# 998. *Nitrosation, Diazotisation, and Deamination. Part IX.* The Influence of Neutral Salts on the Kinetics of Diazotisation.*

By B. C. CHALLIS and J. H. RIDD.

In an extension of earlier kinetic studies of diazotisation to more acidic media, the effect of large concentrations of neutral salts (mainly perchlorates and nitrates) on the kinetics of diazotisation has first been examined at low acidities. Most of the salts have a strong accelerative effect which appears to be derived jointly from the anion and the cation, and to influence both the acid-catalysed and the uncatalysed mechanism of diazotisation (the latter involves nitrous anhydride as an intermediate). For perchlorates and nitrates, the main part of the catalysis is attributed to a medium effect, not to the reaction of the anions ($X^-$) with nitrous acid to form new nitrosating agents (NOX).

THE kinetics and mechanisms of diazotisation in dilute solutions of mineral acids ($[H^+] \leqslant 0{\cdot}5$M) have already been described,[1,2] and the present group of papers is concerned with the extension of this work to hydrogen-ion concentrations of about 3M. The first kinetic

---

* Part VIII, *J.*, 1959, 3304.

[1] Hughes, Ingold, and Ridd, *J.*, 1958, 58, and following papers.

[2] Larkworthy, *J.*, 1959, 3116, 3304.

studies of diazotisation in this range of acidity revealed a very complex form of acid catalysis,[3,4] but a knowledge of related salt effects has enabled us to analyse this catalysis into the sum of contributions from two independent reaction paths. This paper is concerned with the catalytic effect of neutral salts; the following two papers outline the two new kinetic forms. The full details of the work at still higher acidities will be offered shortly.[5]

(1) *Salt Effects on Hydrogen-ion-catalysed Diazotisation.*—This mechanism of diazotisation has the kinetic form of equation (1) and has been interpreted as the reaction of the free amine with the nitrous acidium ion.[1] In this equation the concentration terms refer to the exact molecular species indicated within the brackets. However it is convenient

$$\text{Rate} = k_3[\text{H}^+][\text{Ar·NH}_2][\text{HNO}_2] \qquad (1)$$

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

to report the salt effects in terms of the stoicheiometric * second-order rate-coefficient, $\bar{k}_2$, defined by equation (2). At the acidities used, the nitrous acid is mainly present as molecular $HNO_2$ and the amines are mainly present as their conjugate acids; $\bar{k}_2$ and $k_3$ are therefore related by $k_3K = \bar{k}_2$ where $K$ is the dissociation constant of the substituted anilinium ion.

The effect of ionised perchlorates on the rate of diazotisation of *o*-chloroaniline and *p*-nitroaniline at acidities where equation (1) is obeyed is shown in Table 1. Both reactions are strongly accelerated by the added salts and, as shown in Fig. 1, the values of log $\bar{k}_2$ are linear functions of the salt concentration. The salt effect can therefore be expressed by equation (3), where $[ClO_4^-]$ is the concentration of perchlorate ions derived from the salt and where $m$ depends on the cation present.

TABLE 1.

Effect of ionised perchlorates on the rate of diazotisation of *o*-chloroaniline and *p*-nitroaniline in dilute perchloric acid at 0° ($\bar{k}_2$ in l. mole$^{-1}$ sec.$^{-1}$).

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| (1) *p*-Nitroaniline * in 0·5M-$HClO_4$. | | | | | | | | | |
| $[NaClO_4]$ ...... | 0 | 0·5 | 1·5 | 2·5 | | | | | |
| $\bar{k}_2$ (eq. 2) ...... | 16·1 | 22·2 | 43·0 | 80·0 | | | | | |
| (2) *o*-Chloroaniline † in 0·1M-$HClO_4$. | | | | | | | | | |
| $[NaClO_4]$ ...... | 0 | 0·5 | 1·0 | 1·5 | 2·0 | 2·5 | 3·0 | 4·0 | |
| $\bar{k}_2$ (eq. 2) ...... | 0·326 | 0·497 | 0·647 | 0·880 | 1·18 | 1·62 | 2·14 | 3·51 | |
| (3) *o*-Chloroaniline † in 0·091M-$HClO_4$. | | | | | | | | | |
| (*a*) $[LiClO_4]$ ...... | 0 | 0·5 | 1·0 | 1·5 | 2·0 | 2·5 | | | |
| $\bar{k}_2$ (eq. 2) ...... | 0·320 | 0·511 | 0·724 | 1·05 | 1·51 | 2·22 | | | |
| (*b*) $[Mg(ClO_4)_2]$ ... | 0 | 0·166 | 0·250 | 0·408 | 0·500 | 0·750 | 0·909 | 1·00 | 1·212 |
| $\bar{k}_2$ (eq. 2) ...... | 0·320 | 0·437 | 0·501 | 0·597 | 0·700 | 0·969 | 1·08 | 1·45 | 1·94 |

* Initial concns.: [Amine] ~5 × $10^{-5}$M; [Nitrous acid] ~3 × $10^{-5}$M.
† Initial concns.: [Amine] ~$10^{-3}$ — $10^{-4}$M; [Nitrous acid] ~$10^{-4}$M.

$$\log \bar{k}_2 = \log \bar{k}_2^{\circ} + m[\text{ClO}_4^-]. \qquad (3)$$

The values of $m$ for *o*-chloroaniline are: $LiClO_4$ 0·33, $NaClO_4$ 0·27, and $Mg(ClO_4)_2$ 0·31; and for *p*-nitroaniline: $NaClO_4$ 0·28.

The influence of lithium, sodium, and magnesium nitrates on the rate of diazotisation of *o*-chloroaniline in dilute perchloric acid is shown in Table 2; the relative catalytic

---

* We retain the convention that a bar over a rate-coefficient indicates that it is calculated with respect to stoicheiometric concentrations and we indicate these concentrations by writing out the name of the species concerned within the concentration brackets.

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

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

[5] Cf. Challis and Ridd, *Proc. Chem. Soc.*, 1960, 245.

effects lie in the same order as for the corresponding perchlorates, but, for the nitrates, the plots in Fig. 2 show that the values of log $\bar{k}_2$ are not a linear function of the salt concentration. The form of the variation from a linear plot would be consistent with the presence of an additional catalytic effect depending directly on the nitrate-ion concentration, but it is not possible to obtain a satisfactory fit for all three nitrates by adding such a term (with a single proportionality constant) to the linear catalytic form exemplified by equation (3).

TABLE 2.

Effect of ionised nitrates on the rate of diazotisation of *o*-chloroaniline in dilute perchloric acid * at 0°.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $[LiNO_3]$ | 0 | 0·47 | 0·94 | 1·41 | 1·88 | 2·83 | |
| $\bar{k}_2$ (eq. 2) | 0·320 | 0·651 | 1·01 | 1·51 | 2·07 | 4·02 | |
| $[NaNO_3]$ | 0 | 0·5 | 1·0 | 1·5 | 2·0 | 2·5 | 3·0 |
| $\bar{k}_2$ (eq. 2) | 0·320 | 0·608 | 0·892 | 1·24 | 1·60 | 2·04 | 2·56 |
| $[Mg(NO_3)_2]$ | 0 | 0·24 | 0·48 | 0·73 | 0·97 | 1·20 | 1·45 |
| $\bar{k}_2$ (eq. 2) | 0·320 | 0·632 | 0·994 | 1·45 | 2·07 | 2·74 | 4·04 |

* $[HClO_4]$ = 0·091M. Reactant concns.: [Amine] ~$10^{-3}$ – $10^{-4}$M; [Nitrous acid] ~ $10^{-4}$M. $\bar{k}_2$ in l. mole$^{-1}$ sec.$^{-1}$.

TABLE 3.

Evidence for the constancy of $\bar{k}_2$ (eq. (2) with varying reactant concentrations in the diazotisation of *p*-nitroaniline in 0·5M-perchloric acid containing sodium perchlorate at 0°.

| | $[NaClO_4]$ = 0·5M | | | $[NaClO_4]$ = 1·5M | | |
|---|---|---|---|---|---|---|
| $10^5$ [Amine] (M) | 6·3 | 6·3 | 3·15 | 6·3 | 6·3 | 12·6 |
| $10^5$ [Nitrous acid] (M) | 3·15 | 6·3 | 6·3 | 3·15 | 6·3 | 3·15 |
| $\bar{k}_2$ (l. mole$^{-1}$ sec.$^{-1}$) | 22·2 | 23·3 | 22·2 | 43·0 | 43·5 | 43·1 |

The catalytic effects of two other salts on the diazotisation of *o*-chloroaniline have also been examined. Studies of diazotisation in dilute nitric acid have shown that the catalytic effect of M-tetramethylammonium nitrate is about equal to that of 0·4M-sodium nitrate; for univalent cations the catalytic order is therefore $Li^+ > Na^+ > Me_4N^+$. The catalytic effect of sodium toluene-*p*-sulphonate is also rather low; in 0·091M-perchloric acid, a 0·5M-solution of the salt increases the reaction rate by about 20%.

The order with respect to nitrous acid in the presence of added salts has been checked because some salts are known to increase the rate of formation of nitrous anhydride (see following section) and this nitrosating agent provides an additional reaction path for diazotisation. However, the values of the initial reaction rates, of the total reaction order, and of the rate coefficients all indicate that there is no significant incursion of the nitrous anhydride mechanism. One group of results indicating this is given in Table 3; the constancy of $\bar{k}_2$ when the relative reactant concentrations are changed confirms that the kinetic form obeys equation (2) in the presence of added salts and hence that the order with respect to nitrous acid remains unity.

(2) *Salt Effects on the Formation of Nitrous Anhydride.*—The formation of nitrous anhydride in aqueous solution has been considered as the reaction of nitrite ions with the nitrous acidium ion; it is therefore of interest to compare the salt effects on this nitrosation with those on the direct nitrosation of amines.

The diazotisation of aniline in feebly acidic solutions occurs predominantly by the formation of nitrous anhydride, thus:

$$\text{Stage 1: } 2HNO_2 \underset{v_{-1}}{\overset{v_1}{\rightleftharpoons}} N_2O_3 + H_2O$$

$$\text{Stages 2 and 3: } Ar{\cdot}NH_2 \xrightarrow[v_2]{N_2O_3} Ar{\cdot}NH{\cdot}NO \xrightarrow[\text{Fast}]{} ArN_2^+.$$

When stage (1) is rate-determining the kinetic form is as equation (4): when stage (2) is rate-determining the kinetic form is as equation (5).

$$\text{Rate} = k_2[\mathrm{HNO_2}]^2 \qquad (4)$$

$$\text{Rate} = k_3[\mathrm{Ph{\cdot}NH_2}][\mathrm{HNO_2}]^2 \qquad (5)$$

However, it is convenient to report the salt effects in terms of a stoicheiometric second-order rate-coefficient $\bar{k}_2$ defined by equation (6):

$$\text{Rate} = \bar{k}_2[\text{Nitrous acid}]^2; \qquad (6)$$

the transition in the kinetic form from equation (4) to equation (5) is then marked by the increasing dependence of $\bar{k}_2$ on the amine concentration.

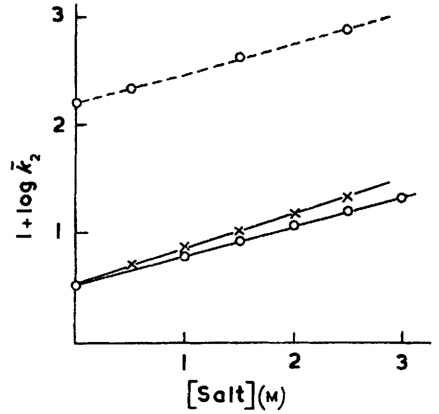

FIG. 1. Effect of ionised perchlorates on the rate of diazotisation of *o*-chloroaniline (solid line) and *p*-nitroaniline (broken line). (o) $NaClO_4$; (×) $LiClO_4$.

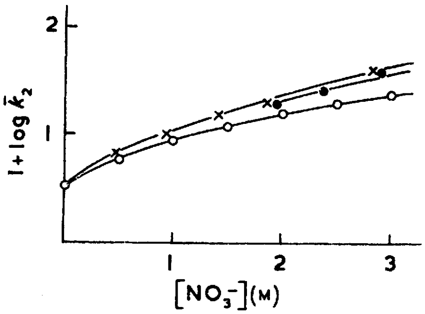

FIG. 2. Effect of ionised nitrates on the rate of diazotisation of *o*-chloroaniline. (o) $NaNO_3$; (●) $Mg(NO_3)_2$; (×) $LiNO_3$.

The variation of $\bar{k}_2$ with the concentration of sodium perchlorate is listed in Table 4 for conditions where, in the absence of sodium perchlorate, the rate of formation of nitrous anhydride is largely rate-determining. Results are given for two amine concentrations and also for the effective order ($n$) with respect to the amine; this quantity is calculated for a given concentration of sodium perchlorate from equation (7);

TABLE 4.

Effect of sodium perchlorate on the rate of diazotisation of aniline at 0°.

[$HClO_4$] = 0·02M; [Nitrous acid] = 0·001M.

| | $\bar{k}_2$ (eq. 6) (l. mole$^{-1}$ sec.$^{-1}$) | | |
|---|---|---|---|
| [$NaClO_4$] (M) | [Amine] = 0·01M | [Amine] = 0·02M | Order ($n$) |
| 0 | 1·13 | 1·34 | 0·25 |
| 0·5 | 1·77 | 2·14 | 0·28 |
| 1·0 | 2·17 | 2·97 | 0·46 |
| 2·0 | 4·15 | 6·35 | 0·62 |
| 3·0 | 6·43 | 10·95 | 0·77 |

$$\log \bar{k}_2 = \text{Constant} + n \log [\text{Amine}]. \qquad (7)$$

The results show that the presence of sodium perchlorate increases both the value of $\bar{k}_2$ and that of $n$.

The initial rates listed in Table 5 show that the order with respect to the nitrous acid remains even in the presence of the sodium perchlorate; the increase in the value of $\bar{k}_2$ must therefore arise from an increase in the rate of formation of nitrous anhydride ($v_1$). The increase in $n$ can only arise from an increase in the ratio $v_{-1}/v_2$; this presumably occurs by an increase in $v_{-1}$. Thus sodium perchlorate appears to increase both the rate of formation and the rate of hydrolysis of nitrous anhydride.

The dependence of $n$ on the concentration of sodium perchlorate restricts the useful comparisons of the $\bar{k}_2$ values in Tables 1 and 4 to the lower salt concentrations. Such a comparison then indicates that sodium perchlorate has a slightly greater effect on the nitrosation of nitrite ions than on the nitrosation of amines; the presence of 0·5N-sodium perchlorate increases the rate of formation of nitrous anhydride by 60% and increases the rate of diazotisation of *o*-chloroaniline by 52%. Nevertheless the similarity between these results suggests that they should be considered together as examples of a general salt effect on the acid-catalysed nitrosation of nucleophilic reagents.

TABLE 5.

Dependence of the initial rate on the concentration of nitrous acid in the diazotisation of aniline ([Amine] = 0·02M) in 0·02M-perchloric acid at 0°.

| $[NaClO_4]$ = 0·5M | | $[NaClO_4]$ = 3·0M | |
|---|---|---|---|
| $10^3$ [Nitrous acid] | Initial rate ($10^{-6}$ mole l.$^{-1}$ sec.$^{-1}$) | $10^3$ [Nitrous acid] | Initial rate ($10^{-6}$ mole l.$^{-1}$ sec.$^{-1}$) |
| 0·5 | 0·52 | 0·5 | 1·9 |
| 1·0 | 1·90 | 1·0 | 7·5 |

(3) *Interpretation of the Catalysis.*—Other studies have shown that some salts, notably the alkali halides, catalyse diazotisation by the formation of new nitrosating agents (*e.g.*, NOBr).[1,6] The catalytic effect of bromide ions can be observed with salt concentrations as low as $10^{-4}$M. However, the catalytic effect of perchlorates and nitrates reported above is of a very different magnitude, and for the several reasons outlined below seems to require a different explanation. Thus the halide-ion catalysis depends linearly on the concentration of salt, while the perchlorate-ion catalysis depends exponentially on the concentration of salt [cf. eq. (3)]. The greater catalytic effect of bromide than of chloride ions can be simply understood from the difference in the equilibrium concentrations of the corresponding nitrosyl halides:[7] in contrast, 3M-solutions of sodium nitrate and perchlorate have almost identical catalytic effects, although $N_2O_4$ is a well-known covalent species and nitrosyl perchlorate has not yet been obtained as a covalent species under any conditions.[8] There is no evidence that halide-ion catalysis depends on the nature of the cation, but catalysis by perchlorates and nitrates is clearly dependent on this factor. These differences have been stressed because other workers have explained the related catalytic effect of perchlorate ions from aqueous perchloric acid in terms of nitrosation by nitrosyl perchlorate.[4,9] It seems unlikely that this process can be significant under our conditions, although the slightly different kinetic form observed with the catalysis by nitrate ions is consistent with a small contribution from nitrosation by dinitrogen tetroxide.

Comparison with acidity-function measurements shows that the catalytic effect of sodium perchlorate cannot be derived from the effect of the salt on the $H_0$ acidity of the medium. The presence of 3M-sodium perchlorate in 0·1M-perchloric acid increases the acidity of the medium by 0·6 $H_0$ unit (cf. Appendix to Part XI), and this change in acidity would increase $\bar{k}_2$ by about 8% (cf. Part XI). In comparison, the catalytic effect of sodium perchlorate at this concentration increases $\bar{k}_2$ by over 1000%. Primary salt

---

[6] Schmid, *Z. Electrochem.*, 1937, **43**, 626.

[7] Schmid and Hallaba, *Monatsh.*, 1956, **87**, 560; Schmid and Fouad, *ibid.*, 1957, **88**, 631; Schmid and Essler, *ibid.*, p. 1110.

[8] Cf. Angus and Leckie, *Proc. Roy. Soc.*, 1935, *A*, **150**, 615; *Trans. Faraday Soc.*, 1935, **31**, 958.

[9] Schmid and Essler, *Monatsh.*, 1960, **91**, 484.

effects depending on differences between the charges of the reactants and the transition state should also be unimportant, for, in the nitrosation of amines, both the reactants and the transition state have a unit positive charge. The reaction of a nitrite ion with a nitrous acidium ion involves a loss of charge, but this should not be kinetically significant in terms of the Brönsted equation because the bulk of the nitrous acid is present as molecular $HNO_2$. Hence, both the initial state of the reactants and the transition state have zero charge.

These arguments eliminate the simpler explanations usually given for catalysis by added salts. Of the remaining interpretations, we consider that the exponential form of the catalysis by added perchlorates is more consistent with a medium effect on diazotisation by the nitrous acidium ion than with the incursion of any new reaction path. Electrolytes could give rise to such a medium effect either by facilitating the loss of water in the transition state (a primary salt effect) or by increasing the equilibrium concentration of the nitrous acidium ion (a secondary salt effect). For the purpose of the kinetic analysis in the two following papers, the exact source of this medium effect is immaterial; however, from other considerations, it seems probable that the increase in the equilibrium concentration of the nitrous acidium ion is the more important factor. The lack of discrimination in the reactions of the nitrous acidium ion with a number of nucleophiles [10] and the analogy with the reactions of the nitrosyl halides [10] suggest that the nitrosation of the substrates discussed above by the nitrous acidium ion approximates to a diffusion-controlled process; such a reaction should be more sensitive to changes in the concentrations of the reactants than to a primary salt effect on the stability of the " transition state."

This argument implies that salt effects on the equilibrium concentration of the nitrosating agent are greater than those on the $H_0$ function, so that the increase in the concentration of the nitrosating agent more than outweighs the decrease in the concentration of the free amine. If the nitrosating agent were the nitrosonium ion, then this difference would be expected, for the equilibrium concentration of the nitrosonium ion should be determined by the $J_0$ function [11] and should therefore be very sensitive to the composition of the medium. The suggestion that this kind of medium dependence applies in part to the equilibrium concentration of the nitrous acidium ion is not consistent with the original theory of acidity functions,[11] but it should be noted that several examples are now available where the protonation of neutral substrates deviates in this way from the $H_0$ function.[12] The formal similarity of the hydrated nitrosonium ion with the nitrous acidium ion supports the view that medium effects on the two equilibria may be similar. At intermediate and high acidities, it may therefore be unprofitable to stress the mechanistic distinction between reactions of the nitrous acidium ion and those of the nitrosonium ion, although, at low acidities, the slow rate of oxygen exchange between nitrous acid and water is sufficient to rule out the nitrosonium ion as an effective nitrosating agent.[10] The duality of mechanism outlined in the following papers depends on equilibria involving the amine, not on this kind of distinction in the nitrosating agent concerned.

*Experimental.—Materials.* Purification of the amines and the sodium nitrite has been described.[1,2] Great care had to be taken over the purification of the salts because of the presence of halide ions and nitrite ions as impurities. Sodium perchlorate was prepared from " AnalaR " sodium hydroxide and " AnalaR " perchloric acid; the salt was recrystallised from water and dried at 140°. The other perchlorates and the nitrates were obtained as reagent-grade chemicals and were repeatedly recrystallised from water until free from halide and nitrite ions, respectively. The perchlorates and nitrates of lithium and sodium were dried and used as the anhydrous salts; the other salts were weighed as their hydrates. Stock solutions of these salts ($\sim$6M) were prepared and the concentrations of the perchlorate and nitrate ions were checked by gravimetric analysis with " nitron " ($C_{20}H_{16}N_4$).

---

[10] Ridd, *Quart. Rev.*, 1961, **15**, 418.
[11] Paul and Long, *Chem. Rev.*, 1957, **57**, 1.
[12] Ridd, *Ann. Reports*, 1961, **58**, 153.

TABLE 6.

Diazotisation of *o*-chloroaniline in aqueous perchloric acid (0·099M) containing sodium perchlorate (1·5M) at 0°.

[Amine] = 7·27 × $10^{-4}$M; [Nitrous acid] = 0·91 × $10^{-4}$M.

| Time (min.) | Reaction (%) | $k_2$ (l. mole$^{-1}$ sec.$^{-1}$) | Time (min.) | Reaction (%) | $k_2$ (l. mole$^{-1}$ sec.$^{-1}$) |
|---|---|---|---|---|---|
| 1·22 | 6·5 | — | 15·05 | 44·4 | 0·884 |
| 2·18 | 9·9 | 0·880 | 20·08 | 53·4 | 0·880 |
| 4·22 | 16·6 | 0·860 | 30·00 | 67·0 | 0·880 |
| 6·95 | 25·1 | 0·890 | 45·50 | 80·0 | 0·854 |
| 11·03 | 35·2 | 0·925 | ∞ | 98·0 | — |

*Kinetic runs.* These were carried out as previously described,[1,2] except for the substitution of a Unicam S.P. 500 spectrophotometer for the Hilger Spekker instrument. An example of a typical kinetic run is set out in Table 6 and illustrates the calculation of one of the rate coefficients listed in Table 1.

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

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