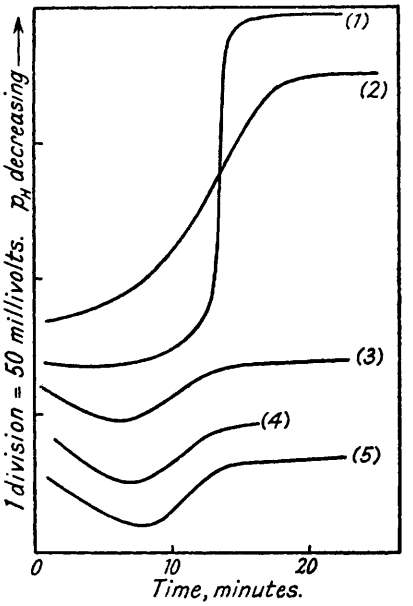
A circuit, based on that of Hemingway (*Ind. Eng. Chem., Anal.*, **1935**, **7**, 203), was found satisfactory for the purpose, although rather subject to disturbance by unknown outside influences. The results of the observations are recorded in the form of millivolt–time curves. The reaction mixtures were of the same composition as those used for the conductivity experiments and the measurements were made at the same temperature, namely, 25°. In Fig. 1 are given the millivolt–time curves for methylaniline with different additions of hydrochloric acid.

Fig. 1.



Millivolt–time curves for methylaniline.

Fig. 2.



(1) N-*Benzyl*-p-*toluidine* (0·6 *mol.* HCl).
(2) N-*Benzyl*-o-*toluidine* (0·5 *mol.* HCl).
(3) *Aniline* (0·6 *mol.* HCl).
(4) *Aniline* (0·52 *mol.* HCl).
(5) *Aniline* (0·55 *mol.* HCl).

The resemblance to the conductivity curves is close, the principal difference being in the early stages. Since the millivolt readings are directly proportional to p_H and therefore logarithmically related to the reciprocal of the actual hydrogen-ion concentration, it follows that the early parts of the curves accentuate the actual hydrogen-ion concentration changes much more than the later parts. The results show clearly that the changes in hydrogen-ion concentration are responsible for the principal characteristics of the conductivity–time curves.

Other amines were also examined (Fig. 2). *N*-Benzyl-*p*-toluidine behaved in very much the same way as methylaniline, but with *N*-benzyl-*o*-toluidine the rise in hydrogen-ion concentration was not so abrupt. A similar difference was observed between the conductivity–time curves of these two amines. For aniline the millivolt–time curve is very similar to the conductivity–time curve (*J. Proc. Roy. Soc. N.S.W.*, **1936**, **70**, 322).

Any explanation of the mechanism of the nitrosation of secondary amines in methanol solution must allow for an initial stage in which there is a slight increase in hydrogen-ion concentration, followed by a rapid reaction involving the liberation of hydrogen ions. Probably, as has already been pointed out, the same initial changes take place prior to

the formation of diazo-compounds from primary amines, although here the masking effect of secondary reactions enters.

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