Comparison of the Reactivity of Nine Nitrous Acid Scavengers

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Rate constants have been measured for the reaction of nitrous acid in aqueous solution at 25 °C with urea, 2,4-dinitroaniline, hydroxylamine, sulphanilic acid, hydrazoic acid, sulphanilamide, hydrazine, sulphamic acid, and 4-nitroaniline, as a function of acidity up to *ca.* 1.5M. The acid–rate profiles, which are all consistent with mechanisms involving electrophilic nitrosation and various protonation equilibria, give the order of reactivity at each acidity of these potential nitrous acid scavengers. The order of reactivity varies with the acidity because of the different acidity dependences, *e.g.* the ' best ' scavenger at 0.05M-acid is 4-nitroaniline followed by sulphamic acid, whilst at 1.3M-acid the most reactive is the hydrazinium ion followed by hydrazoic acid. The effect of added halide ion, thiocyanate ion, and thiourea was also examined. Nitrosation of urea, 2,4-dinitroaniline, hydrazinium ion, and sulphamic acid was not catalysed by any added nucleophile, probably because of the importance, for these substrates containing electron-withdrawing groups, of the reversibility of the initial nitrosation. For the remaining five substrates normal nucleophilic catalysis was observed; analysis of the kinetic data enables the second-order rate constant for attack by the nitrosyl halide, *etc.* to be evaluated. The reactivity sequence NOCl > NOBr > NOSCN > $\mathrm{NO\overset{+}{S}C(NH_2)_2}$ was found in each case.

Nitrous acid can readily be decomposed, often yielding gaseous products, by reaction with a number of species, mainly amines and related compounds, where the rate-limiting step is usually one of *N*-nitrosation. These reactions are of some interest from a mechanistic point of view where it is instructive to correlate the reactivity with structure, but also are of practical interest in cases where it is important to remove traces of nitrous acid from reaction solutions, *e.g.* for some nitration reactions in concentrated nitric acid,[1] and also in some nuclear fuel reprocessing reactions where reoxidation of plutonium(III) to plutonium(IV) can occur.[2] Further, decomposition of nitrous acid is important in the prevention of nitrosamine formation possibly *in vivo*, and in the analysis of nitrosamine yields it is sometimes necessary to remove quantitatively, rapidly, and irreversibly excess of nitrous acid from solution. A number of species such as urea, sulphamic acid, ascorbic acid *etc.* have been used for this purpose and some have been examined kinetically from a mechanistic point of view, *e.g.* sulphamic acid,[3] hydrazine,[4,5] hydroxylamine,[6] and hydrazoic acid.[5,7] However, the reactions are dependent on the acidity of the medium, in different ways, depending on various protonation equilibria, and so extrapolation of data from one acidity to another is difficult. In this paper we have set out to examine the reactivity of nine potential nitrous acid scavengers, urea, hydroxylamine, sulphanilic acid, hydrazoic acid, hydrazine, sulphanilamide, sulphamic acid, 4-nitroaniline, and 2,4-dinitroaniline, over a range of acidity, typically 0—1.5M-HClO$_4$. In addition we have noted the effect of added nucleophiles such as halide ion and thiocyanate ion for each substrate since catalysis occurs in some cases and not in others. In this way it was hoped to present data which enable the correct choice of scavenger to be made under given experimental conditions. An indirect method of establishing a relative reactivity scale has been presented,[8] based on the rates of denitrosation of nitrosamines in the presence of such scavengers, but suffers from the disadvantage that it is useful only in the high acid region necessary to bring about such denitrosations at convenient rates. Clearly a series of direct measurements of the rate constants over a wide acid range is the more desirable procedure.

$$\mathrm{HNO_2 + H^+ \rightleftharpoons H_2NO_2^+}$$
$$\mathrm{H_2NO_2^+ + S \longrightarrow Product}$$
$$\mathrm{S + H^+ \rightleftharpoons SH^+}$$

Scheme 1.

Results and Discussion

Acid-catalysed Reactions.—Reaction rate constants were determined for many of the substrates in the acid range 0—1.5M-HClO$_4$. Under these conditions and with $[\mathrm{substrate}]_{\mathrm{Total}} \gg [\mathrm{HNO_2}]$ all the reactions were first order in [HNO$_2$], indicating that the pathway involving N$_2$O$_3$ is not important here. Reaction is believed to occur by the attack of the nitrous acidium ion $\mathrm{H_2NO_2^+}$, present in very low equilibrium concentration, or possibly by the free nitrosonium ion NO$^+$. These two possibilities, which are indistinguishable kinetically have been discussed fully recently [9,10] and this is not a point which is at issue in this work. We shall assume the pathway set out in Scheme 1 involving $\mathrm{H_2NO_2^+}$. Under these acid conditions we can neglect the ionisation of nitrous acid to give nitrite ion, but need to consider the protonation equilibria of many of the substrates S. The general rate equation derived from Scheme 1 is that given by equation (1), where K_a is the acid dissociation constant of [SH$^+$], $[\mathrm{S}]_{\mathrm{T}}$ is the total

$$\mathrm{Rate} = \frac{kK_a[\mathrm{H^+}][\mathrm{S}]_{\mathrm{T}}[\mathrm{HNO_2}]}{K_a + [\mathrm{H^+}]} \qquad (1)$$

stoicheiometric concentration of the substrate (=[S] + [SH$^+$]) and k is the product of the rate constant for reaction of $\mathrm{H_2NO_2^+}$ the equilibrium constant for its formation. Clearly two limiting forms are to be expected, (a) when $K_a \gg$ [H$^+$] and (b) when $K_a \ll$ [H$^+$]; these are given by equations (2) and (3) respectively in the form of the first-order observed

$$k_0 = k[\mathrm{H^+}][\mathrm{S}]_{\mathrm{T}} \qquad (2)$$

$$k_0 = kK_a[\mathrm{S}]_{\mathrm{T}} \qquad (3)$$

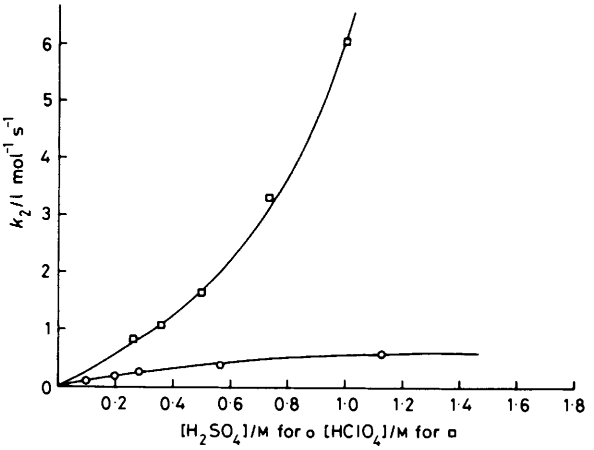

Figure 1. Acid–rate profiles for the nitrosation of urea (○) and the diazotisation of 2,4-dinitroaniline (□)

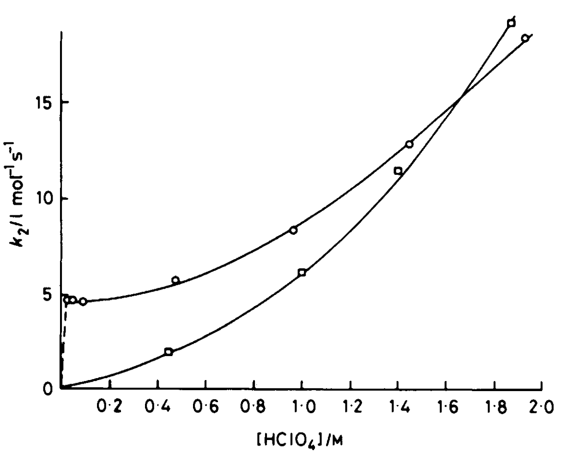

Figure 2. Acid–rate profiles for the diazotisation of sulphanilic acid (○) and for the nitrosation of the hydroxylammonium ion (□)

rate constant k_0 defined by $-d[HNO_2]/dt = k_0[HNO_2]$. Acid-catalysis is thus to be expected only when $K_a \gg [H^+]$. We have used in this treatment $[H^+]$ as the measure of the acidity, and at low $[H^+]$ this is in order, but at higher acidities, typically >0.5M, this should be replaced by an appropriate acidity function.

Throughout this paper we represent the reactivity of any substrate towards nitrosation by the second-order rate constant k_2 defined by $k_0/[S]_T$ at each and every acidity. For two substrates, 4-nitroaniline and 2,4-dinitroaniline, the experimental conditions were different, because of solubility difficulties. Again the reactions were carried out under first-order conditions but with $[HNO_2] \gg [S]_T$ and so k_2 is given by $k_0/[HNO_2]$. In both cases reactions were so rapid that the spontaneous decomposition of nitrous acid was not a problem.

Urea.—This has been extensively used as a nitrous acid trap, particularly to cut out the pathway in nitration involving nitrosation, usually in concentrated nitric acid solutions. Previous work [8] has indicated that urea is the least effective trap, but has the advantage of a high solubility in water. The reaction yields gaseous products, as shown by equation (4),

$$CO(NH_2)_2 + 2HNO_2 \longrightarrow CO_2 + 2N_2 + 3H_2O \quad (4)$$

but has never been studied kinetically, as far as we are aware. We found the reaction to be first order both in $[HNO_2]$ and in [urea] and to be acid-catalysed at low acidities, but this effect levelled off at higher acidities as expected from equation (1) if K_a and $[H^+]$ are comparable. The acidity dependence of k_2 is shown in Figure 1. The reciprocal form of equation (1) allows K_a to be determined from a plot of $(k_0)^{-1}$ *versus* $(h_0)^{-1}$. We find a pK_a value of 0.14 compared with the literature value of 0.18.[11] We have used the Hammett acidity function h_0 here to represent the protonation equilibrium, which is indistinguishable from h_A, the function appropriate to amide protonation, under these acidities. It is clear from Figures 1—4 that urea is by far the least effective trap for nitrous acid at all acidities considered here. The k value [equation (1)] was deduced as 0.89 l^2 mol^{-2} s^{-1}.

2,4-*Dinitroaniline*. Again reaction was first order in [substrate] and $[HNO_2]$, k_2 is shown as a function of acidity in Figure 1. Acid catalysis over the whole acid range is found and is expected when $[H^+] \ll K_a$ applies. The plot is not linear in $[H^+]$ because of the necessity to use an appropriate acidity function for the protonation of HNO_2. So even though 2,4-dinitroaniline is rather unreactive at low acidity, the form of acid catalysis suggests that at very high acidities diazotisation should proceed rapidly, since no significant protonation is likely to occur until very high acid concentrations are used (pK_a −4.5). A limiting value for k at low acidities (assuming a linear H^+ dependence in that region) is 2.5 l^2 mol^{-2} s^{-1}. This compares with a value* of 0.37 l^2 mol^{-2} s^{-1} reported by Larkworthy [12] for reaction at 0°, where a similar acid dependence was found.

Hydroxylammonium Ion.—The nitrosation of hydroxylamine has been extensively studied kinetically at 0°.[6,13] We have obtained k_2 values at 25° for comparison purposes with the other substrates. The results, shown in Figure 2, are of the same form as those reported for reaction at 0°, including a levelling-off of k_2 and subsequent reduction in k_2 at even higher acidities (not shown in the Figure). The rate profile up to 1.8M-$HClO_4$ is of the same form as that of 2,4-dinitroaniline, which is consistent with a mechanism proposed by Stedman *et al.*,[6,13] involving nitrosation of the hydroxylammonium ion $\overset{+}{N}H_3OH$. The limiting value of k [equation (1)] at low acidities is 3.6 l^2 mol^{-2} s^{-1} compared with the reported value at 0° of 0.24 l^2 mol^{-2} s^{-1}.[13]

Sulphanilic Acid.—This has been much used as a nitrous acid trap and also synthetically in the production of azo dyes. The kinetics do not appear to have been examined previously. Our results are shown in Figure 2. Here the amine is significantly more basic than either 4-nitroaniline or 2,4-dinitroaniline, with a pK_a value of 3.2. It is thus difficult to pick up acid catalysis since $[H^+] \gg K_a$ except at very low acidity. Initially the graph shows the expected constancy of k_0 with $[H^+]$ as expected from equation (3), but above *ca.* 0.2M-$HClO_4$ there is a further acid catalysis. This has been interpreted [14] for aniline derivatives of basicity greater than pK_a *ca.* 3, in terms of another mechanistic pathway involving the nitrosation of the *protonated* form of the amine, possible *via* some complex where NO^+ is bound initially to the aromatic ring. The limiting k value at low acidities (ignoring this additional catalysis) is calculated as 7.3 × 10^3 l^2 mol^{-2} s^{-1} [from equation (3)]. This is one of the largest values reported at 25° and is quite close to the values reported for thiourea and some alkylthioureas for *S*-nitrosation,[15] and it is believed [9]

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* The value usually quoted is 3.7 l^2 mol^{-2} s^{-1}, but there is an error in the original paper and the correct value should be 0.37 l^2 mol^{-2} s^{-1}

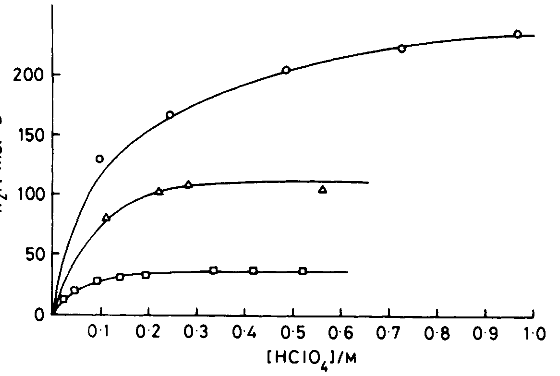


Figure 3. Acid–rate profiles for the diazotisation of 4-nitroaniline (○), sulphanilamide (□), and the nitrosation of sulphamic acid (△)

that k values in this region represent the diffusion-controlled limit.

Sulphanilamide.—This aniline derivative has also been much used in diazotisation and coupling reactions but there appears to be no data on the kinetics of diazotisation other than a comparison between diazotisation by nitrous acid and by an alkyl nitrite.[16] Our results are presented graphically in Figure 3, and show the expected behaviour predicted by equation (1) with $K_a \sim [H^+]$. The double reciprocal plot yields a value of 1.3 for the pK_a which does not agree very well with the literature values [11] of 2.3, 2.06, 2.02, and 2.10. However this procedure yields good agreement for the pK_a values of urea, 4-nitroaniline, and sulphamic acid (see later) so we have some confidence in the value of 1.3. The value of k, also deduced from the double reciprocal plot is 900 l^2 mol^{-2} s^{-1}, significantly below the value for sulphanilic acid as expected for the less basic and less nucleophilic sulphanilamide.

Sulphamic Acid.—This is probably the most widely used trap for nitrous acid, reacting according to equation (5). The

$$NH_2SO_3H + HNO_2 = N_2 + HSO_4^- + H_2O + H^+ \quad (5)$$

reaction was studied at 0° by Hughes,[3] who showed that at low acidity reaction occurred *via* the sulphamate ion. We find a similar acid dependence at 25° as shown in Figure 3, the levelling off of k_2 being entirely consistent with the protonation of the sulphamate ion to the less reactive sulphamic acid. We find from these data a pK_a value of 1.1, in reasonable agreement with the value 0.98 of Hughes at 0°. Sulphamic acid thus behaves in a similar fashion to sulphanilamide showing the intermediate behaviour of equation (1) when $K_A \sim [H^+]$ generally, but tending to a zero order H^+ dependence at higher acidity.

4-*Nitroaniline.*—The acid–rate profile is also included in Figure 3 and shows again the same pattern as for sulphanilamide and sulphamic acid. Again rate constants have not previously been reported at 25° but the rate law has been established [12] at 0°. Analysis of the data by a double reciprocal plot yields a value of 1.0 for the pK_a (literature value 1.0 [11]) and a value of k [equation (1)] of 2.7×10^3 l^2 mol^{-2} s^{-1} (below that expected for diffusion controlled reactions).

Hydrazoic Acid.—Since the reactive species in acid solution HN_3 is not expected to undergo further protonation in the acid range studied here, it is to be expected therefore that the limiting rate equation (2) will apply. Figure 4 shows the

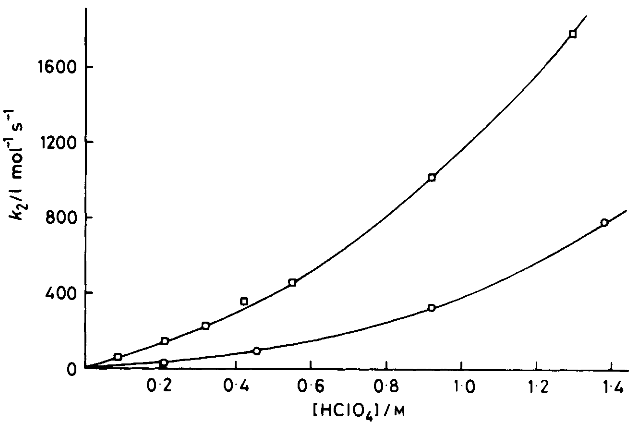


Figure 4. Acid–rate profiles for the nitrosation of hydrazoic acid (○) and the hydrazinium ion (□)

expected acid catalysis, which is not linear in $[H^+]$ as for 2,4-dinitroaniline and hydroxylamine (and hydrazinium ion later) because of the activity effects which are not allowed for. Hydrazoic acid is significantly more reactive than either 2,4-dinitroaniline or hydroxylamine with a k value [equation (2)] of 160 l^2 mol^{-2} s^{-1} (assuming a linear $[H^+]$ dependence as $[H^+] \longrightarrow 0$), which is compatible with the reported value [7] of 33.7 l^2 mol^{-2} s^{-1} at 0°.

Hydrazinium Ion.—The observed rate profile (Figure 4) is consistent with the reaction of the protonated form $NH_2NH_3^+$ as has been established by Stedman *et al.*[4,5] The limiting value of k as $[H^+] \longrightarrow 0$ is 620 l^2 mol^{-2} s^{-1} which agrees well with that reported by Stedman *et al.* (611 l^2 mol^{-2} s^{-1}).

The overall efficiency of a nitrous acid trap thus depends crucially on the acidity of the medium. Table 1 collects the data (expressed as the second-order rate constant k_2 defined by rate $= k_2[HNO_2][S]_T$) for all of the substrates studied here at three different acidities (0.05, 0.5, and 1.3M-H^+) so that easy direct comparison can be made at each of three acidities.

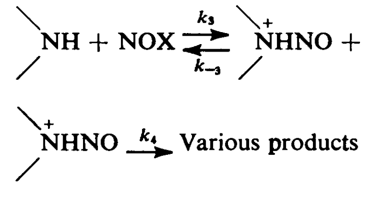
At low acidities (0.05M) the increasing order of overall reactivity of the substrates examined is given by the order in the first column, *i.e.* urea is the least reactive and 4-nitroaniline the most. At higher acidities however, the order changes significantly as various protonation equilibria come into play so that at 1.3M-H^+ the hydrazinium ion and hydrazoic acid become the most efficient traps. The results are included (in Table 1) also for three thiol-carboxylic acids examined in a parallel study.[17] The k_2 values clearly show that these substrates are indeed the most efficient of nitrous acid traps, and although the acid catalysis was not extended to very high acid concentrations, it is likely that protonation of the sulphur atom (and consequent reduction in efficiency in nitrosation) is not an important factor contrasting with many basic nitrogen containing species.

If reaction occurs in these systems *via* $H_2NO_2^+$ then it is not possible to evaluate the actual second-order rate constants for the process $H_2NO_2^+ + S \longrightarrow S^+\text{-NO}$, since the dissociation constant of $H_2NO_2^+$ is not known. However, other arguments, notably the relative insensitivity of the third-order rate constant k [equation (1)] to substrate structure for some reactive species, have been used to put the case for diffusion controlled processes here. A value of k of *ca.* 7×10^3 l^2 mol^{-2} s^{-1} has been regarded [9] as this limiting value at 25°. The only substrate studied in the present work with a value of k in this region is sulphanilic acid (7.3×10^3 l^2 mol^{-2} s^{-1})

Table 1. Data (expressed as second-order rate constants) for all substrates studied, at three different acidities

Substrate	k_2/l mol^{-1} s^{-1} at 25°		
	0.05M-H$^+$	0.5M-H$^+$	1.3M-H$^+$
Urea	0.03	0.36	0.59
2,4-Dinitroaniline	0.12	1.7	~14 *
Hydroxylammonium ion	0.15	2.1	9.6
Sulphanilic acid	4.6	5.5	11
Hydrazoic acid	8.0	105	680
Sulphanilamide	20	37	37 *
Hydrazinium ion	31	390	1 820
Sulphamic acid	47	112	112 *
4-Nitroaniline	72	207	250 *
Cysteine †	26	~200 *	
Mercaptosuccinic acid †	64	~600 *	
Mercaptopropanoic acid †	233	~2 000 *	

* Not measured directly at these acidities, but are extrapolated values. † Measured in a parallel study.[17]



Scheme 2.

Table 2. Nucleophilic catalysis in the diazotisation of sulphanilic acid. [H$^+$] 4.8 × 10^{-2}M, [NaNO$_2$] 5.0 × 10^{-5}M, [sulphanilic acid] 1.22 × 10^{-2}M, 25°

[Cl$^-$]/M	k_0/s^{-1}	[Br$^-$]/M	k_0/s^{-1}
0.025	0.382	0.025	7.2
0.050	0.708	0.050	11.5
0.075	0.963	0.075	14.6
0.100	1.26	0.100	16.9
10^3[SCN$^-$]/M	k_0/s^{-1}	10^3[I$^-$]/M	k_0/s^{-1}
1.74	1.30	1.01	0.69
3.49	2.55	2.02	1.36
6.97	4.65	3.03	1.94
10.5	6.58	4.04	2.57

Table 3. Absence of catalysis in the nitrosation of hydrazinium ion (1.0 × 10^{-2}M). [H$^+$] 0.21M, [NaNO$_2$] 1.0 × 10^{-3}M, 25°

[Cl$^-$]/M	k_0/s^{-1}	[Br$^-$]/M	k_0/s^{-1}
0.01	1.46	0.01	1.47
0.03	1.55	0.03	1.59
0.05	1.53	0.05	1.80
0.10	1.81	0.10	2.05
[SCN$^-$]/M	k_0*/s^{-1}		
0.01	0.38		
0.05	0.37		
0.10	0.41		
0.20	0.40		

* At 0°.

which suggests that diffusion control operates. As expected 4-nitroaniline has a smaller k value (2.3 × 10^3 l^2 mol^{-2} s^{-1}). The modest overall reactivity of sulphanilic acid (Table 1) is of course attributable to its relatively high basicity.

Nucleophile Catalysed Reactions.—A further complication arises when comparing reactivities of various nitrite traps, if non-basic nucleophiles such as halide ion or thiocyanate ion (X^-) are present, since these produce equilibrium concentrations of NOX species which can themselves effect nitrosation. Thus many cases of catalysis of nitrosation and diazotisation by added halide ion and thiocyanate ion have been noted. However this seems to be confined to amine substrates and attention has been drawn[18] to the fact that amide nitrosation shows no such catalysis. This question has been further examined and a pattern has emerged[19] in which substrates containing a powerful electron-withdrawing group (such as the carbonyl group) show no catalysis. An explanation has been put forward[20] in terms of the reversibility of the initial *N*-nitrosation (see Scheme 2); if $k_{-3}[X^-] \gg k_4$ no X^- catalysis should result. Scheme 2 should also include a mechanism for reaction *via* $H_2NO_2^+$, which could either be a dominating or insignificant term. The same argument can be (and has been) applied to the reverse reaction in the denitrosation of nitrosamines,[21] nitrosamides,[20,22] and nitrososulphonamides[23] and leads to the same conclusion that when $k_{-3}[X^-] \gg k_4$ no catalysis by X^- of the denitrosation reaction occurs.

We have in this paper examined each substrate given in Table 1 for catalysis by added Cl$^-$, Br$^-$, I$^-$, SCN$^-$, and SC(NH$_2$)$_2$, and find catalysis for hydroxylammonium ion, hydrazoic acid, sulphanilamide, sulphanilic acid, and 4-nitroaniline, and no catalysis for urea, hydrazinium ion, sulphamic acid, and 2,4-dinitroaniline. The results fit into the general pattern that when there are powerful electron-withdrawing groups present, $>C{=}O$, $\overset{+}{N}H_3$, SO_3H, and two nitro-substituents, no catalysis occurs. These substrates should have a much larger value of k_{-3} and so allow $k_{-3}[X^-] \gg k_4$ to be achieved more readily. The only apparent exception is the reaction of the hydroxylammonium ion $\overset{+}{N}H_3OH$ where it is believed that *O*-nitrosation is followed by rearrangement.

Thus the reactivity order is affected not only by the acidity of the medium but also by the presence of nucleophilic species. This explains why hydrazoic acid appears to be a better trap than hydrazinium ion (as measured by the indirect method earlier[8]) when the reaction medium was hydrochloric acid or contained added bromide ion.

Typical sets of data are included in Tables 2 and 3 showing respectively catalysis of nitrosation of sulphanilic acid and the absence of catalysis in the nitrosation of hydrazine. Nucleophilic catalysis has previously been reported for hydroxylamine ion, hydrazoic acid,[5,7] and 4-nitroaniline[12,24] whereas the absence of catalysis for the sulphamic acid reaction has also been noted;[3] the data for the other substrates are new. Contrary to a report in the literature[4] we find no catalysis in the nitrosation of the hydrazinium ion (see Table 3) either at 25 or 0°, other than a very small effect attributable to a salt effect. It is interesting to note the difference in behaviour between 4-nitroaniline and 2,4-dinitroaniline, where the introduction of the second nitro-group is sufficient to remove catalysis completely. Presumably the increased nucleophilicity is sufficient to ensure that $k_{-3}[X^-] \gg k_4$. Even for 4-nitroaniline the reversibility is important as shown[24] by the curved plots of k_0 *versus* $[X^-]$. The full expression for the rate from Scheme 2 is given in equation (6), with an

$$\text{Rate} = \frac{k_3 k_4 [S]_T [HNO_2][X^-][H^+] K_{NOX} K_a}{(K_a + H^+)(k_{-3}[X^-] + k_4)} \qquad (6)$$

Table 4. Values of k_3 (from Scheme 2) at 25°

	k_3/l mol^{-1} s^{-1}			
	NOCl	NOBr	NOSCN	$NO\overset{+}{S}C(NH_2)_2$
NH_2OH	5.9×10^8	1.7×10^8	1.2×10^7	
HN_3	1.9×10^6	$\left\{\begin{matrix} 1.3 \times 10^6 \\ 2.0 \times 10^6 \end{matrix}\right\}$ †		
Sulphanilic acid	1.4×10^9	0.99×10^9	2.0×10^6	5.9×10^3
Sulphanilamide	1.8×10^8	4.4×10^7	7.3×10^4	2.0×10^2
4-Nitroaniline *	2.1×10^8	4.3×10^7		

* From ref. 24. † Two values were obtained, one at constant [HN_3] and varying [Br^-] and the other at constant [Br^-] and varying [HN_3].

Table 5. Values of k_7 [equation (7)]/l^2 mol^{-2} s^{-1} at 25°

SCN^-	11 740	From measurements at different [SCN^-]
	11 700	From measurements at different [HN_3]
	1 460	Literature value at 0° (ref. 7)
$SC(NH_2)_2$	7 091	From measurements at different [$SC(NH_2)_2$]
	7 200	From measurements at different [HN_3]
	6 960	Direct measurement (ref. 26)

additional term due to the uncatalysed reaction. Thus k_0 *versus* [X^-] is linear if $k_{-3}[X^-] \ll k_4$ and k_0 is independent of [X^-] if $k_{-3}[X^-] \gg k_4$. The intermediate situation can readily be analysed by taking the reciprocal form of equation (6) and plotting $(k_0)^{-1}$ *versus* $[X^-]^{-1}$. Values of k_3 are collected in Table 4 for the five substrates for which we have found nucleophilic catalysis. For most of the reactions k_0 *versus* [X^-] was linear over the concentration range studied but for some, curved plots were found and analysis was carried out by the double reciprocal plot. The results show clearly the now established trend [19] of reactivity NOCl > NOBr > NOSCN > $NO\overset{+}{S}C(NH_2)_2$ with the values for both NOBr and NOCl approaching the diffusion controlled limit for the sulphanilic acid case. The values for both sulphanilic acid and sulphanilamide (again for NOBr and NOCl) fit reasonably well on the log k_3 *versus* pK_a plot (from ref. 24), illustrating that the nucleophilicities of aniline derivatives towards electrophilic nitrosation by a variety of reagents, show the same trend as their basicities.

One further point of mechanistic interest emerges regarding the nucleophile catalysed reactions of hydrazoic acid. Whilst for [X^-] = bromide the reaction was first order in [HN_3], for both thiocyanate and thiourea the reaction became zero order in the substrate. This has previously been noted for diazotisation at low acidities of aniline [25] and nitrosation of HN_3[7] at 0° for halide ion catalysed reactions. This has now been extended to thiocyanate ion and thiourea catalysed reactions at 25°. Zero-order dependence on HN_3 is to be expected when (Scheme 3) $k_6[HN_3] \gg k_{-5}$ and attack by SCN^- (or thiourea) is rate limiting. The rate equation is then given by equation (7). Values of k_7 are included in Table 5

$$H_2\overset{+}{N}O_2 + SCN^- \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} NOSCN + H_2O$$

$$NOSCN + HN_3 \xrightarrow{k_6} \text{Products}$$

Scheme 3.

$$\text{Rate} = k_7[HNO_2][H^+][SCN^-] \text{ (or } [SC(NH_2)_2]) \quad (7)$$

and were obtained in two ways, (a) from the variation of k_0 with [SCN^-] (or [$SC(NH_2)_2$]) and (b) from measurements at different [HN_3]. There is good agreement between the two methods. No rate constant for the reaction of an anion with nitrous acid has been reported at 25°, but it has been argued [9] on the basis of the similarity of values for different anions at 0°, that the reaction rate is close to diffusion limit. Our value of 11 700 l^2 mol^{-2} s^{-1} is perhaps rather larger than expected, given the reported value at 0° of 1 460 l^2 mol^{-2} s^{-1}, and corresponds to an activation energy of *ca.* 56 kJ mol^{-1} which is significantly larger than that expected for a diffusion-controlled reaction. For the thiourea reaction there is excellent agreement between our k_7 values and that reported [26] for the direct reaction between thiourea and nitrous acid in acid solution. If both reactions are at the diffusion controlled limit then the difference between 11 700 l^2 mol^{-2} s^{-1} for SCN^- and 7 000 l^2 mol^{-2} s^{-1} for $SC(NH_2)_2$ may be due to the different charge type of the reactants.

Experimental

All materials were of the highest purity grade available and were used as such. Fresh sodium nitrite solutions were used daily. All the kinetic experiments were carried out under first-order conditions with [substrate] $\gg$ [HNO_2] except for 4-nitroaniline and 2,4-dinitroaniline where the nitrous acid was in large excess. Most of the reactions were followed by stopped-flow spectrophotometry noting the disappearance of the absorbance at 360 nm due to HNO_2 or for the aniline derivatives, the appearance of the absorption due to the diazonium ion or the disappearance of the amine absorption. The spectrophotometer was interfaced with an Apple II Europlus microcomputer using Hitech stopped-flow data acquisition software. The mean value of at least five separate kinetic runs was taken. For the less reactive substrates, *e.g.* urea and 2,4-dinitroaniline, reaction was followed in a conventional spectrophotometer.

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