1000. *Nitrosation, Diazotisation, and Deamination. Part XI.* The Acid-catalysed Diazotisation of the Anilinium and Related Ions in Aqueous Perchloric Acid (up to* 3·0M*).*

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The kinetics of diazotisation of aniline and *p*-toluidine in concentrations of perchloric acid $\geqslant$ 0·5M show that diazotisation by nitrous anhydride is replaced by another mechanism with a kinetic form that is of the first order with respect to both the amine and the nitrous acid. This reaction is catalysed by sodium perchlorate and strongly catalysed by perchloric acid; the extent of acid catalysis is much greater than that observed in the diazotisation of *p*-nitroaniline (Part X). In media where the ionic strength is maintained constant by sodium perchlorate, the acid catalysis follows a simple kinetic law, and this is interpreted as the direct diazotisation of the anilinium ion. This mechanism of diazotisation and that described in Part X contribute independently to the diazotisation of *o*-chloroaniline.

The effect of perchloric acid on the kinetics of diazotisation of aniline and some related amines has been studied recently by Schmid and his co-workers;[1] the acid catalysis is ascribed mainly to diazotisation by nitrosonium perchlorate. We are in general agreement with their kinetic observations (*e.g.*, on the kinetic order with respect to the amine and the nitrous acid) and on these points our results are presented briefly below. However, our studies of the effect of sodium perchlorate on the reaction rate lead us to a different view of the mechanisms involved.

(1) *Aniline.*—As the concentration of perchloric acid is increased above 0·1M, the kinetic form characteristic of the nitrous anhydride mechanism of diazotisation (equation 1)

$$\text{Rate} = k_3[\text{ArNH}_2][\text{HNO}_2]^2 \qquad (1)$$

is replaced by another kinetic form that is of the first order with respect to both the amine and the nitrous acid. The total order (n) of the reaction with respect to the amine and the nitrous acid therefore decreases from three to two as the acidity is increased. This is illustrated by the results below, calculated from the equation $\log t_{\frac{1}{2}} = \text{Constant} - (n - 1)\log a$, and obtained by using concentrations (a) of the reactants mainly in the range 10^{-3}—10^{-2}M:

[HClO$_4$] (M)	0·5	1·0	1·5	2·0	3·0
Order (n)	2·88	2·43	2·25	2·02	2·03

The results for these acidities are given in detail in the Experimental section. At concentrations of nitrous acid $\sim 10^{-4}$M, the total order is about two for acidities as low as 0·5M.

This new kinetic form is conveniently discussed in terms of the stoicheiometric second-order rate coefficient ($\bar{k}_2$) defined by equation (2):

$$\text{Rate} = \bar{k}_2[\text{Amine}][\text{Nitrous acid}]. \qquad (2)$$

Evidence for the constancy of $\bar{k}_2$ with different reactant concentrations is given in Table 1. The results confirm that the reaction is indeed of the first order with respect to both the amine and the nitrous acid.

The rate coefficient $\bar{k}_2$ increases rapidly with acidity, as shown in the first section of Table 2. This coefficient also increases rapidly with the concentration of sodium perchlorate (Table 2), and the latter increase is much greater than would be expected from the effect of the salt on the H_0 acidity of the medium. For instance, the reaction rate is

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* Part X, preceding paper.

[1] (*a*) Schmid and Sami, *Monatsh.*, 1955, **86**, 904; (*b*) Schmid and Essler, *ibid.*, 1959, **90**, 222; 1960, **91**, 484.

greater in M-perchloric acid containing 2M-sodium perchlorate than in 2M-perchloric acid, although the former solution is the less acidic (the values of H_0 are -0.71 and -0.78, respectively, see Appendix). Part of the catalysis by sodium perchlorate is therefore attributed to a medium effect of the kind discussed in Part IX. The plot in Fig. 1 shows that log $\bar{k}_2$ is a linear function of the salt concentration.

TABLE 1.

Diazotisation of aniline at 0°: evidence for the constancy of $\bar{k}_2$ (eq. 2) at a given acidity.

	$[HClO_4] = 3$M			$[HClO_4] = 0.5$M		
10^4 [Amine]	8	4	4	40	40	80
10^4 [Nitrous acid]	1	1	2	2	4	4
$10^2\bar{k}_2$ (mole^{-1} sec.$^{-1}$ l.)	255	262	260	2·53	2·75	2·78

The factor of ~100 between the values of $\bar{k}_2$ at the different concentrations of perchloric acid is accidental.

TABLE 2.

Diazotisation of aniline at 0°; the dependence of $\bar{k}_2$ (eq. 2) on the concentrations of perchloric acid and of sodium perchlorate.

$[HClO_4]$ (M)	0·5	1·0	1·5	2·0	2·5	3·0	
Perchloric acid alone:							
$10^2\bar{k}_2$ (mole^{-1} sec.$^{-1}$ l.)	2·53 *	8·09 *	19·6	49·0	123	260	
Perchloric acid + sodium perchlorate to ionic strength of 3·0:							
$10^2\bar{k}_2$ (mole^{-1} sec.$^{-1}$ l.)	39·8	74·5	112	161	209	260	
Perchloric acid (1·0M) + sodium perchlorate:							
$[NaClO_4]$	0	0·5	1·0	1·5	2·0	2·5	3·0
$10^2\bar{k}_2$ (mole^{-1} sec.$^{-1}$ l.)	8·09 *	15·0	24·6	44·5	74·5	134	232

* Diazotisation by the nitrous anhydride mechanism may contribute significantly to the rate of these kinetic runs.

TABLE 3.

Diazotisation of aniline at 0°: the solvent isotope effect in deuterium oxide.

$[HClO_4]$ (M)	10^4[Amine] (M)	10^4[Nitrous acid] (M)	$10^2\bar{k}_2$ (mole^{-1} sec.$^{-1}$ l.) H_2O	D_2O	$\bar{k}_2(H_2O)/\bar{k}_2(D_2O)$
1	80	1	5·6	3·2	1·74 *
2	8	1	44	26	1·69 †

Atom fraction of deuterium = * 0·92, † 0·86.

TABLE 4.

Diazotisation of aniline: variation of $\bar{k}_2$ (eq. 2) with temperature.

$[HClO_4]$ (M)	$10^2\bar{k}_2$ (mole^{-1} sec.$^{-1}$ l.) 0°	10·2°	24·6°	E_A (kcal. mole^{-1})
1	8·0	23·5	90	15·9
2	48·6	127	378	13·8
3	262	586	—	12·4

By analogy with the kinetic analysis in Part X, the catalytic effect of perchloric acid should be derived partly from a medium effect depending exponentially on the concentration of the acid and partly from acid catalysis depending on the H_0 acidity function. To isolate the dependence on acidity, the reaction rate has been studied as a function of H_0 in solutions of perchloric acid containing sufficient sodium perchlorate to bring the total ionic strength to 3·0. These results are included in Table 2 and the values of log $\bar{k}_2$ are plotted against the appropriate values of $-H_0$ (see Appendix) in Fig. 2; the slope is unity, so that $\bar{k}_2$ is proportional to h_0. Since the stoicheiometric concentration of the amine is effectively equal to the concentration of the conjugate acid, the full kinetic equation can be written as either (3) or (4):

$$\text{Rate} = k_3{}^0[\text{Ar·NH}_3{}^+][\text{HNO}_2]h_0. \qquad (3)$$

$$\text{Rate} = k_4{}^0[\text{Ar·NH}_2][\text{HNO}_2]h_0{}^2. \qquad (4)$$

The superscript zero on these rate coefficients indicates that they refer to conditions where the medium effect is approximately constant.

The distinction between this kinetic form and that reported in Part X is best seen when these results are compared with those obtained in the same way for *p*-nitroaniline.

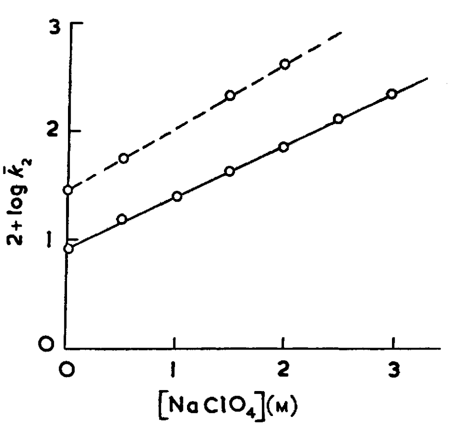

FIG. 1. Effect of sodium perchlorate on the rate coefficient $\bar{k}_2$ (eq. 2) for the diazotisation of aniline (——) and *p*-toluidine (– – –).

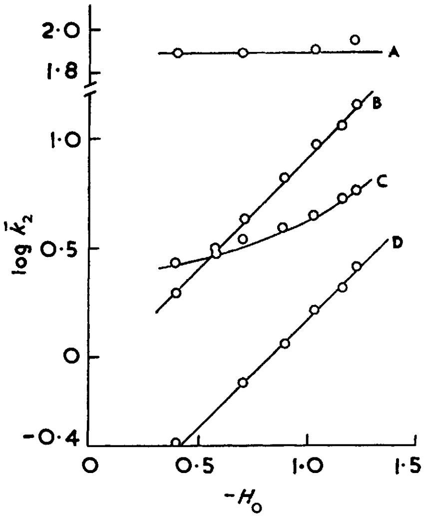

FIG. 2. Logarithmic plot of $\bar{k}_2$ (eq. 2) against $-H_0$ for perchloric acid media containing sufficient sodium perchlorate to bring the ionic strength to 3·0; (A) *p*-nitroaniline; (B) *p*-toluidine; (C) *o*-chloroaniline; (D) aniline. The straight lines B and D are drawn with a slope of unity.

A plot of $\bar{k}_2$ for the diazotisation of *p*-nitroaniline under these conditions is included in Fig. 2: the slope is about zero.

Details of the solvent isotope effect with deuterium oxide on the diazotisation of aniline according to equation (3) are given in Table 3; the reaction is a little slower in the deuterated solvent, and the isotope effect does not seem to be dependent on acidity. The variation of $\bar{k}_2$ with temperature is given in Table 4; the activation energy is clearly a function of acidity. This matter is not discussed further because of some uncertainty over the contribution of the nitrous anhydride mechanism at the lowest acidity listed in Table 4.

(2) p-*Toluidine.*—The diazotisation of this amine was studied in the same way as that of aniline and with similar results; at low concentrations of nitrous acid the reaction obeys equation (2) in concentrations of perchloric acid from 0·5 to 3·0M. The variation of $\bar{k}_2$ with the concentration of perchloric acid, with and without the presence of sodium perchlorate, is given in Table 5. The main features of these results are as follows: (1) the catalytic effect of perchloric acid on the diazotisation of *p*-toluidine is greater than that on the diazotisation of aniline, thus the ratios $\bar{k}_2(2\text{M-HClO}_4)/\bar{k}_2(1\text{M-HClO}_4)$ are 8·5 and 6·1,

respectively; (2) the catalytic effect of sodium perchlorate is also greater (Fig. 1); (3) at constant ionic strength, the slope of log $\bar{k}_2$ against $-H_0$ is unity (Fig. 2). The last result appears significant; it shows that, when the medium effect is approximately constant, the kinetic form for the diazotisation of *p*-toluidine accords with that of aniline and is accurately represented by equation (3) or (4).

(3) *o-Chloroaniline*.—The diazotisation of *o*-chloroaniline at low acidities appears to be a reaction of the free amine with the nitrous acidium ion and this reaction path at higher acidities should give the kinetic form of equation (5) (cf. Part X):

TABLE 5.

Diazotisation of *p*-toluidine at 0°: dependence of $\bar{k}_2$ (eq. 2) on the concentration of perchloric acid and of sodium perchlorate.

$[HClO_4]$ (M)	0·5	1·0	1·5	2·0	2·5	3·0
Perchloric acid alone:						
$10^2\bar{k}_2$ (mole^{-1} sec.$^{-1}$ l.)	6·25	28·5	86	245	570	1500
Perchloric acid + sodium perchlorate to ionic strength of 3·0:						
$10^2\bar{k}_2$ (mole^{-1} sec.$^{-1}$ l.)	199	427	672	985	1170	1500
Perchloric acid (1·0M) + sodium perchlorate:						
$[NaClO_4]$ (M)	0	0·5	1·5	2·0		
$10^2\bar{k}_2$ (mole^{-1} sec.$^{-1}$ l.)	28·5	58	225	427		

$$\text{Rate} = k_3{}^0[\text{Ar·NH}_2][\text{HNO}_2]h_0. \qquad (5)$$

Any incursion of the kinetic form given by equation (4) should change only the dependence on acidity, not the order with respect to the amine and the nitrous acid. As expected, the results at a given acidity always obey equation (2); some values indicating the constancy of $\bar{k}_2$ with varying concentrations of the amine and of the nitrous acid are given in Table 6.

TABLE 6.

Diazotisation of *o*-chloroaniline at 0°: evidence for the constancy of $\bar{k}_2$ (eq. 2) at a given acidity.

	$[HClO_4]$ = 3·0M			$[HClO_4]$ = 0·5M + $[NaClO_4]$ = 2·5M		
10^4[Amine]	4	2	2	2	4	2
10^4[Nitrous acid]	2	2	1	2	2	1
$10^2\bar{k}_2$ (mole^{-1} sec.$^{-1}$ l.)	590	583	577	273	277	277

TABLE 7.

Diazotisation of *o*-chloroaniline at 0°: the variation of $\bar{k}_2$ (eq. 2) with the concentration of perchloric acid at a constant ionic strength (3·0) maintained by sodium perchlorate.

$[HClO_4]$ (M)	0	0·5	0·75	1·00	1·25	1·50	2·00	2·25	2·50	3·00
h_0 *	—	2·52	3·67	5·12	6·56	7·92	11·0	12·9	14·9	17·0
$10^2\bar{k}_2$ (mole^{-1} sec.$^{-1}$ l.)	(216)	274	315	348	363	394	451	497	537	583
$10^2\bar{k}_2 - 2·16$ (mole^{-1} sec.$^{-1}$ l.)	·0	58	99	132	147	178	235	281	321	365

* See Appendix.

Values of $\bar{k}_2$ for various concentrations of perchloric acid at constant ionic strength are given in Table 7. A plot of log $\bar{k}_2$ against $-H_0$ is included in Fig. 2, the slope varies with the acidity, but at all points is intermediate between that for the diazotisation of *p*-nitroaniline and that for the diazotisation of aniline.

It is important to know whether this degree of acid catalysis arises from the sum of contributions from the kinetic terms in equations (4) and (5) or whether it is more correctly represented by some intermediate kinetic form. On the first hypothesis, the kinetics of diazotisation of *o*-chloroaniline should follow equation (6):

$$\text{Rate} = k_3{}^0[\text{Ar·NH}_2][\text{HNO}_2]h_0 + k_4{}^0[\text{Ar·NH}_2][\text{HNO}_2]h_0{}^2. \qquad (6)$$

From the relationship $[\text{Ar·NH}_2]h_0 = [\text{Ar·NH}_3{}^+]K$, where K is the thermodynamic dissociation constant of the anilinium ion, equation (6) can be written as (7):

$$\text{Rate} = (k_3{}^0K + k_4{}^0Kh_0)[\text{Ar·NH}_3{}^+][\text{HNO}_2]. \qquad (7)$$

Since the amine is almost entirely present as the conjugate acid, the comparison of equations (2) and (7) shows that at constant ionic strength, the variation of the stoicheiometric rate coefficient ($\bar{k}_2$) with acidity should follow equation (8):

$$\bar{k}_2 = k_3{}^0K + k_4{}^0Kh_0. \qquad (8)$$

A plot of $\bar{k}_2$ against h_0 should therefore be linear, with an intercept that is equal to the value of $\bar{k}_2$ for diazotisation of the free *o*-chloroaniline molecule by the nitrous acidium ion.

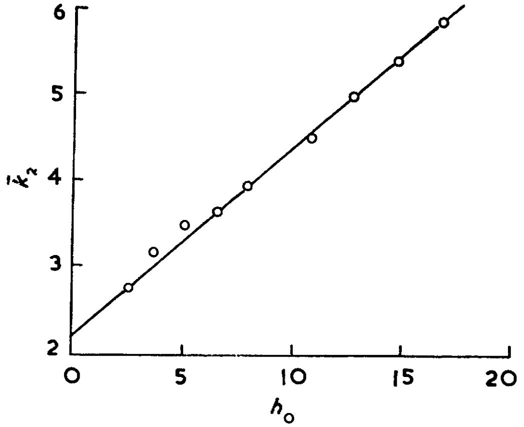

FIG. 3. Plot of $\bar{k}_2$ (eq. 2) against h_0 for the diazotisation of *o*-chloroaniline in aqueous perchloric acid containing sufficient sodium perchlorate to bring the ionic strength to 3·0.

Such a plot is shown in Fig. 3; it is linear with an intercept of 2·16 mole^{-1} sec.$^{-1}$ l., in satisfactory agreement with the value of 2·14 mole^{-1} sec.$^{-1}$ l. recorded in Part IX for the diazotisation of *o*-chloroaniline in 0·1M-perchloric acid–3·0M-sodium perchlorate. The alternative hypothesis, that the acid catalysis of the diazotisation of *o*-chloroaniline corresponds to a kinetic form intermediate between that of equation (4) and that of equation (5), would imply a non-integral order with respect to h_0 and hence a non-linear plot in Fig. 3; this is not supported by the facts. For these experimental conditions, it seems therefore that the two kinetic forms in equations (4) and (5) are sufficient to account completely for the diazotisation of *o*-chloroaniline.

If the contribution of the kinetic form given by equation (5) is subtracted from the values of $\bar{k}_2$ in Table 7, the remainder ($\bar{k}_2$ — 2·16) should be comparable with the values of $\bar{k}_2$ obtained in the diazotisation of aniline and *p*-toluidine. These differences are listed in the last line of Table 7; at each acidity they are intermediate between the values obtained for aniline and *p*-toluidine.

(4) *Interpretation of the Kinetic Equations.*—If the diazotisation of these amines is studied in aqueous perchloric acid containing no sodium perchlorate, the form of the acid catalysis is extremely complex; the slopes of log $\bar{k}_2$ against $-H_0$ are different for different amines and do not approximate to integral values. The kinetics of diazotisation of a number of amines over this acidity range have been analysed by Schmid and Essler [1b] using a kinetic equation containing four terms, three of which are of first-order with

respect to the amine and the nitrous acid and differ only in the effective order with respect to the perchloric acid. It is not surprising that the acid catalysis can be represented in this way, for this approach is equivalent to approximating to an arbitrary function by taking the first three terms of a power series in the independent variable. The agreement then obtained does not imply that the individual kinetic terms have physical significance as independent reaction paths, and since two of the suggested mechanisms appear to require nitrosation by nitrosonium perchlorate their physical reality seems to us to be doubtful.* The inadequacy of this type of analysis can be seen from the large catalytic effect of sodium perchlorate. None of the mechanisms suggested by Schmid and his co-workers [1] involves an order with respect to perchlorate ions of more than unity, yet, in the diazotisation of aniline in M-perchloric acid, doubling the concentration of sodium perchlorate from 1·5 to 3·0M multiplies the reaction rate by a factor of more than five. The increase in the total concentration of perchlorate ions is by a factor of only 1·7.

We consider that the type of kinetic analysis proposed by Schmid and Essler [1b] is misleading because it does not take account of the large medium effect on the rate of diazotisation and of the fact that this medium effect appears to depend exponentially on the electrolyte concentration. The assumption that perchloric acid and sodium perchlorate have similar medium effects enables the dependence of the reaction rate on the acidity function to be observed directly, and the kinetic form of the diazotisation of aniline is then reduced to the single term in equation (4). The kinetics of diazotisation of the other amines studied are simplified in the same way and the complete account of the acid catalysis in all the reactions studied in this and the preceding paper requires only the kinetic terms in equations (4) and (5), both of which lead to integral slopes of log $\bar{k}_2{}^0$ against $-H_0$. This simplification is unlikely to be an accident; it suggests that, over this range of anions and conditions, only two independent, acid-catalysed, mechanisms of diazotisation need be considered. One of these mechanisms was identified in Part X as the reaction of the free amine with the nitrous acidium ion; the other, associated with equation (4), remains to be determined here.

The kinetic form of equation (4) has been observed recently in the *N*-nitrosation of *N*-methylaniline over the same acidity range; [3] this indicates that the *N*-nitrosation stage of diazotisation is still rate-determining. The simplest interpretation of equation (4) then involves a rate-determining reaction between the molecular amine and the nitrosonium ion. The contribution of this reaction path should increase rapidly with acidity and could lead to the observed kinetic form, for the concentration of the nitrosonium ion should be proportional [4] to $[HNO_2]j_0$ † and, in aqueous perchloric acid, j_0 is approximately proportional to $h_0{}^2$.

Nevertheless, it seems that this interpretation cannot be sustained. The fact that the kinetic form of equation (4) first becomes predominant with the more basic amines provides a hint that this interpretation is incorrect, for diazotisation through the nitrosonium ion should be detected most easily with the least basic amines, since, of all nitrosating agents, the nitrosonium ion should discriminate least between different nucleophiles. Further evidence comes from substituent effects on the rate of diazotisation according to equation (4).

The dependence of the rate of diazotisation on the basicity of the amine and on the reactivity of the nitrosating agent is now known in considerable detail.[6] The rate of

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* There is no evidence for covalent nitrosonium perchlorate, either in the solid state or in solution.[2]

† The acidity function nomenclature follows that of ref. 5. Other authors have used the symbol H_R or C_0 for the acidity function J_0.

[2] Angus and Leckie, *Proc. Roy. Soc.*, 1935, *A*, **150**, 615.

[3] Kalatzis and Ridd, unpublished results.

[4] Deno, Berkheimer, Evans, and Peterson, *J. Amer. Chem. Soc.*, 1959, **81**, 2344; note correction, p. 6535.

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

[6] Ridd, *Quart. Rev.*, 1961, **15**, 418.

diazotisation by nitrous anhydride depends considerably on the basicity of the amine; thus, the aniline molecule is more reactive than the *p*-chloroaniline molecule by a factor of 3·4. As the reactivity of the nitrosating agent increases, this discrimination decreases, and for diazotisation by nitrosyl chloride the factor above is reduced to 1·4. For diazotisation by the nitrous acidium ion (and presumably also for that by the nitrosonium ion) the discrimination between all but the feebly basic amines is negligible.[7] At a given acidity, the relative rates of diazotisation are proportional to the relative amounts of free amine in the solution.

The figures below compare the relative rates of diazotisation in 3·0M-perchloric acid [where equation (4) is obeyed] with the relative concentrations of free amine in the solutions, as calculated from the thermodynamic dissociation constants. There is no correspondence whatever. If these reaction rates are to be attributed to the reaction of the free amine with *any* nitrosating agent, it is necessary to assume that the *p*-toluidine molecule is 17 times as reactive as aniline and 800 times as reactive as *o*-chloroaniline. No known nitrosating agent discriminates in this way between different amine molecules.

	p-Toluidine	Aniline	*o*-Chloroaniline
Rel. rate (Tables 2, 5, 7)	1	0·17	0·24 †
Rel. [$Ar{\cdot}NH_2$]	1	3	200

† The contribution of diazotisation according to equation (5) is allowed for as described in section (3).

This difficulty cannot be overcome by assuming that the nitrosonium ion is a particularly weak nitrosating agent. The approximate concentration of the nitrosonium ion in these solutions can be calculated from the J_0 function and the relevant equilibrium constant;[4] this concentration is barely sufficient to account for the observed reaction rate even if reaction is assumed to occur on encounter with the amine molecules. The overall reaction rate is far too high to be explained in this way if the nitrosation is assumed to require a considerable activation energy. It is difficult to conceive any other nitrosating agent which could satisfy the requirements above, and it seems therefore that equation (4) cannot be interpreted as the rate-determining nitrosation of the free amine.

In comparison, the interpretation of equation (4) as the direct nitrosation of the protonated amine has a number of advantages. It explains why this kinetic form first becomes predominant with the more basic amines, for in these the contribution of diazotisation through the free amine is relatively low. It also explains why equations (4) and (5) differ by one power of h_0, for the transition states corresponding to the nitrosation of the protonated amine and the free amine differ in composition by a single proton. The substituent effects still present some difficulty, but substituent effects for the direct nitrosation of the protonated amines are difficult to predict and the rather similar reactivity of the three conjugate acids (as indicated by the relative reaction rates above) is not inconsistent with any theoretical principles.

Probably the main weakness of this interpretation comes from the lack of any other evidence of bimolecular electrophilic substitution at a positive nitrogen atom. Although the details of this transition state are still uncertain, the following account indicates why this unusual reaction path could be important in this system.

The key factor concerns the possibility of proton loss from the conjugate acid during interaction with the electrophile. The protonation of aniline is probably an encounter reaction with a rate coefficient of $\sim 3 \times 10^{10}$ mole^{-1} sec.$^{-1}$ l.,[8] and, from the equilibrium constant of $2{\cdot}6 \times 10^{-5}$, it follows that the rate coefficient for proton loss from the anilinium ion in dilute mineral acid is $\sim 10^{6}$ sec.$^{-1}$. This implies a half-life for the conjugate acid of aniline of $\sim 10^{-6}$ sec.—a time greatly exceeding the time of molecular encounters in solution.

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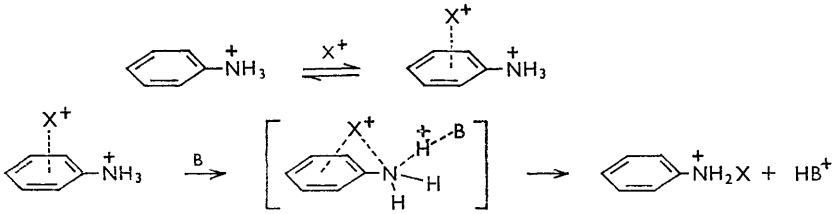
[7] Larkworthy, *J.*, 1959, 3304.

[8] Cf. Bell, *Quart. Rev.*, 1959, **13**, 169.

However, the aromatic ring of the anilinium ion provides a site which can interact with an electrophile and prolong the time of encounter; such interaction would also increase the acidity of the conjugate acid. Thus the interaction could greatly increase the probability of proton loss during the encounter. If the reaction of the electrophile with the free amine does not require an activation energy, then proton loss during the encounter should be automatically followed by reaction with the electrophile. Such a reaction path would have the kinetic characteristics of an attack on the conjugate acid * but could give the same products as an attack on the free amine. As shown below, this reaction path in some ways resembles a saturated electrophilic rearrangement,[9] the initial interaction of the electrophile with the aromatic ring taking the place of one σ-bond. The range of reaction paths of this kind must be limited at low acidities by the incursion of reaction through the free amine and at high acidities by the low mobility of the N–H protons.



It seems likely that such a process may occur with the diazotisation of aniline under the conditions described in this paper. The lack of discrimination shown by the nitrous acidium ion in reaction with the nitrogen atom of amine molecules suggests that the activation energy of this reaction is very low; the reaction path above would therefore have the kinetic form of attack on the conjugate acid. With more reactive electrophiles, this mechanism would be expected to lead to some substitution in the aromatic ring. In deuterated solvents, the concentration of the nitrous acidium ion is probably increased by a factor of about two (see Part X), but the rate of loss of a deuteron from the amino-nitrogen atom is probably less than that of a proton by a somewhat larger factor, so it is reasonable that the reaction rate should be slower (Table 3). The role of the aromatic π-electrons in stabilising the transition state receives support from the apparent absence of the kinetic form of equation (4) in the reaction of aliphatic amines, and of the ethyl ester of glycine, with nitrous acid.[3] The range of this new mechanism of nitrosation is being studied further.

The mechanism proposed above is not a return to the old theory that the protonation of amines is necessary before diazotisation can occur. Reaction should occur much more readily through the free amine, but, if the amine is almost entirely protonated, the interaction of the nitrosating agent with the protonated amine can apparently become kinetically significant.

EXPERIMENTAL

The experimental procedure followed that described previously.[10,11] Tables 8 and 9 illustrate the constancy of $\bar{k}_2$ (eq. 2) throughout a single kinetic run in the diazotisation of *o*-chloroaniline and the dependence of the half-life on the reactant concentration in the diazotisation of aniline.

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* If the reaction of the electrophile with the free amine is relatively slow, so that the proton transfers are reversible, the kinetic form would be indistinguishable from an attack on the free amine.

[9] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 523.

[10] Part IX of this series and references there quoted.

[11] Challis, Ph.D. Thesis, London, 1960.

TABLE 8.

Diazotisation of *o*-chloroaniline at 0°: details of a typical kinetic run (No. 265).

$[\mathrm{HClO_4}] = 3{\cdot}0\,\mathrm{M}$; $[\text{Amine}] = 2 \times 10^{-4}\,\mathrm{M}$; $[\text{Nitrous acid}] = 2 \times 10^{-4}\,\mathrm{M}$.

Time (min.)	$10^4[\mathrm{Ar{\cdot}N_2^+}]$ (M)	k_2 * (mole^{-1} sec.$^{-1}$ l.)	Time (min.)	$10^4[\mathrm{Ar{\cdot}N_2^+}]$ (M)	k_2 * (mole^{-1} sec.$^{-1}$ l.)
1·10	0·207	—	16·63	1·08	5·74
2·03	0·306	5·7	23·47	1·26	5·78
3·97	0·490	6·18	34·18	1·40	5·56
6·92	0·691	5·90	50·92	1·53	—
11·10	0·905	5·92	∞	1·92	—

* Integrated from the time of the first reading.

TABLE 9.

Diazotisation of aniline at 0°: variation of half-life (min.) with the initial concentration of the reactants.

$[\text{Amine}] = [\text{Nitrous acid}] = a$.

10^4a:	100	80	40	20	10	8	4	2	1
$[\mathrm{HClO_4}]$ (M)									
0·5	9·6	14·9	57·0	190	—	—	—	—	—
1·0	—	15·7	44·0	114	—	—	—	—	—
1·5	—	8·2	19·8	44·0	—	—	—	—	—
2·0	—	—	—	—	35·6	43·8	90·5	—	—
3·0	—	—	—	—	—	—	16·0	25·5	58·0

The calculated values of the reaction order are given in the text.

APPENDIX

Values of H_0 in Solutions of Perchloric Acid containing Sodium Perchlorate.—Some information concerning the effect of sodium perchlorate on the values of H_0 in aqueous perchloric acid is already available,[12] but unfortunately those results refer to higher ionic strengths than those used in the kinetic studies of diazotisation. Results at lower ionic strengths were therefore determined by conventional means, by using *o*-nitroaniline as the indicator. The indicator ratio was determined from the optical densities of the solution at several wavelengths near that of the absorption maximum of the indicator base and the values of H_0 were calculated from the indicator ratio with a pK_a of $-0{\cdot}29$ for the *o*-nitroanilinium ion. Further experimental details are given elsewhere [11] and the results are collected in Table 10.

Reference has already been made (Part X) to the fact that perchloric acid and sodium perchlorate, in concentrations up to 3M, have a similar effect on the deviation of log h_0 from log $C_{\mathrm{H^+}}$. Some results illustrating this are annexed, for the addition of either sodium perchlorate or further perchloric acid to M-perchloric acid.

Concn. of electrolyte ($\mathrm{HClO_4}$ or $\mathrm{NaClO_4}$) added to M-perchloric acid	0	0·5	1·0	1·5	2·0
log h_0 − log $C_{\mathrm{H^+}}$ (added $\mathrm{HClO_4}$)	0·25	0·35	0·48	0·61	0·75
log h_0 − log $C_{\mathrm{H^+}}$ (added $\mathrm{NaClO_4}$)	0·25	0·38	0·49	0·60	0·71

Hence, when the ionic strengths of solutions of perchloric acid are brought to 3·0 by the addition of sodium perchlorate, the values of h_0 should be approximately proportional to those of $C_{\mathrm{H^+}}$. The results in Table 7 show that this is correct, but, at higher ionic strengths, this simple relation no longer applies.[12]

TABLE 10.

Values of $-H_0$ in aqueous solutions of perchloric acid containing sodium perchlorate at 25°.

$[\mathrm{NaClO_4}]$ (M)	0 *	0·5	1·0	1·5	2·0	2·5
$[\mathrm{HClO_4}]$ (M)						
0·5	−0·110	−0·018	0·085	0·185	0·302	0·402
1·0	0·250	0·383	0·495	0·603	0·709	0·846
1·5	0·530	—	—	0·899		
2·0	0·780	—	1·042			
2·5	1·01	1·172				
3·0	1·23					

* Taken in part from ref. 5.

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[12] Harbottle, *J. Amer. Chem. Soc.*, 1951, **73**, 4024.

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