Kinetics and Mechanism of the Fischer–Hepp Rearrangement and De-nitrosation. Part VI.[1] The Relative Reactivity of a Number of Nitrogen-containing Species towards Nitrosation, and Further Evidence against an Intermolecular Mechanism for the Rearrangement

D. Lyn H. Williams, Department of Chemistry, Durham University, Durham City

The constant value found for the rearrangement : denitrosation product ratio from *N*-methyl-*N*-nitrosoaniline in sulphuric acid containing a wide variety of ' nitrite traps ' at various concentrations at any one acidity. argues very strongly against a mechanism for the Fischer–Hepp rearrangement involving prior denitrosation and *C*-nitrosation of *N*-methylaniline (NMA) by the free nitrosating agent. The result is however consistent with a previously proposed intramolecular mechanism which occurs concurrently with denitrosation. The observed rate constant k_0 is decreased as NMA is added, thus reversing the denitrosation step. From the variation of k_0 with [NMA] it is possible to obtain values for the relative reactivity towards nitrosation, of a number of ' nitrite traps,' urea, sulphamic acid, hydroxylamine, hydrazoic acid, aniline, and hydrazine. This establishes the reactivity sequence of these compounds towards nitrosation by nitrosyl chloride, nitrosyl bromide, and the nitrous acidium ion. The observed selectivity of these three reagents NOBr > NOCl > $H_2\overset{+}{N}O_2$ is discussed in terms of their relative reactivities.

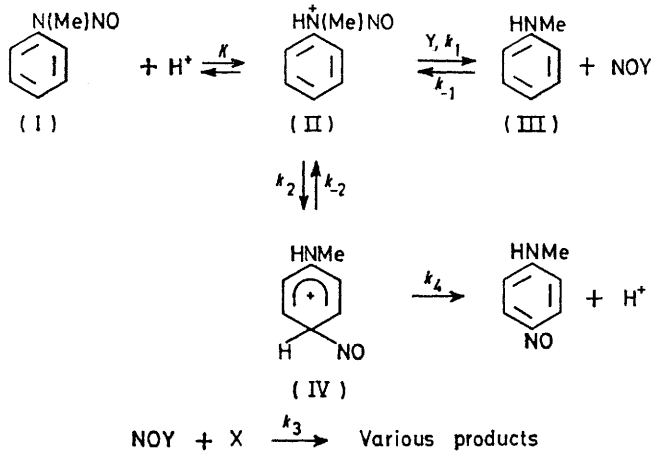
ARGUMENTS have recently been presented [2,3] in favour of an intramolecular mechanism for the acid-catalysed rearrangement of aromatic *N*-nitrosoamines (the Fischer–Hepp rearrangement [4]), which occurs concurrently with the normally reversible de-nitrosation to the secondary amine and a free nitrosating agent (NOY) such as nitrous acid or nitrosyl chloride. NOY may undergo further reaction, *e.g.* with the solvent, or bring about nitrosation of an added amine such as urea. This mechanism differs from the hitherto generally accepted mechanism [5] of denitrosation followed by a direct *C*-nitrosation at the *para*-position of the secondary amine by the free nitrosating agent. In spite of its widespread acceptance, this intermolecular mechanism has in fact never been substantiated quantitatively and was originally proposed [6] on the basis of some rather inconclusive product analyses. Dewar has stated [7] that there is in fact no evidence available concerning the mechanism. The fact that the nitroso-chloride adduct of a reactive olefin is among the products [8] when the rearrangement is carried out in the presence of that olefin, does not *necessarily* mean that nitrosyl chloride is an intermediate in the rearrangement. There are at least two other mechanistic possibilities, *viz.* (*a*) that the nitrosyl chloride is formed by a denitrosation process, but that rearrangement occurs by some other parallel and quite independent route, and (*b*) that the nitroso-amine itself (or more probably its protonated form) acts directly as a nitrosating agent, transferring the NO group to the olefin without the intermediacy of nitrosyl chloride or any other nitrosating agent.

Some doubt was cast regarding the intermolecular rearrangement when it was found [2] that rearrangement occurred, although to a lesser extent, in the presence of quite large quantities of urea, a well known trap for free nitrosating agents, and also when the rate of the reaction was found to be approximately proportional to h_0 and not to the product $h_0[Cl^-]$ (*cf.* the Orton rearrangement of *N*-chloroanilides [9]). Russian workers [10] had also observed the rearrangement reaction in the presence of urea and sulphamic acid. Subsequently, the intramolecular mechanism has been supported (*a*) on the basis of the absence of chloride or bromide ion catalysis for the rearrangement reaction itself [11] and (*b*) by the observed variation in the observed rate constant with added *N*-methylaniline,[3] when it is possible to suppress denitrosation completely, and observe only the rearrangement reaction. We now present further evidence, of a more direct kind, which argues very strongly against *C*-nitrosation of a secondary amine by a free nitrosating agent, and which is consistent with the intramolecular mechanism.

Product Ratios.—Scheme 1 outlines the proposed reaction paths for the reaction of *N*-methyl-*N*-nitrosoaniline (I) in acid solution, *i.e.* for concurrent rearrangement and de-nitrosation, which arise by two separate reactions of (II), the protonated form of (I). For simplicity we write the reaction (II) ⟶ (IV) in one stage, although clearly some intermediate must be involved, because of the large distance involved from the amino nitrogen atom to the *para*-position in the ring. Such an intermediate could be a π-complex, although, as yet, there is no evidence as to its exact nature. This simplification in no way affects the general form of the rate equation, but merely means that k_2 and k_{-2} are

[1] Part V, I. D. Biggs and D. L. H. Williams, *J.C.S. Perkin II*, 1975, 107.
[2] T. D. B. Morgan and D. L. H. Williams, *J.C.S. Perkin II*, 1972, 74.
[3] T. D. B. Morgan, D. L. H. Williams, and J. A. Wilson, *J.C.S. Perkin II*, 1973, 473.
[4] O. Fischer and E. Hepp, *Ber.*, 1886, **19**, 2991.
[5] H. J. Shine, 'Aromatic Rearrangements,' Elsevier, Amsterdam, 1967, pp. 231—235.
[6] J. Houben, *Ber.*, 1913, **46**, 3984.
[7] M. J. S. Dewar, 'Molecular Rearrangements,' ed. P. de Mayo, Wiley-Interscience, New York, 1963, ch. 5, p. 310.
[8] P. W. Neber and H. Rauscher, *Annalen*, 1942, **550**, 182.
[9] Ref. 5, pp. 221—230.
[10] T. I. Aslapovskaya, E. Y. Belyaev, V. P. Kumarev, and B. A. Porai-Koshits, *Reakts. sposobnost. org. Soedinenii*, 1968, **5**, 456.
[11] D. L. H. Williams, *Internat. J. Chem. Kinetics*, 1975, in the press.

composite rate constants. In general Y can be Cl^-, Br^-, I^-, SCN^-, or H_2O and we have used the following X compounds, all of which react irreversibly with a free nitrosating agent, $CO(NH_2)_2$, HN_3, $PhNH_2$, NH_2SO_3H, NH_2OH, and N_2H_4. The final proton transfer from (IV) is no doubt brought about by some base B, but its concentration is included in k_4. A rate equation has



SCHEME 1

been derived [11] for Scheme 1 by assuming steady state treatments for (IV) and for NOY. It is also assumed that (I) behaves as a Hammett base and that the extent of protonation is small; the latter assumption is borne out by examination of the u.v. spectra of solutions of (I) in water and in acid solution. The observed first-order rate coefficient k_0 {defined by $-d[(I)]/dt = k_0[(I)]$} is then given by equation (1). Good first-order behaviour would thus only be expected when Y, X, and (III) are present in large excess over (I). The specific

$$k_0 = \left(\frac{k_2k_4}{k_{-2} + k_4}\right)Kh_0 + \frac{k_1k_3[Y][X]Kh_0}{k_{-1}[III] + k_3[X]} \quad (1)$$

$$k_0 = \left(\frac{k_2k_4}{k_{-2} + k_4}\right)Kh_0 + k_1[Y]Kh_0 \quad (2)$$

i.e. $k_0 = k_r + k_d$

question of catalysis by Y (which applies only to denitrosation) has been discussed elsewhere.[11] If [X] is sufficiently high such that $k_3[X] \gg k_{-1}[(III)]$, then equation (1) reduces to the simpler equation (2). We have observed [12] this limiting form of k_0 which is independent of the nature and concentration of X for all the X compounds listed {so long as sufficient X is present to ensure that $k_3[X] \gg k_{-1}[(III)]$}. In physical terms this limiting form simply means that the nitrosating agent (NOY) is being removed by X as soon as it is formed, thus making denitrosation irreversible and reducing the reaction scheme to two parallel irreversible reactions of (II). The first term of equation (2) now represents that part of the reaction leading to rearrangement (k_r) whilst the second term represents denitrosation (k_d). The product ratio, according to this mechanism is thus governed only by the bulk reactivity of Y. For the very powerful nucleophiles Br^-, SCN^-, and I^-, we might expect $k_1[Y]Kh_0$ to dominate equation (2), yielding no rearrangement product. This is observed in practice for these nucleophiles and also for Cl^- except at very low concentrations of Cl^-. However for reactions in sulphuric acid, without added salts, where Y might now be H_2O (there being no catalysis of denitrosation by HSO_4^-), both products are observed. This is reasonable and consistent with k_1 being much smaller for the less nucleophilic H_2O. Table 1 shows

TABLE 1

The % rearrangement product and the observed rate constant as a function of added X

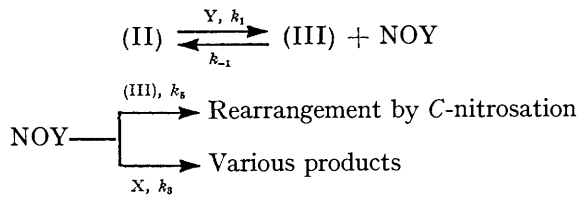
Added X	[X]/M	$10^4k_0/s^{-1}$	Rearrangement (%)
HN_3	$6{\cdot}53 \times 10^{-4}$	0·65	21
HN_3	$16{\cdot}3 \times 10^{-4}$	0·67	21
NH_2SO_3H	$3{\cdot}1 \times 10^{-3}$	0·65	21
NH_2SO_3H	$7{\cdot}8 \times 10^{-3}$	0·64	22
$CO(NH_2)_2$	0·10	0·62	21
NH_2OH	$2{\cdot}58 \times 10^{-3}$	0·62	20
NH_2NH_2	$1{\cdot}56 \times 10^{-3}$	0·66	20

the results of experiments carried out in 2·75M-sulphuric acid at 31°. Not only is the reaction obviously zero order in X as shown by the constancy of k_0 over the whole range of X compounds, but also the % rearrangement is constant over the same range at 21 ± 1%. Similar results were obtained at the higher acidity of 4·5M-H_2SO_4 where 10% rearrangement was found over a range of X compounds. According to equation (2), the product ratio should be independent of the acidity of the medium. This has been found not to be the case, the % rearrangement decreasing steadily from 21 at 2·75M-H_2SO_4 to 7% at 4·66M-H_2SO_4. This trend arises because the rearrangement and denitrosation reactions do not have exactly the same acidity dependences, the rate of rearrangement is proportional to $(h_0)^{1.2}$ (ref. 3) whilst denitrosation is proportional to $(h_0)^{1.6}$ (ref. 1). This difference, which is discussed in more detail elsewhere,[1] is thought to be due to the intervention of a second mechanism of denitrosation at high acidities involving attack by H_3O^+ rather than H_2O. As expected, because of their differing reactivities, the limiting value for [X] varies within the group. For most of those considered, concentrations of *ca.* $1—2 \times 10^{-3}$M are sufficient to ensure that $k_3[X] \gg k_{-1}[(III)]$, but for urea the limit is not reached until its concentration is *ca.* 0·1M. The relative reactivities of X will be discussed quantitatively later, but it is clear that urea is a relatively poor trap for a free nitrosating species, compared with the other X compounds.

The constancy of the product ratio is wholly consistent with the intramolecular mechanism (Scheme 1) for rearrangement, but cannot be accounted for by the alternative intermolecular mechanism shown in Scheme

[12] D. L. H. Williams and J. A. Wilson, *J.C.S. Perkin II*, 1974, 13.

2. Without going into the detailed form expected from this scheme (although that does in fact illustrate



SCHEME 2

the difference also [11]) it is easy to see that there should always be a direct competition between (III) (*N*-methylaniline) and X for capture of the free nitrosating agent (NOY). That being so, the % rearrangement should always decrease (towards zero) as the concentration of X is increased, and should vary with the reactivity of X, even though the overall reaction is kinetically zero-order in X, *i.e.* we are now concerned with the post rate-determining, product-determining stage. Further, since the condition for zero-order kinetics in X is that $k_3[X] \gg k_{-1}[(III)]$, it follows that $k_3[X] \gg k_5[(III)]$, since it is very likely that $k_{-1}[(III)] \gg k_5[(III)]$, *i.e.* the rate of *N*-nitrosation is much greater than that of *C*-nitrosation. It is therefore difficult to account for *any* rearrangement product at all under these conditions by this mechanism. This rules out completely *C*-nitrosation of the secondary amine by NOY as a reaction path to the *p*-nitroso-isomer. Arguments against an alternative mechanism in which direct *C*-nitrosation occurs at the *para*-position of NMA by the protonated nitroso-amine (II), have been presented elsewhere.[11]

As expected, the addition of chloride ion (and Br^-, SCN^-, and I^-) increases k_0 whilst decreasing the yield of rearrangement product, but again, as expected from Scheme 1, at a constant $[Cl^-]$ the yield of rearrangement is independent of the concentration of added X. This is illustrated for some sulphamic acid reactions in Table 2.

TABLE 2

The % rearrangement product and the observed rate constant as a function of added chloride

NaCl/M	$10^3[NH_2SO_3H]$/M	$10^5k_0/s^{-1}$	Rearrangement (%)
0	2·29	3·4	21
0·10	2·29	9·0	11
0·15	2·29	11·8	8
0·20	2·29	14·0	7
0·20	4·58	14·0	7

All at 2·52M-H_2SO_4

Effect of N-*Methylaniline Addition.*—The addition of *N*-methylaniline to the reaction mixture results in a decrease in the value of k_0 towards a limiting value, and an increase in the yield of rearrangement. This other limiting value of k_0 at high *N*-methylaniline concentration has been taken [3] as the overall rate constant for rearrangement alone $\{k_{-1}[(III)]$ is now $\gg k_3[X]\}$ and is given by $k_r = [k_2k_4/(k_{-2} + k_4)]Kh_0$. In the earlier work [3] this limiting value of k_0 at high [NMA] was determined for reactions with no added X, *i.e.* where the only possible decomposition reaction of NOY was with the solvent. Figure 1 shows the same pattern of

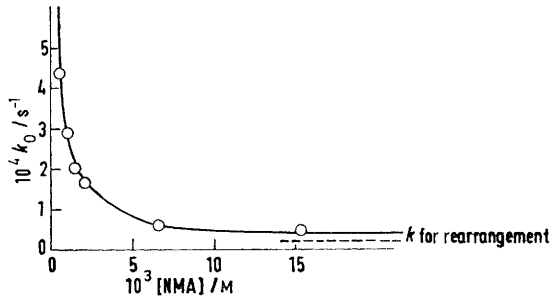


FIGURE 1 Variation of k_0 with added NMA for reaction in the presence of excess of hydroxylamine

behaviour when the reaction contains an excess of added hydroxylamine; k_0 decreases towards the previously obtained limit of k_r as [NMA] is increased, although naturally more NMA is now required to bring about the limiting condition than when there is no added X. At intermediate values of added NMA, neither of the limiting conditions obtain and it is possible to evaluate the ratio $k_{-1} : k_3$. Equation (1) can be rearranged to give equation (3): a plot of $1/(k_0 - k_r)$ against [(III)] at

$$\left(\frac{1}{k_0 - k_r}\right) = \frac{k_{-1}[(III)]}{k_3[X]k_1[Y]Kh_0} + \frac{1}{k_1[Y]Kh_0} \quad (3)$$

constant acidity, [Y] and [X] should be linear of slope $k_{-1}/k_3[X]k_1[Y]Kh_0$. Values of $k_1[Y]Kh_0$, *i.e.* k_d, are readily obtained from the limiting value of k_0 at high [X] so that $k_{-1} : k_3$ is easily determined. Figure 2 shows

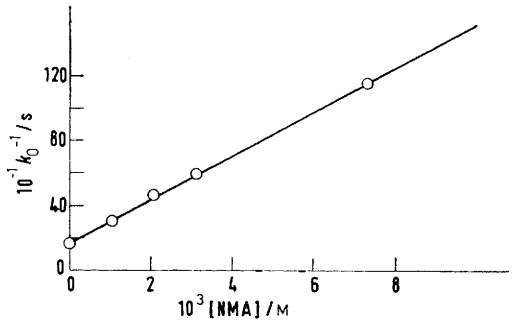


FIGURE 2 A plot of k_0^{-1} against added NMA for reaction in the presence of excess of bromide ion and sulphamic acid

such a plot for reaction in sulphuric acid (4·8M) containing added sodium bromide (0·1M) and sulphamic acid (2×10^{-3}M). Good straight lines have been obtained for a number of X compounds for the three solvent systems, hydrochloric acid (3·0M), sulphuric acid (2·7M) containing 0·2M-sodium bromide, and sulphuric acid (4·8M). Some of the results for the hydrochloric acid

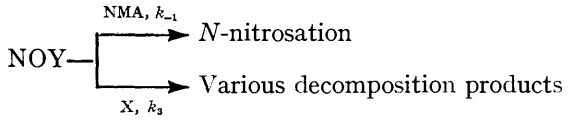
system have been published in a preliminary communication.[13] The $k_{-1} : k_3$ ratio can equally well be obtained from equation (3) by plotting $1/(k_0 - k_r)$ against 1/[X] at constant [(III)]. There is good agreement between values obtained by both procedures. Table 3 shows the results that have been obtained for

TABLE 3

Values of $k_{-1} : k_3$ for various X species for the three nitrosating agents

X	NOCl Reaction	NOBr Reaction	$H_2\overset{+}{N}O_2$ Reaction
HN_3	$2{\cdot}5 \times 10^{-2}$	$3{\cdot}3 \times 10^{-2}$	$1{\cdot}9 \times 10^{-3}$
NH_2NH_2	$2{\cdot}2 \times 10^{-2}$	$4{\cdot}8 \times 10^{-2}$	$6{\cdot}3 \times 10^{-3}$
NH_2SO_3H	0·44	1·7	$7{\cdot}9 \times 10^{-2}$
$C_6H_5NH_2$	1·9		
NH_2OH	9·5	31	5·4
$CO(NH_2)_2$	337, 394 †	1170	39, 32 †

six different X compounds and for the three solvent systems, where it is thought that the free nitrosating agents are NOCl, NOBr, and $H_2\overset{+}{N}O_2$. Most of the results were obtained from measurements at constant [X], whilst those marked † were determined at constant [(III)]. These ratios represent the reactivity of species X, relative to that of NMA towards the three nitrosating agents. Hydrazoic acid is the most reactive, with urea



the least reactive of the substrates studied, with a factor of *ca.* 10^4 covering the reactivity range. This indirect method enables such a sequence of reactivity to be established using conventional kinetic techniques. The individual values of k_3 for a number of these X compounds appear to be so large that in most cases a direct measurement is rather difficult. So far as we are aware, this reactivity sequence has never been established previously even in a qualitative way. Some of these materials (*e.g.* urea and hydrazine) have been used to remove nitrous acid [14] or nitrosyl halides from reaction mixtures, for example in aromatic nitration [15] when it is necessary to prevent nitration *via* nitrosation and oxidation, using nitric acid which contains small quantities of nitrous acid, and also in the formation of nitrate esters,[16] again from nitric acid, where the presence of small quantities of nitrous acid can lead to explosive reactions. The sequence $HN_3 \longrightarrow CO(NH_2)_2$ gives the decreasing effectiveness of those materials as nitrous acid scavengers in acid solution. Urea, which is most commonly used for this purpose, is in fact the least reactive of the series studied: thus sulphamic acid is *ca.* 500 times more effective. Interestingly, Arnall had observed [15] qualitatively that hydrazine was more effective than urea in eliminating the nitrosation accompanying nitration.

This method also allows the comparison of the various nitrosating agents themselves. As expected all three show the same order of reactivity towards the X compounds. However for each X, the rate ratios are greatest for the bromide ion catalysed reactions and smallest for the non-catalysed reactions. This is readily interpreted in terms of reactivity and selectivity, nitrosyl bromide appears to be the most selective reagent, and $H_2\overset{+}{N}O_2$ the least discriminating. The difference between the two nitrosyl halides is that expected from consideration of the relative inductive effects of chlorine and bromine, *i.e.* that nitrosyl chloride should be more reactive than nitrosyl bromide. The well known catalysis $Br^- > Cl^-$ in diazotisation and nitrosation arises from the relative magnitudes of the equilibrium constants for the formation of the nitrosyl halides NOY from Y^- and HNO_2 [equation (4)]. According to the work of Schmid,[17] the reactivities of nitrosyl chloride and nitrosyl bromide are much the same in

$$Y^- + HNO_2 + H^+ \rightleftharpoons NOY + H_2O \qquad (4)$$

diazotisation of aniline derivatives, where it is thought that both reactions proceed at rates near the diffusion-controlled limit. Similar results were obtained for the halide-catalysed nitrosation of hydroxylamines.[18] Our results, however, show that nitrosyl bromide is clearly more selective than nitrosyl chloride (for each X), and are consistent with our earlier work [19] on the nitrosation of olefins, where nitrosyl chloride was found to be about six times more reactive than nitrosyl bromide. Similarly, it might be expected that the positively charged nitrous acidium ion $H_2\overset{+}{N}O_2$, would be a more reactive species than either of the nitrosyl halides. This is borne out by the results in Table 3 where all the $k_{-1} : k_3$ ratios are significantly smaller for the $H_2\overset{+}{N}O_2$ reaction than for either catalysed reaction.

The values of $k_{-1} : k_3$ obtained in this way do not describe the true rate coefficients for the various nitrosation reactions since substantial quantities of some of the X species (as well as *N*-methylaniline itself) exist as the protonated form in the acid solutions used. If we assume that nitrosation occurs largely by reaction of the non-protonated form [20] then the ratio of the true rate constants for nitrosation $k_{-1}' : k_3'$, is given by equation (5), where K_{NMA} and K_X are, respectively, the

$$\frac{k_{-1}'}{k_3'} = \frac{k_1}{k_{-3}} \cdot \frac{h_0}{K_{NMA}} \cdot \left(\frac{1}{\frac{h_0}{K_X} + 1} \right) \qquad (5)$$

[13] D. L. H. Williams, *J.C.S. Chem. Comm.*, 1974, 324.
[14] W. Macmillen and T. H. Reade, *J. Chem. Soc.*, 1929, 585.
[15] F. Arnall, *J. Chem. Soc.*, 1923, **123**, 3111.
[16] A. I. Vogel, *J. Chem. Soc.*, 1948, 1847.
[17] H. Schmid and E. Hallana, *Monatsh.*, 1956, **87**, 560; H. Schmid and M. G. Fouad, *ibid.*, 1957, **88**, 631; H. Schmid and C. Essler, *ibid.*, p. 1110.
[18] T. D. B. Morgan, G. Stedman, and M. N. Hughes, *J. Chem. Soc.* (*B*), 1968, 344.
[19] J. R. Park and D. L. H. Williams, *J.C.S. Perkin II*, 1972, 2158.
[20] B. C. Challis and J. H. Ridd, *Proc. Chem. Soc.*, 1961, 173.

dissociation constants of the protonated forms of *N*-methylaniline and X. We further assume that these dissociations are adequately expressed by the Hammett acidity function. The pK_a values are such that in most cases h_0/K_X is either $\gg 1$ or $\ll 1$. Values of $k_{-1}' : k_3'$ are shown in Table 4. The pK_a value of

TABLE 4

Values of $k_1' : k_3'$ for various X species for the three nitrosating agents

X	pK_a	NOCl Reaction	NOBr Reaction	$H_2\overset{+}{N}O_2$ Reaction
HN_3	−6·21	$2·1 \times 10^4$	$4·5 \times 10^4$	$2·1 \times 10^4$
NH_2NH_2	8·07	$1·3 \times 10^{-5}$	$2·9 \times 10^{-5}$	$3·8 \times 10^{-6}$
$NH_2\overset{+}{N}H_3$		$[1·9 \times 10^4]$	$[6·5 \times 10^4]$	$[7·1 \times 10^4]$
NH_2SO_3H		$[3·7 \times 10^5]$	$[23 \times 10^5]$	$[8·8 \times 10^5]$
$C_6H_5NH_2$	4·60	4·3		
NH_2OH	5·95	0·75	2·5	0·43
$CO(NH_2)_2$	0·13	16×10^6	59×10^6	$2·0 \times 10^6$
$NH_2C\overset{+}{O}NH_3$		$[2·8 \times 10^8]$	$[16 \times 10^8]$	$[4·4 \times 10^8]$

sulphamic acid is apparently not known and the values of the rate ratios for sulphamic acid have been evaluated assuming that the extent of protonation is very small. For hydrazine and urea where there are two basic sites, values have been obtained assuming reaction *via* NH_2NH_2 and $CO(NH_2)_2$ respectively from $pK_a(1)$ and also for reaction *via* $NH_2\overset{+}{N}H_3$ and $NH_2C\overset{+}{O}NH_3$. The $pK_a(2)$ values are not known but are likely to be very small. From the very small rate ratios for reaction *via* NH_2NH_2, it appears likely (and not unreasonable) that reaction occurs *via* $NH_2\overset{+}{N}H_3$; similar behaviour would be expected for urea. The same general pattern of reactivity appears from Table 4 as did in Table 3, *i.e.* that nitrosyl bromide is the most selective reagent, showing the greatest range of 'substituent' effects. The order of reactivity of X has changed a little from Table 3, *e.g.* hydroxylamine itself is in reality more reactive towards nitrosyl chloride than is aniline; the apparent greater reactivity of aniline arises from the greater basicity of hydroxylamine. It is known that at somewhat higher acidities [20] *N*-nitrosation can occur *via* the protonated form of the substrate; this may well occur in our case particularly with the positively charged nitrosating agent.

The 4·3 figure in Table 4 for aniline represents a reasonable value for the activation by the *N*-methyl group towards electrophilic substitution. A similar rate enhancement has been found [21] for nitrosation of aniline and *N*-methylaniline by the nitrous anhydride molecule N_2O_3.

One further point can be made. It appears from the significant differences in the rate ratios for reactions involving nitrosyl bromide and nitrosyl chloride, and also from the significant substituent effects, *e.g.* 4·3, for a methyl substituent, that these reactions in general do not proceed at rates approaching the diffusion-controlled limit, otherwise much smaller rate differences would be expected. This contrasts with the conclusion of Schmid [17] who measured the nitrosations directly, but had to make a number of assumptions in order to evaluate the final true rate coefficients.

TABLE 5

Rate constants from a typical run

t (units of 96·5 s)	0	1	2	3	4	5	6	7
OD (275 nm)	0·768	0·700	0·634	0·582	0·533	0·490	0·447	0·410
$10^4 k_0/s^{-1}$		10·7	11·2	10·9	10·9	10·8	10·9	10·9
t (units of 96·5 s)	8	9	10	11	12	13	∞	
OD (275 nm)	0·378	0·350	0·324	0·301	0·281	0·263	0·082	
$10^4 k_0/s^{-1}$	10·9	10·8	10·8	10·8	10·7	10·6		

Mean value $k_0 = 10·9 \times 10^{-4}\ s^{-1}$. Duplicate runs agreed to ±5%. Guggenheim method used if 'infinity' value not taken.

EXPERIMENTAL

N-Methyl-*N*-nitrosoaniline was prepared and purified by the usual method.[22] Rate measurements were carried out in a cell block of a Pye–Unicam SP 8000 spectrophotometer at 31°. The reaction was followed either by the disappearance of the absorption at fixed wavelength of 275 nm, or by scanning a convenient wavelength range at suitable time intervals. The yield of *N*-methyl-*p*-nitrosoaniline was obtained spectrophotometrically. A typical run is given in Table 5 for reaction of *N*-methyl-*N*-nitrosoaniline (1×10^{-4}M) in sulphuric acid (4·8M) containing sulphamic acid (2×10^{-3}M) and NMA ($17·9 \times 10^{-3}$M).

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[21] E. Kalatzis and J. H. Ridd, *J. Chem. Soc.* (*B*), 1966, 529.
[22] A. I. Vogel, 'Textbook of Practical Organic Chemistry,' Longmans, London, 1954, p. 547.