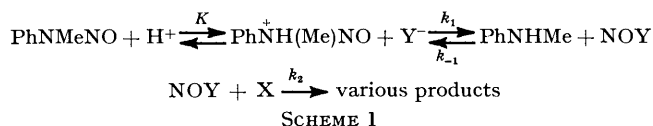


Kinetics and Mechanism of the Diazotisation of Substituted Anilines by Nitrosyl Halides. The Question of Diffusion-controlled Reactions

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Rate measurements have been carried out in water at 25 °C, using a stopped-flow spectrophotometer, on the diazotisation of a number of substituted anilines, under conditions where the effective nitrosating agents are thought to be nitrosyl chloride and nitrosyl bromide. Analysis of the rate data yielded values of k_2 , the true rate coefficient for the *N*-nitrosation step. For both nitrosyl chloride and nitrosyl bromide reactions k_2 increased rapidly with increasing pK_a of the amines, but tended to level off at a value of $4\text{--}5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$, *i.e.* close to the diffusion-controlled limit of $7.4 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. For the amines of low pK_a , nitrosyl chloride was, as expected, the more effective reagent. The reversibility of the *N*-nitrosation step (previously noted for reactions in methanol solvent) explained the apparently large substituent selectivity observed earlier for reactions at high [HCl], measured by an indirect method. For anilines containing electron-withdrawing groups, reaction occurred in two parts and the rate constant for each determined: it is suggested that the first reaction is the initial *N*-nitrosation of the aniline, and the second a tautomerisation of the reactive *N*-nitroso intermediate.

As part of a mechanistic study of the denitrosation reactions of nitrosoamines brought about by nucleophilic species Y^- in acid solution, a method was developed,^{1,2} whereby the relative rate coefficients were obtained indirectly for the reaction of any free nitrosating agent NOY ($\text{H}_2\text{N}^+\text{O}_2$ or NO^+ , NOCl , NOBr , NOSCN , *etc.*) with any species X capable of undergoing nitrosation irreversibly. Results have been reported for such a series of reactions with sulphamic acid, hydrazine, hydrazoic acid, hydroxylamine, urea, and aniline, *i.e.* with reagents which have been commonly used as 'nitrite traps' in acid solution. The method was based on the direct measurement of the rate coefficient for denitrosation of *N*-methyl-*N*-nitrosoaniline at constant $[\text{H}^+]$, $[\text{Y}^-]$, and $[\text{X}]$, as a function of the concentration of added *N*-methylaniline, the product of the denitrosation reaction. Scheme 1 outlines the mechanism of the re-



action, which is in accord with the experimental observations.³ The ratio $k_2:k_{-1}$ can readily be obtained and hence the reactivity sequence of X species established quantitatively. In some cases it was possible to compare these results with those obtained by direct measurements (by fast reaction techniques) of the nitrosation reactions concerned.^{4,5} The same qualitative sequence of reactivity is found for various X species by both methods, but the quantitative agreement is not always good, particularly for those reactions involving the nitrosyl halides, although it must be added that the reaction conditions (particularly the acidity) were substantially different.

In a recent paper by one of us,⁶ results were presented for the relative rate coefficients for the diazotisation of a number of *para*-substituted anilines, (a) in 4.75M-hydrochloric acid and (b) in sulphuric acid containing added thiocyanate ion. For both nitrosating agents NOCl and NOSCN it was found that quite a large range of reactivity covered the *p*-nitro- to *p*-methoxy-anilines.

There was a reasonable $\sigma\text{--}\rho$ relationship with a ρ value of *ca.* -3 . This was a quite unexpected result, since it is commonly believed⁷ that the diazotisation of aniline and its derivatives by nitrosyl halides is a very fast reaction with rate coefficients close to the diffusion-controlled limit. One would not, therefore, expect such a large selectivity by substituent groups as was apparently indicated by the indirect method.

The direct measurements of the rate coefficients for the diazotisation which formed the basis for the conclusion regarding the diffusion-controlled limit were obtained by Schmid and his co-workers,^{8,9} for the reactions of aniline, *o*-, *m*-, and *p*-toluidine, and *o*-, *m*-, and *p*-chloroaniline. A number of assumptions were made in evaluating the second-order rate coefficients, and the kinetic method usually involved the analysis of one or two quickly taken points. The rate coefficients so obtained, did not vary very much from one substrate to another, and were all in the range $1\text{--}3 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$, at 25 °C. Originally an attempt was made to correlate the results with the basicities of the amines, and it was later⁷ that the suggestion was made that in fact all these rate coefficients approached closely to that expected for a diffusion-controlled process.

The apparent conflict between our indirect measurements and those of Schmid and his co-workers (admittedly under somewhat different reaction conditions), has led us to repeat and to extend the early work of Schmid and his co-workers, using a fast reaction technique now available. We have examined the diazotisation of a range of substituted anilines both at low acidity (*ca.* 0.2M-HCl) and over a wide range of acidity (1–5M-HCl). In addition, results have been obtained for the corresponding reactions in sulphuric acid containing sodium bromide, where, it is believed, the effective nitrosating agent is nitrosyl bromide. The results are presented and discussed in this paper.

EXPERIMENTAL

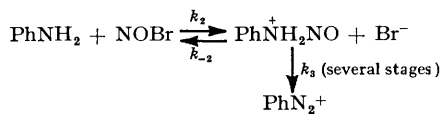
All the aniline derivatives were obtained commercially, and purified by recrystallisation, distillation, or vacuum sublimation, as appropriate, before use in the kinetic studies. A sample of *p*-chlorobenzenediazonium hydrogen sulphate

was prepared by the method of Piercey and Ward¹⁰ from nitrosium hydrogen sulphate and *p*-chloroaniline in acetic acid.

Rate measurements were carried out at 25 °C using a Canterbury stopped-flow spectrophotometer. Equal volumes of aqueous sodium nitrite and the aniline derivative in hydrochloric acid (or in sulphuric acid containing sodium bromide) were rapidly mixed and the increasing absorbance due to the diazonium ion measured at a suitable wavelength (usually in the range 320–360 nm). For some of the reactions at high acidity the sodium nitrite solutions were also made up in hydrochloric acid, to avoid large temperature changes upon mixing. The amine was always in at least 20-fold excess over sodium nitrite. First-order rate coefficients (k_0) were obtained usually by the Guggenheim method. Each individual run gave a k_0 value with a standard deviation of $\pm 2\%$ or less, and each k_0 was reproducible within $\pm 4\%$. It was shown that k_0 was quite independent of the wavelength chosen for the measurement. For the anilines containing electron-withdrawing groups, a second relaxation was observed, sufficiently separated from the first to enable both rate coefficients to be measured.

RESULTS AND DISCUSSION

(i) *Bromide Ion Catalysed Reactions.*—These reactions were carried out in 0.2M-sulphuric acid containing sodium bromide over the range 0–0.08M. The total initial nitrous acid concentration was generally in the range $0.5\text{--}5 \times 10^{-4}\text{M}$ and the total amine concentration was always at least 20-fold in excess of this. Good first-order behaviour in nitrous acid was found, from the individual plots, and also from the constancy of the rate coefficient k_0 (defined by $-\text{d}[\text{HNO}_2]/\text{d}t = k_0[\text{HNO}_2]$, where $[\text{HNO}_2]$ refers to the 'total nitrite' concentration) upon doubling the initial sodium nitrite concentration. Further, the values of k_0 were unchanged on doubling the acidity at any one bromide ion concentration. In all cases k_0 was directly proportional to the total amine concentration, and refers to reaction in 0.23M- H_2SO_4 containing *ca.* $1.5 \times 10^{-2}\text{M}$ -sodium bromide. A set of results was also obtained for each amine for the variation of k_0 with [bromide ion] at constant [total amine]. In all cases bromide ion catalysis was observed. The experimental results are all consistent with a reaction scheme involving diazotisation *via* the nitrosyl bromide species, rather than any of the other possible nitrosating agents, NO^+ , H_2NO_2^+ , or N_2O_3 . Whereas the plots of k_0 *versus* $[\text{Br}^-]$ are linear for aniline, *p*-methoxy-, and *p*-methyl-aniline, these plots are distinctly curved for the remaining amines, with k_0 tending to level off at high $[\text{Br}^-]$. An example of each (for *p*-methoxyaniline and *p*-aminobenzoic acid) is shown in Figure 1. The levelling off of k_0 at high $[\text{Br}^-]$ suggests that under these



SCHEME 2

conditions, the initial formation of the *N*-nitroso species is reversible. A mechanism incorporating this is out-

lined in Scheme 2. Generally it has been assumed that the decomposition of the *N*-nitroso intermediate PhNH_2NO to give the diazonium ion *via* a number of stages, is very rapid. It is however conceivable, that particularly at high $[\text{Br}^-]$, the kinetic term $k_{-2}[\text{Br}^-]$ might become comparable in magnitude with k_3 . The latter is, of course, a composite function, but is retained as one overall rate coefficient for simplicity. The expression for k_0 deduced from Scheme 2 (assuming that the total amine concentration is virtually constant) is given in equation (1). In this equation K_{NOBr} is the

$$k_0 = \frac{k_2 k_3 K_{\text{NOBr}} K_A [\text{Br}^-] [\text{A}_T]}{k_{-2} [\text{Br}^-] + k_3} \quad (1)$$

$$k_0 = k_2 K_{\text{NOBr}} K_A [\text{Br}^-] [\text{A}_T] \quad (2)$$

equilibrium constant for NOBr formation⁹ ($5.1 \times 10^{-2} \text{mol}^{-2} \text{dm}^6$ at 25 °C), K_A the equilibrium constant for the dissociation of the protonated amine (values taken from

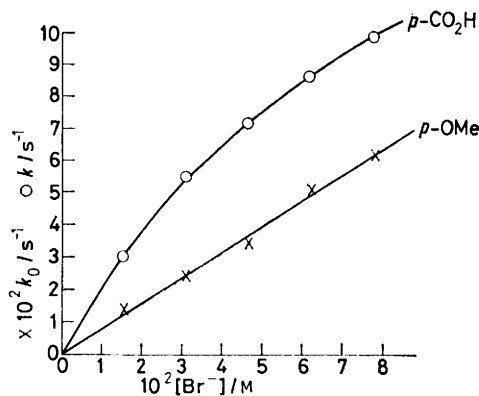


FIGURE 1 Variation of k_0 with $[\text{Br}^-]$ for *p*-aminobenzoic acid (○), and *p*-methoxyaniline (×)

ref. 11), and $[\text{A}_T]$ the total amine concentration (\approx [protonated amine]). This treatment assumes that reaction occurs *via* the unprotonated form of the amine. There has been no report of a reaction of a nitrosyl halide with the protonated form of the amine (although at high acidity H_2NO_2^+ or NO^+ can react with the protonated form¹²). It is difficult to interpret our substituent effect results in terms of reaction *via* the protonated form.

If $k_3 \gg k_{-2}[\text{Br}^-]$ then (1) reduces to the simple form (2) where k_0 is now $\propto [\text{Br}^-]$. For aniline and its *p*-methoxy and *p*-methyl derivatives, k_2 was obtained (a) from the appropriate k_0 *versus* $[\text{Br}^-]$ plot, and also (b) from the k_0 *versus* $[\text{A}_T]$ plot. The agreement between both methods is generally encouraging. The value obtained by Schmid and Fouad⁹ earlier for aniline is $3.2 \times 10^9 \text{l mol}^{-1} \text{s}^{-1}$, compared with our value of $1.7 \times 10^9 \text{l mol}^{-1} \text{s}^{-1}$. We have made no allowance for activity effects [but see NOCl reactions (ii) later] which would tend to increase the value of k_2 somewhat. For the remaining anilines studied, values of k_2 were obtained from plots of $(k_0)^{-1}$ *versus* $([\text{Br}^-])^{-1}$. Figure 2 shows a typical plot for the reaction of *p*-aminobenzoic

acid. Values of k_2 together with those of the ratios $k_{-2} : k_3$, also obtained from the double reciprocal plots, are in Table 1.

TABLE 1
Collected results for nitrosyl bromide reactions

Aniline derivative	$10^{-9}k_2/l \text{ mol}^{-1} \text{ s}^{-1}$	$k_{-2} : k_3$	Slope *	
			Calculated	Observed
<i>p</i> -NO ₂	0.043	25	1 780	1 910
<i>m</i> -NO ₂	0.11	11		
<i>p</i> -CO ₂ H	0.43	13	900	1 070
<i>p</i> -Cl	2.5	5.6	130	180
<i>m</i> -OMe	2.2	6.6	96	100
H	1.7 ^a			
	1.7 ^b			
	3.2 ^c			
<i>p</i> -Me	2.5 ^a			
	2.9 ^b			
<i>p</i> -OMe	2.8 ^a			
	3.2 ^b			

* Slope of k_0 versus $[A_T]$ plot. ^a From k_0 versus $[Br^-]$ plot. ^b From k_0 versus $[A_T]$ plot. ^c From ref. 9.

For the less reactive aniline derivatives (*p*-nitro, etc.) a check on the internal consistency of the method can be

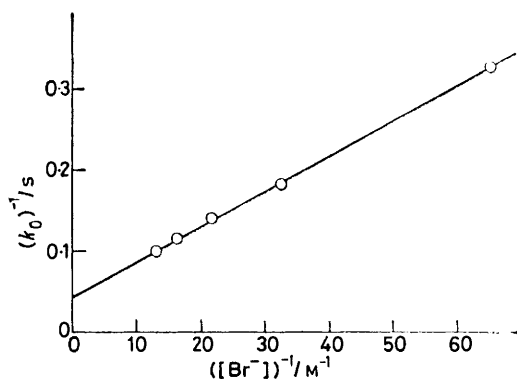


FIGURE 2 Double reciprocal plot $(k_0)^{-1}$ versus $([Br^-])^{-1}$ for the reaction of *p*-aminobenzoic acid

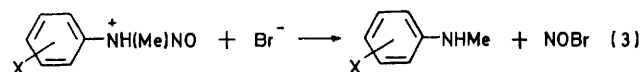
made by comparison of the measured slope of the k_0 versus $[A_T]$ line, with that calculated using the k_2 and $k_{-2} : k_3$ values obtained from the double reciprocal plots. These results are also given in Table 1 and again show reasonable agreement.

The main point to note regarding the results in Table 1 is the way that the k_2 values increase quite significantly with the pK_a value of the amines from $0.043 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ for *p*-nitro- to $2.5 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ for *p*-chloro-aniline, and thereafter show a pronounced tendency to level off at $ca. 3-4 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. This effect is shown more clearly in Figure 3, where the corresponding data for the nitrosyl chloride reactions are also given. These results generally accord with an earlier suggestion⁷ that the rate coefficients for these diazotisation reactions approach the diffusion-controlled limit of $7.4 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$, for reactions in water at 25°. It seems that this is particularly true for aniline derivatives of $pK_a > 4$.

Woppmann and Sofer¹⁴ have found that the diazotisation of aniline in methanolic hydrobromic and hydrochloric acids involves the reversibility of the initial

N-nitrosation as a kinetically important step. Their kinetic results showed k_0 levelling off at high $[HBr]$, and yielded linear double reciprocal plots. The rate coefficients were however $ca. 10^2$ less than the diffusion controlled limit for that solvent, and nitrosyl chloride was about three times more reactive than nitrosyl bromide.

Although $k_{-2} : k_3$ ratios could not be determined for all the substituted anilines studied here (for the NOBr reactions), it is clear that, generally there is a tendency for this ratio to increase with the electron-attracting power of the substituent. Results are available on the effect of substituents on the equivalent of step k_{-2} , with stable nitrosoamines [*i.e.* for equation (3)] in their



denitrosation reactions with nucleophiles such as halide ion. Here the trend in the rate coefficients for various X substituents is $p\text{-OMe} < p\text{-Me} < \text{H} < p\text{-NO}_2 \sim m\text{-OMe} \sim p\text{-Cl} \sim m\text{-NO}_2$, although only a factor of six covers the reactivity of the whole range. It appears that the $k_{-2} : k_3$ ratios whilst following the same qualitative order, are more sensitive to the nature of the substituent X. This suggests that the effect on k_3 is in the opposite sense. The results for the corresponding nitrosyl chloride reactions (see later) cover a wider range of substituents, and show the same pattern.

(ii) *Chloride Ion Catalysed Reactions.*—Reactions here were carried out in hydrochloric acid. Good first-order behaviour was observed in both total nitrous acid and in total amine concentrations. In one set of experiments k_0 values were determined for each aniline derivative over a range of 1–5M-hydrochloric acid, at constant total amine concentration. Plots of k_0 versus $[HCl]$ were curved; this is to be expected now (a) because of the importance at these concentrations of activity effects and (b) if the reverse step (denitrosation) is kinetically important as for some of the nitrosyl bromide reactions. If a reaction scheme analogous to Scheme 2 is taken, together with appropriate account of activity coefficients, then equation (4) can be deduced. This again

$$k_0 = \frac{k_2 k_3 K_{\text{NOCl}} K_A [\text{Cl}^-] f_{\pm}^2 [A_T]}{k_{-2} [\text{Cl}^-] f_{\pm}^2 + k_3} \quad (4)$$

assumes that the total amine concentration $[A_T]$ is given by the concentration of the protonated form. The error introduced here is small even for *p*-nitroaniline. The symbols in equation (4) have the same meaning as previously in equation (1); f_{\pm} is the mean ionic activity coefficient for the hydrochloric acid solution.¹⁵ This equation is exactly analogous to that deduced by Woppmann and Sofer,¹⁴ for the diazotisation of aniline in methanolic hydrochloric acid. If this treatment is correct then a plot of $(k_0)^{-1}$ versus $([\text{Cl}^-] f_{\pm}^2)^{-1}$ should be linear. This was the case for all the aniline derivatives. The detailed results are given in Table 2 for the seven amines studied. From the slopes and intercepts

of these plots it is possible to obtain k_2 and the ratio $k_{-2} : k_3$ as for the bromide ion catalysed reactions. The

TABLE 2

Variation of k_0 with $[\text{HCl}]$ at constant total amine concentration *

[HCl]/M	PhNH ₂ k_0/s^{-1}	<i>m</i> -MeC ₆ H ₄ NH ₂ k_0/s^{-1}	<i>p</i> -MeC ₆ H ₄ NH ₂ $10^2 k_0/\text{s}^{-1}$	<i>p</i> -MeC ₆ H ₄ NH ₂ $10^2 k_0/\text{s}^{-1}$
1.01	0.33	0.15	4.2	5.6
2.08	0.90	0.45	12.2	21
3.07	1.87	0.86	35.9	48
4.08	3.31	1.39	71.7	98.7
5.25	3.89	2.94	114.2	144

[HCl]/M	<i>p</i> -ClC ₆ H ₄ NH ₂ k_0/s^{-1}	<i>p</i> -CO ₂ HC ₆ H ₄ NH ₂ k_0/s^{-1}	<i>p</i> -NO ₂ C ₆ H ₄ NH ₂ k_0/s^{-1}
1.13	0.32	5.6	8.4
2.08	0.81	11.3	11.5
2.96	1.54	15.2	13.8
3.86	2.73	19.7	14.5
4.90	3.27		15.2

* The total amine concentration is not the same for each substrate.

collected values are given in Table 3. A series of measurements was also carried out at a single low

TABLE 3

Collected k_2 values (all in $\text{l mol}^{-1} \text{s}^{-1}$) and $k_{-2} : k_3$ ratios for nitrosyl chloride reactions

Aniline derivative	$10^{-9} k_2^a$	$10^{-9} k_2^b$	$10^{-9} k_2^c$	$k_{-2} : k_3$
<i>p</i> -NO ₂	0.21	0.27		1.6
<i>m</i> -NO ₂		1.2		
<i>p</i> -CO ₂ H	1.1	1.1		0.42
<i>p</i> -Cl	1.8	2.3	1.9	0.096
<i>m</i> -OMe	3.0	3.3		0.083
H	2.2	2.5	2.6	0.088
<i>p</i> -Me	4.1	3.4	3.0	0.034
<i>p</i> -OMe	5.9	5.1		0.03

^a Determined over the range 1–5M-HCl using equation (6).

^b Obtained from measurements at 0.2M-HCl using equation (7).

^c From ref. 8.

acidity (0.2M-HCl) for each of these anilines. Here it is reasonable to assume, knowing the $k_{-2} : k_3$ ratios, that $k_3 \gg k_{-2}[\text{Cl}^-]f_{\pm}^2$ for each of the substrates, even *p*-nitroaniline. Under these conditions equation (4) is simplified to give equation (5), from which k_2 may readily be

$$k_0 = k_2 K_{\text{NOCl}} K_A [\text{Cl}^-] f_{\pm}^2 [\text{A}_T] \quad (5)$$

obtained from measurements at one $[\text{Cl}^-]$ and $[\text{A}_T]$. The values of k_2 so obtained are also given in Table 3, alongside the values obtained over the range 1–5M-hydrochloric acid. It is clear that the agreement between the two sets of results is good. Also included in Table 3 (in the third column of figures) are the values of k_2 obtained by Schmid and his co-workers⁸ earlier from measurements at 0.2M-HCl. Where a comparison is possible (for aniline, *p*-chloroaniline, and *p*-toluidine), it can be seen that the agreement is very good. The feature of the results is again the increasing values of k_2 from *p*-nitroaniline to *p*-chloroaniline with pK_a , and thereafter the levelling off of k_2 as the calculated diffusion-controlled limit is approached. The data for both nitrosyl chloride and nitrosyl bromide reactions are shown graphically (Figure 3) as a function

of pK_a . At low pK_a , particularly for *p*-nitroaniline, it is clear that nitrosyl chloride is significantly more reactive than nitrosyl bromide, as is expected from simple electronegativity arguments. This has recently been observed⁴ in the halide-catalysed nitrosation of the hydrazinium ion (NH_2NH_3^+), and also earlier in the electrophilic addition of the nitrosyl halides to alkenes in water.¹⁶ Woppmann and Sofer¹⁴ also found the same order for diazotisation in methanol.

Significance of the $k_{-2} : k_3$ Ratios.—It is clear from Tables 1 and 3 that the $k_{-2} : k_3$ ratios decrease in magnitude with increasing pK_a value of the amine, for both nitrosyl halides. Before discussing this trend it is worth noting that for the same amine the ratio is significantly greater (20–80 fold) for the bromide ion catalysed reaction than for the chloride ion catalysed reaction. Since k_3 is expected to be independent of the halide ion, this gives a direct comparison of the efficiencies of the two halide ions in step k_{-2} , *i.e.* the denitrosation

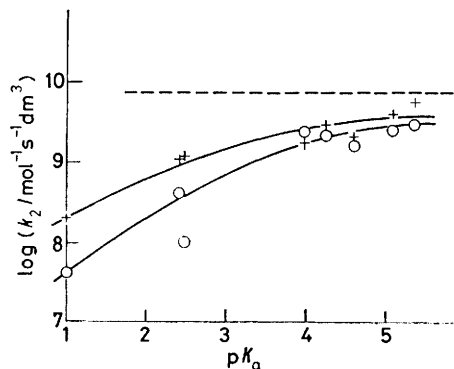
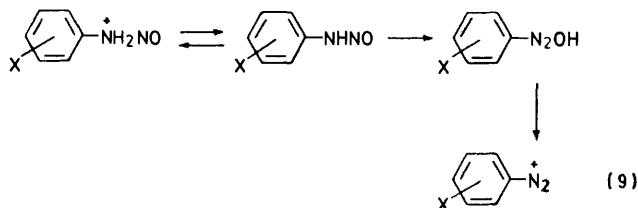
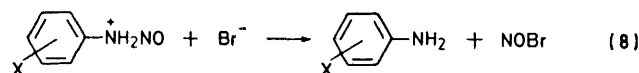


FIGURE 3 $\log k_2$ versus pK_a for NOCl (+) and NOBr (O) reactions

of a nitrosoamine. As expected from their nucleophilicities bromide ion is the more reactive. This point has been established³ by the direct measurement of the rate coefficients for the reactions of halide ions with nitrosoamines in acid solution. In that case $(k)_{\text{Br}^-} : (k)_{\text{Cl}^-}$ was *ca.* 50.

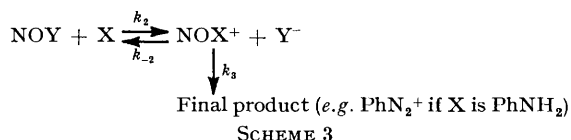
The effect of ring substitution on the rate coefficient for denitrosation of *N*-methyl-*N*-nitrosoaniline has also been investigated recently.¹⁷ It was found that electron-withdrawing substituents increased the rate of denitrosation and *vice versa*. The range of reactivity was however quite small, a factor of six covering *p*-nitro to *p*-methoxy, and it was argued that two factors were involved: (a) the effect of substitution upon the pK_a of the nitrosoamine and (b) the substituent effect upon the substitution reaction itself [equation (3)]. It is to be expected that (a) and (b) would operate in opposing directions, thus resulting in the relatively small overall effect as observed. It is reasonable to expect substituent effects of similar magnitude for step k_{-2} from Scheme 2, *i.e.* equation (8). No independent results are available for the sequence of fast reactions leading to the diazonium ion [equation (9)]. It could be argued that substitution would affect the different steps in opposite directions,

making the overall effect on k_3 small. It is not possible to predict the direction or magnitude of this overall effect, but the $k_{-2} : k_3$ rate ratios measured in this work



suggest that the overall substituent effect upon k_3 is in the *opposite* sense to that upon k_{-2} , resulting in a larger substituent effect for the ratio than those found for the simple denitrosation reaction.¹⁷

It is now clear that the reversibility of *N*-nitrosation of anilines by nitrosyl halides is a step of kinetic importance, particularly at high concentration of halide ion and also for aniline derivatives containing electron-withdrawing groups. In Scheme 1 therefore, the final stage is generally better represented by Scheme 3. If



$k_3 \gg k_{-2}[\text{Y}^-]$ then the reversibility is not important. This means that any relative ' k_2 ' values obtained by the indirect procedure⁶ are not necessarily the true k_2 values, but $k_2 k_3 : (k_{-2}[\text{Y}^-] + k_3)$ values. This adds to the complexity of interpretation of substituent effects, and accounts for the apparently greater selectivity shown by substituents at high than at low $[\text{HCl}]$, for the diazotisation of anilines. It simply means that at high $[\text{Cl}^-]$ the reversibility is important and the rate coefficient determined is a composite quantity. This is probably the reason why there is always not good quantitative agreement between the relative reactivities of some of the 'nitrite traps' X, when measured by the indirect method,¹ compared with those measured directly.^{4,5} Assumptions regarding the rapid and *irreversible* destruction of free nitrosating species by X need to be examined more carefully in some cases.

For those aniline derivatives containing electron-withdrawing groups (NO_2 , Cl, and CO_2H), a second, slower reaction was observed. Data for both processes for the reaction of *p*-nitroaniline in hydrochloric acid solutions are given in Table 4. The rate constants of the two reactions are separated sufficiently for both to be accurately measured. This second reaction had quite different characteristics from the first, in that although it was found to be first order in total nitrous acid, it was

first-order in $[\text{H}^+]$ and independent of both the [amine] and [halide ion]. These results are not compatible with

TABLE 4

Rate data for reaction of 4-nitroaniline at 25 °C

$10^3[\text{4-nitroaniline}]/\text{M}$	$10^4[\text{NaNO}_2]/\text{M}$	$[\text{HCl}]/\text{M}$	k_0/s^{-1}	$k_{\text{slow}}/\text{s}^{-1}$
2.02	1.0	1.04	8.2	0.090
4.04	1.0	1.04	17	0.090
2.02	1.0	2.04	10.5	0.27
2.02	1.0	3.04	13	0.60
2.02	1.0	4.04	14.5	1.55
2.02	1.0	0.54*	11	0.12

* Contains sodium chloride.

a reaction involving the coupling of the diazonium ion with the excess of amine, which could be observed usually over a much longer time scale. Further it was shown that this second reaction was not a further reaction of the diazonium ion, by synthesis of *p*-chlorobenzenediazonium hydrogen sulphate, and by its examination under the kinetic reaction conditions; no corresponding absorbance change was observed. It appears that this second reaction is one leading to the formation of the diazonium ion, and could well be the tautomerisation $\text{PhNHNO} \longrightarrow \text{PhN}_2\text{OH}$. This would accord with the observed kinetic results (particularly the independence upon halide ion, and the first order behaviour in acid). Moreover the $k_{-2} : k_3$ rate ratios suggest that the composite rate coefficient k_3 is decreased by electron-withdrawing groups, thus allowing, in these cases, the observation of this step, which would normally be too fast to measure as a separate process, for anilines containing electron-releasing groups.

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