999. *Nitrosation, Diazotisation, and Deamination. Part X.* The Acid-catalysed Diazotisation of* p-*Nitroaniline and 2,4-Dinitroaniline in Aqueous Perchloric Acid (up to* 3·0M*).*

By B. C. CHALLIS, L. F. LARKWORTHY, and J. H. RIDD.

The kinetics of diazotisation of *p*-nitro- and 2,4-dinitro-aniline are reported for aqueous solutions of perchloric acid up to 3·0M. The analysis of the kinetics assumes that perchloric acid can be considered to influence the reaction rate (1) by modifying prototropic equilibria as expected from the values of the H_0 acidity function, and (2) by an additional medium effect, the magnitude of which for a given reaction is similar to that of alkali perchlorates. After allowance for the medium effect, the kinetics are shown to fit a simple equation and this is considered to be derived from a rate-determining reaction between the free amine and the nitrous acidium ion.

THE first results on the diazotisation of a range of amines at moderate acidities revealed a very complex pattern of acid catalysis [1,2] but, after the recognition of the medium effect described in Part IX, it was seen that the amines fell mainly into two groups, apparently depending on their basicity, and that each group obeyed a simple kinetic equation. The two amines forming the subject of this paper were the least basic of the amines studied and illustrate one of the new kinetic forms.

In the analysis of the kinetics in this and the following paper it has been assumed that perchloric acid has a medium effect similar to that of the alkali perchlorates and defined by equation (3) of Part IX. The justification for this assumption lies largely in the resultant simplification of the kinetics, but the assumption is reasonable, for the relative catalytic effect of the different salts (in particular the order $Li^+ > Na^+ > NMe_4^+$) gives some evidence of a correlation with salt effects on the H_0 function,[3] and these are probably derived, in part, from salt effects on the activity of water. The effect of perchloric acid

---

* Part IX, preceding paper.

[1] Larkworthy, Ph.D. Thesis, London, 1953.

[2] Schmid and Essler, *Monatsh.*, 1959, **90**, 222.

[3] Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

on the activity of water is similar to that of lithium perchlorate,[4] and, up to concentrations of 3·0M, the effect of perchloric acid on the deviation of H_0 from $-\log[H^+]$ is very similar to that of sodium perchlorate (see Appendix to Part XI). The medium effect of perchloric acid has, therefore, been assigned a value between that of sodium perchlorate and that of lithium perchlorate.

(1) p-*Nitroaniline.*—At low acidities,[5] the diazotisation of this amine follows equation (1) with $k_3 = 161$ mole^{-2} sec.$^{-1}$ l.^{2}:

$$\text{Rate} = k_3[\text{ArNH}_2][\text{HNO}_2][\text{H}^+]. \qquad (1)$$

This equation has been interpreted [5] as the reaction of the free amine with the nitrous acidium ion. As the acidity is increased above 0·5M, the total order with respect to the nitrous acid and the amine remains two,[1] but the reaction rate increases far more rapidly than predicted by equation (1). In discussing this variation with acidity, it is helpful to define a rate-coefficient (k_2) by equation (2):

$$\text{Rate} = k_2[\text{ArNH}_2][\text{HNO}_2]. \qquad (2)$$

If the reaction involves the nitrous acidium ion then, to a first approximation, k_2 should be proportional to h_0; if the reaction involves the nitrosonium ion then, to a first approximation, k_2 should be proportional * to j_0.

TABLE 1.

Diazotisation of *p*-nitroaniline in aqueous perchloric acid at 0°.

$[\text{HClO}_4]$ (M)	H_0	J_0 *	$\bar{k}_2$ (eq. 5)	k_2 (eq. 2)	$\log k_2^\circ$ (eq. 3)
0·10	+1·00	+0·97	7·8	15·6	1·16
0·50	+0·20	−0·20	16·1	117	1·92
1·00	−0·22	−0·99	24·0	422	2·32
1·50	−0·53	−1·60	35·0	1200	2·63
2·00	−0·78	−2·18	51·5	3150	2·90
2·50	−1·01	−2·74	71·5	7430	3·12
3·00	−1·23	−3·25	92·5	15,900	3·30

Rate coefficients in mole^{-1} sec.$^{-1}$ l.

* Calc. from the values given in terms of percentage of HClO_4 by Deno, Berkheimer, Evans, and Peterson (*J. Amer. Chem. Soc.*, 1959, **81**, 2344). The values in terms of molarities in that paper contain numerical errors.

Values of k_2 as a function of acidity are given in the fifth column of Table 1 and are plotted logarithmically against $-H_0$ in Fig. 1; the graph is curved and the slope exceeds unity. However, to allow for the medium effect of perchloric acid, values of k_2° have been calculated from equation (3), by analogy with equation (3) of Part IX. The value of m has been set at 0·3; the m-values for lithium and sodium perchlorates are 0·33 and 0·27, respectively.†

$$\log k_2 = \log k_2^\circ + m[\text{HClO}_4]. \qquad (3)$$

The values of $\log k_2^\circ$ are included in Table 1 and Fig. 1; as expected, they lie on a straight line of about unit slope (0·95). Thus k_2° is proportional to h_0, and the kinetics of diazotisation therefore follow equation (4); the superscript zero on the rate coefficient indicates that the kinetic form refers to conditions where the medium effect is constant.

$$\text{Rate} = k_3^\circ[\text{ArNH}_2][\text{HNO}_2]h_0. \qquad (4)$$

---

* The nomenclature for acidity functions used in these papers is taken from ref. 3.

† These values of m are for *o*-chloroaniline. However, the results in Part IX suggest that the medium effects are very similar for *o*-chloroaniline and *p*-nitroaniline.

[4] Robinson and Stokes, "Electrolyte Solutions," Butterworths Scientific Publns., London, 1959, Appendix 8.10.

[5] Larkworthy, *J.*, 1959, 3304.

The validity of equation (4) can be more directly seen from the dependence of the rate of diazotisation on acidity in perchloric acid solutions containing sufficient sodium perchlorate to maintain the medium effect approximately constant. The values of the stoicheiometric rate coefficient $\bar{k}_2$ [defined by equation (5)] under these conditions at 0° are as follows for acidities where the amine is largely present as the conjugate acid.

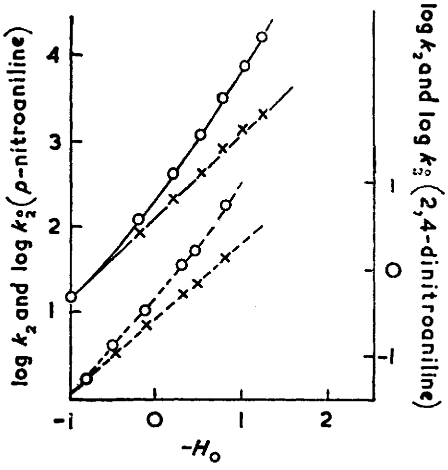

Fig. 1. Plot of log k_2 (eq. 2) (○) and log $k_2°$ (eq. 3) (×) for the diazotisation of p-nitroaniline (——) and 2,4-dinitroaniline (- - -) as a function of $-H_0$.

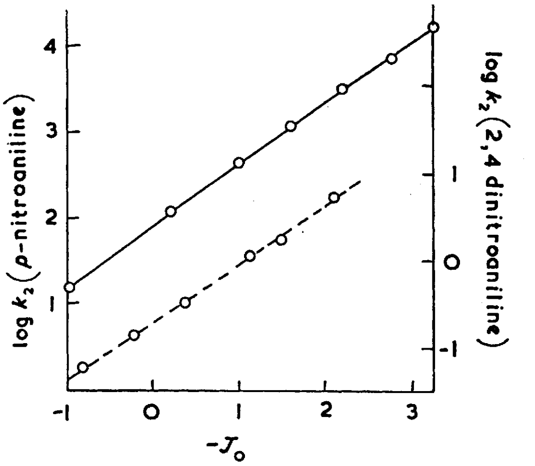

Fig. 2. Plot of log k_2 (eq. 2) for the diazotisation of p-nitroaniline (——) and 2,4-dinitroaniline (- - -) as a function of $-J_0$.

The constancy of $\bar{k}_2$ then follows directly from equation (4), for the product $[ArNH_2]h_0$ is proportional to the concentration of the conjugate acid and this is effectively equal to the stoicheiometric concentration of the amine.

$$\text{Rate} = \bar{k}_2[\text{Amine}][\text{Nitrous acid}]. \qquad (5)$$

$[HClO_4]$ (M)	0·5	1·0	2·0	3·0
$[NaClO_4]$ (M)	2·5	2·0	1·0	0
$\bar{k}_2$ (mole^{-1} sec.$^{-1}$ l.)	80·0	81·1	84·1	93·0

The alternative correlation of log k_2 (eq. 2) with J_0 is shown in Fig. 2. The slope is only 0·7 and there is no sign of an increase in the slope with increasing acidity; indeed the trend is in the other direction. This is evidence against the gradual incursion of nitrosation by the nitrosonium ion as the acidity is increased.

A comparison of the reaction rate in water and deuterium oxide is given in Table 2 in

TABLE 2.

Determination of the solvent isotope effect in the diazotisation of *p*-nitroaniline in aqueous acids at 0°.

Acid	Concn. (M)	$\bar{k}_2$ (eq. 5) H_2O	 D_2O *	$\bar{k}_2$ $(H_2O)/\bar{k}_2$ (D_2O)
H_2SO_4	0·0215	7·02	7·02	1
$HClO_4$	0·0425	5·58	5·73	0·97

Rate coefficients in mole^{-1} sec.$^{-1}$ l.

* Atom fraction of deuterium ~0·8.

TABLE 3.

Variation of $\bar{k}_2$(eq. 5) with temperature in the diazotisation of *p*-nitroaniline.

$[HClO_4]$ (M)	$\bar{k}_2$ (mole^{-1} sec.$^{-1}$ l.) * 273°	 283·2°	 297·6°	*E* (kcal. mole^{-1})
0·5	16·1	58·2	237	17·5 ± 0·5
1·0	24·0	82·8	371	17·7 ± ,,
1·5	35·0	108·0	—	17·4 ± ,,

* Mean value based on two or more kinetic runs.

terms of the stoicheiometric rate coefficient ($\bar{k}_2$); there appears to be no deuterium isotope effect. The variation of the stoicheiometric rate coefficient ($\bar{k}_2$) with temperature is shown in Table 3, together with the corresponding values of the Arrhenius activation energy.

(2) 2,4-*Dinitroaniline.*—This amine (pK_a − 4·53) is effectively unprotonated over the acid range 0·5—3·0M and so the stoicheiometric rate coefficients ($\bar{k}_2$, eq. 5) are equal to the molecular rate coefficients (k_2, eq. 2). The values of $\bar{k}_2$ for different concentrations of perchloric acid are given in Table 4 and plotted logarithmically against $-H_0$ in Fig. 1. As with *p*-nitroaniline, the graph has a slope greater than unity and shows some curvature.

TABLE 4.

Diazotisation of 2,4-dinitroaniline in aqueous perchloric acid at 0°.

$[HClO_4]$	0·159	0·313	0·581	1·12	1·40	2·07
$\bar{k}_2$ (eq. 5)	0·059 *	0·132 *	0·325 *	1·11	1·65	5·45
log $k_2°$ (eq. 3)	$\bar{2}$·72	$\bar{1}$·02	$\bar{1}$·34	$\bar{1}$·71	$\bar{1}$·80	0·11

Rate coefficients in mole^{-1} sec.$^{-1}$ l.

* Taken from ref. 5.

An attempt has been made to correct these rate coefficients for the medium effect discussed above. The effect of sodium perchlorate on the rate of diazotisation of 2,4-dinitroaniline was not investigated but there is some evidence that, for this kinetic form, the medium effects of different salts are not very sensitive to the nature of the amine (see Fig. 1, Part IX). Values of log $k_2°$ have therefore been calculated for 2,4-dinitroaniline by using equation (3) with the same value of *m* (0·3) as for *p*-nitroaniline. These values of log $k_2°$ are included in Table 4 and in Fig. 1; they show more scatter than for *p*-nitroaniline but again approximate well to a straight line of unit slope. Hence the diazotisation of 2,4-dinitroaniline appears to follow equation (4) over this range of acidity.

The variation of log k_2 with J_0 is shown in Fig. 2. The graph is very similar to that for *p*-nitroaniline.

(3) *Discussion.*—The above results, leading to the kinetic form of equation (4), suggest that diazotisation under these conditions proceeds by the rate-determining attack of the free amine on the nitrous acidium ion, and that this reaction is subject to a medium effect of the type described in the preceding paper. Equation (4) is then the natural extension of equation (1) to solutions of moderate acidity. The results do not support a rate-determining attack of the nitrosonium ion on the free amine, for the incursion of this

mechanism should cause the slope of log k_2 against J_0 to increase with increasing acidity to a value of about unity. This is not observed.

Although this result has been described as a nitrosation by the nitrous acidium ion, the kinetic form would also be consistent with a proton transfer to the nitrous acid at the same time as the interaction of this acid with the amine. The solvent isotope effect k_{H_2O}/k_{D_2O} has been frequently used in attempts to resolve uncertainties of this kind; it has been argued that a pre-equilibrium formation of the conjugate acid causes the reaction to be faster in the deuterated solvent, whereas a rate-determining proton transfer causes the reaction to be faster in water.[6] Although this analysis of the results is an oversimplification,[7] it is still of some value in determining the reaction mechanism.

The results in Table 2 show that the solvent isotope effect, when expressed in terms of the stoicheiometric rate coefficients, is about unity. However, in applying these results to a reaction of the free amine, it is necessary to take account of the difference in the dissociation of the *p*-nitroanilinium ion in the two media. At the concentration of perchloric acid listed in Table 2, the percentage dissociation of the *p*-nitroanilinium ion can be calculated[8] to be: H_2O, 72%; D_2O, 41%. Expressed in terms of the molecular rate coefficients (eq. 1), the reaction is therefore faster in the deuterated solvent by a factor of about 1·7. A similar isotope effect (a factor of 2·2) has been observed in the nitrosation of iodide ions by the nitrous acidium ion at low acidities.[9] These results suggest that the proton transfer to the nitrous acid is effectively complete before the interaction with the nucleophile (iodide ion or free amine). The increase in the reaction rate by a factor of about 2 can be ascribed to an increase in the concentration of the nitrous acidium ion in the deuterated medium.[10]

At the present time, it is difficult to draw mechanistic conclusions from the values of the activation energy given in Table 3 because the values of ΔH for the relevant nitrous acid equilibria are unknown. The value of ΔH for the protonation of *p*-nitroaniline is known[11] to be 4·6 kcal. mole^{-1}, and, since the amine is largely protonated under the conditions of Table 3, the activation energy expressed in terms of the free amine should be about 13 kcal. mole^{-1}. This result is similar to that for the nitrosation of iodide ions by the nitrous acidium ion at lower acidities ($\sim$14 kcal. mole^{-1});[12] and this is reasonable, for the rate coefficients for the reaction of these nucleophiles with the nitrous acidium ions are within a factor of ten.[13]

Experimental.—The experimental procedure followed that described previously. The results for a typical kinetic run are given in Table 5 and illustrate the constancy of $\bar{k}_2$ throughout a single run.

TABLE 5.

Diazotisation of *p*-nitroaniline in aqueous perchloric acid (1·5M) at 0°.

Initial concns.: [Amine] = 5 × 10^{-5}M; [Nitrous acid] = 5 × 10^{-5}M.

Time (min.)	Reaction (%)	$\bar{k}_2$ (eq. 5) (sec.$^{-1}$ mole^{-1} l.)	Time (min.)	Reaction (%)	$\bar{k}_2$ (eq. 5) (sec.$^{-1}$ mole^{-1} l.)
1·98	19·5	35·0	13·0	54·2	33·3
4·00	31·8	34·7	18·4	66·0	35·5
6·00	40·2	35·7	25·0	71·6	33·3
9·00	49·2	34·4	35·0	77·6	34·7

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE,
GOWER STREET, LONDON, W.C.1.

[*Received, June* 26*th*, 1962.]

---

[6] Bell, " Acid–Base Catalysis," Oxford University Press, 1941, p. 143.
[7] Bunton and Shiner, *J. Amer. Chem. Soc.*, 1961, **83**, 3214.
[8] Högfeldt and Bigeleisen, *J. Amer. Chem. Soc.*, 1960, **82**, 15.
[9] Challis, Ph.D. Thesis, London, 1960.
[10] Cf. Bunton and Shiner, *J. Amer. Chem. Soc.*, 1961, **83**, 42.
[11] Gel'bstein, Shcheglova, and Temkin, *Doklady Akad. Nauk S.S.S.R.*, 1956, **107**, 108.
[12] Challis and Ridd, unpublished results; cf. ref. 9.
[13] Ridd, *Quart. Rev.*, 1961, **15**, 418.